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PHYSICAL

**E** **CHEMISTRY**





# Chapter Contents

## 01

## MOLE CONCEPT & EUDIOMETRY

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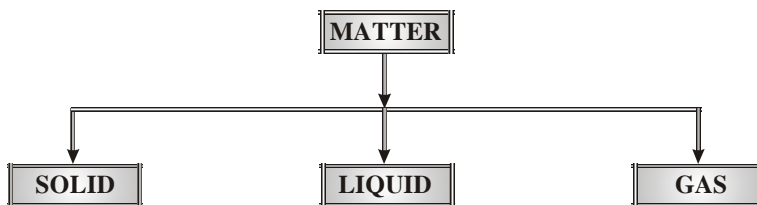
MOLE CONCEPT

1. **MATTER** : Matter is anything that has mass and occupies space.

Two ways of classifying matter :

- I. Physical classification                      II. Chemical classification

1.1 **Physical classification :**

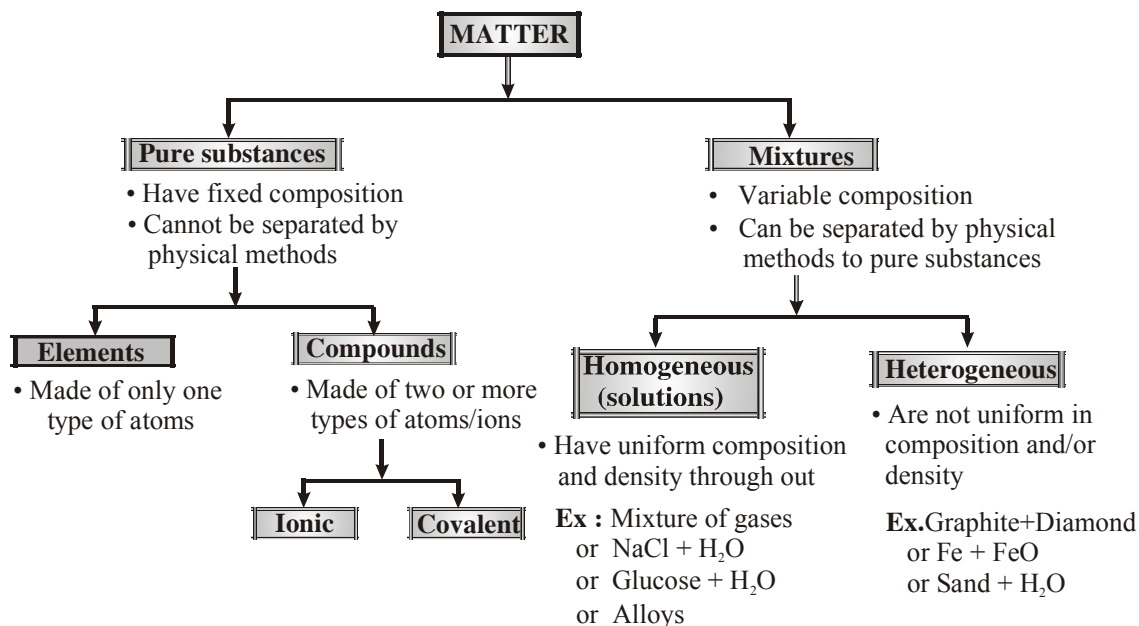


- |   |  |   |
|---|--|---|
| (i) Particles held very closely packed in ordered manner. | Particles are less closely packed.       | Particles are farthest apart                |
| (ii) No freedom of movement of particles                  | Particles can move around to some extent | Movement of particles is very easy and fast |
| (iii) Definite shape and volume                           | Definite volume, indefinite shape        | indefinite shape and volume                 |
| (iv) Exists at low T and high P                           | Exists at intermediate P & T             | Exists at high T and low P                  |

**Note : For same substance :**

- Solid and Liquid co-exist at **MELTING POINT**.
- Liquid and gas co-exist at **BOILING POINT**.
- Solid and gas co-exist at **SUBLIMATION POINT**.
- Solid, liquid and gas co-exist at **TRIPLE POINT**.

1.2 **Chemical classification :**



- Note**
- **PHASE** : It is the state of matter uniform in density and composition.
  - Homogeneous mixtures have single phase while heterogeneous mixtures are multi-phase.
- Ex** : NaCl + H<sub>2</sub>O mixture has one phase  
**Ex** : Graphite + Diamond mixture has 2 phases.

## 2 SOME SPECIFIC PROPERTIES OF SUBSTANCES

### 2.1 Deliquescence :

The property of certain compounds of taking up the moisture present in atmosphere and becoming wet when exposed, is known as deliquescence. These compounds are known as deliquescent. Sodium hydroxide, potassium hydroxide, anhydrous calcium chloride, anhydrous magnesium chloride, anhydrous ferric chloride, etc., are the examples of deliquescent compounds.

### 2.2 Hygroscopicity :

Certain compounds combine with the moisture of atmosphere and are converted into hydroxides or hydrates. Such substances are called hygroscopic. Anhydrous copper sulphate, quick lime (CaO), anhydrous sodium carbonate, etc., are of hygroscopic nature.

### 2.3 Efflorescence :

The property of some crystalline substances of losing their water of crystallisation on exposure and becoming powdery on the surface is called efflorescence and such salts are known as efflorescent. The examples are : Ferrous sulphate (FeSO<sub>4</sub>·7H<sub>2</sub>O), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O), sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O), potash alum [K<sub>2</sub>SO<sub>4</sub>·Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O], etc.

### 2.4 Malleability :

This property is shown by metals. When metallic solid is being beaten, it does not break but is converted into thin sheet. It is said to possess the property of malleability. Copper, gold, silver, aluminium, lead, etc., can be easily hammered into sheets. Gold is the most malleable metal.

### 2.5 Ductility :

The property of metal to be drawn into wires is termed ductility. Copper, silver, gold, aluminium, iron, etc., are ductile in nature. Platinum is the most ductile metal.

### 2.6 Brittleness :

The solid materials which break into small pieces on hammering are called brittle. The solids of non-metals and ionic solid are generally brittle in nature.

**Ex: Ice, Diamond etc.**

### 3. THE LAW OF CHEMICAL COMBINATION

*Aoine Lavoisier, John Dalton* and other scientists formulated certain laws concerning the composition of matter and chemical reactions. These laws are known as the law of chemical combination.

#### 3.1 Law of indestructibility of matter or conservation of Mass :

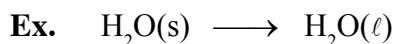
- This law was proposed by *Lavoisier in 1789*.
- According to this law, in all physical or chemical changes the total mass of the system remains constant or in a physical or chemical change, mass is neither created nor destroyed. Thus, in a physical or chemical change.



Antoine Lavoisier  
(1743-1794)

Antoine-Laurent de Lavoisier, the "father of modern chemistry," was a French nobleman prominent in the histories of chemistry and biology. He named both oxygen and hydrogen and predicted silicon.

**Total mass of reactant reacted = Total mass of products formed**



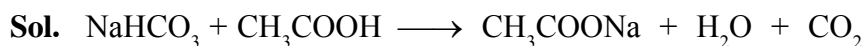
Above reaction shows the physical change and the wt. of  $\text{H}_2\text{O}(\text{s}) = \text{wt. of } (\text{H}_2\text{O})(\ell)$

In case the reacting materials are not completely consumed, the relationship will be.

Total masses of reactants = Total masses of product + masses of unreacted reactants

- In nuclear reactions (Mass + energy) is conserved, not the mass separately.

**Ex.1** When 4.2 g  $\text{NaHCO}_3$  is added to a solution of  $\text{CH}_3\text{COOH}$  weighing 10.0 g, it is observed that 2.2 g  $\text{CO}_2$  is released into atmosphere. The residue is found to weigh 12.0 g. Show that these observations are in agreement with the law of conservation of mass.



$$\text{Initial mass} = 4.2 + 10 = 14.2$$

$$\text{Final mass} = 12 + 2.2 = 14.2$$

Thus, during the course of reaction law of conservation of mass is obeyed.

#### DO YOUR SELF-01

1. 100 gm  $\text{CaCO}_3(\text{s})$  on heating decompose completely and gives 44 gm  $\text{CO}_2(\text{g})$ . The residue is found to weight 56 gms. show that these observations proof the law of conservation of mass.
2. 12 gm  $\text{C}(\text{s})$  react with 32 gm  $\text{O}_2(\text{g})$  to form  $\text{CO}_2(\text{g})$ . Find amount of  $\text{CO}_2(\text{g})$  obtained if no reactant left at end of reaction .

**Answers :**

1. Initial mass = final mass
2. 44 gm

### 3.2. Law of constant or definite proportion :

- This law was given by **Joseph Louis Proust** in 1799.
- Chemical composition of a compound remains constant whether it is obtained by any method or any source.

#### ◆ Example :

In water ( $H_2O$ ), Hydrogen and Oxygen combine in 1 : 8 mass ratio, the ratio remains constant whether it is tap water, river water or sea water or produced by any chemical reaction.



Joseph Proust  
(1754 - 1826)

Proust was born the son of an apothecary at Angers in north-west France. He studied in Paris. He lived in poverty for some years before being awarded a pension by Louis XVIII.

**Ex.2** 1.80 g of a certain metal burnt in oxygen gave 3.0 g of its oxide. 1.50 g of the same metal heated in steam gave 2.50 g of its oxide. Show that these results illustrate the law of constant proportion.

**Sol.** In the first sample of the oxide,

$$\text{wt. of metal} = 1.80 \text{ g}, \quad \text{wt. of oxygen} = (3.0 - 1.80) \text{ g} = 1.2 \text{ g}$$

$$\therefore \frac{\text{wt. of metal}}{\text{wt. of oxygen}} = \frac{1.80 \text{ g}}{1.2 \text{ g}} = 1.5$$

In the second sample of the oxide,

$$\text{wt. of metal} = 1.50 \text{ g}, \quad \text{wt. of oxygen} = (2.50 - 1.50) \text{ g} = 1 \text{ g}$$

$$\therefore \frac{\text{wt. of metal}}{\text{wt. of oxygen}} = \frac{1.50 \text{ g}}{1 \text{ g}} = 1.5$$

Thus, in both samples of the oxide the proportions of the weights of the metal and oxygen are fixed. Hence, the results follow the law of constant proportion.

**Note:** This law is not applicable in case of isotopes.

#### DO YOUR SELF-02

- 12 gm C(s) burnt in oxygen gave 28 gm CO(g). 36 gm C(s) reduce  $Al_2O_3(s)$  to gave 84 gm CO(g). Show that these results illustrate the law of constant proportion.
- Is proportion of hydrogen and oxygen in  $H_2O$  different if source of  $H_2O$  changed?

**Answers :**

1. In both sample of CO the proportions of C and O are fixed
2. No

### 3.3. The law of multiple proportion :

- This law was given by Dalton in 1803.
- If two elements combine to form more than one compound, then the different masses of one element which combine with a fixed mass of the other element, bear a simple ratio to one another.



**Ex.** Nitrogen and oxygen combine to form five stable oxides –

$N_2O$	Nitrogen 28 parts	Oxygen 16 parts
$N_2O_2$	Nitrogen 28 parts	Oxygen 32 parts
$N_2O_3$	Nitrogen 28 parts	Oxygen 48 parts
$N_2O_4$	Nitrogen 28 parts	Oxygen 64 parts
$N_2O_5$	Nitrogen 28 parts	Oxygen 80 parts

The masses of oxygen which combine with same mass of nitrogen in the five compounds bear a ratio 16 : 32 : 48 : 64 : 80 or 1 : 2 : 3 : 4 : 5.

**Note:** This law is not applicable in case of isotopes.

**Ex.3** Carbon forms two oxides. One contains 27.27 % carbon & another contains 42.86% carbon. Show that the data illustrate the law of multiple proportion.

**Sol.** The mass ratio of C : O in first oxide = 27.27 : 72.73 = 3 : 8

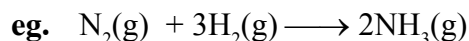
The mass ratio of C : O in second oxide = 42.86 : 57.14 = 3 : 4

Hence for each 3 gm of carbon the masses of oxygen combined is in 2 : 1 ratio.

Hence the data is according the law of multiple proportion.

### 3.4 Law of Gaseous volumes :

- This law was given by **Gay-Lussac**. in 1808.
- According to this law, gases react with each other in the simple ratio of their volumes and if products are also gases then they are also in simple ratio of volume provided that all volumes are measure at same temp. & pressure.



1 vol.    3vol.            2vol.

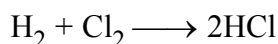


Joseph Louis  
Gay Lussac  
(1778 - 1850)

Joseph Louis Gay-Lussac also ; 6 December 1778 – 9 May 1850) was a French chemist and physicist. He is known mostly for two laws related to gases, and for his work on alcohol-water mixtures, which led to the degrees Gay-Lussac used to measure alcoholic beverages in many countries.

**Ex.4** For the gaseous reaction,  $H_2 + Cl_2 \longrightarrow 2HCl$ . If 40 ml of hydrogen completely reacts with chlorine then find out the required volume of chlorine and volume of produced HCl ?

**Sol.** According to Gay Lussac's Law :



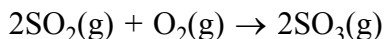
$\therefore$  1 ml of  $H_2$  will react will 1 ml of  $Cl_2$  and 2 ml of HCl will produce.

$\therefore$  40 ml of  $H_2$  will react with 40 ml of  $Cl_2$  and 80 ml of HCl will produce.

required vol. of  $Cl_2$  = 40 ml, produced vol. of HCl = 80 ml

## DO YOUR SELF-03

1. 2ml SO<sub>2</sub>(g) react with 1 ml of O<sub>2</sub>(g) completely to form SO<sub>3</sub>(g)



Is it true that 3ml of SO<sub>3</sub>(g) obtained at end of reaction.

## Answer

1. No.

- 3.5. **Avogadro's law (1811)** : Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules.

## 4. DALTON'S ATOMIC THEORY

Ancient Indian and Greek philosophers have always wondered about the unknown and unseen form of matter. The idea of divisibility of matter was considered long back in India, around 500 BC. An Indian philosopher **Maharishi Kanad**, postulated that if we go on dividing matter ( padarth ), we shall get smaller and smaller particles. Ultimately, a time will come when we shall come across the smallest particle beyond which further division will not be possible. He named these particles **Parmanu**. Another Indian philosopher, Pakudha Katyayama, elaborated this doctrine and said that these particles normally exist in a combined form which gives us various forms of matter. Around the same era, the Greek philosopher Democritus expressed the belief that all matter consists of very small, indivisible particles, which he named **atomos** (meaning uncuttable or indivisible).



**John Dalton** (1766 - 1844) , an Englishman, began teaching at a Quaker school when he was 12. His fascination with science included an intense interest in meteorology (he kept careful daily weather records for 46 years), which led to an interest in the gases of the air and their ultimate components, atom. Dalton is best known for his atomic theory, in which he postulated that the fundamental differences among atoms are their masses. He was the first to prepare a table of relative atomic weight.

Although Democritus' ideal was not accepted by many of his contemporaries (notably Plato and Aristotle), somehow it endured. Experimental evidence from early scientific investigations provided support for the notion of "atomism" and gradually gave rise to the modern definitions of elements and compounds. It was in **1808**, **John Dalton**, formulated a precise definition of the indivisible building blocks of matter that we call atoms. Dalton's work marked the beginning of the modern era of chemistry. The hypotheses about the nature of matter on which Dalton's atomic theory is based can be summarized as follows :

- (i) Matter consists of indivisible atoms.
- (ii) All atoms of a given element are identical, having the same size, mass and chemical properties. The atoms of one element are different from the atoms of all other elements.

- (iii) Compounds are formed when atoms of different elements combine in a fixed ratio.
- (iv) A chemical reaction involves only the separation, combination or rearrangement of atoms. It does not result in their creation or destruction.

## 5. ATOMIC AND MOELCULAR MASSES :

The mass of an atom depends on the number of electrons, protons, and neutrons it contains. Knowledge of an atom's mass is important in laboratory work. But atoms are extremely small particles - even the smallest speck of dust that our unaided eyes can detect contains as many as  $1 \times 10^{16}$  atoms ! Clearly we cannot weigh a single atom, but it is possible to determine the mass of one atom relative to another experimentally. The first step is to assign a value to the mass of one atom of a given element so that it can be used as a standard.

### 5.1 RELATIVE ATOMIC MASS :

Hydrogen, being lightest atom was arbitrarily assigned a mass of 1 (without any units) and other elements were assigned masses relative to it. However, the present system of atomic masses is based on carbon - 12 as the standard and has been agreed upon in 1961. Here, Carbon - 12 is one of the isotopes of carbon and can be represented as  $^{12}\text{C}$ . In this system,  $^{12}\text{C}$  is assigned a mass of exactly 12 atomic mass unit (**amu**) and masses of all other atoms are given relative to this standard. **Relative Atomic Mass is defined as the number which indicates how many times the mass of one atom of an element is heavier in comparison to 1/12th part of the mass of one atom of C-12.**

$$\begin{aligned} \text{Relative atomic mass of an element} &= \frac{\text{mass of one atom of an element}}{\frac{1}{12}[\text{mass of one C - 12 atom}]} \\ &= \frac{\text{Mass of one atom of an element}}{1 \text{ amu}} \end{aligned}$$

**5.1.1 ATOMIC MASS UNIT (a.m.u. or u) :** The quantity  $1/12^{\text{th}}$  mass of an atom of  $\text{C}^{12}$  is known as atomic mass unit.

Since mass of 1 atom of C - 12 =  $1.992648 \times 10^{-23}$  g

$$\therefore 1/12^{\text{th}} \text{ part of the mass of 1 atom} = \frac{1.992648 \times 10^{-23} \text{ g}}{12} = 1.67 \times 10^{-24} \text{ g} = \frac{1}{6.022 \times 10^{23}} \text{ g}$$

It may be noted that the atomic masses as obtained above are the relative atomic masses and not the actual masses of the atoms. These masses on the atomic mass scale are expressed in terms of atomic mass units (abbreviated as amu). Today, 'amu' has been replaced by 'u' which is known as **unified mass**.

### 5.1.2 GRAM ATOMIC MASS OR MASS OF 1 G ATOM :

When numerical value of atomic mass of an element is expressed in grams then the value becomes gram atomic mass or GAM.

gram atomic mass (GAM) = mass of 1 **g atom** = mass of 1 **mole atoms**

$$= \text{mass of } N_A \text{ atoms} = \text{mass of } 6.022 \times 10^{23} \text{ atoms.}$$

**Ex.** GAM of oxygen = mass of 1 g atom of oxygen = mass of 1 mol atoms of oxygen.

$$= \text{mass of } N_A \text{ atoms of oxygen} = \left( \frac{16}{N_A} \text{ g} \right) \times N_A = 16 \text{ g}$$

**Ex.** Mass of one atom of Oxygen = 16 amu or  $16 \times 1.66 \times 10^{-24} \text{ g}$

$$\text{Mass of } N_A \text{ atoms of Oxygen} = 16 \times 1.66 \times 10^{-24} \times 6.022 \times 10^{23} \text{ g} = 16 \text{ g}$$

Now see the table given below and understand the definition given before.

Element	R.A.M. (Relative Atomic Mass)	Atomic mass (mass of one atom)	Gram Atomic mass or weight
N	14	14 amu	14 gm
He	4	4 amu	4 gm
C	12	12 amu	12 gm

### 5.1.3 AVERAGE ATOMIC MASS :

If an element exists in different isotopic forms having relative abundance  $X_1\%$ ,  $X_2\%$  .....  $X_n\%$ , with relative atomic masses  $M_1, M_2$  .....  $M_n$  respectively then ,

$$\text{Avg. Atomic mass of element} = \frac{X_1}{100}(M_1) + \frac{X_2}{100}(M_2) + \dots + \frac{X_n}{100}(M_n) = \sum_{i=1 \text{ to } n} \frac{X_i}{100}(M_i)$$

**Ex.5** The atomic mass of an element is 50

(i) Calculate the mass of one atom, in amu

(ii) Calculate the mass of  $6.022 \times 10^{23}$  atoms, in gm

(iii) Calculate the number of atoms in its 10 gm

(iv) What mass of the element contains  $3.011 \times 10^{20}$  atoms

**Sol.** (i) 50 amu

(ii) 50 gm

(iii)  $\therefore$  50 gm of element contains  $6.022 \times 10^{23}$  atoms

$$\therefore 10 \text{ gm of element will contain } \frac{6.022 \times 10^{23}}{50} \times 10 = 1.2044 \times 10^{22} \text{ atoms}$$

(iv)  $\therefore$   $6.022 \times 10^{23}$  atoms weighs 50 gm

$$\therefore 3.011 \times 10^{20} \text{ atoms weighs } \frac{50}{6.022 \times 10^{23}} \times 3.011 \times 10^{20} = 0.025 \text{ gm}$$

**Ex.6** An element exist in nature in two isotopic forms :  $X^{30}$  (90%) and  $X^{32}$ (10%). What is the average atomic mass of element ?

$$\text{Sol. Av. atomic mass} = \frac{\Sigma(\% \text{abundance} \times \text{atomic mass})}{100} = \frac{90 \times 30 + 10 \times 32}{100} = 30.2$$

### DO YOUR SELF-04

- Calculate mass of 1 atom of  $^{16}_8\text{O}$  in gram.
- Calculate mass of  $6.022 \times 10^{20}$  atoms of  $^{14}_7\text{N}$  in gm.
- Find no. of  $^4_2\text{He}$  atoms present in 52 amu He sample ?
- Element B exist in nature in two isotopic form B-10 (20%) and B -11 (80%). What is average atomic mass of B ?

**Answers :**

- $2.66 \times 10^{-23} \text{ gm}$
- $1.4 \times 10^{-2} \text{ gm.}$
- 13
- 10.8

## 5.2 RELATIVE MOLECULAR MASS :

The number which indicates how many times the mass of one molecule of a substance is heavier in comparison to 1/12th part of the mass of an atom of C-12.

OR

The molecular mass of a substance is the sum of atomic masses of all the atoms present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together.

<b>Ex.</b> molecular mass of oxygen (O <sub>2</sub> )	=	32
molecular mass of (O <sub>3</sub> )	=	48
molecular mass of HCl	=	1 + 35.5 = 36.5
molecular mass of H <sub>2</sub> SO <sub>4</sub>	=	2 + 32 + 64 = 98

### 5.2.1 GRAM MOLECULAR MASS (MASS OF 1 G MOLECULE) :

When numerical value of molecular mass of the substance is expressed in grams then the value becomes gram molecular mass or GMM.

$$\begin{aligned} \text{gram molecular mass (GMM)} &= \text{mass of 1 g molecule} = \text{mass of 1 mole molecules} \\ &= \text{mass of } N_A \text{ molecules} = \text{mass of } 6.022 \times 10^{23} \text{ molecules} \end{aligned}$$

<b>Ex.</b> GMM of H <sub>2</sub> SO <sub>4</sub>	=	mass of 1 g molecule of H <sub>2</sub> SO <sub>4</sub>
	=	mass of 1 mole molecules of H <sub>2</sub> SO <sub>4</sub>
	=	mass of N <sub>A</sub> molecules of H <sub>2</sub> SO <sub>4</sub>
	=	$\left(\frac{98}{N_A}\right) \times N_A = 98 \text{ g}$

<b>Ex.</b> Molecular Mass of N <sub>2</sub> = 28 amu	=	$28 \times 1.66 \times 10^{-28} \text{ g}$
Mass of N <sub>A</sub> molecules of N <sub>2</sub>	=	$28 \times 1.66 \times 10^{-24} \times 6.022 \times 10^{23} \text{ g} = 28 \text{ g}$

### 5.2.2 AVERAGE MOLECULAR MASS OF NON-REACTING GAS MIXTURE :

$$M_{\text{avg.}} = \frac{\text{Total mass of mixture}}{\text{Total mole}} = \frac{\sum(\% \text{vol} \times \text{molecular mass})}{100} = \frac{100}{\sum\left(\frac{\% \text{mass}}{\text{molecular mass}}\right)}$$

**Ex.7** The molecular mass of a compound is 75

(i) Calculate the mass of 100 molecules, in amu.

(ii) Calculate the mass of 5000 molecules, in gm.

(iii) What is the mass of  $6.022 \times 10^{20}$  molecules, in gm

(iv) How many molecules are in its 2.5 mg

Sol. (i) mass of 1 molecules = 75 amu

∴ mass of 100 molecules = 7500 amu

(ii) Mass of 5000 molecules =  $5000 \times 75$  amu  
 =  $5000 \times 75 \times 1.66 \times 10^{-24} = 6.225 \times 10^{-19}$  gm

(iii)  $\therefore 6.022 \times 10^{23}$  molecules weighs 75 gm

$\therefore 6.022 \times 10^{20}$  molecules weighs  $\frac{75}{6.022 \times 10^{23}} \times 6.022 \times 10^{20} = 0.075$  gm

(iv)  $\therefore 75$  gm compound contains  $6.022 \times 10^{23}$  molecules

$\therefore 2.5 \times 10^{-3}$  gm will contain  $\frac{6.022 \times 10^{23}}{75} \times 2.5 \times 10^{-3} = 2.007 \times 10^{19}$  molecules.

**Ex.8** A gaseous mixture contains 40%  $H_2$  and 60% He, by volume. What is the average molecular mass of mixture ?

**Sol.**  $M_{av} = \frac{\Sigma(\% \text{ by vol.} \times \text{molecular mass})}{100} = \frac{40 \times 2 + 60 \times 4}{100} = 3.20$

### DO YOUR SELF-05

1. What is the molar mass of  $CO_2$ ,  $SO_2$ ,  $SO_3$ , urea ( $NH_2CONH_2$ ), glucose ( $C_6H_{12}O_6$ ), sucrose (cane sugar) ( $C_{12}H_{22}O_{11}$ ),  $PCl_5$ ,  $PCl_3$ ,  $Cl_2$ ,  $KClO_3$ ,  $Na_2CO_3$ ,  $NaHCO_3$ ,  $CaCO_3$  and  $CaCl_2$ .
2. What is the mass of one  $CO_2$  molecule in gm?
3. Calculate mass of 50 molecules of  $CO_2$  in gm.
4. Calculate mass of 5 molecule of  $CO_2$  in amu.
5. A gaseous mixture contains 2 moles of He and 6 moles  $H_2$  gas. What is the average molecular mass of mixture ?
6. A gases mixture contains 40%  $H_2$  and 60% He, by moles. What is the average molecular mass of mixture?

**Answers :**

1. 44 gm, 64 gm, 80 gm, 60 gm, 180 gm, 342 gm, 208.5 gm, 137.5 gm, 71 gm, 122.5 gm, 106 gm, 84 gm, 100 gm and 111 gm.
2.  $7.3 \times 10^{-23}$  gm      3.  $3.67 \times 10^{-21}$  gm      4. 220 amu
5. 2.50      6. 3.20

## 6 INTRODUCTION TO MOLE

Atoms and molecules are extremely small in size and their numbers in even a small amount of any substance is really very large. To handle such large numbers, a unit of similar magnitude is required. The 14<sup>th</sup> Geneva conference on weight and measures adopted **mole** as a *seventh basic SI unit of the amount of a substance*. Mole concept is essential tool for the fundamental study of chemical calculations. This concept is simple but its application requires a thorough practice. There are many ways of measuring the amount of substance, weight and volume being the most common, but basic unit of chemistry is the atom or a molecule and measuring the number of molecule is more important.

### 6.1 DEFINITION OF MOLE AND MOLAR MASS :

- A mole is the amount of a substance that contains as many entities (Atoms, Molecules, Ions or any other particles) as there are atoms in exactly 12 g of C-12 isotope.
- A mole of a substance contains Avogadro's number ( $6.022 \times 10^{23}$ ) of particles.  
The term mole, like a dozen or a gross, thus refers to a particular number of things. A dozen eggs equals 12 eggs, a gross of pencils equals 144 pencils, and a mole of ethanol equal  $6.022 \times 10^{23}$  ethanol molecules.
- The **molar mass** of a substance is the mass of one mole of the substance. Carbon-12 has a molar mass of exactly 12 g/mol, by definition.
- 1 g-atom = 1 mole atoms =  $N_A$  atoms
- 1 g-molecule = 1 mole molecules =  $N_A$  molecules
- 1 g-ion = 1 mole ions =  $N_A$  ions

### 6.2 Methods to calculate moles :

- (i) If number of particles (molecules or atoms) is given then,

$$\text{mole} = \frac{\text{Given number of molecule / atom}}{N_A}$$

- (ii) If mass is given then, number of mole =  $\frac{\text{Given mass of substance (in gm)}}{\text{GAM / GMM}}$

- (iii) If volume of gas is given then, mole

$$= \frac{\text{Volume of gas at STP}}{22.7 \text{ L}} = \frac{\text{Volume of gas at } 0^\circ\text{C and 1 atm}}{22.4 \text{ L}}$$

(Standard molar volume is the volume occupied by 1 mole of an ideal gas at STP (Standard temperature and pressure which is 273.15 K & 1 bar respectively), which is equal to 22.7 L).

1 mole of an ideal gas occupy 22.4 L at  $0^\circ\text{C}$  and 1 atm.

- (iv) Under any condition of temperature and pressure, moles of gases may be calculated using IDEAL GAS EQUATION :  $PV = nRT$ ,

where, R = Universal Gas Constant

$$= 0.082 \text{ L-atm/K-mol}$$

$$= 8.314 \text{ J/K-mol}$$

$$\approx 2 \text{ cal/K-mol}$$

#### Units of pressure and their relation:

$$1 \text{ atm} = 76 \text{ cm Hg}$$

$$= 760 \text{ mm Hg}$$

$$= 760 \text{ torr} \quad (1 \text{ torr} = 1 \text{ mm Hg})$$

$$= 1.01325 \times 10^6 \text{ dyne/cm}^2$$

$$= 1.01325 \times 10^5 \text{ N/m}^2 \text{ or Pa}$$

$$= 1.01325 \text{ bar} \quad (1 \text{ bar} = 10^5 \text{ Pa})$$

$$1 \text{ bar} = 75 \text{ cm Hg}$$

**Units of Volume and their relation:**

$$1 \text{ ml} = 1 \text{ cm}^3 = 1 \text{ c.c.}$$

$$1 \text{ Litre} = 1000 \text{ ml} = 1 \text{ dm}^3$$

$$1 \text{ m}^3 = 1000 \text{ L}$$

**Units of Temperature and their relation:**

$$T = 273.15 + t$$

where, T = Absolute temperature (in Kelvin) and t = temperature in °C

(Normally, we take 273K in calculation)

- (v) Sometimes gas is collected over water. In this case, the measured pressure is sum of pressure of gas and the vapour pressure of water (also called Aqueous Tension). In order to calculate moles of gas, the vapour pressure of water should be deducted from the measured pressure.

**Ex.9 Calculate the number of g-molecules (mole of molecules) in the following :**

(i) 3.2 gm  $\text{CH}_4$

(ii) 70 gm nitrogen

(iii)  $4.5 \times 10^{24}$  molecules of ozone

(iv)  $2.4 \times 10^{21}$  atoms of hydrogen

(v) 11.2 L ideal gas at  $0^\circ\text{C}$  and 1 atm

(vi) 4.54 ml  $\text{SO}_3$  gas at STP

(vii) 8.21 L  $\text{C}_2\text{H}_6$  gas at 400K and 2atm

(viii) 164.2 ml He gas at  $27^\circ\text{C}$  and 570 torr [ $N_A = 6 \times 10^{23}$ ]

**Sol.** (i) 3.2 gram  $\text{CH}_4$

$$\text{number of moles (CH}_4) = \frac{w}{M} = \frac{3.2}{16} = 0.2 \text{ moles}$$

(ii) 70 gram  $\text{N}_2$

$$\text{Number of moles} = \frac{w}{M} = \frac{70}{28} = 2.5$$

(iii)  $4.5 \times 10^{24}$  molecules of  $\text{O}_3$

$$\text{Number of moles} = \frac{\text{no. of molecules}}{N_A} = \frac{4.5 \times 10^{24}}{6 \times 10^{23}} = 7.5$$

(iv)  $2.4 \times 10^{21}$  atoms of hydrogen

$$\text{Number of gram molecules of H}_2 = \frac{\text{no. of molecules}}{N_A} = \frac{2.4 \times 10^{21}}{2 \times 6 \times 10^{23}} = 0.002$$

(v) 11.2 litre ideal gas at  $0^\circ\text{C}$  and 1 atm

$$\text{Number of moles} = \frac{\text{Volume at } 0^\circ\text{C \& 1 atm}}{22.4 \text{ litre}} = \frac{11.2}{22.4} = 0.5$$

(vi) 4.54 ml  $\text{SO}_3$  gas at STP



$$\text{Number of moles} = \frac{V_{\text{STP}}(\text{ml})}{22700\text{ml}} = \frac{4.54}{22700} = 2 \times 10^{-4}$$

(vii) 8.21 litre  $\text{C}_2\text{H}_6$  at 400 K and 2 litre

$$n = \frac{PV}{R.T} = \frac{2 \times 8.21}{0.0821 \times 400} = 0.5$$

(viii) 164.2 ml He gas at  $27^\circ\text{C}$  and 570 torr

$$n = \frac{PV}{RT} = \left( \frac{570}{760} \text{atm} \right) \times \frac{164.2 \times 10^{-3} \text{litre}}{0.0821 \times 300} = 0.005$$

**Ex.10** Find no. of protons in 180 ml  $\text{H}_2\text{O}$ . Density of water = 1 gm/ml.

**Sol.** Mass of water = density  $\times$  volume = 180 g

$$\text{Moles of water} = \frac{180}{18} = 10$$

1 mol water has 10 mol protons

$$\begin{aligned} \therefore 10 \text{ mol water has } 100 \text{ mol protons} &= 100 \times 6.022 \times 10^{23} \text{ protons} \\ &= 6.022 \times 10^{25} \text{ protons.} \end{aligned}$$

**Ex.11** What mass of  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  contains exactly  $6.022 \times 10^{22}$  atoms of oxygen ?

**Sol.** Molar mass of  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  = 275 gm.

1 mole  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  has 11 mol O-atoms.

$\Rightarrow$  11  $N_A$  O – atoms are in 275 g  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$

$$\Rightarrow 6.022 \times 10^{22} \text{ O – atoms are in } = \frac{275}{11 \times 6.022 \times 10^{23}} \times 6.022 \times 10^{22} \text{ g} = 2.5 \text{ g}$$

**Ex.12** What is number of atoms and molecules in 112 L of  $\text{O}_3(\text{g})$  at  $0^\circ\text{C}$  and 1atm ?

**Sol.** Moles of molecules =  $\frac{112}{22.4} = 5$

Moles of atoms =  $5 \times 3 = 15$

No. of molecules =  $5 N_A$

No. of atoms =  $15 N_A$ .

## DO YOUR SELF-06

- A box contains  $12 \times 10^{22}$  number of oxygen atoms. Find moles of O-atoms? ( $N_A = 6 \times 10^{23}$ )
- If a closed container contain 5 moles of  $\text{CO}_2$  gas, then find total number of  $\text{CO}_2$  molecules in the container ( $N_A = 6 \times 10^{23}$ )
- A flask of 8.2 L contains  $\text{CH}_4$  gas at a pressure of 2 atm. Find moles of  $\text{CH}_4$  gas at 400K?
- Find moles of O-atom in 5.6 litres of  $\text{SO}_3$  at  $0^\circ\text{C}$ , 1 atm?
- How many atoms are there in 5 moles of silver ( $N_A = 6 \times 10^{23}$ )
- How many moles of O-atom are there in 1 mole  $\text{CaCO}_3$
- How many moles of O-atom are in  $2.7 \times 10^{25}$  molecules of  $\text{CO}_2$  ( $N_A = 6 \times 10^{23}$ )
- Find number of O-atoms in 1 mole  $\text{O}_2$
- Find moles of Cu atom and number of Cu atoms in it's 0.635 gm ( $\text{Cu} = 63.5$ )
- Find number of molecules in 11.35 litre  $\text{SO}_2$  gas at STP.
- 2 moles of  $\text{H}_2\text{SO}_4$  is kept in a beaker. Find
  - Moles of H-atom
  - Moles of S-atom
  - Moles of O-atom
  - Number of O-atoms
- A flask contains 16 gm helium ( ${}^4_2\text{He}$ ) gas (Gram atomic mass of He = 4). Find
  - Moles of He
  - Moles of proton
  - Total number of neutrons
- 6.4 gm of  $\text{SO}_2$  will contain how many
  - Moles of  $\text{SO}_2$  molecule
  - Number of  $\text{SO}_2$  molecules

## Answers :

- |                          |                           |                                     |
|--------------------------|---------------------------|-------------------------------------|
| 1. 0.2                   | 2. $3 \times 10^{24}$     | 3. 0.5 mole                         |
| 4. 0.75 moles            | 5. $3 \times 10^{24}$     | 6. 3 mole                           |
| 7. 90                    | 8. $2N_A$                 | 9. 0.01 mole, ( $0.01 \times N_A$ ) |
| 10. ( $0.5 \times N_A$ ) | 11. (i) 4                 | (ii) 2                              |
|                          |                           | (iii) 8                             |
|                          |                           | (iv) $8N_A$                         |
| 12. (i) 4                | (ii) 8                    | (iii) $8N_A$                        |
| 13. (i) 0.1 mole         | (ii) ( $0.1 \times N_A$ ) |                                     |

**7 DENSITY :**

It is of two types.

- I. Absolute density
- II. Relative density

**7.1 For liquids and solids :**

$$\text{Absolute density} = \frac{\text{mass}}{\text{volume}}$$

$$\text{Relative density or specific gravity} = \frac{\text{density of the substance}}{\text{density of water at } 4^\circ\text{C (1 gm ml}^{-1}\text{)}}$$

**7.2 For gases :**

$$\text{Absolute density} = \frac{\text{mass}}{\text{volume}} = \frac{PM}{RT}$$

where P is pressure of gas, M = molar mass of gas, R is the gas constant, T is absolute temperature.

**Vapour Density :**

Vapour density is defined as the density of the gas with respect to hydrogen gas at the same temperature and pressure.

$$\text{Vapour density} = \frac{d_{\text{gas}}}{d_{\text{H}_2}} = \frac{PM_{\text{gas}}/RT}{PM_{\text{H}_2}/RT}$$

$$\text{V.D.} = \frac{M_{\text{gas}}}{M_{\text{H}_2}} = \frac{M_{\text{gas}}}{2} \Rightarrow \boxed{M_{\text{gas}} = 2 \times \text{V.D.}}$$

**Ex.13** A gaseous mixture of  $\text{H}_2$  and  $\text{NH}_3$  gas contains 68 mass % of  $\text{NH}_3$ . The vapour density of the mixture is –

**Sol.** No. of moles of  $\text{NH}_3$  in 100g mixture =  $\frac{68}{17} = 4$

No. of moles of  $\text{H}_2$  in 100g mixture =  $\frac{32}{2} = 16$

$$M_{\text{average}} = \frac{\text{Total mass}}{\text{Total moles}} = \frac{100}{4 + 16} = 5$$

$$\text{V D} = \frac{5}{2} = 2.5$$

**DO YOUR SELF-07**

1. Find V.D. of  $\text{SO}_3$
2. A glass contains 36 ml of liquid water (density = 1 gm/ml). Find
  - (i) Moles of  $\text{H}_2\text{O}$
  - (ii) Number of  $\text{H}_2\text{O}$  molecules
  - (iii) Number of H-atoms

**Answers :**

1. 40
2. (i) 2 mole (ii)  $2 \times N_A$  (iii)  $4 \times N_A$

## 8. STOICHIOMETRY

Stoichiometry is the calculation of amounts of reactants and products involved in a reaction. Stoichiometric calculations require a balanced chemical equation of the reaction.

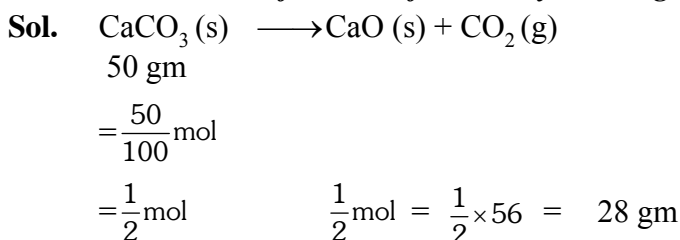
A balanced chemical equation is one which contains an equal number of atoms of each element on both sides of equation.

## 8.1 SIGNIFICANCE OF STOICHIOMETRIC COEFFICIENTS :

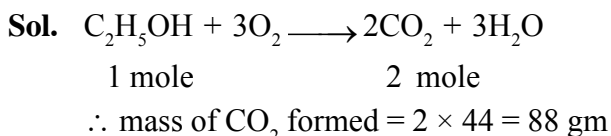
Stoichiometric coefficients of chemical equation tells us about the ratio in which moles of reactants react and moles of products form.

<b>Ex.</b>	$2\text{H}_2(\text{g})$	+	$\text{O}_2(\text{g})$	$\longrightarrow$	$2\text{H}_2\text{O}(\text{g})$
1 <sup>st</sup> interpretation	2 moles		1 mole		2 moles
2 <sup>nd</sup> interpretation	$2\text{N}_\text{A}$ molecules		$\text{N}_\text{A}$ molecules		$2\text{N}_\text{A}$ molecules
3 <sup>rd</sup> interpretation	2 molecules		1 molecules		2 molecules

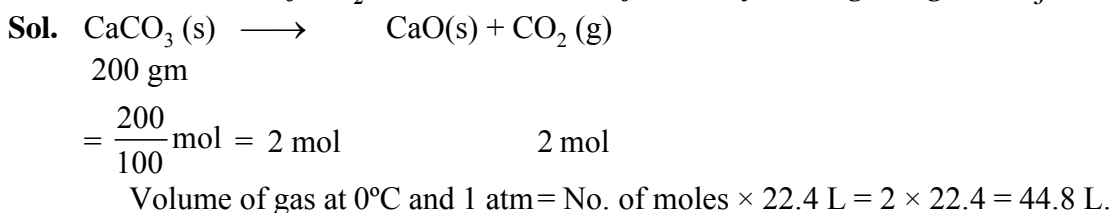
**Ex.14** What mass of CaO is formed by heating 50 g CaCO<sub>3</sub> in air ?



**Ex.15** If 1 mole of ethanol (C<sub>2</sub>H<sub>5</sub>OH) completely burns to form carbon dioxide and water, mass of carbon dioxide formed is about



**Ex.16.** What volume of CO<sub>2</sub> at 0°C and 1 atm is formed by heating 200 g CaCO<sub>3</sub> ?



## DO YOUR SELF-08

- $2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$   
Find moles of H<sub>2</sub> produced from 4 moles of NH<sub>3</sub>
- $\text{NH}_2\text{COONH}_4 \xrightarrow{\Delta} 2\text{NH}_3 + \text{CO}_2$   
If 6 moles of NH<sub>3</sub> is produced then find moles of NH<sub>2</sub>COONH<sub>4</sub> intially taken.
- $\text{KClO}_3 \rightarrow \text{KCl} + \text{O}_2$  (unbalanced) ,  
If in above reaction 5 moles of KClO<sub>3</sub> was heated, then find moles of O<sub>2</sub> produced on completion of reaction
- $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$   
If at the end of reaction , 18 mole of H<sub>2</sub> is produced then find moles of NH<sub>3</sub> initially taken

**Answers :**

1. 6                      2. (3)                      3. (7.5)                      4. (12)

□ **LIMITING REAGENT (L.R.) :**

- (i) The reactant which is completely consumed when a reaction goes to completion is called **Limiting Reactant or Limiting reagent**.  
 (ii) The reactant whose stoichiometric amount is least, is limiting reactant.

$$\text{where ; stoichiometric amount} = \frac{\text{Given moles of reactant}}{\text{Stoichiometric coefficient of reactant in balance Reaction}}$$

- (iii) When amounts of two or more than two reactants are given :



$$\text{Stoichiometric amount} \quad \frac{n_A}{a} \qquad \qquad \frac{n_B}{b}$$

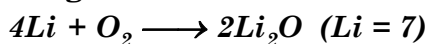
$$\text{If } \frac{n_A}{a} < \frac{n_B}{b} \quad \Rightarrow \text{A is limiting reagent.}$$

$$\text{If } \frac{n_A}{a} = \frac{n_B}{b} \text{ then reaction occurs to completion \& no reactant is left at the end.}$$

$$\text{If } \frac{n_A}{a} > \frac{n_B}{b} \quad \Rightarrow \text{B is limiting reagent.}$$

For calculation of moles of product, LR should be used.

**Ex.17. 28 gm Lithium is mixed with 48 gm O<sub>2</sub> to reacts according to the following reaction.**



**The mass of Li<sub>2</sub>O formed is**

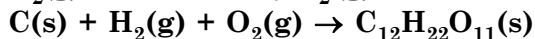
**Sol.**

	4Li	+	O <sub>2</sub>	→	2Li <sub>2</sub> O
moles taken	$\frac{28}{7}$		$\frac{48}{32}$		
	=4		=1.5		
$\frac{\text{mole taken}}{\text{stoich. coeff.}}$	$\frac{4}{4} = 1$		$\frac{1.5}{1} = 1.5$		
	(L.R.)				

$$\text{Moles of Li}_2\text{O formed} = \frac{2}{4} \times 4 = 2$$

$$\text{Mass of Li}_2\text{O formed} = 2 \times 30 = 60 \text{ gm}$$

**Ex.18 Calculate the mass of sucrose C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> (s) produced by mixing 78 g of C(s), 11 g of H<sub>2</sub>(g) & 67.2 litre of O<sub>2</sub> (g) at 0°C and 1 atm according to given reaction (unbalanced) ?**



**Sol.**

	12C(s)	+	11 H <sub>2</sub> (g)	+	$\frac{11}{2}$ O <sub>2</sub>	→	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (s)
Moles taken	$\frac{78}{12}$		$\frac{11}{2}$		$\frac{67.2}{22.4}$		
	= 6.5		= 5.5		= 3		
$\frac{\text{mole taken}}{\text{stoich. coeff.}}$	$\frac{6.5}{12}$		$\frac{5.5}{11}$		$\frac{3}{5.5}$		
	= 0.54		= 0.5		= 0.545		
			(L.R.)				

$$\therefore \text{Moles of C}_{12}\text{H}_{22}\text{O}_{11} \text{ formed} = \frac{5.5}{11} = 0.5$$

$$\text{Mass of sucrose obtained} = 0.5 \times 342 = 171 \text{ grams.}$$

## DO YOUR SELF-9

- 3 moles  $\text{N}_2(\text{g})$  is allowed to react with 6 moles of  $\text{H}_2(\text{g})$  to form  $\text{NH}_3(\text{g})$  in a close container. Find limiting reagent.
- $\text{CaCO}_3 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$   
0.2 mole  $\text{CaCO}_3$  is reacted with 0.5 moles  $\text{HCl}$ . Find mass of  $\text{CO}_2$  produced?
- Maximum mass of sucrose  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  produced by mixing 84 gm of carbon, 12 gm of hydrogen and 56 lit.  $\text{O}_2$  at 1 atm & 273 K is  
 $\text{C}(\text{s}) + \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$   
(A) 138.5                      (B) 155.5                      (C) 186.5                      (D) 199.5

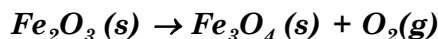
## Answers:

- ( $\text{H}_2$ )                      2. 8.80 gm                      3. (B)

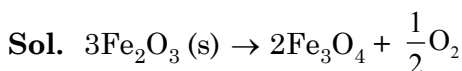
## 8.3 PROBLEMS BASED ON MIXTURE :

The composition of any mixture may be determined by reacting the mixture with some substance, by which either one or more component of mixture may react.

**Ex.19** 1.5 gm mixture of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  on very strong heating leave a residue weighing 1.46 gm. The reaction responsible for loss of weight is



What is the percentage by mass of  $\text{Fe}_2\text{O}_3$  in original sample.



$$3 \times 160 \qquad \qquad \frac{1}{2} \times 32$$

$$= 480 \text{ gm} \qquad \qquad = 16 \text{ gm}$$

$$\text{loss of 16 gm} \rightarrow 480 \text{ gm Fe}_2\text{O}_3$$

$$\text{loss of 0.04 gm} \rightarrow 0.04 \times \frac{480}{16} = 1.2 \text{ gm Fe}_2\text{O}_3$$

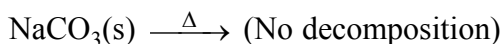
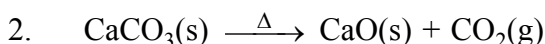
$$\% \text{ by mass} = \frac{1.2}{1.5} \times 100 = 80\%$$

## DO YOUR SELF-10

- 19 gm mixture of  $\text{Na}_2\text{CO}_3(\text{s})$  and  $\text{NaHCO}_3(\text{s})$  on heating gives 2.2 gm  $\text{CO}_2$  gas. Find %  $\text{NaHCO}_3$  (by mass) in mixture.
- Write decomposition reaction of  $\text{CaCO}_3(\text{s})$  and  $\text{Na}_2\text{CO}_3(\text{s})$  on heating.

## Answers :

- 44.21 %



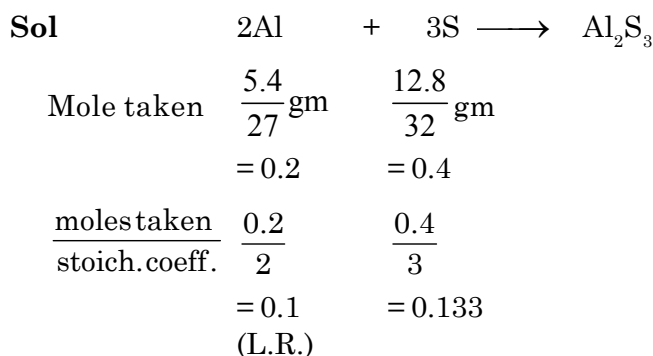
### 8.4 PERCENTAGE YIELD :

In general, when a reaction is carried out in the laboratory we do not obtain the theoretical amount of the product, in reality. The amount of the product that is actually obtained is called the **actual yield**. Knowing the actual yield and theoretical yield the percentage yield can be calculate as :

$$\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

The percentage yield of any product is always equal to the percentage extent of that reaction.

**Ex.20 Aluminium reacts with sulphur to form aluminium sulphide. If 5.4 gm of Aluminium reacts with 12.8gm sulphure gives 12gm of aluminium sulphides, then the percent yield of the reaction is. (Al = 27, S = 32)**



$$\text{moles of Al}_2\text{S}_3 \text{ formed} = \frac{1}{2} \times 0.2 = 0.1$$

$$\text{mass of Al}_2\text{S}_3 \text{ formed} = 0.1 \times 150 = 15 \text{ gm}$$

But, from equation, only 12 gm  $\text{Al}_2\text{S}_3$  is formed.

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = \frac{12}{15} \times 100 = 80 \%$$

### DO YOUR SELF-11

1. 5 moles of  $\text{CaCO}_3$  on heating yielded 2 moles of  $\text{CO}_2$ . Find % yield of reaction
2. 245 gm of  $\text{KClO}_3$  on heating yielded 64 gm  $\text{O}_2$ . Find % yield of reaction.  
(K = 39, Cl = 35.5)

**Answers :**

1. 40%
2. 66.67

### 8.5 DEGREE OF DISSOCIATION, $\alpha$ :

It represents the mole of substance dissociated per mole of the substance taken.

$$\text{A} \rightarrow n \text{ particles; } \alpha = \frac{M_0 - M}{(n - 1)M}$$

where, n = number of product particles per particle of reactant

$M_0$  = Molar mass of 'A'

M = Molar mass of final mixture

Dissociation decreases the average molar mass of system while association increases it.

Same formula is applicable for association, taking the correct value of 'n'.

**Ex.21** For the reaction  $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$

Calculate degree of dissociation ( $\alpha$ ) if observed molar mass of mixture is 13.6

**Sol.**  $M_0 = M_{\text{NH}_3} = 17$ ,  $M = 13.6$  (given),  $n = \frac{4}{2} = 2$

$$\alpha = \frac{M_0 - M}{(n-1)M} = \frac{17 - 13.6}{(2-1) \times 13.6} = 0.25$$

### DO YOUR SELF-12

- Find value of  $\alpha$  if % dissociation is 25%
- 'A' dissociate into 'B' and 'C' according reaction.



If 5 moles of 'A' is 40% dissociated, then find moles of 'A' left.

**Answers :**

- 0.25
- 3 mol

### 8.6 PERCENTAGE PURITY :

The percentage of a specified compound or element in an impure sample may be given as

$$\% \text{purity} = \frac{\text{Actual mass of pure substance}}{\text{Total mass of sample}} \times 100$$

If impurity is unknown, it is always considered as inert (unreactive) material.

**Ex.22** A chalk sample exactly requires 17.52 gram HCl for complete reaction with all  $\text{CaCO}_3$  present in it. If the chalk sample is 72% pure, the mass of sample taken is

**Sol.**  $\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$

$$\text{Moles of HCl} = \frac{17.52}{36.5}$$

$$\text{Moles of CaCO}_3 = \frac{1}{2} \times \frac{17.52}{36.5}$$

$$\text{Weight of CaCO}_3 \text{ required} = \frac{1}{2} \times \frac{17.52}{36.5} \times 100$$

Mass of sample taken :

$$= \frac{1}{2} \times \frac{17.52}{36.5} \times \frac{100 \times 100}{72} = 33.33 \text{ gm}$$



## DO YOUR SELF-13

1. A 2000 gm sample of  $\text{CaCO}_3$  is 80% pure. Find weight (in gm) of pure  $\text{CaCO}_3$
2. An impure sample (having 60% purity) of  $\text{KClO}_3$  contains 30 gm of pure  $\text{KClO}_3$ . Find weight of impure sample.
3. A 200 gm sample of  $\text{CaCO}_3$  having 40% purity is heated. Find moles of  $\text{CO}_2$  obtained.

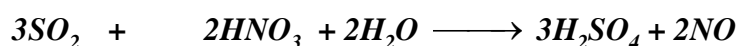
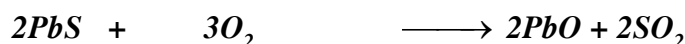
Answers :

1. 1600 gm
2. 50 gm
3. 0.8 moles

## 8.7 PROBLEMS RELATED WITH SEQUENTIAL REACTION :

When one of products formed in previous reaction is consumed in the next one.

**Ex.23** How many grams  $\text{H}_2\text{SO}_4$  can be obtained from 1320 gm  $\text{PbS}$  as per reaction sequence ?



[At. mass :  $\text{Pb} = 208$ ,  $\text{S} = 32$ ]

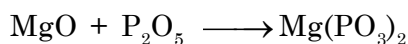
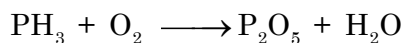
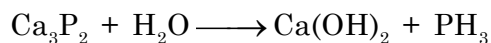
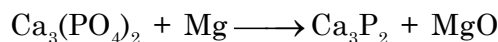
**Sol.** Moles of  $\text{PbS} = \frac{1320}{240} = 5.5 \text{ mol}$

Moles of  $\text{SO}_2 = 5.5 \text{ mol} = \text{moles of } \text{H}_2\text{SO}_4$

Mass of  $\text{H}_2\text{SO}_4 = 5.5 \times 98 = 539 \text{ gm}$

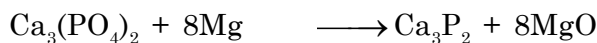
[When amount of only one reactant is given generally other is assumed in excess.]

**Ex.24** Calcium phosphide  $\text{Ca}_3\text{P}_2$  formed by reacting magnesium with excess calcium orthophosphate  $\text{Ca}_3(\text{PO}_4)_2$  was hydrolysed by excess water. The evolved phosphine  $\text{PH}_3$  was burnt in air to yield phosphorous pentoxide ( $\text{P}_2\text{O}_5$ ). How many gram of magnesium metaphosphate would be obtain if 192 gram  $\text{Mg}$  were used (Atomic weight of  $\text{Mg} = 24$ ,  $\text{P} = 31$ )

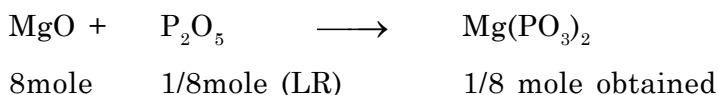
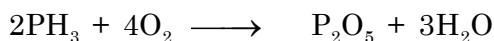
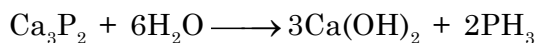


magnesium metaphosphate.

**Sol.** Balanced chemical reaction :

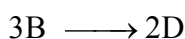
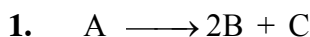


excess  $\frac{192}{24} = 8 \text{ mole}$   $\frac{1}{8} \text{ mole}$  8mole

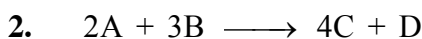


$$W_{\text{Mg}(\text{PO}_3)_2} = 1/8 \times 182 = 22.75 \text{ Mg}$$

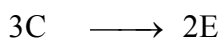
### DO YOUR SELF-14



Find moles of D produced if initially 3 moles of A are taken -



(excess)



If in the above reaction 6 moles of E are produced, find moles of 'A' initially taken.

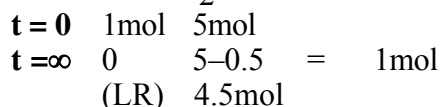
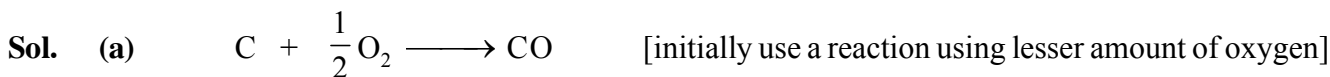
Answers :

1. (4)                      2. (4.5 mole)

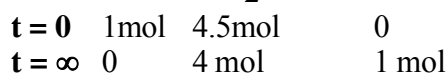
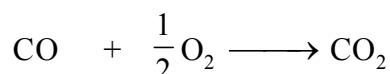
### 8.8 PROBLEM RELATED WITH PARALLEL REACTION :

When same two reactants form two or more products by independent reactions.

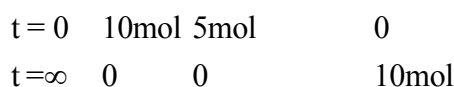
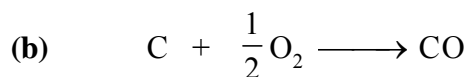
**Ex.25** Carbon reacts with oxygen forming carbon monoxide and/or carbon dioxide depending on availability of oxygen. Find moles of each product obtained when 160 gm oxygen reacts with (a) 12 g carbon (b) 120 g carbon (c) 72 g carbon.



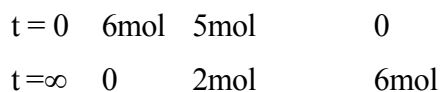
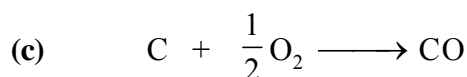
Since CO & O<sub>2</sub> are left, CO<sub>2</sub> will also formed.



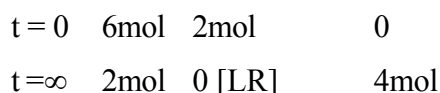
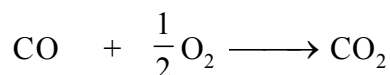
At end, 1 mole CO<sub>2</sub> & no CO present



At end only 10 mol CO present.



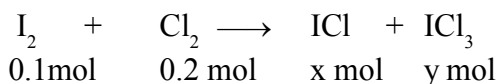
[LR]



At end [2mol CO + 4mol CO<sub>2</sub>] left.

**Ex.26** 25.4 gm of iodine and 14.2 gm of chlorine are made to react completely to yield mixture of ICl and ICl<sub>3</sub>. Ratio of moles of ICl & ICl<sub>3</sub> formed is (Atomic mass : I = 127, Cl = 35.5)

**Sol.**



Applying conservations of I and Cl -atom

$$0.2 = x + y \quad \Rightarrow \quad x = 0.1$$

$$0.4 = x + 3y \quad \Rightarrow \quad y = 0.1$$

$$\therefore n_{ICl} : n_{ICl_3} = x : y = 1 : 1$$

### DO YOUR SELF-15

1. 2 moles carbon and 1.5 moles of oxygen gas are reacted in a container to produce CO or CO<sub>2</sub> or both. Find moles of CO, CO<sub>2</sub> produced.

**Answer :**

1. CO = 1 mole, CO<sub>2</sub> = 1 mole

### 8.9 PRINCIPLE OF ATOM CONSERVATION (POAC)

POAC is nothing but the conservation of atoms of reactants and products involved in a chemical reaction. And if atoms are conserved, moles of atoms shall also be conserved. The principle is fruitful for the students when they don't get the idea of balanced chemical equation. In the problem using POAC we do not need to balance a reaction and we can even add two or more reactions. This principle can be understood by the following example.

**Consider the decomposition of KClO<sub>3</sub> (s) → KCl (s) + O<sub>2</sub> (g) (unbalanced chemical reaction)**

Apply the principle of atom conservation (POAC) for K atoms.

or moles of K atoms in KClO<sub>3</sub> = moles of K atoms in KCl

Now, since 1 molecule of KClO<sub>3</sub> contains 1 atom of K

Thus, moles of K atoms in KClO<sub>3</sub> = 1 × moles of KClO<sub>3</sub>

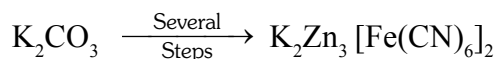
and moles of K atoms in KCl = 1 × moles of KCl

$$\therefore \text{moles of KClO}_3 = \text{moles of KCl} \quad \text{or} \quad \frac{\text{wt. of KClO}_3 \text{ in g}}{\text{mol. wt. of KClO}_3} = \frac{\text{wt. of KCl in g}}{\text{mol. wt. of KCl}}$$

- The above equation gives the mass-mass relationship between  $\text{KClO}_3$  and  $\text{KCl}$  which is important in stoichiometric calculations. Again, applying the principle of atom conservation for O atoms,  
 moles of O in  $\text{KClO}_3 = 3 \times \text{moles of KClO}_3$   
 moles of O in  $\text{O}_2 = 2 \times \text{moles of O}_2$   
 $\therefore 3 \times \text{moles of KClO}_3 = 2 \times \text{moles of O}_2$   
 or  $3 \times \frac{\text{wt. of KClO}_3}{\text{mol. wt. of KClO}_3} = 2 \times \frac{\text{vol. of O}_2 \text{ at 1atm and } 0^\circ\text{C}}{\text{Molar vol. (22.4lt)}}$
- The above equations thus gives the mass-volume relationship of reactants and products.

**Ex.27** 27.6 g  $\text{K}_2\text{CO}_3$  was treated by a series of reagents so as to convert all of its carbon to  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ . Calculate the weight of the product. [mol. wt. of  $\text{K}_2\text{CO}_3 = 138$  and mol. wt. of  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 = 698$ ]

**Sol.** Here we have no knowledge about series of chemical reactions but we know about initial reactant and final product, accordingly.



Since C atoms are conserved, applying POAC for C atoms,

$$\text{moles of C in K}_2\text{CO}_3 = \text{moles of C in K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$$

$$1 \times \text{moles of K}_2\text{CO}_3 = 12 \times \text{moles of K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$$

$$\frac{\text{wt. of K}_2\text{CO}_3}{\text{mol. wt. of K}_2\text{CO}_3} = 12 \times \frac{\text{wt. of the product}}{\text{mol. wt. of product}}$$

$$\text{wt. of K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 = \frac{27.6}{138} \times \frac{698}{12} = 11.6 \text{ g}$$

### DO YOUR SELF-16

- 3 moles of  $\text{S}_8$  was treated by a series of reagents so as to convert all of its S to  $\text{H}_2\text{SO}_4$ . Calculate weight of product.

**Answers :**

- 2352 gm.

### 9. PERCENTAGE COMPOSITION OF ANY ELEMENT IN ANY COMPOUND :

Percentage of particular element present in a compound given as ,

Mass % of an element

$$= \frac{\text{mass of that element in the compound}}{\text{molar mass of the compound}} \times 100$$

$$= \frac{\text{no. of atoms of that element} \times \text{Atomic mass}}{\text{molar mass of the compound}} \times 100$$

Let us understand it by taking the example of water ( $\text{H}_2\text{O}$ ). Since water contains hydrogen and oxygen, the percentage composition of both these elements can be calculated as follows :

$$\text{Mass \% of an element} = \frac{\text{mass of that element in the compound} \times 100}{\text{molar mass of the compound}}$$

$$\text{Molar mass of water} = 18 \text{ g}$$

$$\text{Mass \% of hydrogen} = \frac{2 \times 1}{18} \times 100 = 11.11$$

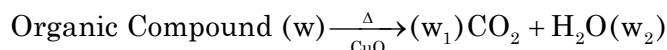
$$\text{Mass \% of oxygen} = \frac{16}{18} \times 100 = 88.89$$

### 9.1 PERCENTAGE DETERMINATION OF ELEMENTS IN ORGANIC COMPOUNDS :

All these methods are applications of POAC

Do not remember the formulae, derive them using the concept, its easy.

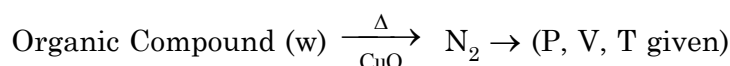
(a) **Liebig's method** : (for Carbon and hydrogen)



$$\% \text{ of C} = \frac{w_1}{44} \times \frac{12}{w} \times 100$$

$$\% \text{ of H} = \frac{w_2}{18} \times \frac{2}{w} \times 100$$

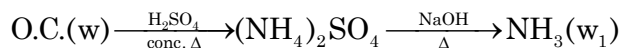
(b) **Duma's method** : (for nitrogen)



use  $PV = nRT$  to calculate moles of  $\text{N}_2$ ,  $n$ .

$$\therefore \% \text{ of N} = \frac{n \times 28}{w} \times 100$$

(c) **Kjeldahl's method** : (for nitrogen)



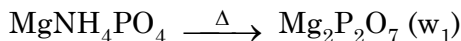
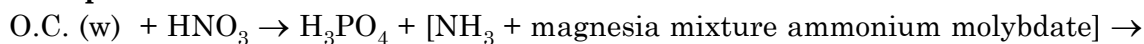
$$\% \text{ of N} = \frac{14}{17} \times \frac{w_1}{w} \times 100$$

(d) **Sulphur** :



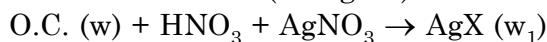
$$\Rightarrow \% \text{ of S} = \frac{w_1}{233} \times \frac{1 \times 32}{w} \times 100.$$

(e) **Phosphorus** :



$$\% \text{ of P} = \frac{w_1}{222} \times \frac{2 \times 31}{w} \times 100$$

(f) **Carius method** : (Halogens)



If X is Cl then colour = curdy white

If X is Br then colour = dull yellow

If X is I then colour = bright yellow

Flourine can't be estimated by this

$$\% \text{ of X} = \frac{w_1}{(\text{M. weight of AgX})} \times \frac{1 \times (\text{At. wt. of X})}{w} \times 100$$

**Ex.28** In which of the following has same % composition of C,  
HCHO, CH<sub>3</sub>COOH, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, CH<sub>3</sub>COCH<sub>3</sub>

**Sol.** HCHO, CH<sub>3</sub>COOH, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>

$$\% \text{ C(HCHO)} = \frac{1 \times 12}{30} \times 100 = 40\%$$

$$\% \text{ C(CH}_3\text{COOH)} = \frac{2 \times 12}{60} \times 100 = 40\%$$

$$\% \text{ C(C}_6\text{H}_{12}\text{O}_6) = \frac{6 \times 12}{180} \times 100 = 40\%$$

$$\% \text{ C(CH}_3\text{COCH}_3) = \frac{3 \times 12}{58} \times 100 = 62.07\%$$

**Ex.29** A sample of 0.5 gm of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed by 2.45 gm of H<sub>2</sub>SO<sub>4</sub>. The residual acid required solution containing 1.2 gm. NaOH for neutralisation. Find the percentage composition of nitrogen in the compound ?

**Sol.**  $2 \text{ NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2 \text{SO}_4$   
 $\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$

$$\text{Moles of H}_2\text{SO}_4 \text{ taken} = \frac{2.45}{98} = 0.025$$

$$\text{Moles of NaOH} = \frac{1.2}{40} = 0.03$$

$$\therefore \text{Moles of H}_2\text{SO}_4 \text{ reacted with NaOH} = \frac{0.03}{2} = 0.015$$

$$\text{Remaining mol of H}_2\text{SO}_4 = 0.025 - 0.015 = 0.01$$

$$\text{mol of NH}_3 \text{ evolved} = 0.01 \times 2 = 0.02$$

$$\% \text{ N in sample} = \frac{0.02 \times 14}{0.5} \times 100 = 56\%$$

### DO YOUR SELF-17

- Find % oxygen in C<sub>2</sub>H<sub>5</sub>OH
- Calculate the molar mass of a compound in the Dumas method at 100°C for which volume of experimental container was 452 ml and the pressure was 745.1 torr. The difference in mass between the empty container and the final measurement was 1.129 gm.

**Answers :**

- 34.78%
- 78.0 gm/mol .

## 10. EMPIRICAL AND MOLECULAR FORMULA

We have just seen that knowing the molecular formula of the compound we can calculate percentage composition of the elements. Conversely if we know the percentage composition of the elements initially, we can calculate the relative number of atoms of each element in the molecules of the compound. This gives us the empirical formula of the compound. Further if the molecular mass is known then the molecular formula can be easily determined.

Thus, the **empirical** formula of a compound is a chemical formula showing the relative number of atoms in the simplest ratio, the **molecular formula** gives the actual number of atoms of each element in a molecule.

i.e. **Empirical formula** : Formula depicting constituent atoms in their simplest ratio.

**Molecular formula** : Formula depicting actual number of atoms in one molecule of the compound.

The molecular formula is generally an integral multiple of the empirical formula.

i.e.  $\text{molecular formula} = \text{empirical formula} \times n$

where  $n = \frac{\text{molecular formula mass}}{\text{empirical formula mass}}$

**Example :**

Molecular Formula	$\text{H}_2\text{O}_2$	$\text{C}_6\text{H}_6$	$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_4\text{O}_2$
	2 : 2	6 : 6	2 : 6	2 : 4 : 2
Simplest ratio	1 : 1	1 : 1	1 : 3	1 : 2 : 1
Empirical Formula	H O	C H	$\text{CH}_3$	$\text{CH}_2\text{O}$

### 10.1 DETERMINATION OF EMPIRICAL FORMULA :

Following steps are involved in determining the empirical formula of the compounds –

- First of all find the % by wt. of each element present in the compound.
- The % by wt of each element is divided by its atomic weight. It gives atomic ratio of elements present in the compounds.
- Atomic ratio of each element is divided by the minimum value of atomic ratio so as to get simplest ratio of atoms.
- If the value of simplest atomic ratio is fractional then raise the value to the nearest whole number or multiply with suitable coefficient to convert it into nearest whole number
- Write the Empirical formula as we get the simplest ratio of atoms.

### 10.2 DETERMINATION OF MOLECULAR FORMULA :

- Find out the empirical formula mass by adding the atomic masses of all the atoms present in the empirical formula of compound.
- Divide the molecular mass (determined experimentally by some suitable method) by the empirical formula mass and find out the value of  $n$ .
- Multiply the empirical formula of the compound with ' $n$ ' so as to find out the molecular formula of the compound.

**Ex.30.** An organic compound contains 49.3% carbon, 6.84% hydrogen and its vapour density is 73. Molecular formula of compound is :-

**Sol.** V.D. = 73  $\Rightarrow$  M = 2  $\times$  73 = 146

$$C = 146 \times \frac{49.3}{100} = 71.978 \text{ g} = \frac{71.978}{12} \approx 6 \text{ mole}$$

$$H = 146 \times \frac{6.84}{100} = 9.9864 \text{ g} = \frac{9.9864}{1} \approx 10 \text{ mole}$$

$$O = 146 \times \frac{100 - (49.3 + 6.84)}{100} = \frac{64.86}{16} = 4.05375 \approx 4 \text{ mol}$$

$$\text{M.F.} = \text{C}_6\text{H}_{10}\text{O}_4$$

**Ex.31** The empirical formula of an organic compound containing carbon & hydrogen is  $\text{CH}_2$ . The mass of 1 litre of organic gas is exactly equal to mass of 1 litre  $\text{N}_2$  therefore molecular formula of organic gas is.

**Sol.** Empirical Mass of  $\text{CH}_2 = 12 + 2 = 14$

$\therefore$  Mass of 1 litre of organic gas = Mass of 1 litre of  $\text{N}_2$

Since V, P, T, n are same.

Therefore from  $PV = \frac{m}{M}RT$  implies that molar mass should also be same.

$\therefore$  Molecular mass of organic compound will be 28 g

$$n = \frac{\text{Molecular mass}}{\text{Empirical mass}} = \frac{28}{14} = 2$$

So molecular formula = 2  $\times$   $\text{CH}_2 = \text{C}_2\text{H}_4$

### DO YOUR SELF-18

- In which of following has same empirical formula -  
 $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_6\text{H}_6$
- Determine the empirical formula of an oxide of iron, which has 70% Fe and 30% 'O' by mass. (Fe = 56)

**Answers :**

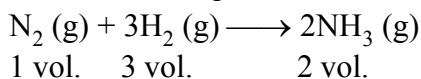
- $\text{C}_2\text{H}_2$ ,  $\text{C}_6\text{H}_6$ ,
- $\text{Fe}_2\text{O}_3$



**11. EUDIOMETRY :**

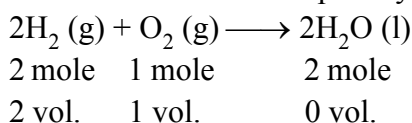
Eudiometry or gas analysis involves the calculations based on gaseous reactions or the reactions in which at least two components are gaseous, in which the amounts of gases are represented by their volumes, measured at the same pressure and temperature. Some basic assumptions related with calculations are:

- (i) Gay-Lussac's law of volume combination holds good. According to this law, the volumes of gaseous reactants reacted and the volumes of gaseous products formed, all measured at the same temperature and pressure, bear a simple ratio.



Problem may be solved directly in terms of volume, in place of mole. The stoichiometric coefficients of a balanced chemical reactions gives the ratio of volumes in which gaseous substances are reacting and products are formed, at same temperature and pressure.

- (ii) The volumes of solids or liquids is considered to be negligible in comparison to the volume of gas. It is due to the fact that the volume occupied by any substance in gaseous state is even more than thousand times the volume occupied by the same substance in solid or liquid states.



- (iii) Air is considered as a mixture of oxygen and nitrogen gases only. It is due to the fact that about 99% volume of air is composed of oxygen and nitrogen gases only.
- (iv) Nitrogen gas is considered as a non- reactive gas. It is due to the fact that nitrogen gas reacts only at very high temperature due to its very high thermal stability. Eudiometry is performed in an eudiometer tube and the tube can not withstand very high temperature. This is why, nitrogen gas can not participate in the reactions occurring in the eudiometer tube.
- (v) The total volume of non-reacting gaseous mixture is equal to sum of partial volumes of the component gases (**Amagat's law**).

$$V = V_1 + V_2 + \dots$$

Partial volume of gas in a non-reacting gaseous mixture is its volume when the entire pressure of the mixture is supposed to be exerted only by that gas.

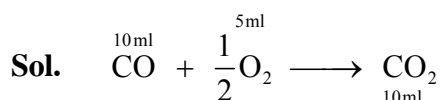
- (vi) The volume of gases produced is often given by certain solvent which absorb contain gases.

<b>Solvent</b>	<b>Gases absorb</b>
KOH	CO <sub>2</sub> , SO <sub>2</sub> , Cl <sub>2</sub>
Ammonical Cu <sub>2</sub> Cl <sub>2</sub>	CO
Turpentine oil	O <sub>3</sub>
Alkaline pyrogallol	O <sub>2</sub>
water	NH <sub>3</sub> , HCl
CuSO <sub>4</sub> /CaCl <sub>2</sub>	H <sub>2</sub> O

**(vii) EUDIOMETER**

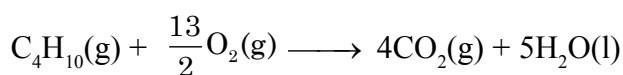
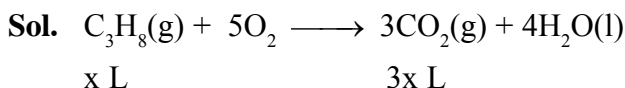
An eudiometer is a laboratory device that measures the change in volume of a gas mixture following a physical or chemical change.

**Ex.32** 10 ml of CO is mixed with 25 ml air (20% O<sub>2</sub> by volume). Find final volume (in ml) after complete combustion.



$$V_f = V_{\text{CO}_2} + \text{Volume of remaining air} = 10 + 20 = 30 \text{ ml}$$

**Ex.33** A 3 L gas mixture of propane (C<sub>3</sub>H<sub>8</sub>) and butane (C<sub>4</sub>H<sub>10</sub>) on complete combustion at 25°C produced 10 L CO<sub>2</sub>. Assuming constant P and T conditions what was volume of butane present in initial mixture ?

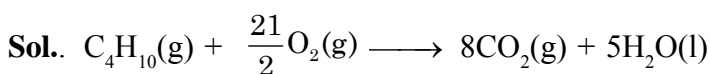


$$\text{from question } 3x + 4(3-x) = 10 \Rightarrow x = 2$$

$$\therefore \text{Volume of butane, C}_4\text{H}_{10} = (3-x) = 1 \text{ L}$$

**Ex.34** 100 ml gaseous meta Xylene  undergoes combustion with excess of oxygen at

room temperature and pressure. Volume contraction / expansion (in ml) during reaction is

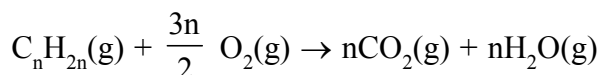


$$\begin{array}{ccccccc} 100 \text{ ml} & \frac{21}{2} \times 100 & & 800 \text{ ml} & & & 0 \\ & = 1050 \text{ ml} & & & & & \end{array}$$

$$\therefore \text{Contraction in volume} = (100 + 1050) - 800 = 350 \text{ ml}$$

**Ex.35** An alkene upon combustion produces CO<sub>2</sub>(g) and H<sub>2</sub>O(g). In this combustion process if there is no volume change occurs then the no. of C atoms per molecule of alkene will be :

**Ans.(2)**

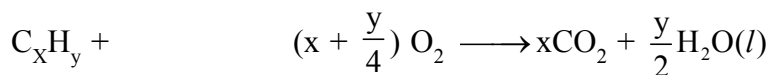


if there no volume changes i.e.  $\Delta_{\text{ng}} = 0$

$$(n+n) - \left(1 + \frac{3n}{2}\right) = 0 \Rightarrow n = 2$$

**Ex.36** A gaseous hydrocarbon ( $C_xH_y$ ) requires 6 times of its own volume of  $O_2$  for complete oxidation and produces 4 times of its volume of  $CO_2$ . Find out the volume of  $x + y$ .

**Ans. (012)**



$$a \qquad a\left(x + \frac{y}{4}\right) \qquad ax$$

$$\text{Given that : } a(x + y/4) = 6a$$

$$\text{and } ax = 4(a)$$

$$x = 4 \text{ and } y = 8 \qquad \dots(2)$$

$$\therefore x + y = 4 + 8 = 12$$

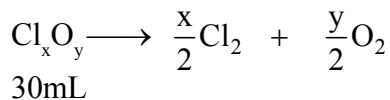
**Ex.37** On heating 60 ml mixture containing equal volume of chlorine gas and its gaseous oxide, volume becomes 75 ml due complete decomposition of oxide. On treatment with KOH volume becomes 15 ml. What is the formula of oxide of chlorine ?

**Ans.  $Cl_2O$**

**Sol.** Let oxide of Cl is  $Cl_xO_y$

So in 60 mL  $\Rightarrow$  30 mL  $Cl_xO_y$  and 30 mL  $Cl_2$ .

Now,



30mL

$$\frac{30 \cdot x}{2} \text{ mL} \qquad \frac{30 \cdot y}{2} \text{ mL}$$

Given :

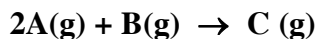
$$75 = 30 + \frac{30x}{2} + \frac{30y}{2} \qquad \Rightarrow \qquad x + y = 3 \dots\dots\dots(i)$$

KOH absorbs  $Cl_2$  and volume becomes 15 mL so,

$$(75 - 15) = V_{Cl_2} = 30 + \frac{30x}{2} \qquad \Rightarrow \qquad x = 2 \text{ and } y = 1$$

So the oxide :  $Cl_2O$

**Ex.38** 5 L of A (g) & 3 L of B(g) measured at same T & P are mixed together which react as follows



What will be the total volume (in litre) after the completion of the reaction at same T & P.

**Ans. (3)**

**Sol.**  $2A(g) + B(g) \longrightarrow C(g)$

5L      3L

L.R. is A

$$\text{So, volume of C produced} = \frac{1}{2} \times 5 = 2.5 \text{ L}$$

$$\text{and, volume of B reacted} = \frac{1}{2} \times 5 = 2.5 \text{ L}$$

$$\text{So, volume fo B remained} = 3 - 2.5 = 0.5 \text{ L}$$

$$\text{Hence, } V_{\text{total}} = V_C + V_B = 2.5 + 0.5 = 3 \text{ L}$$

## DO YOUR SELF-19

- KOH solvent can absorb in which of following gas.  
(A)  $\text{Cl}_2$  (B)  $\text{SO}_2$  (C)  $\text{CO}_2$  (D)  $\text{H}_2$
- $\text{O}_2$  gas can be absorb by  
(A) Turpentine oil (B) Alkaline pyragallol solution  
(C) KOH solvent (D) Ammonical  $\text{Cu}_2 \text{Cl}_2$  solution
- How much volume in ml of  $\text{CO}_2$  gas obtain at root temperature after complete combustion of 16 ml  $\text{CH}_4$  gas.
- Write and balance the combustion reactions of following hydrocarbons.  
(i)  $\text{CH}_4$  (ii)  $\text{C}_2\text{H}_4$  (iii)  $\text{C}_3\text{H}_8$  (iv)  $\text{C}_4\text{H}_8$   
(iv)  $\text{C}_2\text{H}_2$  (iv)  $\text{C}_2\text{H}_5 \text{OH}$
- Complete the following table related to combustion of hydrocarbon in Eudiometer tube. (All volume measurements are done at room temperature and pressure.)

Volume of hydro carbon	Volume of oxygen ( $\text{O}_2$ )	Initial volume( $V_i$ ) of gases	Final volume( $V_f$ ) of gases	Volume contraction
10 ml $\text{CH}_4$	20 ml $\text{O}_2$			
30 ml $\text{C}_2\text{H}_4$	90 ml $\text{O}_2$			
30 ml $\text{C}_2\text{H}_4$	100 ml $\text{O}_2$			
50 ml $\text{C}_3\text{H}_8$	300 ml $\text{O}_2$			
20 ml $\text{C}_2\text{H}_5\text{OH}$	80 ml $\text{O}_2$			

## Answers :

- (A,B,C)
- (B)
- (16 ml)
- (i)  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$   
(ii)  $\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$   
(iii)  $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$   
(iv)  $\text{C}_4\text{H}_8 + 6\text{O}_2 \rightarrow 4\text{CO}_2 + 4\text{H}_2\text{O}$   
  
(iv)  $\text{C}_2\text{H}_2 + \frac{5}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + \text{H}_2\text{O}$   
  
(iv)  $\text{C}_2\text{H}_5 \text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
- Ans.

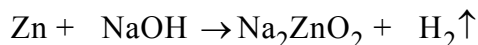
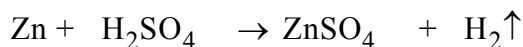
Volume of hydro carbon	Volume of oxygen ( $\text{O}_2$ )	Initial volume( $V_i$ ) of gases	Final volume( $V_f$ ) of gases	Volume contraction
10 ml $\text{CH}_4$	20 ml $\text{O}_2$	30 ml	10 ml	20 ml
30 ml $\text{C}_2\text{H}_4$	90 ml $\text{O}_2$	120 ml	60 ml	60 ml
30 ml $\text{C}_2\text{H}_4$	100 ml $\text{O}_2$	130 ml	70 ml	60 ml
50 ml $\text{C}_3\text{H}_8$	300 ml $\text{O}_2$	350 ml	200 ml	150 ml
20 ml $\text{C}_2\text{H}_5\text{OH}$	80 ml $\text{O}_2$	100 ml	60 ml	40 ml

## SOLVED EXAMPLES

**Ex.1** When the same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volume of hydrogen evolved is. **[JEE-1979]**

- (A) 1 : 1                      (B) 1 : 2                      (C) 2 : 1                      (D) 9 : 4

**Ans. (A)**



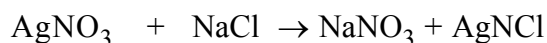
**Ex.2** If 0.50 mole of  $\text{BaCl}_2$  is mixed with 0.20 mol of  $\text{Na}_3\text{PO}_4$ , the maximum number of moles of  $\text{Ba}_3(\text{PO}_4)_2$  that can be formed is - **[JEE-1981]**

- (A) 0.70                      (B) 0.50                      (C) 0.20                      (D) 0.10

**Ans.(D)**

**Ex.3** What weight of  $\text{AgCl}$  will be precipitated when a solution containing 4.77 g of  $\text{NaCl}$  is added to a solution of 5.77 g of  $\text{AgNO}_3$ . ( $\text{Ag} = 108$ )

**Ans. (4.879 gm)**



$$5.77 \text{ gm} \quad 4.77 \text{ gm}$$

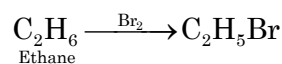
$$0.034 \text{ mole (LR)} \quad 0.082 \text{ mole}$$

$$\text{wt. of AgCl} = 0.034 \times 143.5 = 4.879 \text{ gm}$$

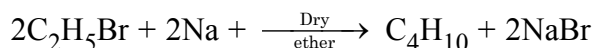
**Ex.4** n-butane is product by the monobromination of ethane followed by the Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55g n-butane, if the bromination takes place with 90% yield and the Wurtz reaction with 85% yield. **[JEE-1984]**

**Ans. (55.50 litre)**

(i) Monobromination of ethane



(ii) Wurtz reaction :



Molecular weight of

$$\text{C}_4\text{H}_{10} = (12 \times 4) + (10 \times 1) = 58$$

$$\therefore \text{Amount of n-butane to be produced} = \frac{55}{58} \text{ mol} = 0.948 \text{ mol}$$

$$\therefore \text{Amount of C}_2\text{H}_5\text{Br required to obtain 0.948 mol}$$

But the conversion is only 85%

$$\text{Hence, the amount of C}_2\text{H}_5\text{Br required} = \frac{1.896}{85} \times 100 = 2.23 \text{ mol}$$

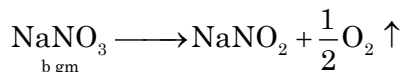
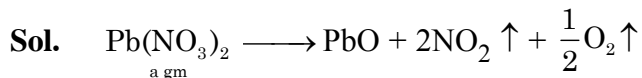
To obtain  $\text{C}_2\text{H}_5\text{Br}$  from  $\text{C}_2\text{H}_6$ , the same amount of  $\text{C}_2\text{H}_6$  would be required. But the percent

$$\text{conversion of C}_2\text{H}_6 \text{ to required} = \frac{2.23}{90} \times 100 = 2.478 \text{ mol.}$$

Thus , required volume of ethane of NTP =  $22400 \times 2.478 = 55507.2 \text{ ml} = 55.50 \text{ L.}$

**Ex.5** A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the weight of the residue was constant. If the loss in weight is 20% find the amount of lead nitrate and sodium nitrate in the mixture. [JEE-1990]

**Ans.**  $\text{Pb}(\text{NO}_3)_2 = 3.32 \text{ gm}$ ,  $\text{NaNO}_3 = 1.68 \text{ gm}$



$\therefore a + b = 5 \quad \dots (1)$

The loss in weight for 5 g mixture =  $5 \times \frac{28}{100} = 1.4 \text{ g}$

$\therefore$  Residue left =  $5 - 1.4 = 3.6 \text{ g}$

The residue contain  $\text{PbO} + \text{NaNO}_2$

$\therefore 331 \text{ g Pb}(\text{NO}_3)_2 \text{ gives} = 223 \text{ g PbO}$

$\therefore a \text{ g Pb}(\text{NO}_3)_2 \text{ gives} = \frac{223 \times a}{332} \text{ g PbO}$

Similarly,

$\therefore 85 \text{ g NaNO}_3 \text{ gives} = 69 \text{ g NaNO}_2$

$\therefore b \text{ g NaNO}_3 \text{ gives} = \frac{69 \times b}{85} \text{ g NaNO}_2$

Solving equation, (1) and (2)

$a = 3.32 \text{ g}$  and  $b = 1.68 \text{ g}$

**Ex.6** The weight of  $2.01 \times 10^{23}$  molecules of CO is-

[AIEEE 2002]

- (1) 9.3 g                      (2) 7.2 g                      (3) 1.2 g                      (4) 3 g

**Ans. (1)**

**Sol.** Mass =  $\frac{2.01 \times 10^{23}}{6.02 \times 10^{23}} \times 28 = 9.3 \text{ gm}$

**Ex.7** In an organic compound of molar mass  $108 \text{ g mol}^{-1}$  C, H and N atoms are present in 9 : 1 : 3.5 by weight. Molecular formula can be : [AIEEE 2002]

- (1)  $\text{C}_6\text{H}_8\text{N}_2$                       (2)  $\text{C}_7\text{H}_{10}\text{N}$                       (3)  $\text{C}_5\text{H}_6\text{N}_3$                       (4)  $\text{C}_4\text{H}_{18}\text{N}_3$

**Ans. (1)**

**Sol.**

	C	H	N
	9	1	3.5
Mole	$\frac{9}{12}$	$\frac{1}{1}$	$\frac{3.5}{14}$
	0.75	1	0.25
	$\text{C}_3 \text{H}_4 \text{N} = \text{emp. formula}$		
	mol. formula = $\text{C}_6\text{H}_8\text{N}_2$		

**Ex.8** How many moles of magnesium phosphate,  $\text{Mg}_3(\text{PO}_4)_2$  will contain 0.25 mole of oxygen atoms?

[AIEEE 2006]

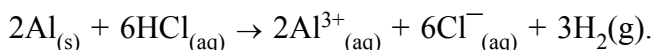
- (1)  $3.125 \times 10^{-2}$       (2)  $1.25 \times 10^{-2}$       (3)  $2.5 \times 10^{-2}$       (4) 0.02

**Ans. (1)**

**Sol.**  $x \times 8 = 0.25 \Rightarrow x = 3.125 \times 10^{-2}$

**Ex.9** In the reaction

[AIEEE-2007]

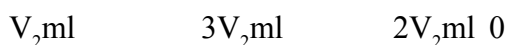
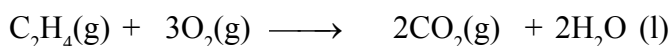
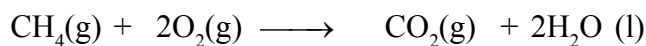


Select the correct information(s)

- (1) 6L  $\text{HCl}_{(aq)}$  is consumed for every 3L  $\text{H}_2(\text{g})$  produced  
 (2) 33.6 L  $\text{H}_2(\text{g})$  is produced regardless of temperature and pressure for every mole of Al that reacts  
 (3) 67.2 L  $\text{H}_2(\text{g})$  at STP is produced for every mole of Al that reacts  
 (4) 11.2 L  $\text{H}_2(\text{g})$  at STP is produced for every mole of of  $\text{HCl}_{(aq)}$  consumed

**Ans.(4)**

**Ex.10** 30 ml gaseous mixture of methane and ethylene in volume ratio X : Y requires 350 ml air containing 20% of  $\text{O}_2$  by volume for complete combustion. If ratio of methane and ethylene changed to Y : X. What will be volume of air (in ml) required for complete reaction under similar condition of temperature and pressure.



For given data :  $V_1 + V_2 = 30$

$$\text{and } 2V_1 + 3V_2 = 350 \times \frac{20}{100} = 70$$

$$\therefore V_1 = 20, V_2 = 10$$

For required data :  $V_1 = 10$  and  $V_2 = 20$

$$\therefore \text{Volume of } \text{O}_2 \text{ required} = 2V_1 + 3V_2 = 80 \text{ ml and volume of air required} = 80 = \frac{100}{20} = 400 \text{ml}$$

**Ex.11** 5 ml of gas containing only carbon and hydrogen was mixed with an excess of oxygen (30 ml) and the mixture exploded by means of an electric spark. After the explosion, the volume of the mixed gases remaining was 25 ml. On adding a concentrated solution of potassium hydroxide, the volume further diminished to 15 ml the residual gas being pure oxygen. All volumes have been reduced to NTP. Calculate the molecular formula of the hydrocarbon. [JEE-1979]

**Ans. ( $\text{C}_2\text{H}_4$ )**

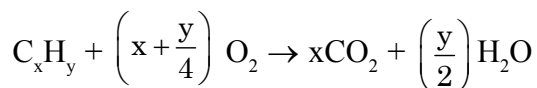
**Sol.** Volume of oxygen taken = 30 ml

Volume of unused oxygen = 15 ml

Volume of  $\text{O}_2$  used = Volume of  $\text{O}_2$  added - volume of  $\text{O}_2$  left =  $30 - 15 = 15$  ml.

and volume of  $\text{CO}_2$  produced =  $25 - 15 = 10$  ml

General equation of the combustion of a hydrocarbon is as following lows.



$$5 \text{ ml } 5\left(x + \frac{y}{2}\right) \text{ ml } \quad 5x$$

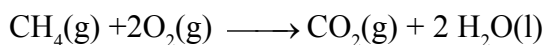
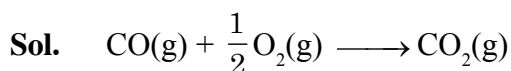
$$\therefore 5x = 10 \Rightarrow x = 2$$

$$\text{and } 5\left(x + \frac{y}{2}\right) = 15$$

$\therefore$  Molecular formula of hydrocarbon =  $\text{C}_2\text{H}_4$

**Ex.12** A 20.0 ml mixture of  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{He}$  gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be  $13.0 \text{ cm}^3$ . A further contraction of  $14.0 \text{ cm}^3$  occurs when the residual gas is treated with  $\text{KOH}$  solution. Find out the composition of the gaseous mixture in terms of volume percentage. **[JEE-1995]**

**Ans.** (%  $\text{CH}_4 = 20$ , %  $\text{CO} = 50$ , %  $\text{He} = 30$  )



'x' is the volume of  $\text{CO}$  and y is the volume of  $\text{CH}_4$

$$\text{Thus, } \frac{1}{2}x + 2y = 13 \quad (1)$$

$$x + y = 14 \quad (2)$$

$$x = 10 \text{ and } y = 4$$

Thus, %  $\text{CH}_4 = 20$ , %  $\text{CO} = 50$ , %  $\text{He} = 30$



## EXERCISE S-I

## PROBLEMS RELATED WITH DIFFERENT TYPES OF ATOMIC MASSES &amp; BASIC CONCEPT OF MOLE

- Find :
  - No. of moles of Cu atom in  $10^{23}$  atoms of Cu. MC0001
  - Mass of 200  $^{16}_8\text{O}$  atoms in amu MC0001
  - Mass of 100 atoms of  $^{14}_7\text{N}$  is  $y \times 10^{-22}$  in gm, then value of  $y$  is ( $1 \text{ amu} = 1.67 \times 10^{-24} \text{ gm}$ ) MC0001
  - No. of molecules & atoms in 54 gm  $\text{H}_2\text{O}$  is  $y \times 10^{23}$  and  $z \times 10^{23}$  respectively then value of  $y$  &  $z$  is ( $N_A = 6.022 \times 10^{23}$ ) MC0002
  - No. of molecules in 88 gm  $\text{CO}_2$  is  $y \times 10^{23}$ , then value of  $y$  is ( $N_A = 6.022 \times 10^{23}$ ) MC0002
- If mass of one  $^{12}\text{C}$  atom is  $y \times 10^{-23}$  gm, then value of  $y$  is ? MC0003
- Calculate mass (in gm) of O atoms in 6 gm  $\text{CH}_3\text{COOH}$  ? MC0004
- Calculate mass of water (in gm) present in 499 gm  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  ?  
(Atomic mass : Cu = 63.5, S = 32, O = 16, H = 1) MC0005
- What mass (in gm) of  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  contains exactly  $6.022 \times 10^{22}$  atoms of oxygen ?  
( $N_A = 6.022 \times 10^{23}$ ) MC0006
- The weight (in gram) of pure potash Alum ( $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ ) which contains 6.4 gm oxygen is. (Atomic weight of K = 39, S = 32, Al = 27) MC0007
- The Kohinoor diamond was the largest diamond ever found. How many moles of carbon atom were present in it, if it is weigh 3300 carat. [Given: 1 carat = 200 mg] MC0008
- Calculate volume (in litre) of  $\text{H}_2$  gas kept at STP if it contains as many H atoms as in 98 gm  $\text{H}_3\text{PO}_4$ .  
[Atomic mass of P = 31] MC0009
- 80gm of  $\text{SO}_x$  gas occupies 14 litre at 2atm & 273K. The value of  $x$  is : MC0010

10. 40 mg of gaseous substance ( $X_2$ ) occupies 4.8 mL of volume at 1 atm and  $27^\circ\text{C}$ . Atomic mass of element X is : (R : 0.082 atm L/mole-K)

MC0011

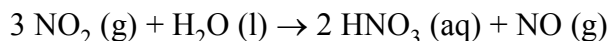
**STOICHIOMETRY**

11. How many gm of HCl is needed for complete reaction with 21.75 gm  $\text{MnO}_2$  ?  
(Mn = 55, Cl = 35.5)



MC0012

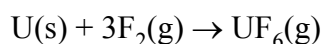
12. Nitric acid is manufactured by the Ostwald process, in which nitrogen dioxide reacts with water.



How many grams of nitrogen dioxide are required in this reaction to produce 25.2 gm  $\text{HNO}_3$  ?

MC0013

13. Fluorine reacts with uranium to produce uranium hexafluoride,  $\text{UF}_6$ , as represented by this equation



If no. of fluorine molecules are required to produce 7.04 mg of uranium hexafluoride,  $\text{UF}_6$ , from an excess of uranium is  $y \times 10^{19}$  then value of y is ? The molar mass of  $\text{UF}_6$  is 352 gm/mol.

( $N_A = 6.022 \times 10^{23}$ )

MC0014

14. What total volume, in litre at  $627^\circ\text{C}$  and 82.1 atm, could be formed by the decomposition of 16 gm of  $\text{NH}_4\text{NO}_3$  ? Reaction :  $2 \text{NH}_4\text{NO}_3 \rightarrow 2\text{N}_2 + \text{O}_2 + 4\text{H}_2\text{O}(\text{g})$ . (R : 0.0821 atm L/mole-K)

MC0015

15. Calculate mass of phosphoric acid (in gm) required to obtain 53.4g pyrophosphoric acid.



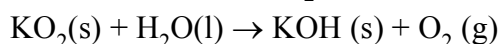
MC0016

**LIMITING REACTANT**

16. Carbon reacts with chlorine to form  $\text{CCl}_4$ . 36 gm of carbon was mixed with 142 g of  $\text{Cl}_2$ . If ratio of mass of  $\text{CCl}_4$  produced and the remaining mass of excess reactant is y : 1, then value of y is

MC0017

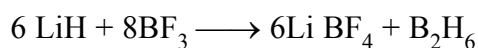
17. Potassium superoxide,  $\text{KO}_2$ , is used in rebreathing gas masks to generate oxygen :



If a reaction vessel contains 0.158 mol  $\text{KO}_2$  and 0.10 mol  $\text{H}_2\text{O}$ , how many moles of  $\text{O}_2$  can be produced ?

MC0018

18. A chemist wants to prepare diborane ( $\text{B}_2\text{H}_6$ ) by the reaction



If he starts with 2.0 moles each of LiH &  $\text{BF}_3$ . How many moles of  $\text{B}_2\text{H}_6$  can be prepared.

MC0019

19. Sulphuric acid is produced when sulphur dioxide reacts with oxygen and water in the presence of a catalyst :  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2\text{SO}_4$ . If 5.6 mol of  $\text{SO}_2$  reacts with 4.8 mol of  $\text{O}_2$  and a large excess of water, what is the maximum number of moles of  $\text{H}_2\text{SO}_4$  that can be obtained ?

MC0020

**PROBLEMS RELATED WITH MIXTURE**

20. One gram of an alloy of aluminium and magnesium when heated with excess of dil. HCl forms magnesium chloride, aluminium chloride and hydrogen. The evolved hydrogen collected at  $0^\circ\text{C}$  has a volume of 1.12 litres at 1 atm pressure. Calculate the composition of (% by mass) of the alloy.

(Al = 27, Mg = 24)

MC0021

21. A sample containing only  $\text{CaCO}_3$  and  $\text{MgCO}_3$  is ignited to  $\text{CaO}$  and  $\text{MgO}$ . The mixture of oxides produced weight exactly half as much as the original sample. Calculate the percentages of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  (by mass) in the sample.

MC0022

22. Determine the percentage composition (by mass) of a mixture of anhydrous sodium carbonate and sodium bicarbonate from the following data:

wt. of the mixture taken = 2g

Loss in weight on heating = 0.124 gm.

MC0023

23. A sample of mixture of  $\text{CaCl}_2$  and  $\text{NaCl}$  weighing 2.22 gm was treated to precipitate all the Ca as  $\text{CaCO}_3$  which was then heated and quantitatively converted to 0.84 gm of  $\text{CaO}$ . Calculate mass fraction of  $\text{CaCl}_2$  in the mixture.

MC0024

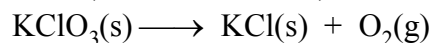
24. When 4 gm of a mixture of  $\text{NaHCO}_3$  and  $\text{NaCl}$  is heated, 0.66 gm  $\text{CO}_2$  gas is evolved. If ratio of the percentage composition (by mass) of the  $\text{NaHCO}_3$  and  $\text{NaCl}$  is  $y : 1$  then value of  $y$  is.

MC0025

25. A power company burns approximately 500 tons of coal per day to produce electricity. If the sulphur content of the coal is 1.20 % by weight, how many tons  $\text{SO}_2$  are dumped into the atmosphere per hour ?

MC0026

26. Calculate the percent loss in weight after complete decomposition of a pure sample of potassium chlorate. (K = 39, Cl = 35.5)

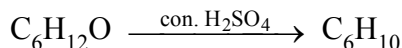


MC0027

27. A sample of calcium carbonate is 80% pure, 25 gm of this sample is treated with excess of HCl. How much volume (in litre) of  $\text{CO}_2$  will be obtained at 1 atm & 273 K?

MC0028

28. Cyclohexanol is dehydrated to cyclohexene on heating with conc.  $\text{H}_2\text{SO}_4$ . If the yield of this reaction is 75%, how much cyclohexene (in gm) will be obtained from 100 g of cyclohexanol ?



MC0029

29. If the yield of chloroform obtainable from acetone and bleaching powder is 58%. What is the weight of acetone (in gm) required for producing 239 mg of chloroform ?



MC0030

30. Calculate % yield of the reaction if 200g  $\text{KHCO}_3$  produces 22g of  $\text{CO}_2$  upon strong heating. (K = 39)

MC0031

31. The vapour density of a sample of  $\text{N}_2\text{O}_4$  gas is 35. What percent of  $\text{N}_2\text{O}_4$  molecules are dissociated into  $\text{NO}_2$  ?

MC0032

32. If a sample of pure  $\text{SO}_3$  gas is heated to  $600^\circ\text{C}$ , it dissociates into  $\text{SO}_2$  and  $\text{O}_2$  gases upto 50%. If the average molar mass of the final sample is  $M_{\text{avg}}$  find value of  $\left(\frac{M_{\text{av}}}{100}\right)$ .

MC0033

33. When silent electric discharge is passed through  $\text{O}_2$  gas, it converts into  $\text{O}_3$ . If the density of final sample is 20 times the density of hydrogen gas under similar conditions, calculate the mass percent of  $\text{O}_2$  in the final sample.

MC0034

34. When acetylene ( $\text{C}_2\text{H}_2$ ) gas is passed through red hot iron tube, it trimerises into benzene ( $\text{C}_6\text{H}_6$ ) vapours. If the average molar mass of vapours coming out through the tube is 50, calculate the degree of trimerisation of acetylene.

MC0035

### SEQUENTIAL & PARALLEL REACTIONS

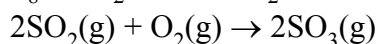
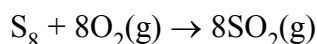
35.  $\text{Br}_2(l)$  reacts with  $\text{Cl}_2(g)$  to form  $\text{BrCl}$  and  $\text{BrCl}_3$ , simultaneously. How many moles of  $\text{Cl}_2(g)$  reacts completely with 0.03 moles of  $\text{Br}_2(l)$  to form  $\text{BrCl}$  and  $\text{BrCl}_3$  in 5 : 1 molar ratio

MC0036

36. When 80 gm  $\text{CH}_4$  is burnt,  $\text{CO}$  and  $\text{CO}_2$  gases are formed in 1 : 4 mole ratio. If the mass of  $\text{O}_2$  gas used in combustion is w gm then find value of (w/100).

MC0037

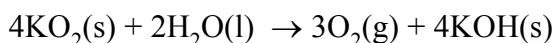
37. Sulphur trioxide may be prepared by the following two reactions :



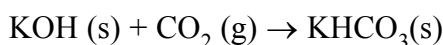
If amount of  $\text{SO}_3$  will be produced from 1 mol of  $\text{S}_8$  is w gm, then value of w/100 is.

MC0038

38. Potassium superoxide,  $\text{KO}_2$ , is utilised in closed system breathing apparatus. Exhaled air contains  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , both of which are removed and the removal of water generates oxygen for breathing by the reaction



The potassium hydroxide removes  $\text{CO}_2$  from the apparatus by the reaction :



(a) What mass of  $\text{KO}_2$  (in gm) generates 0.24 gm of oxygen ?

(b) What mass of  $\text{CO}_2$  (in gm) can be removed from the apparatus by 100 gm of  $\text{KO}_2$  ? (K = 39)

**MC0039**

### PRINCIPLE OF ATOM CONSERVATION

39. In a determination of P, an aqueous solution of  $\text{NaH}_2\text{PO}_4$  is treated with a mixture of ammonium and magnesium ions to precipitate magnesium ammonium phosphate  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . This is heated and decomposed to magnesium pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$  which is weighed. A solution of  $\text{NaH}_2\text{PO}_4$  yielded 1.11 g of  $\text{Mg}_2\text{P}_2\text{O}_7$ . What weight of  $\text{NaH}_2\text{PO}_4$  (in gm) was present originally ? (P = 31)

**MC0040**

40. 6 gm nitrogen on successive reaction with different compounds gets finally converted into 30 gm  $[\text{Cr}(\text{NH}_3)_x\text{Br}_2]$  Value of x is [Atomic mass : Cr = 52, Br = 80]

**MC0041**

41. A 5.00 gm sample of a natural gas, consisting of methane ( $\text{CH}_4$ ), and ethylene, ( $\text{C}_2\text{H}_4$ ) was burned in excess oxygen, yielding  $\frac{44}{3}$  gm of  $\text{CO}_2$  and some  $\text{H}_2\text{O}$  as products. What mole percent of the sample was ethylene?

**MC0042**

42. All carbon atom present in  $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  weighing 7.62 gm is converted to  $\text{CO}_2$ . How many gm of  $\text{CO}_2$  were obtained. (K = 39)

**MC0043**

### PERCENTAGE COMPOSITION, EMPIRICAL AND MOLECULAR FORMULA

43. Haemoglobin contains 0.25% iron by mass. The molecular mass of Haemoglobin is 89600. The number of iron atoms per molecule of Haemoglobin (Atomic mass of Fe = 56) -

**MC0044**

44. 1.6 g of an organic compound containing sulphur, when treated with series of reagents, produces  $\text{H}_2\text{SO}_4$  which on reaction with  $\text{BaCl}_2$  produces 0.233 g of  $\text{BaSO}_4$ . Calculate % by mass of S in the organic compound. (Given : Atomic weight of Ba = 137)

**MC0045**

45. When 2.0 gm of an organic compound is burnt completely, 150 ml  $\text{N}_2$  gas at  $27^\circ\text{C}$  and 0.821 atm is obtained. The mass fraction of nitrogen in the compound is.

(R = 0.0821 atm L/mole - K)

**MC0046**

46. A polystyrene of formula  $\text{Br}_3\text{C}_6\text{H}_2(\text{C}_8\text{H}_8)_n$  was prepared by heating styrene with tribromobenzyl peroxide in the absence of air. It was found to contain 10.48% bromine by weight. Find the value of  $n$ . (Br = 80). MC0047
47. A moth repellent has the composition 49% C, 2.7% H and 48.3% Cl. Its molecular weight is 147 gm. Determine its molecular formula MC0048
48. 0.5 g of NaOH is required by 0.4 gm of a polybasic acid  $\text{H}_n\text{A}$  (Molecular weight = 96gm) for complete neutralization. Value of 'n' would be : (Assume all H atom are replaced)– MC0049
49. The empirical formula of a compounds is  $\text{CH}_2\text{O}$ . 0.25 mole of this compound contains 1 gm hydrogen. The molecular formula of compound is - MC0050
50. A compound has 62 % carbon, 10.4 % hydrogen and 27.6 % oxygen. If molar mass of compound is 58, if ratio of no. of C atom to H-atom is  $y : 1$  then value of  $y$  is. MC0051

### EUDIOMETRY

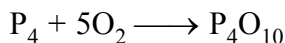
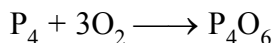
51. What volume (in ml) of  $\text{O}_2(\text{g})$  is needed for complete combustion of 40 ml ethane gas ( $\text{C}_2\text{H}_6$ ) ? MC0052
52. 10 ml of CO is mixed with 25 ml air having 20%  $\text{O}_2$  by volume. What would be the final volume (in ml) if none of CO and  $\text{O}_2$  is left after the reaction? MC0053
53. Calculate the volume (in ml) of  $\text{CO}_2$  evolved by the combustion of 50 ml of a mixture containing 40%  $\text{C}_2\text{H}_4$  and 60%  $\text{CH}_4$  (by volume) MC0054
54. 10 moles of a mixture of CO (g) and  $\text{CH}_4(\text{g})$  was mixed with 22 moles of  $\text{O}_2$  gas and subjected to sparking. Find the moles of gas absorbed when the residual gases are passed through alc. KOH. MC0055
55. 60 ml of a mixture of nitrous oxide and nitric oxide was exploded with excess of hydrogen. If 38 ml of  $\text{N}_2$  was formed, calculate % volume of NO gas in the mixture. MC0056
56. When 100 ml of a  $\text{O}_2 - \text{O}_3$  mixture was passed through turpentine, there was reduction of volume by 20 ml. If 100 ml of such a mixture is heated, what will be the increase in volume (in ml)? MC0057

57. 10 ml of an oxide of nitrogen produce 20 ml  $\text{NO}_2$  and 5 ml  $\text{O}_2$  on complete decomposition. The oxide of nitrogen is-
- MC0058**
58. A gaseous alkane is exploded with  $\text{O}_2$ . The volume of  $\text{O}_2$  required for complete combustion and the volume of  $\text{CO}_2$  formed after combustion are in 7 : 4 ratio. What is the molecular formula of alkane ?
- MC0059**
59. When a certain quantity of oxygen was ozonised in a suitable apparatus, the volume decreased by 4 ml. On addition of turpentine the volume further decreased by 8 ml. All volumes were measured at the same temperature and pressure. From these data, if formula of ozone is  $\text{O}_x$  then find x.
- MC0060**
60. A 20 ml mixture of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  undergoes sparking in gas eudiometer with just sufficient amount of  $\text{O}_2$  and shows contraction of 37.5 ml. The volume (in ml) of  $\text{C}_2\text{H}_2$  in the mixture is.
- MC0061**

## EXERCISE S-II

## MOLE

1. Two substance  $P_4$  &  $O_2$  are allowed to react completely to form mixture of  $P_4O_6$  &  $P_4O_{10}$  leaving none of the reactants. Using this information calculate the moles of  $P_4O_6$  and  $P_4O_{10}$  in the final mixture when the following amounts of  $P_4$  &  $O_2$  are taken.



- (i) If 1 mole  $P_4$  & 4 mole of  $O_2$   
 (ii) If 3 mole  $P_4$  & 11 mole of  $O_2$   
 (iii) If 3 mole  $P_4$  & 13 mole of  $O_2$

MC0062

2. By the reaction of carbon and oxygen, a mixture of CO and  $CO_2$  is obtained. What is the mass percent of CO in of the mixture obtained when 20 grams of  $O_2$  reacts with 12 grams of carbon ?

MC0063

3. Nitrogen (N), phosphorus (P), and potassium (K) are the main nutrients in plant fertilizers. According to an industry convention, the numbers on the label refer to the mass % of N,  $P_2O_5$ , and  $K_2O$ , in that order. If the N : P : K ratio of a 28 : 11.75 : 11.75 fertilizer in terms of moles of each elements, and express it as x : y : 1. Find value of y (P = 31, K = 39)

MC0064

4. A 10 g sample of a mixture of calcium chloride and sodium chloride is treated with  $Na_2CO_3$  to precipitate calcium as calcium carbonate. This  $CaCO_3$  is heated to convert all the calcium to CaO and the final mass of CaO is 1.12gm. Calculate % by mass of NaCl in the original mixture.

MC0065

5. A mixture of Ferric oxide ( $Fe_2O_3$ ) and Al is used as a solid rocket fuel which reacts to give  $Al_2O_3$  and Fe. No other reactants and products are involved. On complete reaction of 1 mole of  $Fe_2O_3$ , 200 units of energy is released.

- (a) Write a balance reaction representing the above change.  
 (b) If the ratio of masses of  $Fe_2O_3$  and Al taken so that maximum energy per unit mass of fuel is released is y : 1 then value of y is  
 (c) What would be energy released if 16 kg of  $Fe_2O_3$  reacts with 2.7 kg of Al.

MC0066

6. 5.33 mg of salt  $[Cr(H_2O)_5Cl].Cl_2 \cdot H_2O$  is treated with excess of  $AgNO_3(aq.)$ , then mass (in mg) of AgCl precipitate obtained will be :

Given : [Cr = 52, Cl = 35.5, Ag = 108]

MC0067

7. If mass % of oxygen in monovalent metal carbonate is 48%, If the number of atoms of metal present in 5mg of this metal carbonate sample is  $y \times 10^{19}$  then value of y is ( $N_A = 6.022 \times 10^{23}$ ).

MC0068



8. The formula of compound composed of A & B which is given by  $A_xB_y$ , it is strongly heated in oxygen as per reaction-



If 2.5 gm of  $A_xB_y$  on oxidation gives 3 gm oxide of A, If ratio of  $x : y$  is  $z : 1$  then value of  $z$  is.

[Atomic mass of A = 24 & B = 14]

MC0069

9. Calculate the maximum mass of  $CaCl_2$  produced when  $2.4 \times 10^{24}$  atoms of calcium is taken with 96 litre of  $Cl_2$  gas at 380 mm pressure and at  $27^\circ C$ .

[R = 0.08 atm L/mole-K &  $N_A = 6 \times 10^{23}$ ]

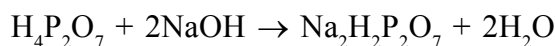
MC0070

10.  $P_4S_3 + 8O_2 \longrightarrow P_4O_{10} + 3SO_2$

Calculate mass in gm of  $P_4S_3$  is required to produce at least 9.6 gm of each product. (P = 31, S = 32)

MC0071

11. Consider the given reaction



If 534 gm of  $H_4P_2O_7$  is reacted with  $3.0 \times 10^{24}$  formula units of NaOH, then the total number of moles of  $H_2O$  produced is ( $N_A = 6 \times 10^{23}$ ) (P = 31)

MC0072

### Comprehension based on "Law of Conservation of Mass" (12 & 13)

It states that matter can neither be created nor destroyed.

This law was put forth by Antoine Lavoisier in 1789. He performed careful experimental studies for combustion reactions for reaching to the above conclusion. This law formed the basis for several later developments in chemistry. Infact, this was the result of exact measurement of masses of reactants and products, and carefully planned experiments performed by Lavoisier.

12. What weight (in gm) of silver nitrate will react with 0.585 gm NaCl to produce 1.435 gm AgCl and 0.85 gm  $NaNO_3$

MC0073

13. 6.3 gm sodium bicarbonate is added to 15 gm acetic acid solution.  $CO_2$  formed is allowed to escape. The weight of the solution left is 18 gm. What is the mass (in gm) of  $CO_2$  formed.

MC0073

### Comprehension based on “Law of Definite Proportions” (14 & 15)

This law was given by, a French chemist, Joseph Proust. He stated that a given compound always contains exactly the same proportion of elements by weight.

Proust worked with two samples of cupric carbonate—one of which was of natural origin and the other was synthetic one. He found that the composition of elements present in it was same for both the samples as shown below :

	% of copper	% of oxygen	% of carbon
Natural Sample	51.35	9.74	38.91
Synthetic Sample	51.35	9.74	38.91

Thus, irrespective of the source, a given compound always contains same elements in the same proportion. The validity of this law has been confirmed by various experiments. It is sometimes also referred to as **Law of constant composition**.

#### Limitation :

The law is not applicable if the compound is formed from different isotopes of an element. The two isotopes of carbon C-12 and C-14 form carbondioxide  $C^{12}O_2$  and  $C^{14}O_2$ . The ratio of C : O is 12 : 32 and 14 : 32 respectively. It is not a constant ratio.

14. 0.5 gm silver is dissolved in excess of nitric acid. This solution is treated with excess of NaCl solution when 0.66 gm AgCl is formed. One gram metallic silver wire is heated in dry  $Cl_2$ , 1.32 gm AgCl is formed. Show that these data confirm the law of constant proportion.

MC0074

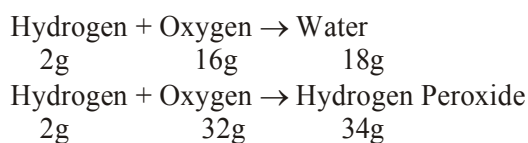
15. 6.488 gm lead reacts with 1.002 gm oxygen to form an oxide. This oxide is also obtained by heating  $Pb(NO_3)_2$ . It is found that % of lead in this oxide is 86.62. Show that these data illustrate the law of definite proportions.

MC0075

### Comprehension based on “Law of Multiple Proportions” (16 to 17)

This law was proposed by Dalton in 1803. According to this law, if two elements combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.

For example, hydrogen combines with oxygen to form two compounds, namely, water and hydrogen peroxide.



Here, the masses of oxygen (i.e. 16 gm and 32 gm) which combine with a fixed mass of hydrogen (2 gm) bear a simple ratio, i.e. 16:32 or 1: 2.

16. An element forms two oxides. In one oxide, one gram of the oxide contains 0.5 gm of the element. In another oxide, 4 gm of the oxide contains 0.8 gm of the element. Show that these data confirm the law of multiple proportion.
- MC0076**
17. 0.11 gm of an oxide of nitrogen gives 56 mL  $N_2$  at 273 K and 1 atm. 0.15 gm of another oxide of nitrogen gives 56 mL  $N_2$  at 1 atm, 273K. Show that these data confirm the law of multiple proportion.
- MC0077**
18. 10 ml of a mixture of  $CH_4$ ,  $C_2H_4$  and  $CO_2$  were exploded with excess of air. After explosion and further cooling, there was contraction of 17 ml and after treatment with KOH, there was further reduction of 14 ml. What is the composition of the mixture (in ml)?
- MC0078**
19. 40 ml of a mixture of  $C_2H_2$  and CO is mixed with 100 ml of  $O_2$  gas and the mixture is exploded. The residual gases occupied 104 ml and when these are passed through KOH solution, the volume becomes 48 ml. All the volume are at same temperature and pressure. If ratio of volume of  $C_2H_2$  & CO is  $y : 1$ , then value of  $y$  is
- MC0079**
20. 10 mL of gaseous organic compound containing C, H and O only, was mixed with 100 mL of  $O_2$  and exploded under identical conditions and then cooled. The volume left after cooling was 90 mL. On treatment with KOH a contraction of 20 mL was observed. If vapour density of compound is 23, if molecular formula of the compound is  $C_xH_yO_z$ , then find  $(x + y + z)$ .

**MC0080**

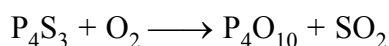
## EXERCISE O-I

## Single Correct :

- 1 One atomic mass unit in kilogram is  
 (A)  $1/N_A$  (B)  $12/N_A$  (C)  $1/1000 N_A$  (D)  $1000/N_A$  **MC0081**
- 2 A gaseous mixture contains  $\text{CO}_2$  (g) and  $\text{N}_2\text{O}$  (g) in a 2 : 5 ratio by mass. The ratio of the number of molecules of  $\text{CO}_2$  (g) and  $\text{N}_2\text{O}$  (g) is  
 (A) 5 : 2 (B) 2 : 5 (C) 1 : 2 (D) 5 : 4 **MC0082**
- 3 Which of the following contain largest number of carbon atoms?  
 (A) 15 gm ethane,  $\text{C}_2\text{H}_6$  (B) 40.2 gm sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$   
 (C) 72 gm glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$  (D) 35 gm pentene,  $\text{C}_5\text{H}_{10}$  **MC0083**
- 4 The number of hydrogen atoms in 0.9 gm glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , is same as  
 (A) 0.048 gm hydrazine,  $\text{N}_2\text{H}_4$  (B) 0.17 gm ammonia,  $\text{NH}_3$   
 (C) 0.30 gm ethane,  $\text{C}_2\text{H}_6$  (D) 0.03 gm hydrogen,  $\text{H}_2$  **MC0084**
- 5 Ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , is the substance commonly called alcohol. The density of liquid alcohol is 0.7893 g/ml at 293 K. If 1.2 mole of ethanol are needed for a particular experiment, what volume of ethanol should be measured out?  
 (A) 55 ml (B) 58 ml (C) 70 ml (D) 79 ml **MC0085**
- 6 An iodized salt contains 0.5 % of NaI. A person consumes 3 gm of salt everyday. The number of iodide ions going into his body everyday is ( $I = 127$ )  
 (A)  $10^{-4}$  (B)  $6.02 \times 10^{-4}$  (C)  $6.02 \times 10^{19}$  (D)  $6.02 \times 10^{23}$  **MC0086**
- 7 The percentage by mole of  $\text{NO}_2$  in a mixture of  $\text{NO}_2$ (g) and  $\text{NO}$ (g) having average molecular mass 34 is :  
 (A) 25% (B) 20% (C) 40% (D) 75% **MC0087**
- 8 The number of carbon atoms present in a signature, if a signature written by carbon pencil, weighing  $1.2 \times 10^{-3}$  g is  
 (A)  $12.04 \times 10^{20}$  (B)  $6.02 \times 10^{19}$  (C)  $3.01 \times 10^{19}$  (D)  $6.02 \times 10^{20}$  **MC0088**

- 9 The average atomic mass of a mixture containing 79 mole % of  $^{24}\text{Mg}$  and remaining 21 mole % of  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$ , is 24.31. % mole of  $^{26}\text{Mg}$  is  
 (A) 5 (B) 20 (C) 10 (D) 15  
**MC0089**
10. How many litres of oxygen at 1atm & 273K will be required to burn completely 2.2 g of propane ( $\text{C}_3\text{H}_8$ )  
 (A) 11.2 L (B) 22.4 L (C) 5.6 L (D) 44.8 L  
**MC0090**
11. If  $1/2$  moles of oxygen combine with aluminium to form  $\text{Al}_2\text{O}_3$  then weight of Aluminium metal used in the reaction is (Al= 27)  
 (A) 27 g (B) 18 g (C) 54 g (D) 40.5 g  
**MC0091**
12. Volume of  $\text{CO}_2$  obtained at STP by the complete decomposition of 9.85 g  $\text{BaCO}_3$  is (Ba = 137)  
 (A) 2.24 lit (B) 1.12 lit (C) 1.135 lit (D) 2.27 lit  
**MC0092**
13. The drain cleaner, **Drainex** contains small bits of aluminium (Al = 27) which reacts with caustic soda to produce dihydrogen. What is the volume (in ml) of dihydrogen at  $27^\circ\text{C}$  and 1.013 bar that is produced when 0.27 gm of aluminium reacts :  
 $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2$   
 (A) 0.369 (B) 369.0 (C) 246.0 (D) 540.0  
**MC0093**
14. Volume of  $\text{O}_2$  obtained at 2 atm & 546K, by the complete decomposition of 8.5 g  $\text{NaNO}_3$  is  
 $2\text{NaNO}_3 \rightarrow 2\text{NaNO}_2 + \text{O}_2$   
 (A) 2.24 lit (B) 1.12 lit (C) 0.84 lit (D) 0.56 lit  
**MC0094**
- 15 The minimum mass of mixture of  $\text{A}_2$  and  $\text{B}_4$  required to produce at least 1 kg of each product is :  
 (Given At. mass of 'A' = 10 ; At. mass of 'B' = 120)  
 $5\text{A}_2 + 2\text{B}_4 \longrightarrow 2\text{AB}_2 + 4\text{A}_2\text{B}$   
 (A) 2120 gm (B) 1060 gm (C) 560 gm (D) 1660 gm  
**MC0095**
- 16 The mass of  $\text{CO}_2$  produced from 620 gm mixture of  $\text{C}_2\text{H}_4\text{O}_2$  &  $\text{O}_2$ , prepared to produce maximum energy is (Combustion reaction is exothermic)  
 (A) 413.33 gm (B) 593.04 gm (C) 440 gm (D) 320 gm  
**MC0096**

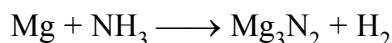
17. The mass of  $P_4O_{10}$  produced if 440 gm of  $P_4S_3$  is mixed with 384 gm of  $O_2$  is



- (A) 568 gm                      (B) 426 gm                      (C) 284 gm                      (D) 396 gm

MC0097

18. The mass of  $Mg_3N_2$  produced if 48 gm of Mg metal is reacted with 34 gm  $NH_3$  gas is



- (A)  $\frac{200}{3}$  gm                      (B)  $\frac{100}{3}$  gm                      (C)  $\frac{400}{3}$  gm                      (D)  $\frac{150}{3}$  gm

MC0098

19. An ideal gaseous mixture of ethane ( $C_2H_6$ ) and ethene ( $C_2H_4$ ) occupies 28 litre at 1atm,  $0^\circ C$ . The mixture reacts completely with 128 gm  $O_2$  to produce  $CO_2$  and  $H_2O$ . Mole fraction of  $C_2H_6$  in the mixture is—

- (A) 0.6                      (B) 0.4                      (C) 0.5                      (D) 0.8

MC0099

20. 280 g of a mixture containing  $CH_4$  and  $C_2H_6$  in 5 : 2 molar ratio is burnt in presence of excess of oxygen. Calculate total moles of  $CO_2$  produced.

- (A) 9                      (B) 18                      (C) 7                      (D) 12

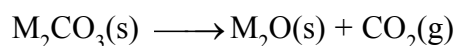
MC0100

21. Mixture of  $MgCO_3$  &  $NaHCO_3$  on strong heating gives  $CO_2$  &  $H_2O$  in 3 : 1 mole ratio. The weight % of  $NaHCO_3$  present in the mixture is:

- (A) 30%                      (B) 80%                      (C) 40%                      (D) 50%

MC0101

22. A metal carbonate decomposes according to following reaction



Percentage loss in mass on complete decomposition of  $M_2CO_3(s)$

(Atomic mass of M = 102)

- (A)  $\frac{100}{3}$  %                      (B)  $\frac{50}{3}$  %                      (C)  $\frac{25}{3}$  %                      (D) 15%

MC0102

23. 90 gm mixture of  $H_2$  and  $O_2$  is taken in stoichiometric ratio and gives  $H_2O$  with 50% yield. The produced mass of  $H_2O$  (in gm) is :

- (A) 45 gm                      (B) 36 gm                      (C) 20 gm                      (D) 90 gm

MC0103

24. An impure sample of  $CaCO_3$  contains 38% of Ca. The percentage of impurity present in the sample is :

- (A) 5%                      (B) 95%                      (C) 10%                      (D) 2.5%

MC0104

25. The vapour density of sample of partially decomposed cyclobutane ( $C_4H_8$ ) gas is 20. The degree of dissociation of  $C_4H_8$  into  $C_2H_4$  gas is -  
 (A) 0.25 (B) 0.50 (C) 0.60 (D) 0.40

MC0105

26. A sample of  $NH_3$  gas is 20% dissociated into  $N_2$  and  $H_2$  gases. The mass ratio of  $N_2$  and  $NH_3$  gases in the final sample is -

- (A)  $\frac{7}{34}$  (B)  $\frac{7}{17}$  (C)  $\frac{14}{17}$  (D)  $\frac{21}{17}$

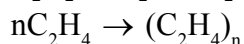
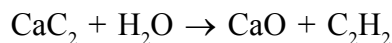
MC0106

27. The density of a sample of  $SO_3$  gas is 2.5 g/L at  $0^\circ C$  and 1 atm. Its degree of dissociation into  $SO_2$  and  $O_2$  gases is -

- (A)  $\frac{6}{7}$  (B)  $\frac{1}{7}$  (C)  $\frac{3}{7}$  (D)  $\frac{5}{7}$

MC0107

28. Polyethene can be prepared by  $CaC_2$  by the following sequence of reactions.



(Polyethene)

The mass in kg of polyethene that can be prepared by 20 kg  $CaC_2$ .

- (A) 4.1 kg (B) 8.75 kg (C) 3.78 kg (D) 10 kg

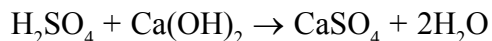
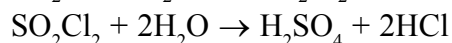
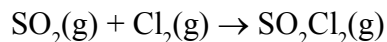
MC0108

29. 25.4 gm of iodine and 14.2 gm of chlorine are made to react completely to yield a mixture of  $ICl$  and  $ICl_3$ . Ratio of moles of  $ICl$  &  $ICl_3$  formed is (Atomic mass : I = 127, Cl = 35.5)

- (A) 1 : 1 (B) 1 : 2 (C) 1 : 3 (D) 2 : 3

MC0109

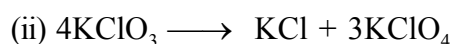
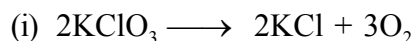
30. One commercial system removes  $SO_2$  emission from smoke at  $95^\circ C$  by the following set of reactions-

Assuming the process to be overall 95% efficient. How many moles of  $CaSO_4$  may be produced from 128 gm  $SO_2$ . [Ca = 40, S- 32, O-16]

- (A) 1.9 moles (B) 2 mol (C) 3.8 mol (D) 0.95 mol

MC0110

31. Equal masses of  $KClO_3$  undergoes different reaction in two different container :

Mass ratio of the  $KCl$  produced in respective reaction is  $x : 1$ . Value of 'x' will be.

- (A) 4 (B) 2 (C) 0.25 (D) 3

MC0111

32. A compound contains  $10^{-2}$  % of phosphorous. If atomic mass of phosphorus is 31, the molecular mass of the compound having one phosphorus atom per molecule is :-  
 (A) 31 (B)  $3.1 \times 10^3$  (C)  $3.1 \times 10^5$  (D)  $3.1 \times 10^4$

MC0112

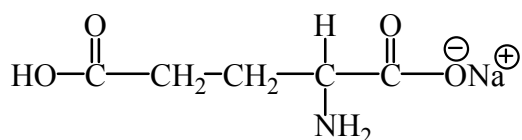
33. 13.4 gm of a sample of unstable hydrated salt :  $\text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$  was strongly heated. Weight loss on heating is found to be equal to 6.3 gm. Calculate the value of x.  
 (A) 6 (B) 5 (C) 7 (D) 8

MC0113

34. An organic compound contains 4% sulphur by mass. Its minimum molecular weight is :  
 (A) 200 (B) 400 (C) 800 (D) 1600

MC0114

35. Monosodium glutamate (MSG) is salt of one of the most abundant naturally occurring non-essential amino acid which is commonly used in food products like in "MAGGI" having structural formula as



Mass % of Na in MSG is-

- (A) 14.8 (B) 15.1 (C) 13.6 (D) 16.5

MC0115

36. Which of the following series of compounds have same mass percentage of carbon ?  
 (A)  $\text{CO}_2$ , CO (B)  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_2$   
 (C)  $\text{C}_2\text{H}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_{10}\text{H}_8$  (D)  $\text{HCHO}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{C}_6\text{H}_{12}\text{O}_6$

MC0116

37. A compound contains 69.5% oxygen and 30.5% nitrogen and its molecular weight is 92. The formula of that compound is :-  
 (A)  $\text{N}_2\text{O}$  (B)  $\text{NO}_2$  (C)  $\text{N}_2\text{O}_4$  (D)  $\text{N}_2\text{O}_5$

MC0117

38. 1 lt. of a hydrocarbon weighs as much as one litre of  $\text{CO}_2$ . The molecular formula of the hydrocarbon is -  
 (A)  $\text{C}_3\text{H}_8$  (B)  $\text{C}_2\text{H}_6$  (C)  $\text{C}_2\text{H}_4$  (D)  $\text{C}_3\text{H}_6$

MC0118

39. Which of the following compounds has same empirical formula as that of glucose:-  
 (A)  $\text{CH}_3\text{CHO}$  (B)  $\text{CH}_3\text{COOH}$  (C)  $\text{CH}_3\text{OH}$  (D)  $\text{C}_2\text{H}_6$

MC0119

40. Two oxides of a metal contains 50% and 40% of a metal respectively. The formula of the first oxide is  $\text{MO}$ . Then the formula of the second oxide is -  
 (A)  $\text{MO}_2$  (B)  $\text{M}_2\text{O}_3$  (C)  $\text{M}_2\text{O}$  (D)  $\text{M}_2\text{O}_5$

MC0120



41. A compound of X and Y has equal mass of them. If their atomic weights are 30 and 20 respectively. The molecular formula of compound is -

- (A)  $X_2Y_2$                       (B)  $X_3Y_3$                       (C)  $X_2Y_3$                       (D)  $X_3Y_2$

MC0121

42. 10 ml  $CH_4$  gas is burnt completely in air ( $O_2 = 20\%$ , by volume). The minimum volume of air needed is -

- (A) 20 ml                      (B) 50 ml                      (C) 80 ml                      (D) 100 ml

MC0122

43.  $C_6H_5OH(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$

Magnitude of volume change if 30 ml of  $C_6H_5OH(g)$  is burnt with excess amount of oxygen, is

- (A) 30 ml                      (B) 60 ml                      (C) 20 ml                      (D) 10 ml

MC0123

44. A mixture of  $C_2H_2$  and  $C_3H_8$  occupied a certain volume at 80 mm Hg. The mixture was completely burnt to  $CO_2$  and  $H_2O(l)$ . The pressure of  $CO_2$  was found to be 230 mm Hg at the same temperature and volume. The fraction of  $C_2H_2$  in mixture is

- (A) 0.125                      (B) 0.5                      (C) 0.85                      (D) 0.25

MC0124

45. 20 mL of a mixture of CO and  $H_2$  were mixed with excess of  $O_2$  and exploded & cooled. There was a volume contraction of 23 mL. All volume measurements corresponds to room temperature ( $27^\circ C$ ) and one atmospheric pressure. Determine the volume ratio  $V_1 : V_2$  of CO and  $H_2$  in the original mixture

- (A) 6.5 : 13.5                      (B) 5 : 15                      (C) 9 : 11                      (D) 7 : 13

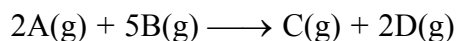
MC0125

46. Each volume of a gaseous organic compound containing C, H and S only produce 1 volume  $CO_2$ , 2 volume  $H_2O$  vapours and 1 volume  $SO_2$  gases on complete combustion. The molecular formula of compound is -

- (A)  $CH_2S$                       (B)  $CH_4S$                       (C)  $C_2H_4S$                       (D)  $C_2H_6S$

MC0126

47. For a chemical reaction occurring at constant pressure and temperature.



- (A) contraction in volume is double the volume of A taken if B is taken in excess.  
(B) contraction in volume is more than the volume of B taken if A is in excess.  
(C) volume contracts by 20 mL if 10 mL A is reacted with 20 mL B.  
(D) no change in volume due to reaction

MC0127

48. When one litre of  $\text{CO}_2$  is passed over hot coke, the volume becomes 1.4 litres. The composition of final products will not be.

- (A)  $V_{\text{CO}_2} : V_{\text{CO}} = 3 : 4$  (B)  $V_{\text{CO}} = 1.6 \text{ ltr.}$  (C)  $n_{\text{CO}_2} : n_{\text{CO}} = 3 : 4$  (D)  $\% \text{ V of CO} = \frac{400}{7}$

MC0128

49. 10 ml of a compound containing 'N' and 'O' is mixed with 30 ml of  $\text{H}_2$  to produce  $\text{H}_2\text{O}$  (l) and 10 ml of  $\text{N}_2$  (g). Molecular formula of compound if both reactants reacts completely, is

- (A)  $\text{N}_2\text{O}$  (B)  $\text{NO}_2$  (C)  $\text{N}_2\text{O}_3$  (D)  $\text{N}_2\text{O}_5$

MC0129

50. When a definite volume of a gaseous alkyne ( $\text{C}_n\text{H}_{2n-2}$ ) is burnt completely in excess of air, a contraction in volume equal to twice the volume of alkyne burnt occurred. The value of 'n' is -

- (A) 4 (B) 6 (C) 3 (D) 20

MC0130

## EXERCISE O-II

1. A sample of iron ore, weighing 0.700g, is dissolved in nitric acid. The solution is then diluted with water, following with sufficient concentrated aqueous ammonia, to quantitative precipitation the iron as  $\text{Fe}(\text{OH})_3$ . The precipitate is filtered, ignited and weighed as  $\text{Fe}_2\text{O}_3$ . If the mass of the ignited and dried precipitate is 0.541g, what is the mass percent of iron in the original iron ore sample (Fe = 56)
- (A) 27.0 %                      (B) 48.1 %                      (C) 54.1 %                      (D) 81.1 %

MC0131

2. A sample of pure Cu (4.00g) heated in a stream of oxygen for some time, gains in weight with the formation of black oxide of copper (CuO). The final mass is 4.90 g. What percent of copper remains unoxidized (Cu = 64)
- (A) 90 %                      (B) 10 %                      (C) 20 %                      (D) 80 %

MC0132

3. 1120 ml of ozonised oxygen ( $\text{O}_2 + \text{O}_3$ ) at 1 atm & 273K weighs 1.76 gm. The reduction in volume on passing this through alkaline pyrogallol solution is -
- (A) 896 ml                      (B) 224 ml                      (C) 448 ml                      (D) 672 ml

MC0133

## ASSERTION REASON:

4. **Statement-1** : When a gaseous hydrocarbon is burnt in excess of oxygen and the products of combustion are cooled to the original temperature and pressure, a contraction in volume occurs.

**Statement-2** : The contraction in volume is solely due to the liquifaction of water vapour.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

MC0134

5. **Statement -1** :  $2\text{A} + 3\text{B} \longrightarrow \text{C}$

$\frac{4}{3}$  moles of 'C' are always produced when 3 moles of 'A' & 4 moles of 'B' are added.

**Statement -2** : 'B' is the limiting reactant for the given data.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is false, statement-2 is true.  
 (D) Statement-1 is true, statement-2 is false.

MC0135

6. **Assertion** : During a chemical reaction, total moles remains constant.

**Reason** : During a chemical reaction, total mass remains constant.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

MC0136

**MULTIPLE CORRECT :**

7. 40 gm of a carbonate of an **alkali metal** or **alkaline earth metal** containing some inert impurities was made to react with excess HCl solution. The liberated  $\text{CO}_2$  occupied 12.315 lit. at 1 atm & 300 K. The correct option is

- (A) Mass of impurity is 1 gm and metal is Be (B) Mass of impurity is 3 gm and metal is Li  
 (C) Mass of impurity is 5 gm and metal is Be (D) Mass of impurity is 2 gm and metal is Mg

MC0137

8. 1 mole of  $\text{H}_2\text{SO}_4$  will exactly neutralise :

- (A) 2 mole of ammonia (B) 1 mole of  $\text{Ba}(\text{OH})_2$   
 (C) 0.5 mole of  $\text{Ca}(\text{OH})_2$  (D) 2 mole of KOH

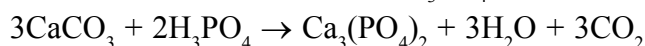
MC0138

9. 12 g of Mg was burnt in a closed vessel containing 32 g oxygen. Which of the following is /are correct.

- (A) 2 gm of Mg will be left unburnt.  
 (B) 0.75 gm-molecule of  $\text{O}_2$  will be left unreacted.  
 (C) 20 gm of MgO will be formed.  
 (D) The mixture at the end will weight 44 g.

MC0139

10. 50 gm of  $\text{CaCO}_3$  is allowed to react with 68.6 gm of  $\text{H}_3\text{PO}_4$  then select the correct option(s)-



- (A) 51.67 gm salt is formed (B) Amount of unreacted reagent = 35.93 gm  
 (C)  $n_{\text{CO}_2}$  formed = 0.5 moles (D)  $n_{\text{H}_2\text{O}}$  formed = 0.7 mole

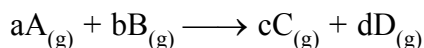
MC0140

11. Select the correct statement(s) for  $(\text{NH}_4)_3\text{PO}_4$ .

- (A) Ratio of number of oxygen atoms to number of hydrogen atoms is 1 : 3  
 (B) Ratio of number of cations to number of anions is 3 : 1  
 (C) Ratio of number of gm-atoms of nitrogen to gm-atoms of oxygen is 3 : 2  
 (D) Total number of atoms in one mole of  $(\text{NH}_4)_3\text{PO}_4$  is 20.

MC0141

12. Two gases A and B which react according to the equation



to give two gases C and D are taken (amount not known) in an Eudiometer tube (operating at a constant Pressure and temperature) to cause the above.

If on causing the reaction there is no volume change observed then which of the following statement is/are correct.

- (A)  $(a + b) = (c + d)$
- (B) average molecular mass may increase or decrease if either of A or B is present in limited amount.
- (C) Vapour Density of the mixture will remain same throughout the course of reaction.
- (D) Total moles of all the component of mixture will change.

MC0142

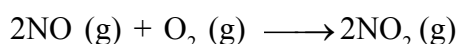
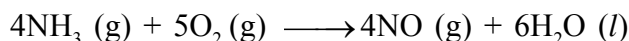
13. 100 ml mixture of CO and CO<sub>2</sub> mixed with 30 mL of O<sub>2</sub> and sparked in eudiometer tube. The residual gas after treatment with aq. KOH has a volume of 10 mL which remains unchanged when treated with alkaline pyrogallol. If all the volumes are under the same conditions, point out **correct** option(s):

- (A) The volume of CO that reacts, is 60 mL
- (B) The volume of CO that remains unreacted, is 10 mL
- (C) The volume of O<sub>2</sub> that remains unreacted, is 10 mL
- (D) The volume of CO<sub>2</sub> that gets absorbed by aq.KOH, is 90 mL.

MC0143

*Paragraph for Q.14 to Q.15*

For the given series of reaction



14. If 20 ml of NH<sub>3</sub> is mixed with 100 ml of O<sub>2</sub>. Volume contraction at the completion of above reactions is

- (A) 20 ml
- (B) 85 ml
- (C) 35 ml
- (D) 100 ml

MC0144

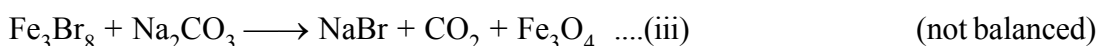
15. Total volume of O<sub>2</sub> used if 20 ml NH<sub>3</sub> is mixed with 100 ml O<sub>2</sub>

- (A) 40
- (B) 60
- (C) 35
- (D) None of these

MC0144

*Paragraph for Q.16 to Q.18*

NaBr, used to produce AgBr for use in photography can be self prepared as follows :



(At. mass : Fe = 56, Br = 80)

16. Mass of iron required to produce  $2.06 \times 10^3$  kg NaBr  
 (A) 420 gm (B) 420 kg (C)  $4.2 \times 10^5$  kg (D)  $4.2 \times 10^8$  gm  
**MC0145**
17. If the yield of (ii) is 60% & (iii) reaction is 70% then mass of iron required to produce  $2.06 \times 10^3$  kg NaBr  
 (A)  $10^5$  kg (B)  $10^5$  gm (C)  $10^3$  kg (D) None  
**MC0146**
18. If yield of (iii) reaction is 90% then mole of  $\text{CO}_2$  formed when  $2.06 \times 10^3$  gm NaBr is formed  
 (A) 20 (B) 10 (C) 9 (D) 440  
**MC0147**

**Comprehension Q.19 and Q.20 (2 questions)**

**Estimation of halogens (Carius method) :** A known mass of compound is heated with conc.  $\text{HNO}_3$  in the presence of  $\text{AgNO}_3$  contained in a hard glass tube known as carius tube in a furnace. C and H are oxidised to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The halogen forms the corresponding  $\text{AgX}$ . It is filtered, dried, and weighed.

**Estimation of sulphur :** A known mass of compound is heated with fuming  $\text{HNO}_3$  or sodium peroxide ( $\text{Na}_2\text{O}_2$ ) in the presence of  $\text{BaCl}_2$  solution in Carius tube. Sulphur is oxidised to  $\text{H}_2\text{SO}_4$  and precipitated as  $\text{BaSO}_4$ . It is filtered, dried and weighed.

19. 0.15gm of an organic compound gave 0.12 gm of silver bromide by the Carius method. Find the percentage of bromine in the compound. ( $\text{Ag} = 108$ ,  $\text{Br} = 80$ )  
 (A) 34.0 (B) 46.0 (C) 80.0 (D) 50.0  
**MC0148**
20. 0.32 gm of an organic substance when treated by Carius method gave 0.466 gm of  $\text{BaSO}_4$ . Calculate the percentage of sulphur in the compound. ( $\text{Ba} = 137$ )  
 (A) 10.0 (B) 34.0 (C) 20.0 (D) 30.0  
**MC0148**

**Comprehension Q.21 and Q.22 (2 questions)**

**Estimation of phosphorous :** A known mass of compound is heated with fuming  $\text{HNO}_3$  or sodium peroxide ( $\text{Na}_2\text{O}_2$ ) in Carius tube which converts phosphorous to  $\text{H}_3\text{PO}_4$ . Magnesia mixture ( $\text{MgCl}_2 + \text{NH}_4\text{Cl}$ ) is then added, which gives the precipitate of magnesium ammonium phosphate ( $\text{MgNH}_4\text{PO}_4$ ) which on heating gives magnesium pyrophosphate ( $\text{Mg}_2\text{P}_2\text{O}_7$ ), which is weighed.

21. 0.124 gm of an organic compound containing phosphorus gave 0.222 gm of  $\text{Mg}_2\text{P}_2\text{O}_7$  by the usual analysis. Calculate the percentage of phosphorous in the compound. ( $\text{Mg} = 24$ ,  $\text{P} = 31$ )  
 (A) 25 (B) 75 (C) 62 (D) 50  
**MC0149**

- 22 An organic compound has 6.2 % of phosphorus. On sequence of reaction, the phosphorous present in the 10 gm of organic compound is converted to  $Mg_2P_2O_7$ . Find the weight of  $Mg_2P_2O_7$  formed.  
 (A) 2.22 gm                      (B) 10.0 gm                      (C) 4.44 gm                      (D) 1.11 gm

**MC0149**

**TABLE TYPE :**

Column-I	Column-II	Column-III
(P) 60 gram sample of hydro carbon that contain 20% H and rest C	(1) %C = 40	(i) No. of atoms of C and O = $8N_A$
(Q) 240 gram urea	(2) %H = $\frac{20}{3}$	(ii) No. of C atoms = $4N_A$
(R) 120 gram acetic acid	(3) % O = $\frac{160}{3}$	(iii) No. of total atoms = $16N_A$
(S) 120 gram glucose	(4) % N = 46.7	(iv) No. of total atoms is 2 times of no. of H atom

23. Out of below correct matching is -  
 (A) P – 1 – i                      (B) P – 1 – ii                      (C) Q – 2 – iii                      (D) S – 2 – iv

**MC0150**

24. In which of following is incorrect -  
 (A) Q – 2 – iv                      (B) R – 3 – iv                      (C) P – 4 – iii                      (D) R – 1 – ii

**MC0150**

25. Out of below correct matching is -  
 (A) S – 4 – iv                      (B) R – 1 – ii                      (C) P – 4 – iii                      (D) P – 2 – ii

**MC0150**

**Table type question :**

Column-I (Gas taken)	Column-II ( $O_2$ needed for complete combustion)	Column-III (Contraction in volume)
(1) 20 ml $C_2H_4$	(i) 60 ml	(I) 50 ml
(2) 25 ml $C_3H_4$	(ii) 100 ml	(II) 40 ml
(3) 30 ml $C_2H_6$	(iii) 70 ml	(III) 75 ml
(4) 35 ml $CH_4$	(iv) 105 ml	(IV) 70 ml

All volumes are measured at 25°C and 1 atm.

26. Which of the following is correct match -  
 (A) 1 – i – II                      (B) 1 – iii – IV                      (C) 2 – iv – II                      (D) 2 – ii – III

**MC0151**

27. Which of the following is correct match -

- (A) 3 – iii – III                      (B) 3 – iv – III                      (C) 4 – iii – III                      (D) 4 – iv – IV

MC0151

28. Which of the following is incorrect (**One or more than one correct**)

- (A) 2 – ii – I                      (B) 4 – iii – IV                      (C) 3 – iv – IV                      (D) 1 – iii – II

MC0151

**Match the column :**

29. One type of artificial diamond (commonly called YAG for yttrium aluminium garnet) can be represented by the formula  $Y_3Al_5O_{12}$ . [Y = 89, Al = 27]

**Column I**

Element

- (A) Y  
(B) Al  
(C) O

**Column II**

Weight percentage

- (P) 22.73%  
(Q) 32.32%  
(R) 44.95%

MC0152

30. The recommended daily dose is 17.6 milligrams of vitamin C (ascorbic acid) having formula  $C_6H_8O_6$ . Match the following. Given :  $N_A = 6 \times 10^{23}$

**Column I**

- (A) O-atoms present in daily dose  
(B) Moles of vitamin C in 1 gm of vitamin C  
(C) Moles of vitamin C that should be consumed daily

**Column II**

- (P)  $10^{-4}$  mole  
(Q)  $5.68 \times 10^{-3}$   
(R)  $3.6 \times 10^{20}$

MC0153

31. Gaseous alkane ( $C_nH_{2n+2}$ ) exploded with oxygen. Ratio of the mol of  $O_2$  for complete combustion to the mole of  $CO_2$  formed is given in column-I & in column II formula is given.

**Column-I**

- (A) 7 : 4  
(B) 2 : 1  
(C) 5 : 3  
(D) 13 : 8

**Column-II**

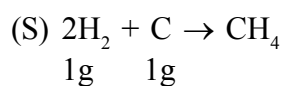
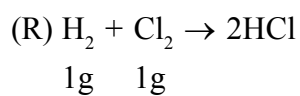
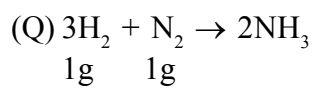
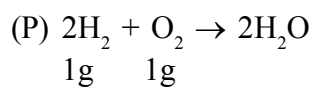
- (P)  $C_3H_8$   
(Q)  $C_4H_{10}$   
(R)  $C_2H_6$   
(S)  $CH_4$

MC0154



Matching list type :

32. Column-I



Column-II  
(mass of product)

(1) 1.028 g

(2) 1.333 g

(3) 1.125 g

(4) 1.214 g

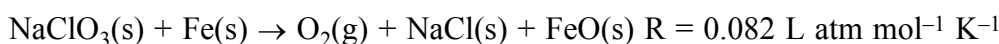
Code :

	P	Q	R	S
(A)	3	4	1	2
(B)	2	4	1	3
(C)	4	3	1	2
(D)	2	3	1	4

MC0155

## EXERCISE JEE -MAINS

1.  $\text{NaClO}_3$  is used, even in spacecrafts, to produce  $\text{O}_2$ . The daily consumption of pure  $\text{O}_2$  by a person is 492L at 1 atm, 300K. How much amount of  $\text{NaClO}_3$ , in grams, is required to produce  $\text{O}_2$  for the daily consumption of a person at 1 atm, 300 K ? [JEE(Main)-2020 (Jan)]



MC0156

2. 5 g of zinc is treated separately with an excess of [JEE(Main)-2020 (Jan)]  
 (a) dilute hydrochloric acid and  
 (b) aqueous sodium hydroxide.

The ratio of the volumes of  $\text{H}_2$  evolved in these two reactions is :

- (1) 1 : 4                      (2) 1 : 2                      (3) 2 : 1                      (4) 1 : 1

MC0157

3. The ammonia ( $\text{NH}_3$ ) released on quantitative reaction of 0.6 g urea ( $\text{NH}_2\text{CONH}_2$ ) with sodium hydroxide ( $\text{NaOH}$ ) can be neutralized by : [JEE(Main)-2020 (Jan)]

- (1) 100 ml of 0.1 N HCl                      (2) 200 ml of 0.4 N HCl  
 (3) 100 ml of 0.2 N HCl                      (4) 200 ml of 0.2 N HCl

MC0158

4. Amongst the following statements, that which was not proposed by Dalton was :  
 (1) all the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.  
 (2) chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction.  
 (3) when gases combine or reproduced in a chemical reaction they do so in a simple ratio by volume provided all gases are at the same T & P. [JEE(Main)-2020 (Jan)]  
 (4) matter consists of indivisible atoms.

MC0159

5. A 10 mg effervescent tablet containing sodium bicarbonate and oxalic acid releases 0.25 ml of  $\text{CO}_2$  at  $T = 298.15 \text{ K}$  and  $p = 1 \text{ bar}$ . If molar volume of  $\text{CO}_2$  is 25.0 L under such condition, what is the percentage of sodium bicarbonate in each tablet ? [Molar mass of  $\text{NaHCO}_3 = 84 \text{ g mol}^{-1}$ ]

- (1) 16.8                      (2) 8.4                      [JEE(Main)-2019 (Jan.)]  
 (3) 0.84                      (4) 33.6

MC0160

6. For the following reaction, the mass of water produced from 445 g of  $\text{C}_{57}\text{H}_{110}\text{O}_6$  is :



- (1) 495 g                      (2) 490 g                      (3) 890 g                      (4) 445 g

MC0161

7. The percentage composition of carbon by mole in methane is : [JEE(Main)-2019 (-april)]  
 (1) 80% (2) 25% (3) 75% (4) 20%  
**MC0162**
8. For a reaction, [JEE(Main)-2019 (-april)]  

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}) ;$$
 identify dihydrogen ( $\text{H}_2$ ) as a limiting reagent in the following reaction mixtures.  
 (1) 14g of  $\text{N}_2$  + 4g of  $\text{H}_2$  (2) 28g of  $\text{N}_2$  + 6g of  $\text{H}_2$   
 (3) 56g of  $\text{N}_2$  + 10g of  $\text{H}_2$  (4) 35g of  $\text{N}_2$  + 8g of  $\text{H}_2$   
**MC0163**
9. 5 moles of  $\text{AB}_2$  weigh  $125 \times 10^{-3}$  kg and 10 moles of  $\text{A}_2\text{B}_2$  weigh  $300 \times 10^{-3}$  kg. The molar mass of A( $M_A$ ) and molar mass of B( $M_B$ ) in  $\text{kg mol}^{-1}$  are : [JEE(Main)-2019 (April)]  
 (1)  $M_A = 50 \times 10^{-3}$  and  $M_B = 25 \times 10^{-3}$   
 (2)  $M_A = 25 \times 10^{-3}$  and  $M_B = 50 \times 10^{-3}$   
 (3)  $M_A = 5 \times 10^{-3}$  and  $M_B = 10 \times 10^{-3}$   
 (4)  $M_A = 10 \times 10^{-3}$  and  $M_B = 5 \times 10^{-3}$   
**MC0164**
10. The minimum amount of  $\text{O}_2(\text{g})$  consumed per gram of reactant is for the reaction :  
 (Given atomic mass : Fe = 56, O = 16, Mg = 24, P = 31, C = 12, H = 1)  
 (1)  $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$  [JEE(Main)-2019 (April)]  
 (2)  $\text{P}_4(\text{s}) + 5 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s})$   
 (3)  $4 \text{Fe}(\text{s}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{FeO}_3(\text{s})$   
 (4)  $2 \text{Mg}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{MgO}(\text{s})$   
**MC0165**
11. At 300 K and 1 atmospheric pressure, 10 mL of a hydrocarbon required 55 mL of  $\text{O}_2$  for complete combustion and 40 mL of  $\text{CO}_2$  is formed. The formula of the hydrocarbon is : [JEE(Main)-2019 (Jan)]  
 (1)  $\text{C}_4\text{H}_8$  (2)  $\text{C}_4\text{H}_7\text{Cl}$  (3)  $\text{C}_4\text{H}_{10}$  (4)  $\text{C}_4\text{H}_6$   
**MC0166**
12. 25 g of an unknown hydrocarbon upon burning produces 88 g of  $\text{CO}_2$  and 9 g of  $\text{H}_2\text{O}$ . This unknown hydrocarbon contains. [JEE(Main)-2019 (Jan)]  
 (1) 20g of carbon and 5 g of hydrogen (2) 24g of carbon and 1 g of hydrogen  
 (3) 18g of carbon and 7 g of hydrogen (4) 22g of carbon and 3 g of hydrogen  
**MC0167**

13. The ratio of mass percent of C and H of an organic compound ( $C_XH_YO_Z$ ) is 6 : 1. If one molecule of the above compound ( $C_XH_YO_Z$ ) contains half as much oxygen as required to burn one molecule of compound  $C_XH_Y$  completely to  $CO_2$  and  $H_2O$ . The empirical formula of compound  $C_XH_YO_Z$  is

[JEE(Main)-2018 (offline)]

- (1)  $C_2H_4O$                       (2)  $C_3H_4O_2$                       (3)  $C_2H_4O_3$                       (4)  $C_3H_6O_3$

MC0168

14. For per gram of reactant, the maximum quantity of  $N_2$  gas is produced in which of the following thermal decomposition reactions ?

[JEE(Main)-2018 (online)]

(Given : Atomic wt. – Cr = 52u, Ba = 137u)

- (1)  $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$                       (2)  $Ba(N_3)_2(s) \rightarrow Ba(s) + 3N_2(g)$   
 (3)  $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + 4H_2O(g)$                       (4)  $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

MC0169

15. An unknown chlorohydrocarbon has 3.55% of chlorine. If each molecule of the hydrocarbon has one chlorine atom only; chlorine atoms present in 1 g of chlorohydrocarbon are :

(Atomic wt. of Cl = 35.5 u; Avogadro constant =  $6.023 \times 10^{23} \text{ mol}^{-1}$ ) [JEE(Main)-2018 (online)]

- (1)  $6.023 \times 10^{21}$                       (2)  $6.023 \times 10^{23}$                       (3)  $6.023 \times 10^{20}$                       (4)  $6.023 \times 10^9$

MC0170

16. The most abundant elements by mass in the body of a healthy human adult are :

Oxygen (61.4%) ; Carbon (22.9%), Hydrogen (10.0%) ; and Nitrogen (2.6%). The weight which a 75 kg person would gain if all  $^1H$  atoms are replaced by  $^2H$  atoms is [JEE(Main)-2017]

- (1) 15 kg                      (2) 37.5 kg                      (3) 7.5 kg                      (4) 10 kg

MC0171

17. 1 gram of a carbonate ( $M_2CO_3$ ) on treatment with excess HCl produces 0.01186 mole of  $CO_2$ . the molar mass of  $M_2CO_3$  in  $g \text{ mol}^{-1}$  is :-

[JEE(Main)-2017]

- (1) 1186                      (2) 84.3                      (3) 118.6                      (4) 11.86

MC0172

18. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is :

(Atomic mass Ag = 108; Br = 80)

[JEE(Main)-2015]

- (1) 48                      (2) 60                      (3) 24                      (4) 36

MC0173

19. The ratio of masses of oxygen and nitrogen in a particular gaseous mixture is 1 : 4. The ratio of number of their molecule is :

[JEE(Main)-2014]

- (1) 1 : 8                      (2) 3 : 16                      (3) 1 : 4                      (4) 7 : 32

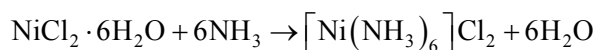
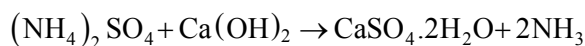
MC0174

20. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of  $\text{CO}_2$ . The empirical formula of the hydrocarbon is [JEE(Main)-2013]  
(1)  $\text{C}_2\text{H}_4$                       (2)  $\text{C}_3\text{H}_4$                       (3)  $\text{C}_6\text{H}_5$                       (4)  $\text{C}_7\text{H}_8$   
MC0175
21. A transition metal M forms a volatile chloride which has a vapour density of 94.8. If it contains 74.75% of chlorine the formula of the metal chloride will be [AIEEE 2012 (Online)]  
(1)  $\text{MCl}_2$                       (2)  $\text{MCl}_4$                       (3)  $\text{MCl}_5$                       (4)  $\text{MCl}_3$   
MC0176
22. The ratio of number of oxygen atoms (O) in 16.0 g ozone ( $\text{O}_3$ ), 28.0 g carbon monoxide (CO) and 16.0 g oxygen ( $\text{O}_2$ ) is :-  
(Atomic mass : C = 12, O = 16 and Avogadro's constant  $N_A = 6.0 \times 10^{23} \text{ mol}^{-1}$ ) [AIEEE 2012 (Online)]  
(1) 3 : 1 : 1                      (2) 1 : 1 : 2                      (3) 3 : 1 : 2                      (4) 1 : 1 : 1  
MC0177

## EXERCISE JEE-ADVANCED

1. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  are used in the preparation, the combined weight (in kg) of gypsum and the nickel-ammonia coordination compound thus produced is \_\_\_\_.

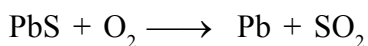
[JEE 2018]



(Atomic weights in  $\text{g mol}^{-1}$ : H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59)

MC0178

2. Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the contents undergo self-reduction. The weight (in kg) of Pb produced per kg of  $\text{O}_2$  consumed is \_\_\_\_\_.



[JEE 2018]

(Atomic weights in  $\text{g mol}^{-1}$ : O = 16, S = 32, Pb = 207)

MC0179

3. If the value of Avogadro number is  $6.023 \times 10^{23} \text{ mol}^{-1}$  and the value of Boltzmann constant is  $1.380 \times 10^{-23} \text{ JK}^{-1}$ , then the number of significant digits in the calculated value of the universal gas constant is

[JEE 2014]

MC0180

## ANSWER KEY

## EXERCISE S-I

- |  |   |  |
|--|---|--|
| 1. (i) 0.16 or 0.17<br>(iii) 23.38<br>(v) 12.04                            | (ii) 3200.00<br>(iv) (18.06 or 18.07), (54.19 or 54.20) |  |
| 2. 1.99  | 3. 3.20   | 4. 180.00  |
| 5. 2.43 or 2.44  | 6. Ans. (9.48)  | 7. Ans.(55.00)   |
| 8. Ans. (34.05)  | 9. Ans.(2.00)   | 10. Ans.(102.50)   |
| 11. 36.50  | 12. 27.60   | 13. 3.61   |
| 14. 0.63   | 15. 58.80   | 16. 6.41 or 6.42   |
| 17. 0.11 or 0.12   | 18. 0.25  | 19. 5.60   |
| 20. %Al = 60; %Mg = 40   |   |  |
| 21. %CaCO <sub>3</sub> = 28.40 or 28.41, %MgCO <sub>3</sub> = 71.59        |   |  |
| 22. %NaHCO <sub>3</sub> = 16.80 ; %Na <sub>2</sub> CO <sub>3</sub> = 83.20 |   |  |
| 23. 0.75   | 24. 1.70  | 25. 0.50   |
| 26. 39.18  | 27. 4.48  | 28. 61.50  |
| 29. 0.20   | 30. Ans. (50.00)  | 31. Ans. (31.42 or 31.43)                                |
| 32. Ans. (0.64)  | 33. Ans. (40.00)  | 34. Ans. (0.72)  |
| 35. Ans.(0.04)   | 36. Ans.(3.04)  | 37. 6.40   |
| 38. (a) 0.71 (b) 61.97   | 39. 1.20  | 40. Ans. (4.00)  |
| 41. Ans. (33.33)   | 42. 5.28  | 43. Ans. (4.00)  |
| 44. Ans.(2.00)   | 45. Ans.(0.07)  | 46. (19.00)  |
| 47. C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>                          | 48. Ans (3.00)  | 49. Ans. (C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> ) |
| 50. Ans. (0.50)  | 51. Ans. 140.00   | 52. 30.00  |
| 53. 70.00  | 54. Ans.(10.00)   | 55. 73.33  |
| 56. 10.00  | 57. Ans.(N <sub>2</sub> O <sub>5</sub> )                | 58. Ans. (C <sub>2</sub> H <sub>6</sub> )                |
| 59. (3.00)   | 60. Ans. (5.00)   |  |

## EXERCISE S-II

- |   |                |                 |
|---|----------------|-----------------|
| 1. (i) 0.5, 0.5 ; (ii) 2, 1 (iii) 1, 2  | 2. (65.62)     | 3. 0.66         |
| 4. %NaCl = 77.80  |                |                 |
| 5. (i) Fe <sub>2</sub> O <sub>3</sub> + 2 Al → Al <sub>2</sub> O <sub>3</sub> + 2Fe; (ii) 2.96 ; (iii) 10,000 units |                |                 |
| 6. Ans. 5.74  | 7. Ans. 6.02   | 8. (1.50)       |
| 9. Ans. (222.00)  | 10. (11.00)    | 11. Ans. (5.00) |
| 12. Ans.(1.70)  | 13. Ans.(3.30) |                 |

$$14. \% \text{ Ag} = \frac{0.5}{0.66} \times 100 = 75.75$$

$$\% \text{ Ag} = \frac{1}{1.32} \times 100 = 75.75$$

In both AgCl, % Ag is same.

15.  $\% \text{ Pb} = \frac{6.488}{(6.488 + 1.002)} \times 100 = 86.62\%$
16. Oxide = 1 gm  $\Rightarrow$  oxygen = 0.5 gm + element = 0.8 gm  
Ratio = 1 : 1  
Oxide = 4 gm  $\Rightarrow$  oxygen = 3.2 gm + element = 0.8 gm  
Ratio = 4 : 1
17. 0.11 gm oxide gives  $\Rightarrow$  0.07 gm N, Hence ; 0.07 gm N + 0.04 gm O  
0.15 gm oxide gives  $\Rightarrow$  0.07 gm N, Hence ; 0.07 gm N + 0.08 gm O
18.  $\text{CH}_4 = 4.50$ ,  $\text{CO}_2 = 1.50$ ,  $\text{C}_2\text{H}_4 = 4.00$
19. (0.66 or 0.67)
20. 9.00

### EXERCISE O-I

- |     |         |     |                 |     |                 |     |         |
|-----|---------|-----|-----------------|-----|-----------------|-----|---------|
| 1   | Ans.(C) | 2   | Ans.(B)         | 3   | Ans.(D)         | 4   | Ans.(C) |
| 5   | Ans.(C) | 6   | Ans.(C)         | 7   | Ans.(A)         | 8   | Ans.(B) |
| 9   | Ans.(C) | 10. | Ans. (C)        | 11. | Ans.(B)         | 12. | Ans.(C) |
| 13. | Ans.(B) | 14. | Ans (B)         | 15  | Ans.(A)         | 16  | Ans.(C) |
| 17  | Ans.(B) | 18  | <b>Ans.</b> (A) | 19. | Ans (B)         | 20. | Ans.(B) |
| 21. | Ans.(D) | 22. | Ans. (B)        | 23. | <b>Ans.</b> (A) | 24. | Ans.(A) |
| 25. | Ans.(D) | 26  | Ans.(A)         | 27. | Ans.(A)         | 28. | Ans.(B) |
| 29. | Ans.(A) | 30. | Ans. (A)        | 31. | Ans(A)          | 32. | Ans(C)  |
| 33. | Ans.(C) | 34. | <b>Ans.</b> (C) | 35. | Ans.(C)         | 36. | Ans.(D) |
| 37. | Ans(C)  | 38. | Ans.(A)         | 39. | Ans(B)          | 40. | Ans.(B) |
| 41. | Ans(C)  | 42. | Ans.(D)         | 43. | Ans.(B)         | 44. | Ans.(A) |
| 45. | Ans.(D) | 46. | Ans.(B)         | 47. | Ans.(A)         | 48. | Ans.(B) |
| 49. | Ans.(C) | 50. | Ans.(C)         |     |                 |     |         |

### EXERCISE O-II

- |     |                                   |     |             |     |                          |     |             |
|-----|-----------------------------------|-----|-------------|-----|--------------------------|-----|-------------|
| 1.  | Ans.(C)                           | 2.  | Ans.(B)     | 3.  | Ans. (A)                 | 4.  | Ans.(C)     |
| 5.  | Ans.(C)                           | 6.  | Ans.(D)     | 7.  | Ans.(B)                  | 8.  | Ans.(A,B,D) |
| 9.  | Ans (B,C,D)                       | 10. | Ans.(A,B,C) | 11. | Ans. (A, B)              | 12. | (A, C)      |
| 13. | (A, B, D)                         | 14. | Ans.(C)     | 15. | Ans.(C)                  | 16. | Ans.(B)     |
| 17. | Ans.(C)                           | 18. | Ans.(B)     | 19  | Ans.(A)                  | 20  | Ans.(C)     |
| 21  | Ans.(D)                           | 22. | Ans.(A)     | 23. | Ans.(D)                  | 24. | Ans.(C)     |
| 25. | Ans.(B)                           | 26. | Ans.(A)     | 27. | Ans.(B)                  | 28. | Ans.(C,D)   |
| 29. | Ans. (A) R, (B) P, (C) Q          |     |             | 30  | Ans. (A) R, (B) Q, (C) P |     |             |
| 31. | Ans.A - R ; B - S ; C - P ; D - Q |     |             | 32. | Ans.(A)                  |     |             |



**EXERCISE JEE -MAINS**

- |                        |             |             |             |
|------------------------|-------------|-------------|-------------|
| 1. Ans. (2120 to 2140) | 2. Ans. (4) | 3. Ans. (3) | 4. Ans. (3) |
| 5. Ans.(2)             | 6. Ans.(1)  | 7. Ans.(4)  | 8. Ans.(3)  |
| 9. Ans.(3)             | 10. Ans.(3) | 11. Ans.(4) | 12. Ans.(2) |
| 13. Ans.(3)            | 14. Ans.(4) | 15. Ans.(3) | 16. Ans.(3) |
| 17. Ans.(2)            | 18. Ans.(3) | 19. Ans.(4) | 20. Ans.(4) |
| 21. Ans.(2)            | 22. Ans.(4) |             |             |

**J-ADVANCE**

- 
- |                |                |             |
|----------------|----------------|-------------|
| 1. Ans. (2.99) | 2. Ans. (6.47) | 3. Ans. (4) |
|----------------|----------------|-------------|





# Chapter Contents

## 02

## CONCENTRATION TERMS

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## CONCENTRATION TERMS

### 1. SOLUTIONS

A solution is a homogenous mixture of two or more pure substances whose composition may be altered within certain limits. Though the solution is homogenous in nature, yet it retains the properties of its constituents.

Generally solution is composed of two components, **solute** and **solvent**. Such type of solution is known as binary solution.

Solvent is that component in solution whose physical state is the same as that of the resulting solution while other component is called as solute. If the physical state of both component is same, then the component in excess is known as solvent and other one is called as solute. Each component in a binary solution can be in any physical state such as liquid, solid and gaseous state.

#### Types of Solutions

Type of Solutions	Solute	Solvent	Common Example
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

### 2. CONCENTRATION OR STRENGTH OF SOLUTION :

The concentration of a solution is the amount of solute dissolved in a known amount of the solvent or solution. Solution can be described as dilute or concentrated solution as per their concentration. A dilute solution has a very small quantity of solute while concentrated solution has a large quantity of solute in solution. Various concentration terms are as follows.

#### 2.1 Mass percentage :

It may be defined as the number of parts of mass of solute per hundred parts by mass of solution.

$$\% \text{ by mass } \left( \frac{w}{W} \right) = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 100$$

[X % by mass means 100 gm solution contains X gm solute and hence = and hence (100 – X) gm solvent]

**2.2 Mass-volume percentage (W/V %) :**

It may be defined as the mass of solute (in gm) present in 100 cm<sup>3</sup> of solution. For example, If 100 cm<sup>3</sup> of solution contains 5 g of sodium hydroxide, then the mass-volume percentage will be 5% solution.

$$\% \left( \frac{w}{V} \right) = \frac{\text{wt. of solute}}{\text{volume of solution}} \times 100$$

$$[X \% \left( \frac{w}{V} \right) \text{ means } 100 \text{ ml solution contains } X \text{ gm solute}]$$

**2.3 Volume Percent :**

It can be represented as % v/v or % volume and normally used for the solutions in which both components are in liquids state. It is the number of parts of by volume solute per hundred parts by volume of solution. Therefore,

$$\% \left( \frac{v}{V} \right) = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100$$

$$\mathbf{2.4 \quad Mole \%} = \frac{\text{Moles of solute}}{\text{Total moles}} \times 100$$

- For gases, % by volume is same as mole %

**2.5 Mole Fraction (X) :**

Mole fraction may be defined as the ratio of number of moles of one component to the total number of moles of all the components (solute and solvent) present in solution. It is denoted by letter X and the sum of all mole fractions in a solution is always equals to one.

$$\text{Mole fraction (X)} = \frac{\text{Moles of solute}}{\text{Total moles}}$$

Mole fraction does not depend upon temperature and can be extended to solutions having more than two components.

**2.6 Molarity (M) :**

Molarity is most common unit for concentration of solution. It is defined as the number of moles of solute present in one litre or one dm<sup>3</sup> of the solution or millimol of solute present in one mL of solution.

$$\text{Molarity (M)} = \frac{\text{Mole of solute}}{\text{volume of solution in litre}}$$

**2.7 Molality (m) :** The number of mole of the solute present in 1000 g of the solvent is known as molality of solution. It represented by letter 'm'.

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

The unit of molality is mol/kg and it does not affect by temperature.

**2.8 Parts per million (ppm) :** The very low concentration of solute in solution can be expressed in ppm. It is the number of parts by mass of solute per million parts by mass of the solution.

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solvent}} \times 10^6 \cong \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

◆ Get yourselves very much comfortable in their inter conversion. It is very handy.

Concentration Type	Mathematical Formula	Concept
Percentage by mass	$\% \left( \frac{w}{w} \right) = \frac{\text{Mass of solute} \times 100}{\text{Mass of solution}}$	Mass (in gm) of solute present in 100 gm of solution.
Volume percentage	$\% \left( \frac{v}{v} \right) = \frac{\text{Volume of solute} \times 100}{\text{Volume of solution}}$	Volume (cm <sup>3</sup> ) of solute present in 100 cm <sup>3</sup> of solution.
Mass-volume percentage	$\% \left( \frac{w}{v} \right) = \frac{\text{Mass of solute} \times 100}{\text{Volume of solution}}$	Mass (in gm) of solute present in 100 cm <sup>3</sup> of solution.
Parts per million	$\text{ppm} = \frac{\text{Mass of solute} \times 10^6}{\text{Mass of solution}}$	Parts by mass of solute per million parts by mass of the solution
Mole fraction	$X_A = \frac{\text{Mole of A}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \dots}$ $X_B = \frac{\text{Mole of B}}{\text{Mole of A} + \text{Mole of B} + \text{Mole of C} + \dots}$	Ratio of number of moles of one component to the total number of moles.
Molarity	$M = \frac{\text{Mole of solute}}{\text{Volume of solution (in L)}}$	Moles of solute
Molality	$m = \frac{\text{Mass of solute} \times 1000}{\text{Molar mass of solute} \times \text{Mass of solvent (g)}}$	in one litre of solution. Moles of solute in one kg of solvent

**Ex.1** Calculate the mole fractions of the components of the solution composed by 92 g glycerol and 90 g water ? ( $M(\text{water}) = 18$  ;  $M(\text{glycerol}) = 92$ )

$$\text{Moles of water} = 90 \text{ g} / 18 \text{ g} = 5 \text{ mol water}$$

$$\text{Moles of glycerol} = 92 \text{ g} / 92 \text{ g} = 1 \text{ mol glycerol}$$

$$\text{Total moles in solution} = 5 + 1 = 6 \text{ mol}$$

$$\text{Mole fraction of water} = 5 \text{ mol} / 6 \text{ mol} = 0.833$$

$$\text{Mole fraction of glycerol} = 1 \text{ mol} / 6 \text{ mol} = 0.167$$

**Ex.2** What will be the molarity of solution when water is added to 16.4g  $\text{Ca}(\text{NO}_3)_2$  to make 100 mL of solution?

$$\text{Mol of } \text{Ca}(\text{NO}_3)_2 = 16.4 / 164 = 0.1$$

$$\text{Molarity} = \text{Mole of solute} / \text{Volume of solution (L)} = 0.10 \text{ mol} / 0.10 \text{ L}$$

$$\text{Therefore, Molarity of given solution} = 1.0 \text{ M}$$

**Ex.3** Calculate the molality of a solution containing 20 g of sodium hydroxide (NaOH) in 250 g of water?

$$\text{Moles of sodium hydroxide} = 20 / 40 = 0.5 \text{ mol NaOH}$$

$$250 \text{ gm} = 0.25 \text{ kg of water}$$

$$\text{Hence molality of solution} = \text{Mole of solute} / \text{Mass of solvent (kg)} = 0.5 \text{ mol} / 0.25 \text{ kg}$$

$$\text{or Molality (m)} = 2.0 \text{ m}$$

**Ex.4** Calculate the gram of copper sulphate ( $\text{CuSO}_4$ ) needed to prepare 250.0 mL of 1.00 M  $\text{CuSO}_4$ ?

$$\text{Moles of } \text{CuSO}_4 = M \times V = 1 \times \frac{250}{1000}$$

$$\text{Molar mass of copper sulphate} = 159.6 \text{ g/mol}$$

$$\text{Hence Mass of copper sulphate (gm)} = \text{Moles of } \text{CuSO}_4 \times \text{Molar mass of copper sulphate.}$$

$$= 1 \times \frac{250}{1000} \times 159.6 \text{ g/mol} = 39.9 \text{ gm of Copper sulphate}$$

**Ex.5** How many gram of  $\text{H}_2\text{SO}_4$  are present in 500 ml of 0.2M  $\text{H}_2\text{SO}_4$  solution ?

$$M = \frac{\text{moles}}{\text{vol.}} \Rightarrow \text{moles of } \text{H}_2\text{SO}_4 = M \times V = 0.2 \times \frac{500}{1000} \text{ L} = 0.1$$

$$\text{Mass of } \text{H}_2\text{SO}_4 = 0.1 \times 98 = 9.8 \text{ g}$$

**Ex.6** Calculate the ppm of mercury in water in a sample containing 30 mg of Hg in 500 ml of solution.

$$\text{Parts per million} = \frac{\text{Mass of solute} \times 10^6}{\text{Mass of solution}}$$



Mass of Hg = 30 mg

Mass of water =  $500/1 = 500\text{g} = 50 \times 10^4 \text{mg}$

(density = mass / volume ; density of water 1 g/ml)  $w = \frac{v}{d}$

Therefore, ppm of mercury =  $\frac{30 \times 10^6}{50 \times 10^4} = 60$  ppm of mercury

**Ex.7** A 100g NaOH solution has 20g NaOH. Find molality.

$$m = \frac{20/40}{100-20} \times 1000 = \frac{500}{80} = 6.25 \text{ mol/kg}$$

**Ex.8** Find molality of aqueous solution of  $\text{CH}_3\text{COOH}$  whose molarity is 2M and density  $d = 1.2 \text{ g/mL}$ .

$$\text{Hint : } \frac{1000 \times M}{1000 \times d - MM_s}$$

where  $d =$  density in  $\text{gL}^{-1}$ ,  $M =$  Molarity,  $m =$  molality,  $M_s =$  molar mass of solute.

$$m = \frac{2}{1200 - 2 \times 60} \times 1000 = 1.85 \text{ m}$$

**Ex.9** A solution has 80%  $\frac{w}{w}$  NaOH with density  $2\text{gL}^{-1}$ . Find (a) Molarity (b) Molality of solution.

Let V be vol. of solution, in L

$$\text{Mass of solute} = (d \times V) \times \left(\frac{\% w}{w}\right) = 2 \times V \times \frac{80}{100} = 1.6V$$

$$(a) M = \frac{1.6V/40}{V} = 0.04 \text{ m} \quad (b) m = \frac{1.6V/40}{2V-1.6V} \times 1000 = 100 \text{ mol kg}^{-1}$$

**Ex.10** 4.450 g sulphuric acid was added to 82.20 g water and the density of the solution was found to be 1.029 g/cc at 25°C and 1 atm pressure. Calculate

(a) the weight percent,

(b) the mole fraction ,

(c) the mole percent,

(d) the molality ,

(e) the molarity of sulphuric acid in the solution under these conditions.

Sulphuric acid = 4.450 g , Water = 82.20 g  $\Rightarrow$  Wt. of solution = 86.65 g

$\therefore$  Density of solution = 1.029 g/cc.

$$(a) \text{ Weight percent} = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 100 = \frac{4.450}{86.65} \times 100 = 5.14$$

(b) Mole fraction :

$$\text{Mole of solute} = \frac{\text{wt. of solute}}{\text{mol wt. of solute}} = \frac{4.45}{98} = 0.0454$$

$$\text{Mole of solvent} = \frac{82.20}{18} = 4.566$$

$$\text{Total moles in solution} = 0.0454 + 4.566 = 4.6114$$

$$\text{Mole fraction of solute} = \frac{0.0454}{4.6114} = 0.0098$$

(c) Mole percent = mole fraction of solute  $\times 100 = 0.0098 \times 100 = 0.98$

(d) Molality =  $\frac{\text{moles of solute}}{\text{mass of solvent (in gm)}} \times 1000$   

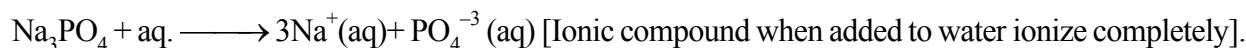
$$= \frac{0.0454 \times 1000}{82.2} = 0.552$$

(e) Molarity =  $\frac{\text{moles of solute}}{\text{litre of solution}}$

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{86.65}{1.029} \text{ ml} = \frac{86.65}{1.029 \times 1000} \text{ litre}$$

$$\text{Molarity} = \frac{0.0454}{\frac{86.65}{1.029 \times 1000}} = \frac{0.0454 \times 1000 \times 1.029}{86.65} = 0.539$$

**Ex.11** Find number of  $\text{Na}^+$  &  $\text{PO}_4^{-3}$  ions in 250 ml of 0.2M  $\text{Na}_3\text{PO}_4$  solution.



$$50 \text{ millimoles (m.m.)} \quad 150 \text{ mm} \quad 50 \text{ mm}$$

$$\text{No. of Na}^+ \text{ ions} = 150 \times 10^{-3} \times N_A ; \text{No. of PO}_4^{-3} \text{ ions} = 50 \times 10^{-3} \times N_A$$

**Ex.12** 80g NaOH was added to 2L water. Find molality of solution if density of water = 1g/mL

**Ans.**  $m = \frac{\text{moles of NaOH}}{\text{mass of H}_2\text{O}} \times 1000 = \frac{80/40}{2 \times 1000} \times 1000 = 1 \text{ molal}$

**Ex.13** The average concentration of  $\text{Na}^+$  ion in human body is 3.0 to 3.9 gm per litre. The molarity of  $\text{Na}^+$  ion is about.

$$0.15 \text{ M}$$

**Sol.**  $M_{\text{Na}^+} = \frac{n_{\text{solute}}}{\text{volume of solution in Lt}} = \frac{3+3.9}{2} = \frac{6.9}{46} = 0.15 \text{ M}$

### DO YOUR SELF-01

Q.1 8 g NaOH is dissolved in one litre of solution. Its molarity is :

- (A) 0.8 M                      (B) 0.4 M                      (C) 0.2 M                      (D) 0.1 M

Q.2 If 18 g of glucose is present in 1000 g of solvent, the solution is said to be :

- (A) 1 molar                      (B) 0.1 molar                      (C) 0.5 molar                      (D) 0.1 molal

- Q.3 The mole fraction of oxygen in a mixture of 7g of nitrogen and 8g of oxygen is :
- (A)  $\frac{8}{15}$  (B) 0.5 (C) 0.25 (D) 1.0
- Q.4 For preparing 0.1 M solution of  $H_2SO_4$  in one litre, we need  $H_2SO_4$  :
- (A) 0.98 g (B) 4.9 g (C) 49.0 g (D) 9.8 g
- Q.5 What is the concentration of chloride ion, in molarity, in a solution containing 10.56 gm  $BaCl_2 \cdot 8H_2O$  per litre of solution ? (Ba = 137)

**Answers :**

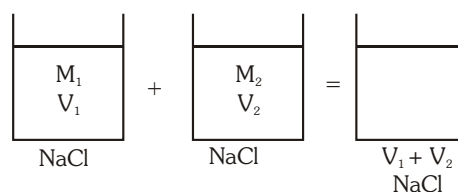
- Q.1 (C)                      Q.2 (D)                      Q.3 (B)                      Q.4 (D)                      Q.5 0.06 M

**3. MIXING OF AND DILUTION SOLUTIONS :**

It is based on law of conservation of moles of solute

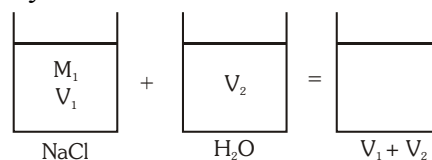
**(i) Two solutions having same solute**

$$\text{Final molarity} = \frac{\text{Total moles}}{\text{Total volume}} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$



**(ii) Dilution Effect :** When a solution is diluted, the moles of solute do not change but molarity changes while on taking out a small volume of solution from a larger volume, the molarity of solution do not change but moles change proportionately.

$$\text{Final molarity} = \frac{M_1V_1}{V_1 + V_2}$$



**n-fold or n-times dilution**

$$\Rightarrow \text{Final volume} = V_1 + V_2 = n(V_1)$$

**Ex.14** 50 ml 0.2 M  $H_2SO_4$  is mixed with 50 ml 0.3M  $H_2SO_4$ . Find molarity of final solution.

$$M_f = \frac{\text{Total moles of } H_2SO_4}{\text{Total volume}} = \frac{50 \times 0.2 \times 10^{-3} + 50 \times 10^{-3} \times 0.3}{(50 + 50) \times 10^{-3}} = 0.25 \text{ M.}$$

**Ex.15** Find final molarity in each case :

- (i) 500 ml 0.1 M HCl + 500 ml 0.2M HCl  
 (ii) 50 ml, 0.1M HCl + 150 ml, 0.3MHCl + 300 ml  $H_2O$   
 (iii) 4.9g  $H_2SO_4$  + 250 ml  $H_2O$  + 250 ml 0.1 M  $H_2SO_4$

**Answer :**

(i)  $M_f = \frac{500 \times 0.1 + 500 \times 0.2}{500 + 500} = 0.15 \text{ M.}$

(ii)  $M_f = \frac{50 \times 0.1 + 150 \times 0.3}{50 + 150 + 300} = \frac{50}{500} = 0.1 \text{ M}$

(iii)  $M_f = \frac{4.9}{98} + \frac{250}{1000} \times 0.1}{\left(\frac{250 + 250}{1000}\right)} = \frac{50 + 25}{500} = 0.15 \text{ M}$

**Ex.16** How much water should be added to 2M HCl solution to form 1 litre of 0.5 M HCl ?

Let V be initial volume

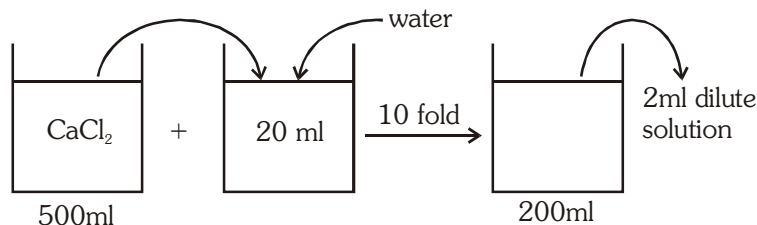
Then mol of HCl = constant

$$2 \times V = 1 \times 0.5 \Rightarrow V = 0.25 \text{ L}$$

$$\text{Volume of water added} = 1 - 0.25 = 0.75 \text{ L}$$

**Ex.17** 1.11g  $\text{CaCl}_2$  is added to water forming 500 ml of solution. 20 ml of this solution is taken and diluted 10 folds. Find moles of  $\text{Cl}^-$  ions in 2 ml of diluted solution.

$$\frac{1.11}{111} = 0.01 \text{ mol CaCl}_2$$



$$\text{Moles of CaCl}_2 \text{ in 20ml solution} = \frac{0.01}{500} \times 20 = \frac{0.01}{25}$$

$$\text{In 200 ml solution, moles of CaCl}_2 = \frac{0.01}{25} \text{ [Note : Dilution does not change moles of solute]}$$

$$\text{In 2 ml of dilute solution moles of CaCl}_2 = \frac{0.01/25}{200} \times 2 = \frac{0.01}{2500} = 4 \times 10^{-6}$$

$$\therefore \text{ moles of Cl}^- = 2 \times 4 \times 10^{-6} = 8 \times 10^{-6}$$

**Ex.18** What volumes of 1M & 2M  $\text{H}_2\text{SO}_4$  solution are required to produce 2L of 1.75M  $\text{H}_2\text{SO}_4$  solution?

Let XL be vol. of 1M solution.

$\therefore (2 - X)\text{L}$  is vol. of 2M solution.

$$\text{Moles of H}_2\text{SO}_4 : 2 \times 1.75 = 1(X) + (2 - X)2 \Rightarrow X = 0.5 \text{ L}$$

i.e. 0.5L of 1M & 1.5 L of 2M solution are required.

**Ex.19** A solution is made by mixing 300 ml 1.5M  $\text{Al}_2(\text{SO}_4)_3$  + 300 ml 2M  $\text{CaSO}_4$  + 400 ml 3.5M  $\text{CaCl}_2$

Find final molarity of (1)  $\text{SO}_4^{2-}$ , (2)  $\text{Ca}^{2+}$ , (3)  $\text{Cl}^-$ . [Assume complete dissociation of these compounds].

$$(1) [\text{SO}_4^{2-}]_f = \frac{\text{Total moles}}{\text{Total volume}} = \frac{300 \times 1.5 \times 10^{-3} \times 3 + 300 \times 2 \times 10^{-3}}{(300 + 300 + 400) \times 10^{-3}} = 1.95\text{M}$$

$$(2) [\text{Ca}^{+2}]_f = \frac{300 \times 2 + 400 \times 3.5}{1000} = 2\text{M}$$

$$(3) [\text{Cl}^-]_f = \frac{400 \times 3.5 \times 2}{1000} = 2.8\text{M}$$

**Ex.20** A solution of KCl has a density of  $1.69 \text{ g mL}^{-1}$  and is 67% by weight. Find the density of the solution if it is diluted so that the percentage by weight of KCl in the diluted solution is 30%.

Let the volume of the KCl solution be 100 mL,

$$\text{Weight of KCl solution} = 100 \times 1.69 = 169 \text{ g}$$

$$100 \text{ g of solution contains} = 67 \text{ g of KCl}$$

$$169 \text{ g of solution} = \frac{67}{100} \times 169 = 113.23 \text{ g}$$

Let  $x$  mL of  $\text{H}_2\text{O}$  be added.

$$\text{New volume of solution} = (100 + x) \text{ mL}$$

$$\text{New weight of solution} = (169 + x) \text{ g}$$

$$(\text{Since } x \text{ mL of } \text{H}_2\text{O} = x \text{ g of } \text{H}_2\text{O}, d_{\text{H}_2\text{O}} = 1)$$

$$\text{New percentage of the solution} = 30\%$$

$$\% \text{ by weight} = \frac{\text{weight of solute} \times 100}{\text{weight of solution}}$$

$$30 = \frac{113.23}{(169 + x)} \times 100$$

$$x = 208.43 \text{ mL} = 208.43 \text{ g}$$

$$\text{New density} = \frac{\text{New weight of solution}}{\text{New volume of solution}} = \frac{(169 + x)}{(100 + x)}$$

$$\therefore d = 1.224 \text{ gm/ml}$$

**Ex.21** Calculate the amount of the water "in mL" which must be added to a given solution of concentration of 40 mg silver nitrate per ml, to yield a solution of concentration of 16 mg silver nitrate per ml ?

1.5 ml

Sol. Before dilution                      After dilution

$$(n_{\text{solute}}) \quad = \quad (n_{\text{solute}})$$

$$M_i V_i \quad = \quad M_f V_f$$

$$\frac{40}{170} \times 1 \quad = \quad \frac{16}{170} (1 + V)$$

$$\Rightarrow V = 1.5 \text{ mL}$$

**Ex.22.** 100 ml, 3%(w/v) NaOH solution is mixed with 100 ml, 9%(w/v) NaOH solution. The molarity of final solution is-

**Ans. (1.5)**

Total NaOH in 100 ml (1st solution) = 3 gm

Total NaOH in 100 ml (2nd solution) = 9 gm

$$\therefore \text{Molarity} = \left( \frac{12/40}{200/1000} \right) = 1.5M$$

**Ex.23.** 1120 gm of 2 'm' urea solution is mixed with 2480 gm of 4 'm' urea solution. Calculate the molality of the resulting solution?

**Ans.** 3.33 m

**Sol.** Let 2 m, 1120 g solution have mass of solute = w gm

$$\therefore \text{solvent} = (1120 - w) \text{ gm}$$

& Let 4 m, 2480 g solution have mass of solute = w' gm

$$\therefore \text{solvent} = (2480 - w) \text{ gm}$$

$$\text{molality} = \frac{n_{\text{solute}}}{\text{wt. of solvent in kg}}$$

$$2 = \frac{w/60}{1120 - w} \times 1000$$

$$w = 120 \text{ gm}$$

$$\& 4 = \frac{w'/60}{2480 - w'} \times 1000$$

$$w' = 480 \text{ gm}$$

$$\text{resulting molality } m = \frac{120 + 480}{1120 - 120 + 2480 - 480} \times 1000 = 3.33 \text{ m}$$

### DO YOUR SELF-02

- Find the resultant molarity obtained by mixing the 2 litre, 0.5M HCl + 3 litre, 0.2 M HCl.
- Find the resultant molarity obtained by mixing the 500 ml, 1M NaCl + 200 ml, 2M NaCl

**Answers:**

- 0.32 M**
- $\frac{9}{7}$  M**

#### 4. SOME TYPICAL CONCENTRATION TERMS

##### 4.1 PERCENTAGE LABELLING OF OLEUM :

Labelled as '% oleum', it means maximum amount of  $\text{H}_2\text{SO}_4$  that can be obtained from 100 gm of such oleum (mixture of  $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$ ) by adding sufficient water. For ex. 109 % oleum sample means, with the addition of sufficient water to 100 gm oleum sample 109 gm  $\text{H}_2\text{SO}_4$  is obtained.

$$\% \text{ labelling of oleum sample} = (100 + x)\%$$

$x$  = mass of  $\text{H}_2\text{O}$  required for the complete conversion of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$

**Ex.24 Find the mass of free  $\text{SO}_3$  present in 100 gm , 109 % oleum sample.**

**Sol.** 109 % means, 9 gm of  $\text{H}_2\text{O}$  is required for 100 gm oleum



9gm

1/2mole

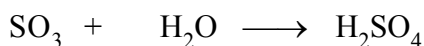
1/2mole

40gm

$\therefore$  Mass of free  $\text{SO}_3 = 40 \text{ gm}$  , Mass of  $\text{H}_2\text{SO}_4 = 60 \text{ gm}$

**Ex.25 Find the % labelling of 100 gm oleum sample if it contains 20 gm  $\text{SO}_3$ .**

**Sol.** % labelling of oleum sample =  $(100 + x)\%$



20gm

1/4mole

1/4mole

4.5gm

$\therefore$  % labelling of oleum sample =  $(100 + 4.5)\% = 104.5\%$

**Ex.26 An oleum sample is labelled as 118 %, Calculate composition of mixture (mass of components) if 40 gm water is added to 30 gm given oleum sample.**

$$\text{H}_2\text{SO}_4 = 35.4 \text{ gm}, \text{H}_2\text{O} = 34.6 \text{ gm}$$

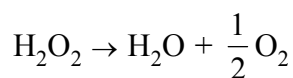
**Sol.** In 100 gm sample requires water = 18 gm

$$30 \text{ gm sample will require water} = \frac{18}{100} \times 30 = 5.4 \text{ gm}$$

Mass of  $\text{H}_2\text{O} = 40 - 5.4 = 34.6 \text{ gm}$  and mass of  $\text{H}_2\text{SO}_4 = 70 - 34.6 = 35.4 \text{ gm}$ .

##### 4.2 VOLUME STRENGTH OF $\text{H}_2\text{O}_2$ SOLUTION :

Labelled as 'volume  $\text{H}_2\text{O}_2$ ', it means volume of  $\text{O}_2$  (in litre) at STP that can be obtained from 1 litre of  $\text{H}_2\text{O}_2$  solution, when  $\text{H}_2\text{O}_2$  when it decomposes according to



**Volume Strength of  $\text{H}_2\text{O}_2$  Solution =  $11.35 \times$  molarity**

**Ex.27** Find the % w/v of "10 V"  $H_2O_2$  solution-

**Sol.** Molarity (M) of solution =  $\frac{\text{volume strength}}{11.35} = \frac{10}{11.35}$

$$\% \left( \frac{w}{v} \right) = \frac{M \times \text{mol. wt. of solute}}{10} = \frac{10}{11.35} \times \frac{34}{10} = 3\%$$

**Ex.28**  $2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$

Under conditions where 1 mole of gas occupies  $24 \text{ dm}^3$ , X L of  $\frac{1}{24} \text{ M}$  solution of  $H_2O_2$  produces  $3 \text{ dm}^3$  of  $O_2$ . Thus X is :-

**Ans.** (6)

$$\text{moles of } H_2O_2 = \frac{1}{24} \times X$$

$$\text{moles of } O_2 = \frac{3}{24} = \frac{1}{8}$$

$$\text{moles of } H_2O_2 = \frac{1}{4} = \frac{X}{24}$$

$$X = 6$$

### DO YOUR SELF-03

- 34 g of hydrogen peroxide is present in 1135 mL of solution. Volume strength of solution is:  
(A) 10 V      (B) 20 V      (C) 30 V      (D) 32 V
- Label an oleum sample which has mass fraction of  $SO_3$  equal to 0.6 :  
(A) 115 %      (B) 109 %      (C) 104.5 %      (D) 113.5 %

#### Comprehension Q.3 and Q.4 (2 questions)

30 gm  $H_2SO_4$  is mixed with 20 gram  $SO_3$  to form mixture.

- Find mole fraction of  $SO_3$  .  
(A) 0.2      (B) 0.45      (C) 0.6      (D) 0.8
- Determine % labelling of oleum solution.  
(A) 104.5      (B) 106      (C) 109      (D) 110

**Answers :**

1. (A)      2. (D)      3. (B)      4. (C)



## PREVIOUS YEARS SOLVED EXAMPLES

- Q.1 One gm of charcoal absorbs 100 ml 0.5 M  $\text{CH}_3\text{COOH}$  to form a monolayer, and thereby the molarity of  $\text{CH}_3\text{COOH}$  reduces to 0.49. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal =  $3.01 \times 10^2 \text{ m}^2/\text{gm}$ . [JEE'2003]

Ans.  $5 \times 10^{-19} \text{ m}^2$

Sol. Final molarity =  $0.5 - 0.49 = 0.01 \text{ M}$

$$\text{mole} = M \times v = 0.01 \times \frac{100}{1000} = 10^{-3}$$

$$\text{no of molecule} = \text{moles} \times N_A = 10^{-3} \times N_A = 6.02 \times 10^{20}$$

$$1 \text{ gm contain charcoal} = 3.01 \times 10^2 \text{ m}^2$$

$$6.02 \times 10^{20} \text{ molecule of acetic acid absorbed charcoal} = 3.01 \times 10^2$$

$$1 \text{ molecule of acetic acid adsorbed charcoal} = 3.01 \times 10^2 \text{ m}^2$$

$$6.02 \times 10^{20} \text{ molecule of acetic acid absorbed charcoal} = 3.01 \times 10^2$$

$$1 \text{ molecule of acetic acid adsorbed charcoal} = \frac{3.01 \times 10^2}{6.02 \times 10^{20}} = 5 \times 10^{-19} \text{ m}^2$$

- Q.2 Calculate the molarity of pure water using its density to be  $1000 \text{ kg m}^{-3}$ . [JEE'2003]

Ans.  $55.5 \text{ mol L}^{-1}$

Sol.  $M = \frac{1000}{\text{MW}} = \frac{1000}{18} = 55.5$

- Q.3  $6.02 \times 10^{21}$  molecules of urea are present in 100 ml of its solution. The concentration of urea solution is - [AIEEE-2004]

(A) 0.001 M                      (B) 0.01 M                      (C) 0.02 M                      (D) 0.1 M

Ans. (D)

$$\text{Moles of urea} = \frac{6.02 \times 10^{21}}{6.02 \times 10^{23}} = \frac{1}{100}$$

$$\text{Molarity} = \frac{1000}{100 \times 100} = 0.1 \text{ M}$$

## EXERCISE # S-I

CONCENTRATION TERMS

- Q.1 Calculate the molarity of the following solutions :
- (a) 4g of caustic (NaOH) soda is dissolved in 200 mL of the solution. CT0001
- (b) 5.3 g of anhydrous sodium ( $\text{Na}_2\text{CO}_3$ ) carbonate is dissolved in 100 mL of solution. CT0001
- (c) 0.365 g of pure HCl gas is dissolved in 50 mL of solution. CT0001
- Q.2 Density of a solution containing 13% by mass of sulphuric acid is 0.98 g/mL. Then molarity of solution will be CT0002
- Q.3 15 g of methyl alcohol is present in 100 mL of solution. If density of solution is  $0.90 \text{ g mL}^{-1}$ , calculate the mass percentage of methyl alcohol in solution CT0003
- Q.4 Units of parts per million (ppm) or per billion (ppb) are often used to describe the concentrations of solutes in very dilute solutions. The units are defined as the number of grams of solute per million or per billion grams of solvent. Bay of Bengal has 2.1 ppm of lithium ions. If the molality of  $\text{Li}^+$  is  $x \times 10^{-4} \text{ m}$ , then find x. ( $\text{Li} = 7$ ) CT0004
- Q.5 A 7.0 M solution of KOH in water contains 28% by mass of KOH. What is density of solution in gm/ml ? ( $\text{K} = 39$ ) CT0005
- Q.6 The concentration of a solution is 8% (w/w) and 10% (w/v). Calculate density (in gm/ml) of solution? CT0006
- Q.7 The mole fraction of solute in aqueous urea solution is 0.2. Calculate the mass percent of solute ? CT0007
- Q.8 The concentration of  $\text{Ca}(\text{HCO}_3)_2$  in a sample of hard water is 405 ppm. The density of water sample is 1.0 gm/ml. If the molarity of solution is  $x \times 10^{-3} \text{ M}$  then find x ? CT0008
- Q.9 How much  $\text{BaCl}_2$  (in gm) would be needed to make 250 ml of a solution having the same concentration of  $\text{Cl}^-$  as one containing 1.825 gm HCl per 100 ml ? ( $\text{Ba} = 137$ ) CT0009
- Q.10 Calculate **molality (m)** of each ion present in the aqueous solution of **2M  $\text{NH}_4\text{Cl}$**  assuming 100% dissociation according to reaction.



**Given :** Density of solution = 3.107 gm / ml.

CT0010

**PROBLEMS RELATED WITH MIXING & DILUTION**

- Q.11 Find out the volume (L) of 98% w/w  $\text{H}_2\text{SO}_4$  (density = 1.8 gm/ml), must be diluted to prepare 12.6 litres of 2.0 M sulphuric acid solution. **CT0011**
- Q.12 500 ml of 2 M NaCl solution was mixed with 200 ml of 1/4 M NaCl solution. Calculate the molarity of NaCl in final solution. **CT0012**
- Q.13 A mixture containing equimolar amounts of  $\text{Ca}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  requires 0.5 L of 4.0 M HCl to react with it completely. Total moles of the mixture is : **CT0013**
- Q.14 500 gm of urea solution of mole fraction 0.2 is diluted to 1500 gm. Calculate the mole fraction of solute in the diluted solution ? **CT0014**
- Q.15 When V ml of 2.2 M  $\text{H}_2\text{SO}_4$  solution is mixed with 10 V ml of water, the volume contraction of 2% take place. Calculate the molarity of diluted solution ? **CT0015**
- Q.16 What volume (in ml) of 0.8 M  $\text{AlCl}_3$  solution should be mixed with 50 ml of 0.2M  $\text{CaCl}_2$  solution to get solution of chloride ion concentration equal to 0.6 M ? **CT0016**
- Q.17 A solution containing 200 ml 0.5 M KCl is mixed with 50 ml 19% w/v  $\text{MgCl}_2$  and resulting solution is diluted 8 times. Molarity of chloride ion is final solution is : **CT0017**

**SOME TYPICAL CONCENTRATION TERMS**

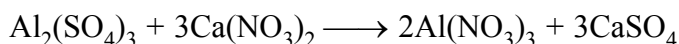
- Q.18 An oleum sample is labelled as 118 %, Calculate
- (i) Mass of  $\text{H}_2\text{SO}_4$  (gm) in 100 gm oleum sample. **CT0018**
- (ii) Maximum mass of  $\text{H}_2\text{SO}_4$  (gm) that can be obtained if 30 gm sample is taken. **CT0018**
- Q.19 A mixture is prepared by mixing 10 gm  $\text{H}_2\text{SO}_4$  and 40 gm  $\text{SO}_3$ . Calculate
- (a) mole fraction of  $\text{H}_2\text{SO}_4$  **CT0019**
- (b) % labelling of oleum **CT0019**
- Q.20 500 ml of a  $\text{H}_2\text{O}_2$  solution on complete decomposition produces 2 moles of  $\text{H}_2\text{O}$ . Calculate the volume strength of  $\text{H}_2\text{O}_2$  solution? **CT0020**
- Q.21 The volume strength of 100 ml  $\text{H}_2\text{O}_2$  solution which produce 5.6 litre of oxygen gas at 1 bar &  $0^\circ\text{C}$ . **CT0021**

## EXERCISE # S-II

Q.1 What volume of 0.2 M NaOH (in L) solution should be mixed to 500 ml of 0.5 M NaOH solution so that 300 ml of final solution is completely neutralised by 20 ml of 2 M  $\text{H}_3\text{PO}_4$  solution.

CT0022

Q.2 How much minimum volume (in L) of  $\left(\frac{5}{51}\right)$  M aluminium sulphate solution should be added to excess calcium nitrate to obtain atleast 1 gm of each salt in the reaction.



CT0023

Q.3 One litre of milk weighs 1.035 kg. The butter fat is 4% (v/v) of milk and has density of  $875 \text{ kg/m}^3$ . If the density of fat free skimmed milk is 'x' gm/L, the value of (x) is ?

CT0024

Q.4 100 ml of 0.1 M solution of AB (d = 1.5 gm/ml) is mixed with 100 ml of 0.2 M solution of  $\text{CB}_2$  (d = 2.5 gm/ml). Calculate the molarity of  $\text{B}^-$  in final solution if the density of final solution is 4 gm/ml. Assuming AB and  $\text{CB}_2$  are non reacting & dissociates completely into  $\text{A}^+$ ,  $\text{B}^-$ ,  $\text{C}^{+2}$ .

CT0025

Q.5 60 ml of a "x" % w/w alcohol by weight (d =  $0.6 \text{ g/cm}^3$ ) must be used to prepare  $200 \text{ cm}^3$  of 12% alcohol by weight (d =  $0.90 \text{ g/cm}^3$ ). Calculate the mass of alcohol (in gm) in original sample.

CT0026

Q.6 If 0.5 M methanol undergo self dissociation like  $\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{O}^- + \text{H}^+$  & if concentration of  $\text{H}^+$  is  $2.5 \times 10^{-4} \text{ M}$  then calculate % dissociation of methanol.

CT0027

Q.7 Determine the volume (in L) of diluted nitric acid (d =  $1.11 \text{ g mL}^{-1}$ , 20% w/v  $\text{HNO}_3$ ) that can be prepared by diluting 50 mL of conc.  $\text{HNO}_3$  with water (d =  $1.42 \text{ g mL}^{-1}$ , 70% w/v).

CT0028

Q.8 50 ml of '20V'  $\text{H}_2\text{O}_2$  is mixed with 200 ml, '10V'  $\text{H}_2\text{O}_2$ . The volume strength of resulting solution is

CT0029

Q.9 500 ml of 0.90M  $\text{CH}_3\text{COOH}$  solution is mixed with 600 ml 12% w/v  $\text{CH}_3\text{COOH}$  solution then calculate the final molarity of solution.

CT0030

Q.10 45.4 V  $\text{H}_2\text{O}_2$  solution (500 ml) when exposed to atmosphere loses 11.2 litre of  $\text{O}_2$  at 1 atm, & 273 K. New molarity of  $\text{H}_2\text{O}_2$  solution (Assume no change in volume)

CT0031

## EXERCISE # O-I

- Q.1 125 ml of 8% w/w NaOH solution (sp. gravity 1) is added to 125 ml of 10% w/v HCl solution. The nature of resultant solution would be \_\_\_\_\_.
- (A) Acidic (B) Basic (C) Neutral (D) Can not be predicted  
CT0032
- Q.2 The molarity of pure water is :
- (A) 100 M (B) 55.6 M (C) 50 M (D) 18M  
CT0033
- Q.3 Mole fraction of  $C_3H_5(OH)_3$  (glycerine) in a solution of 36 g of water and 46 g of glycerine is :
- (A) 0.46 (B) 0.36 (C) 0.20 (D) 0.40  
CT0034
- Q.4 A molal solution is one that contains one mole of a solute in
- (A) 1000 g of the solvent (B) one litre of the solution  
(C) one litre of the solvent (D) 22.4 litres of the solution  
CT0035
- Q.5 The molarity of a solution of sodium chloride in water containing 5.85 gm of sodium chloride in 500 ml of solution is :-
- (A) 0.25 M (B) 2.0 M (C) 1.0 M (D) 0.2 M  
CT0036
- Q.6 The molarity of 98% by wt.  $H_2SO_4$  ( $d = 1.8$  g/ml) is
- (A) 6 M (B) 18 M (C) 10 M (D) 4 M  
CT0037
- Q.7 Which one of the following modes of expressing concentration of solution is independent of temperature -
- (A) Molarity (B) Molality (C) % w/v (D) Grams per litre  
CT0038
- Q.8 Equal weight of NaCl and KCl are dissolved separately in equal volumes of solutions. Molarity of the solutions will be -
- (A) Equal (B) Greater for NaCl (C) Greater for KCl (D) Uncomparable.  
CT0039
- Q.9 How much water should be added to 200 cc of semimolar solution of NaOH to make it exactly decimolar?
- (A) 1000 cc (B) 400 cc (C) 800 cc (D) 600 cc  
CT0040
- Q.10 100 ml of 0.3 M HCl solution is mixed with 200 ml of 0.3 M  $H_2SO_4$  solution. What is the molarity of  $H^+$  in resultant solution ?
- (A) 0.9 M (B) 0.6 M (C) 0.4 M (D) 0.5 M  
CT0041
- Q.11 Molality of 20% (w/w) aq. glucose solution is :
- (A)  $\frac{25}{18}$  m (B)  $\frac{10}{9}$  m (C)  $\frac{25}{9}$  m (D)  $\frac{5}{18}$  m  
CT0042
- Q.12 Molarity of liquid HCl, if density is 1.17 g/cc. :
- (A) 36.5 M (B) 18.25 M (C) 32.05 M (D) 42.10 M  
CT0043

- Q.13. The molarity of a solution made by mixing 50 ml of conc.  $\text{H}_2\text{SO}_4$  (18 M) with 50 ml of water, is:
- (A) 36 M (B) 18 M (C) 9 M (D) 6M
- CT0044**
- Q.14 Equal volumes of 10% (w/v) of HCl is mixed with 10% (w/v) NaOH solution. The resultant solution be.
- (A) basic (B) neutral (C) acidic (D) can't be predicted.
- CT0045**
- Q.15 What volume of 0.2M NaOH solution is needed for complete neutralisation of 0.49 gm orthophosphoric acid -
- (A) 75 ml (B) 300 ml (C) 0.075 ml (D) 50 ml
- CT0046**
- Q.16 If 50 gm oleum sample rated as 118% is mixed with 18 gm water, then the correct option is
- (A) The resulting solution contains 18 gm of water and 118 gm  $\text{H}_2\text{SO}_4$   
 (B) The resulting solution contains 9 gm water and 59 gm  $\text{H}_2\text{SO}_4$   
 (C) The resulting solution contains only 118 gm pure  $\text{H}_2\text{SO}_4$   
 (D) The resulting solution contains 68 gm of pure  $\text{H}_2\text{SO}_4$
- CT0047**
- Q.17 12.5gm of fuming  $\text{H}_2\text{SO}_4$  (labelled as 112%) is mixed with 100 lit water. Molar concentration of  $\text{H}^+$  in resultant solution is :
- [Note : Assume that  $\text{H}_2\text{SO}_4$  dissociate completely and there is no change in volume on mixing]
- (A)  $\frac{2}{700}$  M (B)  $\frac{2}{350}$  M (C)  $\frac{3}{350}$  M (D)  $\frac{3}{700}$  M
- CT0048**
- Q.18 20 ml of '20 vol'  $\text{H}_2\text{O}_2$  solution is diluted to 80 ml. The final volume strength of solution is -
- (A) '80 vol' (B) '25 vol' (C) '5 vol' (D) '8 vol'
- CT0049**
- Q.19 Assuming complete precipitation of AgCl, calculate the sum of the molar concentration of all the ions if 2 lit of 2M  $\text{Ag}_2\text{SO}_4$  is mixed with 4 lit of 1 M NaCl solution is :
- (A) 4M (B) 2M (C) 3 M (D) 2.5 M
- CT0050**
- Q.20 Molarity and Molality of a solute (M. wt = 50 ) in aqueous solution is 9 and 18 respectively. What is the density of solution.
- (A) 1 g/cc (B) 0.95 g/cc (C) 1.05 g/cc (D) 2 g/cc
- CT0051**
- Q.21 The relationship between mole fraction ( $X_A$ ) of the solute & molality 'm' of its solution in ammonia would be
- (A)  $\frac{55.56(X_A)}{1-X_A} = m$  (B)  $\frac{58.82(X_A)}{1-X_A} = m$  (C)  $\frac{58.82(1-X_A)}{X_A} = m$  (D)  $\frac{55.56(1-X_A)}{X_A} = m$
- CT0052**
- Q.22 3.0 molal NaOH solution has a density of 1.12 g/mL. The molarity of the solution is-
- (A) 2.97 M (B) 3 M (C) 3.05 M (D) 3.5 M
- CT0053**

## EXERCISE # O-II

Q.1 **Statement -1** : Molality of pure ethanol is lesser than pure water.

**Statement -2** : As density of ethanol is lesser than density of water.

[Given :  $d_{\text{ethanol}} = 0.789 \text{ gm/ml}$ ;  $d_{\text{water}} = 1 \text{ gm/ml}$ ]

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is false, statement-2 is true.  
 (D) Statement-1 is true, statement-2 is false.

CT0054

Q.2 **Statement-1** : Molarity and molality have almost same value for a very dilute aqueous solution.

**Statement-2** : In all very dilute solution, the mass of solvent ( in gm ) is equal to the volume of solution ( in ml).

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CT0055

Q.3 **Statement-1** : The mass fraction of solute in a solution is always greater than its mole fraction.

**Statement-2** : Mole fraction of solvent in an aqueous solution of ethanol must be greater than that of solute.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CT0056

Q.4 The molar concentration of HCl (aq.) is  $10^{-5} \text{ M}$ . Which of the following statements are correct.

( $d_{\text{solution}} = 1 \text{ gm/cc}$ )

- (A) The mole fraction of HCl  $\cong 1.8 \times 10^{-7}$   
 (B) The concentration of HCl in ppm is 3.65 ppm  
 (C) The molality of HCl solution is approximately  $10^{-5} \text{ m}$   
 (D) The (w/v)% of solution is  $3.65 \times 10^{-5} \%$

CT0057

Q.5 Solution(s) containing 40 gm NaOH is/are

- (A) 50 gm of 80% (w/w) NaOH  
 (B) 50 gm of 80% (w/v) NaOH [ $d_{\text{soln.}} = 1.2 \text{ gm/ml}$ ]  
 (C) 50 gm of 20 M NaOH [ $d_{\text{soln.}} = 1 \text{ gm/ml}$ ]  
 (D) 50 gm of 5m NaOH

CT0058

Q.6 The **incorrect** statement(s) regarding 2M  $\text{MgCl}_2$  aqueous solution is/are ( $d_{\text{solution}} = 1.09 \text{ gm/ml}$ )

- (A) Molality of  $\text{Cl}^-$  is **4.44 m** (B) Mole fraction of  $\text{MgCl}_2$  is exactly **0.035**  
 (C) The conc. of  $\text{MgCl}_2$  is **19% w/v** (D) The conc. of  $\text{MgCl}_2$  is  **$19 \times 10^4 \text{ ppm}$**

CT0059

Q.7 A sample of  $\text{H}_2\text{O}_2$  solution labelled as 56.75 volume has density of 530 gm/L. Mark the correct option(s) representing concentration of same solution in other units. (Solution contains only  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ )

- (A)  $M_{\text{H}_2\text{O}_2} = 6$  (B)  $\% \frac{w}{v} = 17$   
 (C) Mole fraction of  $\text{H}_2\text{O}_2 = 0.25$  (D)  $m_{\text{H}_2\text{O}_2} = \frac{1000}{72}$

CT0060

Q.8 100 mL of 0.06 M  $\text{Ca}(\text{NO}_3)_2$  is added to 50 mL of 0.06 M  $\text{Na}_2\text{C}_2\text{O}_4$ . After the reaction is complete ( $\text{CaC}_2\text{O}_4$  is precipitated)

- (A) 0.003 moles of calcium oxalate will get precipitated  
 (B) 0.003 M  $\text{Ca}^{2+}$  will remain in excess  
 (C)  $\text{Na}_2\text{C}_2\text{O}_4$  is the limiting reagent  
 (D) Oxalate ion ( $\text{C}_2\text{O}_4^{2-}$ ) concentration in final solution is 0.003 M

CT0061

**Comprehension Q.9 and Q.10 (2 questions)**

2 litre of 9.8 % w/w  $\text{H}_2\text{SO}_4$  ( $d = 1.5 \text{ gm/ml}$ ) solution is mixed with 3 litre of 1 M KOH solution.

Q.9 The number of moles  $\text{H}_2\text{SO}_4$  added are

- (A) 1 (B) 2 (C) 3 (D) 0.5

CT0062

Q.10 The concentration of  $\text{H}^+$  if solution is acidic or concentration of  $\text{OH}^-$  if solution is basic in the final solution is

- (A) 0 (B)  $\frac{3}{10}$  (C)  $\frac{3}{5}$  (D)  $\frac{2}{5}$

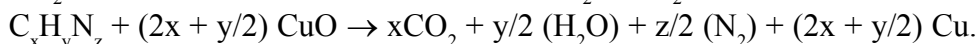
CT0063



## Comprehension Q.11 and Q.14 (4 questions)

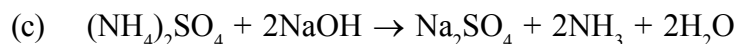
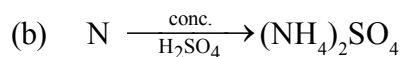
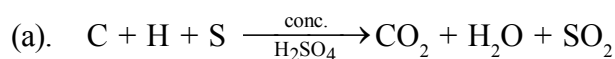
**Estimation of nitrogen :** There are two methods for the estimation of nitrogen (i) Dumas method and (ii) Kjeldahl's method.

- i. Dumas method :** A known mass of compound is heated with copper oxide (CuO) in an atmosphere of  $\text{CO}_2$ , which gives free nitrogen along with  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .



The gaseous mixture is passed over a heated copper gauze which converts traces of nitrogen oxides formed to  $\text{N}_2$ . The gaseous mixture is collected over an aqueous solution of KOH which absorbs  $\text{CO}_2$ , and nitrogen is collected in the upper part of the graduated tube.

- ii. Kjeldahl's method :** A known mass of organic compound (0.5 gm) is mixed with  $\text{K}_2\text{SO}_4$  (10 gm) and  $\text{CuSO}_4$  (1.0 gm) or a drop of mercury (Hg) and conc.  $\text{H}_2\text{SO}_4$  (25 ml), and heated in Kjeldahl's flask.  $\text{CuSO}_4$  or Hg acts as a catalyst, while  $\text{K}_2\text{SO}_4$  raises the boiling point of  $\text{H}_2\text{SO}_4$ . The nitrogen in the organic compound is quantitatively converted to ammonium sulphate. The resulting mixture is then distilled with excess of NaOH solution and the  $\text{NH}_3$  evolved is passed into a known but excess volume of standard HCl or  $\text{H}_2\text{SO}_4$ . The acid left unused is estimated by titration with some standard alkali. The amount of acid used against  $\text{NH}_3$  can thus be known and from this the percentage of nitrogen is calculated.



**iii.** This method is not applicable to compounds containing N in nitro and azo groups, and N present in the ring (e.g., pyridine) as N of these compounds does not change to  $(\text{NH}_4)_2\text{SO}_4$  (ammonium sulphate) under these reaction conditions.

Q.11 0.30 gm of an organic compound gave 82.1 ml of nitrogen collected at 300K and 775 mm pressure in Dumas method. Calculate the percentage of nitrogen in the compound. (Vapour pressure of water or aqueous tension of water at 300K is 15 mm.

- (A) 31.11 (B) 15.56 (C) 28.0 (D) 31.72

CT0064

Q.12 0.50 gm of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5M  $\text{H}_2\text{SO}_4$ . The residual acid required 60 ml of M/2 NaOH solution. Find the percentage of nitrogen in the compound.

- (A) 50 (B) 56 (C) 66 (D) 40

CT0065

Q.13 0.4 gm of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5M  $\text{H}_3\text{PO}_3$ . The residual acid required 30 ml of 0.5M  $\text{Ca}(\text{OH})_2$ . Find the percentage of  $\text{N}_2$  in the compound.

- (A) 20 (B) 50 (C) 70 (D) 45

CT0066

Q.14 0.002 gm of an organic compound was treated according to Kjeldahl's method.  $0.2 \times 10^{-4}$  mol of  $\text{H}_2\text{SO}_4$  was required to neutralise  $\text{NH}_3$ . Calculate the percentage of  $\text{N}_2$ .

- (A) 50 (B) 28 (C) 70 (D) 18

CT0067

## TABLE TYPE QUESTION

Column-I	Column-II	Column-III
(A) 2 M - aqueous NaOH solution (density = 1.25 gm/ml)	(P) 2 mole solute/litre solution	(I) 6 % (w/v) solution
(B) 1.5 m - aqueous NaOH solution (density = 1.06 gm/ml)	(Q) 1.5 mole solute/litre solution	(II) 8 % (w/v) solution
(C) 0.5 M aqueous Glucose solution (density = 1.09 gm/ml)	(R) 0.5 mole solute/litre solution	(III) 9 % (w/v) solution
(D) 1.5 M aqueous Urea solution (density = 1.15 gm/ml)	(S) 1.5 mole solute/kg solvent	(IV) 9 gm solute per 100 gm solvent

Q.15 Which of the following is correct match ?

- (A) A - i - II      (B) B - ii - I      (C) C - iii - IV      (D) D - iv - iii

CT0068

Q.16 Which of the following is correct match ?

- (A) A - i - II      (B) B - iv - I      (C) C - iii - I      (D) D - ii - I

CT0068

Q.17 Which of the following is correct match ?

- (A) A - ii - III      (B) B - ii - III      (C) C - ii - III      (D) D - ii - III

CT0068

## MATCH THE COLUMN :

Q.18 Match the column-

Column-I	Column-II
(Concentration of aqueous solution)	(Density of given solutions is 1.2 g/ml)
(A) 2M NaOH solution	(P) 16gm solute in 240gm solution
(B) $8\% \left( \frac{w}{V} \right)$ KOH solution	(Q) 60gm solute in 240 gm solution
(C) $25\% \left( \frac{w}{W} \right)$ CaCO <sub>3</sub> solution	(R) 8gm solute in 100 ml solution
(D) $X_{C_3H_7OH} = \frac{1}{11}$	(S) 30 gm solute in 100 ml solution
	(T) 1 mole solute in 400 gm solution

CT0069

Q.19 Match the column:

Column I	Column II
(A) 20 V H <sub>2</sub> O <sub>2</sub>	(P) 2.5 M
(B) 24.5 % w/v H <sub>2</sub> SO <sub>4</sub>	(Q) 1.76 M
(C) Pure water	(R) 1.5 M
(D) 5% w/w NaOH (d <sub>solution</sub> = 1.2 gm/ml)	(S) 55.5 M

**CT0070**

Q.20.

Column-I	Column-II
(A) 120 g CH <sub>3</sub> COOH in 1 L solution (d <sub>sol</sub> = 1.2 g/mL)	(P) M = 2
(B) 120 g glucose dissolved in 1 L solution (d <sub>sol</sub> = 1.2 g/mL)	(Q) 10% w/w solution
(C) X <sub>NH<sub>2</sub>CONH<sub>2</sub></sub> = 1/31 (aqueous solution)	(R) 12% w/v solution
(D) 19.6% (w/v) H <sub>2</sub> SO <sub>4</sub> solution → (d <sub>solution</sub> = 1.2 g/mL)	(S) m = 1.85
	(T) m = 0.617

**CT0071**

**EXERCISE # J-MAINS**

1. The molarity of  $\text{HNO}_3$  in a sample which has density 1.4 g/mL and mass percentage of 63% is (Molecular Weight of  $\text{HNO}_3 = 63$ ) **[JEE-Main(Jan)-2020]**  
CT0072
2. 10.30 mg of  $\text{O}_2$  is dissolved into a liter of sea water of density 1.03 g/mL. The concentration of  $\text{O}_2$  in ppm is **[JEE-Main(Jan)-2020]**  
CT0073
3. The ammonia ( $\text{NH}_3$ ) released on quantitative reaction of 0.6 g urea ( $\text{NH}_2\text{CONH}_2$ ) with sodium hydroxide ( $\text{NaOH}$ ) can be neutralized by : **[JEE-Main(Jan)-2020]**  
(A) 100 ml of 0.1 M HCl (B) 200 ml of 0.4 M HCl  
(C) 100 ml of 0.2 M HCl (D) 200 ml of 0.2 M HCl  
CT0074
4. Ferrous sulphate heptahydrate is used to fortify foods with iron. The amount (in grams) of the salt required to achieve 10 ppm of iron in 100 kg of wheat is \_\_\_\_\_. **[JEE-Main(Jan)-2020]**  
Atomic weight : Fe = 55.85 ; S = 32.0 ; O = 16.00  
CT0075
5. The amount of sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) required to prepare 2 L of its 0.1 M aqueous solution is : **[JEE-Main(Jan.)-2019]**  
(A) 68.4 g (B) 17.1 g  
(C) 34.2 g (D) 136.8 g  
CT0076
6. A solution of sodium sulfate contains 92 g of  $\text{Na}^+$  ions per kilogram of water. The molality of  $\text{Na}^+$  ions in that solution in mol  $\text{kg}^{-1}$  is: **[JEE-Main(Jan.)-2019]**  
(A) 16 (B) 8 (C) 4 (D) 12  
CT0077
7. 8g of  $\text{NaOH}$  is dissolved in 18g of  $\text{H}_2\text{O}$ . Mole fraction of  $\text{NaOH}$  in solution and molality (in mol  $\text{kg}^{-1}$ ) of the solutions respectively are : **[JEE-Main(Jan.)-2019]**  
(A) 0.167, 11.11 (B) 0.2, 22.20 (C) 0.2, 11.11 (D) 0.167, 22.20  
CT0078
8. The volume strength of 1M  $\text{H}_2\text{O}_2$  is: (Molar mass of  $\text{H}_2\text{O}_2 = 34 \text{ g mol}^{-1}$ ) **[JEE-Main(Jan.)-2019]**  
(A) 16.8 (B) 11.35  
(C) 22.4 (D) 5.6  
CT0079
9. The strength of 11.2 volume solution of  $\text{H}_2\text{O}_2$  is : [Given that molar mass of H = 1 g  $\text{mol}^{-1}$  and O = 16 g  $\text{mol}^{-1}$ ] **[JEE-Main(april)-2019]**  
(A) 13.6% (B) 3.4% (C) 34% (D) 1.7%  
CT0080
10. What would be the molality of 20% (mass/mass) aqueous solution of KI? (molar mass of KI = 166 g  $\text{mol}^{-1}$ ) **[JEE-Main(april)-2019]**  
(A) 1.08 (B) 1.48 (C) 1.51 (D) 1.35  
CT0081

11. The mole fraction of a solvent in aqueous solution of a solute is 0.8. The molality (in mol kg<sup>-1</sup>) of the aqueous solution is [JEE-Main(april)-2019]  
 (A)  $13.88 \times 10^{-1}$  (B)  $13.88 \times 10^{-2}$  (C) 13.88 (D)  $13.88 \times 10^{-3}$   
 CT0082
12. The amount of BaSO<sub>4</sub> formed upon mixing 100 mL of 20.8% BaCl<sub>2</sub> solution with 50 mL of 9.8% H<sub>2</sub>SO<sub>4</sub> solution will be : [JEE(Main-online)-2014]  
 (Ba = 137, Cl = 35.5, S=32, H = 1 and O = 16)  
 (A) 33.2 g (B) 11.65 g (C) 23.3 g (D) 30.6 g  
 CT0083
13. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of  $\frac{M}{10}$  sulphuric acid. The unreacted acid required 20 mL of  $\frac{M}{10}$  sodium hydroxide for complete neutralization. The percentage of nitrogen in the compound is : [JEE(Main-online)-2014]  
 (A) 3% (B) 5% (C) 6% (D) 10%  
 CT0084
14. 10 mL of 2(M) NaOH solution is added to 200 mL of 0.5 (M) of NaOH solution. What is the final concentration ? [JEE(Main-online)-2013]  
 (A) 0.57 M (B) 5.7 M (C) 11.4 M (D) 1.14 M  
 CT0085
15. The density of 3M solution of sodium chloride is 1.252 g mL<sup>-1</sup>. The molality of the solution will be (molar mass, NaCl = 58.5 g mol<sup>-1</sup>) [JEE(Main-online)-2013]  
 (A) 2.18 m (B) 3.00 m (C) 2.60 m (D) 2.79 m  
 CT0086
16. The concentrated sulphuric acid that is peddled commercially is 95% H<sub>2</sub>SO<sub>4</sub> by weight. If the density of this commercial acid is 1.834 g cm<sup>-3</sup>, the molarity of this solution is :- [JEE-(Main)-2012]  
 (A) 17.8 M (B) 15.7 M (C) 10.5 M (D) 12.0 M  
 CT0087
17. The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity of this solution is [JEE-(Main)-2012]  
 (A) 2.05 M (B) 0.50 M (C) 1.78 M (D) 1.02 M  
 CT0088
18. A 5.2 molal aqueous solution of methyl alcohol, CH<sub>3</sub>OH, is supplied. What is the mole fraction of methyl alcohol in the solution ? [AIEEE-2011]  
 (A) 0.086 (B) 0.050 (C) 0.100 (D) 0.190  
 CT0089

**EXERCISE # JEE-ADVANCED**

Q.1 The mole fraction of urea in an aqueous urea solution containing 900 g of water is 0.05. If the density of the solution is  $1.2 \text{ g cm}^{-3}$ , the molarity of urea solution is [JEE 2019]

(Given data : Molar masses of urea and water are  $60 \text{ g mol}^{-1}$  and  $18 \text{ g mol}^{-1}$ , respectively)

CT0090

Q.2 A compound  $\text{H}_2\text{X}$  with molar weight of 80 g is dissolved in a solvent having density of  $0.4 \text{ g/ml}$ , Assuming no change in volume upon dissolution, the **molality** of a 3.2 molar solution is. [JEE 2014]

CT0091

Q.3 Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density  $1.15 \text{ g/mL}$ . The molarity of the solution is

(A) 1.78 M                      (B) 2.00 M                      (C) 2.05 M                      (D) 2.22 M [JEE 2011]

CT0092

**ANSWER-KEY****EXERCISE # S-I**

Q.1 (a) 0.50 M, (b) 0.50 M, (c) 0.20 M	Q.2 1.30 M
Q.3 16.66 or 16.67	Q.4 3.00
Q.5 1.40	Q.6 1.25
Q.7 45.45	Q.8 2.50
Q.9 13.00 gm	Q.10 0.66 or 0.67
Q.11 1.40	Q.12 1.50 M
Q.13 Ans.(0.80)	Q.14 0.05
Q.15 0.20 M	Q.16 5.55 or 5.56
Q.17 Ans. (0.15 M)	Q.18 (i) 20.00; (ii) 35.40
Q.19 (a) 0.16 or 0.17; (b) 118.00	Q.20 45.40 V
Q.21 Ans. (56.00 V)	

**EXERCISE # S-II**

Q.1 0.25	Q.2 0.02
Q.3 1.04	Q.4 0.50 M
Q.5 21.60	Q.6 0.05
Q.7 0.17 or 0.18	Q.8 Ans.(12.00 V)
Q.9 Ans.(1.50 M)	Q.10 Ans. (2.00 M)

**EXERCISE O-I**

Q.1 Ans.(A)	Q.2 Ans(B)	Q.3 Ans.(C)
Q.4 Ans(A)	Q.5 Ans(D)	Q.6 Ans(B)
Q.7 Ans.(B)	Q.8 Ans.(B)	Q.9 Ans.(C)
Q.10 Ans.(D)	Q.11 Ans. (A)	Q.12 Ans.(C)
Q.13. Ans(C)	Q.14 Ans.(C)	Q.15 Ans.(A)
Q.16 Ans.(B)	Q.17 Ans.(A)	Q.18 Ans.(C)
Q.19 Ans.(B)	Q.20 Ans.(B)	Q.21 Ans.(B)
Q.22 Ans.(B)		

**EXERCISE # O-II**

Q.1 Ans.(B)	Q.2 Ans.(C)	Q.3 Ans.(D)
Q.4 Ans.(A,C,D)	Q.5 Ans.(A, C)	Q.6 Ans.(B, D)
Q.7 (B, D)	Q.8. Ans.(A, C)	Q.9 Ans.(C)
Q.10 Ans.(C)	Q.11 Ans.(A)	Q.12 Ans.(B)

- Q.13 Ans. (C)                      Q.14 Ans.(B)                      Q.15 Ans.(A)  
Q.16 Ans. (B)                      Q.17 Ans.(D)  
Q.18 Ans. (A)-P, R ; (B)- P, R ; (C) - Q, S, T ; (D) – S, Q  
Q.19 Ans. (A) → Q; (B) → P; (C) → S; (D) → R  
Q.20. Ans. (A) →(P,Q,R,S) ; (B) →(Q,R,T) ; (C) →(Q,S) ; (D) →(P)

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**EXERCISE # J-MAINS**

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- |                        |             |             |
|------------------------|-------------|-------------|
| 1. Ans.(14.00)         | 2. Ans.(10) | 3. Ans(C)   |
| 4. Ans. (4.95 to 4.97) | 5. Ans.(A)  | 6. Ans.(C)  |
| 7. Ans.(A)             | 8. Ans.(A)  | 9. Ans.(B)  |
| 10. Ans.(C)            | 11. Ans.(C) | 12. Ans.(B) |
| 13. Ans.(D)            | 14. Ans.(A) | 15. Ans.(D) |
| 16. Ans.(A)            | 17. Ans.(A) | 18. Ans.(A) |

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**EXERCISE # J-ADVANCE**

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- |                        |                |             |
|------------------------|----------------|-------------|
| Q.1 Ans.(2.98 or 2.99) | Q.2 Ans.(8.00) | Q.3 Ans.(C) |
|------------------------|----------------|-------------|





# Chapter Contents

## 03 REDOX & EQUIVALENT CONCEPTS

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## REDOX & EQUIVALENT CONCEPTS (STOICHIOMETRY-II)

### 1. OXIDATION & REDUCTION

Let us do a comparative study of oxidation and Reduction ;

Oxidation	Reduction
(1) Addition of oxygen e.g. $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$	(i) Removal of oxygen e.g. $\text{CuO} + \text{C} \rightarrow \text{Cu} + \text{CO}$
(2) Removal of Hydrogen e.g. $\text{H}_2\text{S} + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{S}$	(ii) Addition of Hydrogen e.g. $\text{S} + \text{H}_2 \rightarrow \text{H}_2\text{S}$
(3) Increase in positive charge e.g. $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$	(iii) Decrease in positive charge e.g. $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$
(4) Increase in oxidation number (+2)    (+4) $\text{SnCl}_2 \rightarrow \text{SnCl}_4$	(iv) Decrease in oxidation number (+7)    (+2) $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$
(5) Removal of electron e.g. $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$	(v) Addition of electron e.g. $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$

### 2. Oxidation Number :

- ◆ It is an imaginary or apparent charge gained by an element when it goes from its elemental free state to combined state in molecules.
- ◆ It is calculated on basis of a arbitrary set of rules.
- ◆ It is a relative charge in a particular bonded state.

#### 2.1 Rules governing oxidation number :

The following rules are helpful in calculating oxidation number of the elements in their different compounds. It is remember that the basis of these rule is the electronegativity of the element.

##### ◆ Fluorine atom :

Fluorine is most electronegativity atom (known). It always has oxidation no. equal to  $-1$  in all its compounds.

##### ◆ Oxygen atom :

In general and as well as in its oxides, oxygen atom has oxidation number equal to  $-2$ .

**In case of :**

- (i) peroxide (e.g.  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{O}_2$ ) is  $-1$
- (ii) super oxide (e.g.  $\text{KO}_2$ ) is  $-\frac{1}{2}$
- (iii) ozonide ( $\text{KO}_3$ ) is  $-\frac{1}{3}$
- (iv) oxygen fluoride  $\text{OF}_2$  is  $+2$  & in  $\text{O}_2\text{F}_2$  is  $+1$

◆ **Hydrogen atom :**

In general, H atom has oxidation number equal to +1. But in metallic hydrides (e.g. NaH, KH) it is -1.

◆ **Halogen atom :**

In general, all halogen atom (Cl, Br, I) has oxidation number equal to -1.

But if halogen atom is attached with an more electronegative atom than halogen atom then it will show positive oxidation numbers.

e.g.  $\overset{+5}{\text{KClO}_3}$   $\overset{+5}{\text{HIO}_3}$   $\overset{+7}{\text{HClO}_4}$   $\overset{+5}{\text{KBrO}_3}$

◆ **Metals :**

(a) Alkali metal (Li, Na, K, Rb, ..... ) always have oxidation number +1.

(b) Alkaline earth metal (Be, Mg, Ca ..... ) always have oxidation number +2.

**Note :** Metal may have positive or zero oxidation number.

(c) Aluminium always have +3 oxidation number

◆ Oxidation number of an element in free state or in allotropic forms is always zero.

e.g.  $\overset{0}{\text{O}_2}$ ,  $\overset{0}{\text{S}_8}$ ,  $\overset{0}{\text{P}_4}$ ,  $\overset{0}{\text{O}_3}$

◆ Sum of the charges of elements in a molecule is zero.

◆ Sum of the charges of all elements in an ions is equal to the charge on the ion.

◆ If the group no. of an element in periodic table is n then its oxidation number may vary from n to n - 8 (but it is mainly applicable in p-block elements)

e.g. N-atom belongs to v group in the periodic table therefore as per rule its oxidation number may vary from

-3 to +5 ( $\overset{-3}{\text{NH}_3}$ ,  $\overset{+2}{\text{NO}}$ ,  $\overset{+3}{\text{N}_2\text{O}_3}$ ,  $\overset{+4}{\text{NO}_2}$ ,  $\overset{+5}{\text{N}_2\text{O}_5}$ )

**Ex.1 Calculate oxidation number of underlined element  $\text{Na}_2\underline{\text{S}_2}\text{O}_3$  :**

**Sol.** Let oxidation number of S-atom is x. Now work accordingly with the rules given before.

$$(+1) \times 2 + (x) \times 2 + (-2) \times 3 = 0$$

$$x = +2$$

**Ex.2  $\text{Na}_2\underline{\text{S}_4}\text{O}_6$  :**

**Sol.** Let oxidation number of S-atom is x

$$(+1) \times 2 + (x) \times 2 + (-2) \times 6 = 0$$

$$x = +2.5$$

◆ It's important to note here that  $\text{Na}_2\underline{\text{S}_2}\text{O}_3$  have two S-atom and there are four S-atom in  $\text{Na}_2\underline{\text{S}_4}\text{O}_6$  but sulphur atom in both the compound have +2 or +2.5 oxidation number, it is the average charge (O. No.) Which reside on each sulphur atom therefore we should work to calculate the individual oxidation number of each sulphur atom in these compound.

**Ex.3** Calculate the O.S. of all the atoms in the following species :

(i)  $\text{ClO}^-$ , (ii)  $\text{NO}_2^-$ , (iii)  $\text{NO}_3^-$  (iv)  $\text{CCl}_4$  (v)  $\text{K}_2\text{CrO}_4$  and (vi)  $\text{KMnO}_4$

**Sol.** (i) In  $\text{ClO}^-$ , the net charge on the species is  $-1$  and therefore the sum of the oxidation states of Cl and O must be equal to  $-1$ . Oxygen will have an O.S. of  $-2$  and if the O.S. of Cl is assumed to be 'x' then  $x - 2$  should be equal to  $-1$ .

$$x \text{ is } +1$$

(ii)  $\text{NO}_2^-$  :  $(2 \times -2) + x = -1$  (where 'x' is O.S. of N)

$$\therefore x = +3$$

(iii)  $\text{NO}_3^-$  :  $x + (3 \times -2) = -1$  (where 'x' is O.S. of N)

$$x = +5$$

(iv) In  $\text{CCl}_4$ , Cl has an O.S. of  $-1$

$$x + 4 \times -1 = 0$$

$$\therefore x = +4$$

(where 'x' is O.S. of C)

(v)  $\text{K}_2\text{CrO}_4$  : K has O.S. of  $+1$  and O has O.S. of  $-2$  and let Cr has O.S. 'x' then,

$$2 \times +1 + x + 4 \times -2 = 0$$

$$\therefore x = +6$$

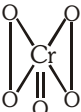
(vi)  $\text{KMnO}_4$  :  $+1 + x + (4 \times -2) = 0$

$$\therefore x = +7$$

(where x is O.S. of Mn).

## 2.2 MISCELLANEOUS EXAMPLES

In order to determine the exact or individual oxidation number we need to take help from the structures of the molecules. Some special cases are discussed as follows :

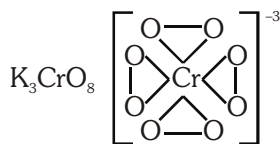
◆ The structure of  $\text{CrO}_5$  is 

From the structure it is evident that in  $\text{CrO}_5$  there are two peroxide linkages and one double bond.

The contribution of each peroxide linkage is  $-2$ . Let the O.N. of Cr is x.

$$\therefore x + (-2)2 + (-2) = 0 \text{ or } x = 6$$

$\therefore$  O.N. of Cr = **+6 Ans.**




From the structure it is evident that in  $\text{CrO}_8^{3-}$  there are four peroxide linkages.

The contribution of each peroxide linkage is  $-2$ . Let the O.N. of Cr is x.

$$\therefore x + (-2)4 = -3 \text{ or } x = +5$$

$\therefore$  O.N. of Cr = **+5 Ans.**

◆ The structure of  $\text{H}_2\text{SO}_5$  is 

From the structure, it is evident that in  $\text{H}_2\text{SO}_5$ , there are one peroxide linkage, two sulphur - oxygen double bond and one OH group. Let the O.N. of S = x.

$$\therefore +1 - 2 + x + (-2) \cdot 2 + (-2) + 1 = 0$$

$$\text{or } x + 2 - 8 = 0$$

$$\text{or } x - 6 = 0$$

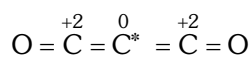
$$\text{or } x = 6$$

$$\therefore \text{O.N. of S in } \text{H}_2\text{SO}_5 \text{ is } +6 \text{ Ans}$$

### 2.3 PARADOX OF FRACTIONAL OXIDATION NUMBER

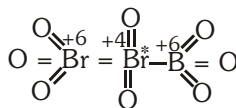
Fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is actually present in different oxidation states. Structure of the species  $\text{C}_3\text{O}_2$ ,  $\text{Br}_3\text{O}_8$  and  $\text{S}_4\text{O}_6^{2-}$  reveal the following bonding situations.

- The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in  $\text{C}_3\text{O}_2$ , two carbon atoms are present in +2 oxidation state each whereas the third one is present in zero oxidation state and the average is  $4/3$ . However the realistic picture is +2 for two terminal carbons and zero for the middle carbon.



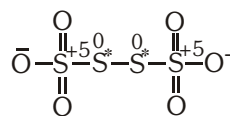
Structure of  $\text{C}_3\text{O}_2$   
(Carbon suboxide)

- Likewise in  $\text{Br}_3\text{O}_8$ , each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality is  $16/3$ .



Structure of  $\text{Br}_3\text{O}_8$  (tribromooctaoxide)

- In the same fashion, in the species  $\text{S}_4\text{O}_6^{2-}$ , is 2.5, whereas the reality being +5, 0, 0 and +5 oxidation number respectively for each sulphur.



Structure of  $\text{S}_4\text{O}_6^{2-}$  (tetrathionate ion)

### 3.1 OXIDISING AND REDUCING AGENT

#### 3.1 Oxidising agent or Oxidant :

Oxidising agents are those compound which can oxidise others and reduced itself during the chemical reaction. Those reagents whose O.N. decrease or which gain electrons in a redox reaction are termed as oxidants

e.g.  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{HNO}_3$ , conc.  $\text{H}_2\text{SO}_4$  etc, are powerful oxidising agents.

#### 3.1 Reducing agent or Reductant :

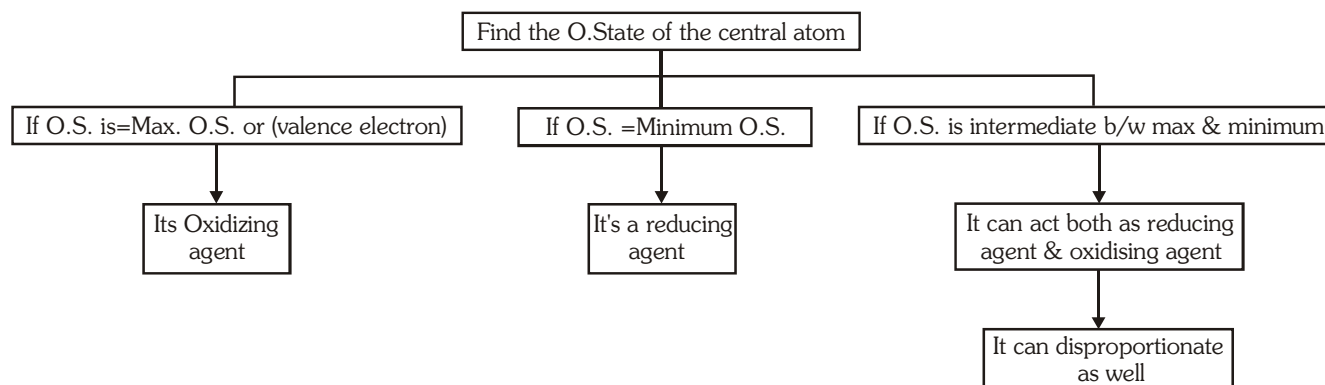
Reducing agents are those compound which can reduce others and oxidise itself during the chemical reaction. Those reagents whose O.N. increase or which loses electrons in a redox reaction are termed as reductants.

e.g.  $\text{KI}$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  are powerful reducing agents.

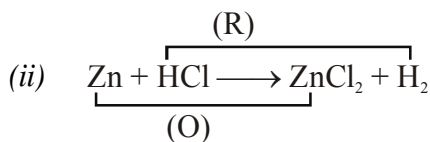
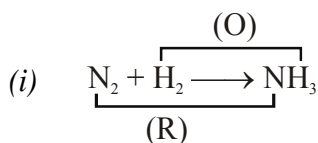
**Note :** There are some compounds also which can work both oxidising agent and reducing agent.

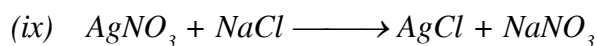
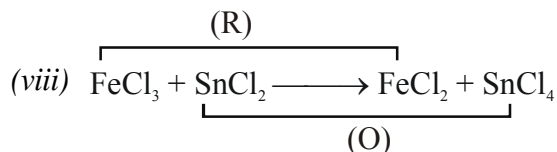
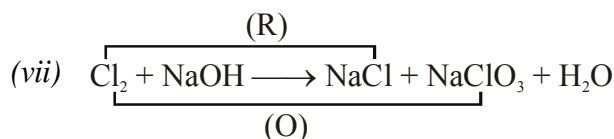
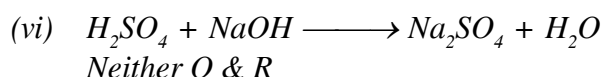
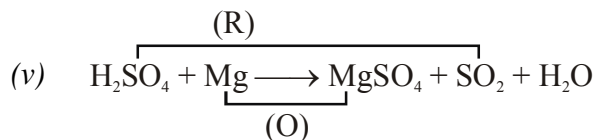
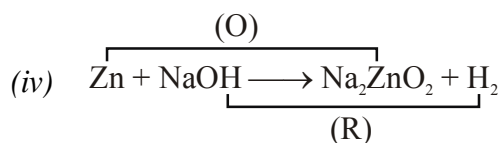
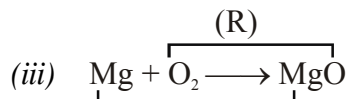
e.g.  $\text{H}_2\text{O}_2$ ,  $\text{NO}_2^-$

### 3.3 HOW TO IDENTIFY WHETHER A PARTICULAR SUBSTANCE IS AN OXIDISING OR REDUCING AGENT



**Ex.4. Identify the species undergoing oxidation and reduction**



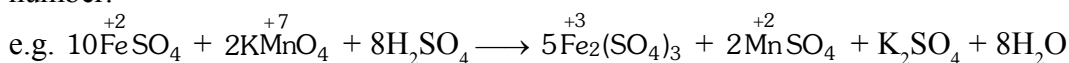


*No oxidation and no reduction.*

#### 4 REDOX REACTION

A reaction in which oxidation and reduction simultaneously take place.

In all redox reactions the total increase in oxidation number must equal the total decrease in oxidation number.

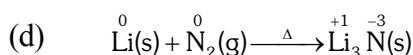
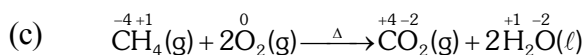
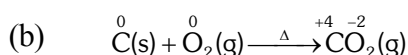
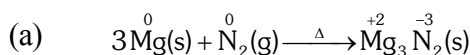
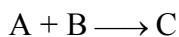


#### 5. TYPE OF REACTION

##### 5.1 Combination Reactions :

When two or more element combine to form compound then such reaction are redox reaction.

For example

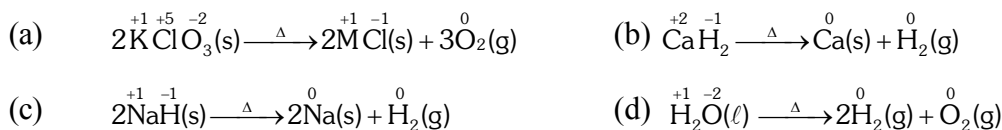


In reaction (c), there is no change in the oxidation number of hydrogen.

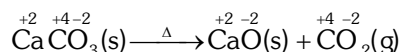


## 5.2 Decomposition Reactions :

Decomposition reactions are opposite of combination. Decomposition reactions are those in which when a molecule breaks down to form two or more components, at least one of them must be in the elemental state. For example :

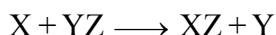


Exception :



## 5.3 Displacement Reactions :

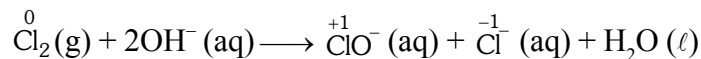
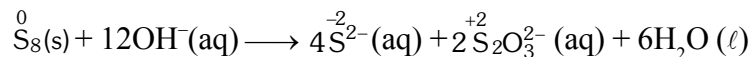
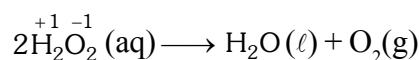
A reaction in which an atom or ion in a compound is replaced by an atom or ion of another element is called a displacement reaction. It may be denoted as :



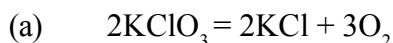
## 5.4 Disproportionations reactions :

A redox reaction in which a same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disproportionation reactions.

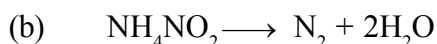
Disproportionation reactions are a special type of redox reactions. One of the reactants in a disproportionation reaction always contains **an element that can exist in at least three oxidation states**. The element in the form of reacting substance is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction.



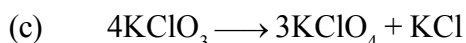
### ◆ Consider following reactions :



$KClO_3$  plays a role of oxidant and reductant both. Because same element is not oxidised and reduced. Here, Cl present in  $KClO_3$  is reduced and O present in  $KClO_3$  is oxidized. So **its not a disproportion reaction** although it looks like one.



Nitrogen in this compound has  $-3$  and  $+3$  oxidation number so it is not a definite value, so its not a disproportion reaction. Its a example of **comproportionation reaction** which is a class of redox reaction in which a element from two different oxidation state gets converted into a single oxidation state.

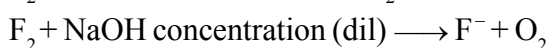
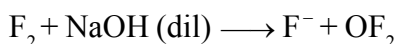


Its a case of disproportionation reaction in which Cl is the atom disproportionating.

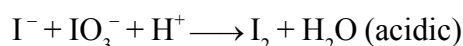
◆ **List of some important disproportionation reaction :**

1.  $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$
2.  $\text{X}_2 + \text{OH}^- (\text{dil.}) \longrightarrow \text{X}^- + \text{XO}^-$
3.  $\text{X}_2 + \text{OH}^- (\text{conc.}) \longrightarrow \text{X}^- + \text{XO}_3^-$

**$\text{F}_2$  does not (can not) undergo disproportionation as it is the most electronegative element.**



- ◆ Reverse of disproportionation is called Comproportionation. In some of the disproportionation reactions by changing the medium (from acidic to basic or reverse) the reaction goes in backward direction and can be taken as an example of Comproportionation.



## 6. BALANCING OF REDOX REACTION

All balanced equations must satisfy two criteria

### 1. Atom balance (mass balance) :

That is there should be the same number of atoms of each kind in reactant and products side.

### 2. Charge balance :

That is the sum of actual charges on both side of the equation must be equal

There are two methods for balancing the redox equations

- (a) Oxidation - number change method
- (b) Ion electron method or half cell method
- (a) **Oxidation number change method :**

This method was given by Jonson. In a balanced redox reaction, total increase in oxidation number must be equal to total decreases in oxidation number. This equivalence provides the basis for balancing redox reactions.

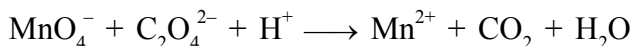
The general procedure involves the following steps :

- (i) Select the atom in oxidising agent whose oxidation number decreases and indicate the gain of electrons.
- (ii) Select the atom in reducing agent whose oxidation number increases and write the loss of electrons.
- (iii) Now cross multiply i.e. multiply oxidising agent by the number of loss of electrons and reducing agent by number of gain of electrons.
- (iv) Balance the number of atoms on both sides whose oxidation numbers change in the reaction.
- (v) In order to balance oxygen atoms, add  $\text{H}_2\text{O}$  molecules to the side deficient in oxygen. Then balance the number of H atoms by adding  $\text{H}^+$  ions in the hydrogen.

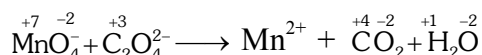
Ex.5 Write the skeleton equation for each of the following processes and balance them by ion electron method :

- (i) Permagnet ion oxidizes oxalate ions in acidic medium to carbon dioxide and gets reduced itself to  $Mn^{2+}$  ions.
- (ii) Chlorine reacts with base to form chlorate ion, chloride ion and water in acidic medium.

Sol. (i) The skeleton equation for the process :



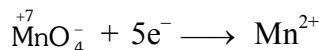
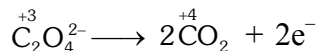
◆ **Step (1)** : Indicating oxidation number :



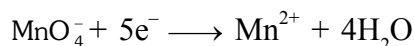
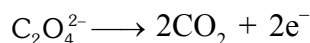
◆ **Step (2)** : Writing oxidation and reduction half reaction :



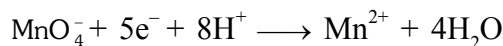
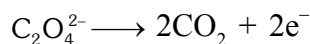
◆ **Step (3)** : Adding electrons to make the difference in O.N.



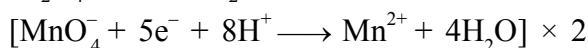
◆ **Step (4)** : Balancing 'O' atom by adding  $H_2O$  molecules



◆ **Step (5)** : Balancing H atom by adding  $H^+$  ions



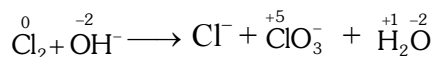
◆ **Step (6)** : Multiply the oxidation half reaction by 2 and reduction half reaction by 5 to equalize the electrons lost and gained and add the two half reactions.



(ii) The skeleton equation for the given process :

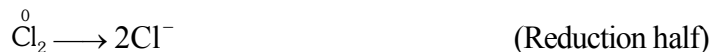


◆ **Step (1)** : Indicate the oxidation number of each atom

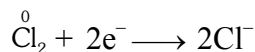


Thus, chlorine is the only element which undergoes the change in oxidation number. It decreases its oxidation number from 0 to 1 and also increases its oxidation number from 0 to 5.

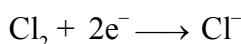
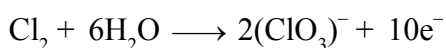
- ◆ **Step (2) :** Write the oxidation and reduction half reactions



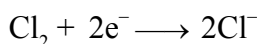
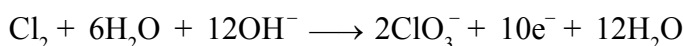
- ◆ **Step (3) :** Add electrons to make up for the difference in O.N.



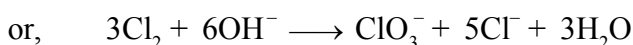
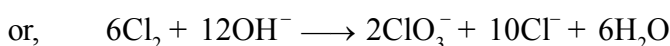
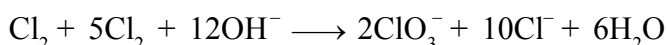
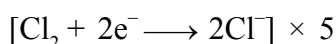
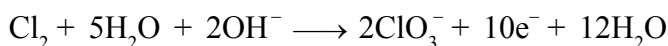
- ◆ **Step (4) :** Balance O atoms by adding H<sub>2</sub>O molecules



- ◆ **Step (5) :** Since medium is basic, balance H atoms by adding H<sub>2</sub>O molecules to the side falling short of H atoms and equal number of OH<sup>-</sup> ions to the other side.



- ◆ **Step (6) :** Multiply the reduction half reaction by 5 and add two half reactions.



**Ex.6** Balance the following chemical reaction by oxidation number method and write their skeleton equation :

- (i) *The nitrate ions in acidic medium oxidize magnesium to Mg<sup>2+</sup> ions but itself gets reduced to nitrous oxide.*

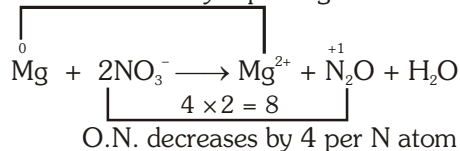
**Sol.** (i) The skeleton equation for the given process is



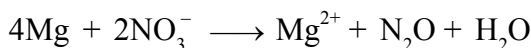
- ◆ **Step (1) :**  $\overset{0}{\text{Mg}} + (\overset{+5}{\text{N}}\overset{-2}{\text{O}})_3^- \longrightarrow \overset{+2}{\text{Mg}} + \overset{+1}{\text{N}}_2\overset{-2}{\text{O}} + \overset{+1}{\text{H}}\overset{-2}{\text{O}}$

Multiply NO<sub>3</sub><sup>-</sup> by 2 to equalize N atoms

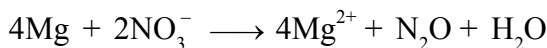
- ◆ **Step (2) :** O.N. increases by 2 per Mg atom



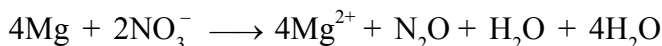
- ◆ **Step (3)** : Equalize increase/decrease in O.N. by multiplying Mg by 4 and  $2\text{NO}_3^-$  by 1.



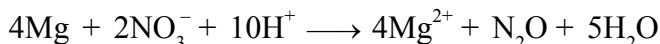
- ◆ **Step (4)** : Balance atoms other than O and H



- ◆ **Step (5)** : Balance O atoms



- ◆ **Step (6)** : Balance H atoms as is done in acidic medium.



**(b) Ion electron method or half cell method :**

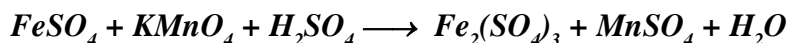
By this method redox equation are balanced in two different medium

- (a) Acidic medium (b) Basic medium

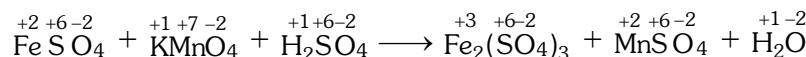
- ◆ **Balancing in acidic medium**

Students are advised to follow the following steps to balance the redox reactions by ion electron method in acidic medium.

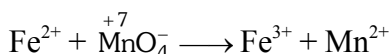
**Ex.7 Balance the following redox reaction.**



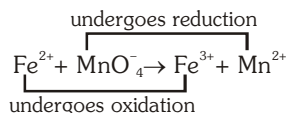
**Sol :** **Step-I** assign the oxidation No. to each elements present in the reaction.



**Step-II** Now convert the reaction in ionic form by eliminating the elements or species which are not going either oxidation or reduction



**Step-III** Now identify the oxidation / reduction occurring into the reaction.



**Step-IV** Split the ionic reaction in two half one for oxidation and other for reduction



**Step-V** Balance the atom other than oxygen and hydrogen atom in both half reactions

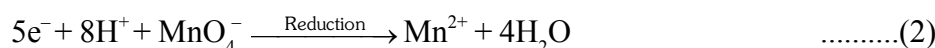


Fe & Mn atom are balanced in both side.

**Step-VI** Now balance O & H atom by  $\text{H}_2\text{O}$  &  $\text{H}^+$  respectively by the following way for one excess oxygen atom add one  $\text{H}_2\text{O}$  on the other side and two  $\text{H}^+$  on the same side.

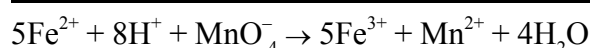
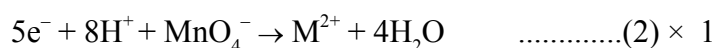


**Step VII** Now see equation (i) & (ii) is balanced atomwise. Now balance both equations chargewise to balance the charge add electrons to the electrically positive side.



**Step VIII** The number of electrons gained and lost in each half-reaction are equalised by multiply suitable factor in both the half reaction and finally the half reactions are added to give the over all balanced reaction.

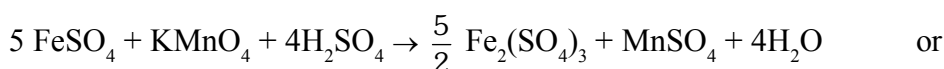
Here we multiply equation (i) by 5 and (ii) by one



(Here at this stage you will get balanced redox reaction in ionic form)

**Step IX** Now convert the ionic reaction in to molecular form by adding the elements or species which are removed instep (II).

Now by some manipulation you will get



### 7. Equivalent weight (E) :

$$\text{Eq. wt (E)} = \frac{\text{Molecular weight}}{\text{valency factor (v.f)}} = \frac{\text{Mol. wt.}}{n - \text{factor}}$$

$$\text{no of Equivalents} = \frac{\text{mass of a sample}}{\text{eq. wt. of that species}}$$

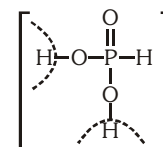
- ◆ Equivalent mass is a pure number when expressed in gram, it is called gram equivalent mass.
- ◆ The equivalent mass of substance may have different values under different conditions.

### 8. Valency factor calculation :

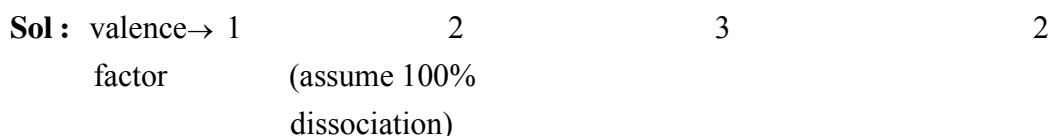
#### ◆ For Acids :

valence factor = number of replaceable  $\text{H}^+$  ions

#### Solved Examples :



{see there are only two replaceable  $\text{H}^+$  ions}



**Self practice problems :**

1. Find the valence factor for following acids

**Answers :**

1. (i) 1      (ii) 2      (iii) 1

**8.2 For Base :**

v.f. = number of replicable  $\text{OH}^-$  ions

**Solved Examples :**

**Ex :**             $\text{NaOH}$              $\text{KOH}$

**Sol :** v.f.  $\rightarrow$     1                    1

E.  $\rightarrow$            $\frac{M}{1}$                      $\frac{M}{1}$

**Self practice problems :**

1. Find the valence factor for following bases

**Answers :**

1. (i) 2      (ii) 1      (iii) 3

**8.3 Acid - base reaction :**

In case of acid base reaction, the valence factor is the actual number of  $\text{H}^+$  or  $\text{OH}^-$  replaced in the reaction. The acid or base may contain more number of replaceable  $\text{H}^+$  or  $\text{OH}^-$  than actually replaced in reaction.

v.f. for base is the number of  $\text{H}^+$  ion form the acid replaced by per molecule of the base.



*Base    Acid*

**Sol :** valency factor of base = 1

valency factor of acid = 2

Here two molecule of  $\text{NaOH}$  replaced  $2\text{H}^+$  ion from the  $\text{H}_2\text{SO}_4$  therefore per molecule of  $\text{NaOH}$  replaced only one  $\text{H}^+$  ion of acid so v.f. = 1

◆ v.f. for acid is number of  $\text{OH}^-$  replaced for the base by per molecule of acid



*Base    Acid*

**Sol :** valence factor of acid = 1

here one of molecule of  $\text{H}_3\text{PO}_4$  replaced one  $\text{OH}^-$  from  $\text{NaOH}$  therefore v.f. for  $\text{H}_3\text{PO}_4$  is = 1

$$E = \frac{\text{mol. wt. of } \text{H}_3\text{PO}_4}{1}$$

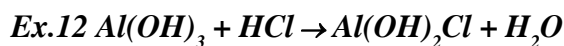


Base Acid

**Sol :** valence factor of acid = 2

here one of molecule of  $\text{H}_3\text{PO}_4$  replaced two  $\text{OH}^-$  from  $\text{NaOH}$  therefore v.f. for  $\text{H}_3\text{PO}_4$  is = 2

$$E = \frac{\text{mol. wt. of } \text{H}_3\text{PO}_4}{2}$$



Base Acid

**Sol :** valence factor of base = 1

here one of molecule of  $\text{Al}(\text{OH})_3$  replaced one  $\text{H}^+$  from  $\text{HCl}$  therefore v.f. for  $\text{Al}(\text{OH})_3$  is = 1

$$E = \frac{\text{mol. wt. of } \text{Al}(\text{OH})_3}{1}$$

#### 8.4 For Salts :

v.f. = Total number of positive charge or negative charge present into the compound.

#### Solved Examples :



**Sol :** V.f.                      2                                       $2 \times 3 = 6$                                       2

E.                                       $\frac{M}{2}$                                        $\frac{M}{6}$                                        $\frac{M}{2}$

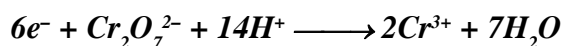
#### 8.5 Eq. wt. of oxidising / reducing agents in redox reaction :

The equivalent weight of an oxidising agent is that weight which accepts one mole electron in a chemical reaction.

(a) Equivalent wt. of an oxidant (get reduced)

$$= \frac{\text{Mol. wt.}}{\text{No. of electrons gained by one mole}}$$

#### Ex.14 In acidic medium



$$\text{Eq. wt. of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{\text{Mol. wt of } \text{K}_2\text{Cr}_2\text{O}_7}{6} = \frac{\text{Mol. wt.}}{6}$$

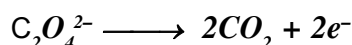
**Note :** [6 in denominator indicates that 6 electrons were gained by  $\text{Cr}_2\text{O}_7^{2-}$  as it is clear from the given balanced equation]

(b) Similarly equivalent wt. of a reductant (gets oxidised)

$$= \frac{\text{Mol. wt.}}{\text{No. of electrons lost by one mole}}$$



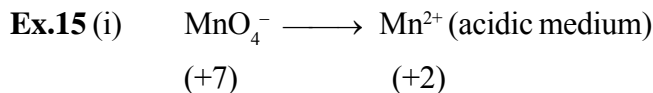
Ex.15 In acidic medium,



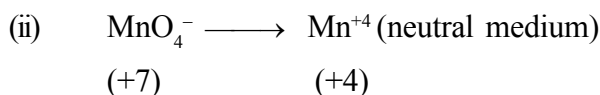
Here, Total electrons lost = 2

$$\text{So, eq. wt.} = \frac{\text{Mol. wt.}}{2}$$

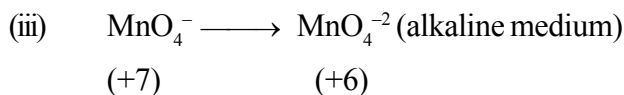
(c) In different condition a compound may have different equivalent weights. Because, it depends upon the number of electrons gained or lost by that compound in that reaction.



$$\text{Here 5 electrons are taken so eq. wt.} = \frac{\text{Mol. wt. of } KMnO_4}{5} = \frac{158}{5} = 31.6$$



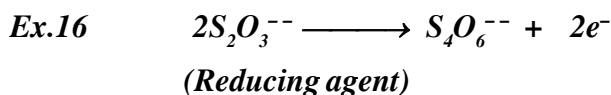
$$\text{Here, only 3 electrons are gained, so eq. wt.} = \frac{\text{Mol. wt. of } KMnO_4}{3} = \frac{158}{3} = 52.7$$



$$\text{Here, only one electron is gained, so eq. wt.} = \frac{\text{Mol. wt. of } KMnO_4}{1} = 158$$

**Note :** It is important to note that  $KMnO_4$  acts as an oxidant in every medium although with different strength which follows the order.

acidic medium > neutral medium > alkaline medium



$$\text{equivalent weight of } S_2O_3^{--} = \frac{2M}{2} = M$$

◆ **Questions based on Equivalent weight :**

- Molecular weight of  $KMnO_4$  in acidic medium and neutral medium will be respectively :  
(A)  $7 \times$  equivalent wt. and  $2 \times$  equivalent wt.      (B)  $5 \times$  equivalent wt. and  $3 \times$  equivalent wt.  
(C)  $4 \times$  equivalent wt. and  $5 \times$  equivalent wt.      (D)  $2 \times$  equivalent wt. and  $4 \times$  equivalent wt.
- In acidic medium, equivalent weight of  $K_2Cr_2O_7$  (Mol. wt. = M) is –  
(A)  $M/3$                       (B)  $M/4$                       (C)  $M/6$                       (D)  $M/2$

**Answers :**

- (1) B                      (2) A                      (3) C

## 9. NORMALITY

Normality of solution is defined as the number of equivalent of solute present in one litre (1000 mL) solutions. Let a solution is prepared by dissolving W g of solute of eq. wt. E in V mL water.

- ◆ No. of equivalent of solute =  $\frac{W}{E}$
- ◆ V mL of solution have  $\frac{W}{E}$  equivalent of solute
- ◆ 1000 mL solution have  $\frac{W \times 1000}{E \times V \text{ mL}}$
- ◆ **Normality (N) =  $\frac{W \times 1000}{E \times V \text{ mL}}$**
- ◆ **Normality (N) = Molarity  $\times$  Valence factor**

Normality (N) = molarity  $\times$  Valence factor (n)

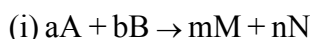
or  $N \times V$  (in mL) =  $M \times V$  (in mL)  $\times$  n

or milli equivalents = millimoles  $\times$  n

## 10. LAW OF EQUIVALENCE

The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction equivalent and mill equivalent of reactants react in equal amount to give same no. of equivalent or milli equivalents of products separately.

**According :**



$$m.\text{eq of A} = m.\text{eq of B} = m.\text{eq of M} = m.\text{eq of N}$$



$$m.\text{eq of } M_xN_y = m.\text{eq of M} = m.\text{eq of N}$$

**Ex.17** The number of moles of oxalate ions oxidized by one mole of  $MnO_4^-$  ion in acidic medium.

(A)  $\frac{5}{2}$

(B)  $\frac{2}{5}$

(C)  $\frac{3}{5}$

(D)  $\frac{5}{3}$

**Sol :** Equivalents of  $C_2O_4^{2-}$  = equivalents of  $MnO_4^-$

$$x (\text{mole}) \times 2 = 1 \times 5$$

$$x = \frac{5}{2}$$

**Ex.18** What volume of 6 M HCl and 2 M HCl should be mixed to get two litre of 3 M HCl ?

**Sol.** Let, the volume of 6 M HCl required to obtain 2 L of 3M HCl = x L

$\therefore$  Volume of 2 M HCl required = (2 - x) L

$$\begin{array}{ccc} M_1V_1 & + & M_2V_2 & = & M_3V_3 \\ 6M \text{ HCl} & & 2M \text{ HCl} & & 3M \text{ HCl} \end{array}$$

$$6 \times (x) + 2 \times (2 - x) = 3 \times 2$$

$$\Rightarrow 6x + 4 - 2x = 6 \Rightarrow 4x = 2$$

$$\therefore x = 0.5 \text{ L}$$

Hence, volume of 6 M HCl required = 0.5 L

Volume of 2M HCl required = 1.5 L

**Ex.19** In a reaction vessel, 1.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.15 M NaOH should be added for this requirement ?

**Sol.** Amount of NaOH present in 1000 mL of 0.15 M NaOH =  $0.15 \times 40 = 6 \text{ g}$

$$\therefore 1 \text{ mL of this solution contain NaOH} = \frac{6}{1000} \times 10^{-3} \text{ g}$$

$$\therefore 1.184 \text{ g of NaOH will be present in} = \frac{1}{6 \times 10^{-3}} \times 1.184 = 197.33 \text{ mL}$$

**Ex.20** What weight of  $\text{Na}_2\text{CO}_3$  of 85% purity would be required to prepare 45.6 mL of 0.235N  $\text{H}_2\text{SO}_4$

**Sol.** Meq. of  $\text{Na}_2\text{CO}_3 = \text{Meq. of H}_2\text{SO}_4 = 45.6 \times 0.235$

$$\therefore \frac{W_{\text{Na}_2\text{CO}_3}}{E_{\text{Na}_2\text{CO}_3}} \times 1000 = 45.6 \times 0.235$$

$$\Rightarrow \frac{W_{\text{Na}_2\text{CO}_3}}{106/2} \times 1000 = 45.6 \times 0.235$$

$$\therefore W_{\text{Na}_2\text{CO}_3} = 0.5679 \text{ g}$$

For 85 g of pure  $\text{Na}_2\text{CO}_3$ , weighed sample = 100 g

$$\therefore \text{For } 0.5679 \text{ g of pure } \text{Na}_2\text{CO}_3, \text{ weighed sample} = \frac{100}{85} \times 0.5679 \\ = 0.6681 \text{ g}$$

### 10.1 Drawbacks of Equivalent concept :

(i) Since equivalent weight of a substance for example oxidising or reducing agent may be variable hence it is better to use mole concept.



$$\therefore \text{Eq. wt of } \text{MnO}_4^- = \frac{\text{MnO}_4^-(\text{mol.wt.})}{5}$$



$$\therefore \text{Eq. wt. of } \text{MnO}_4^- = \frac{\text{MnO}_4^-}{3}$$

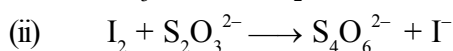
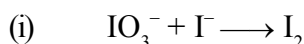
**Thus the no. of equivalents of  $\text{MnO}_4^-$  will be different in the above two cases but no. of moles will be same.**

- (ii) **Normality of any solution depends on reaction while molarity does not.**

For example.

Consider 0.1 mol  $\text{KMnO}_4$  dissolved in water to make 1L solution. Molarity of this solution is 0.1 M. However, its normality is not fixed. It will depend upon the reaction in which  $\text{KMnO}_4$  participates, e.g. If  $\text{KMnO}_4$  forms  $\text{Mn}^{2+}$ , normality =  $0.1 \times 5 = 0.5 \text{ N}$ . This same sample of  $\text{KMnO}_4$ , if employed in a reaction giving  $\text{MnO}_2$  as product (Mn in +4 state) will have normality  $0.1 \times 3 = 0.3 \text{ N}$ .

- (iii) **The concept of equivalents is handy, but it should be used with care.** One must never equate equivalents in a sequence which involves same element in more than two oxidation states. Consider an example  $\text{KIO}_3$  reacts with  $\text{KI}$  to liberate iodine and liberated iodine is titrated with standard hypo solution, The reaction are



meq of hypo = meq of  $\text{I}_2$  = meq of  $\text{IO}_3^-$  + meq of  $\text{I}^-$

$\therefore \text{IO}_3^-$  react with  $\text{I}^- \Rightarrow$  meq of  $\text{IO}_3^-$  = meq of  $\text{I}^-$

- ◆ meq of hypo =  $2 \times$  meq of  $\text{IO}_3^-$

This is wrong. Note that  $\text{I}_2$  formed by (i) have v.f. =  $5/3$  & reacted in equation (ii) have v.f. = 2.

$\therefore$  v.f. of  $\text{I}_2$  in both the equation are different therefore we cannot equate m.eq in sequence. In this type of case students are advised to use mole concept.

**Ex.21** How many milliliters of 0.02000 M  $\text{KMnO}_4$  solution would be required to exactly titrate 25.00 mL of 0.2000 M  $\text{Fe}(\text{NO}_3)_2$  solution.

**Sol : Method - 1 : Mole concept method**

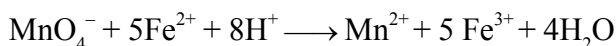
Starting with 25.00 mL of 0.2000M  $\text{Fe}^{2+}$ , we can write.

Millimoles of  $\text{Fe}^{2+} = 25.00 \times 0.2000$

and in volume V (in milliliters of the  $\text{MnO}_4^-$ )

Millimoles of  $\text{MnO}_4^- = V(0.02000)$

The balanced reaction is :



This requires that at the equivalent point,

$$\frac{V(0.02000)}{1} = \frac{(25.00)(0.2000)}{5} \quad V = 50.00 \text{ mL}$$

**Method - 2 : Equivalent Method :**

Equivalents of  $\text{MnO}_4^- = 5 \times$  moles of  $\text{MnO}_4^-$

Normality  $\text{MnO}_4^- = 5 \times$  molarity of  $\text{MnO}_4^-$

For  $\text{Fe}^{2+}$ , moles and equivalents are equal,

At the equivalence point,

$$\text{Equivalents of MnO}_4^- = \text{Equivalents of Fe}^{2+}$$

$$\begin{aligned} \text{or } V_{\text{MnO}_4^-} \times \text{Normality of MnO}_4^- \\ = V_{\text{Fe}^{2+}} \times \text{Normality of Fe}^{2+} \end{aligned}$$

For 0.02000 M MnO<sub>4</sub><sup>-</sup> solution

Normality of MnO<sub>4</sub><sup>-</sup> = (5) (0.02000) = 0.1 N and for 0.2000 M Fe<sup>2+</sup> solution

$$\text{Normality of Fe}^{2+} = 0.2000 \text{ N} \quad V_{\text{MnO}_4^-} = (25.00 \text{ mL}) \left( \frac{0.2000}{0.1000} \right) = 50.00 \text{ mL}$$

### 10.2 FOR ACID-BASE (NEUTRALIZATION REACTION) OR REDOX REACTION

N<sub>1</sub>V<sub>1</sub> = N<sub>2</sub>V<sub>2</sub> is always true.

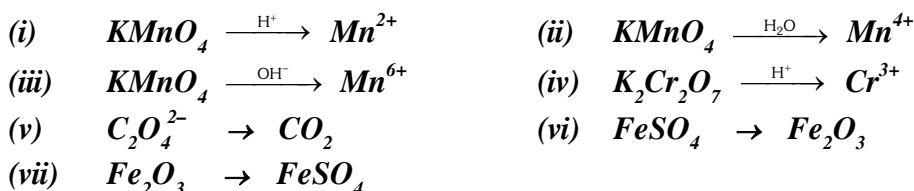
But M<sub>1</sub>V<sub>1</sub> = M<sub>2</sub>V<sub>2</sub> (may or may not be true)

But M<sub>1</sub> × n<sub>1</sub> × V<sub>1</sub> = M<sub>2</sub> × n<sub>2</sub> × V<sub>2</sub> (always true where n terms represent n-factor).

### 10.3 SOME OXIDIZING AGENTS/REDUCING AGENTS WITH EQ. WT.

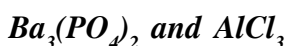
Species	Changed to	Reaction	Electrons exchanged or change in O.N.	Eq. wt.
MnO <sub>4</sub> <sup>-</sup> (O.A.)	Mn <sup>+2</sup> in acidic medium	MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup> → Mn <sup>2+</sup> + 4H <sub>2</sub> O	5	E = $\frac{M}{5}$
MnO <sub>4</sub> <sup>-</sup> (O.A.)	MnO <sub>2</sub> in neutral medium	MnO <sub>4</sub> <sup>-</sup> + 3e <sup>-</sup> + 2H <sub>2</sub> O → MnO <sub>2</sub> + 4OH <sup>-</sup>	3	E = $\frac{M}{3}$
MnO <sub>4</sub> <sup>-</sup> (O.A.)	MnO <sub>4</sub> <sup>2-</sup> in basic medium	MnO <sub>4</sub> <sup>-</sup> + e <sup>-</sup> → MnO <sub>4</sub> <sup>2-</sup>	1	E = $\frac{M}{1}$
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (O.A.)	Cr <sup>3+</sup> in acidic medium	CrO <sub>7</sub> <sup>2-</sup> + 14H <sup>+</sup> + 6e <sup>-</sup> → 2Cr <sup>3+</sup> + 7H <sub>2</sub> O	6	E = $\frac{M}{6}$
MnO <sub>2</sub> (O.A.)	Mn <sup>2+</sup> in acidic medium	MnO <sub>2</sub> + 4H <sup>+</sup> + 2e <sup>-</sup> → Mn <sup>2+</sup> + 2H <sub>2</sub> O	2	E = $\frac{M}{2}$
Cl <sub>2</sub> (O.A.) in bleaching powder	Cl <sup>-</sup>	Cl <sub>2</sub> + 2e <sup>-</sup> → 2Cl <sup>-</sup>	2	E = $\frac{M}{2}$
CuSO <sub>4</sub> (O.A.) in iodometric titration	Cu <sup>+</sup>	Cu <sup>2+</sup> + e <sup>-</sup> → Cu <sup>+</sup>	1	E = $\frac{M}{1}$
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (R.A.)	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup>	2S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> → S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> + 2e <sup>-</sup>	2	E = $\frac{2M}{2} = M$
			(for two molecules)	
H <sub>2</sub> O <sub>2</sub> (O.A.)	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> → 2H <sub>2</sub> O	2	E = $\frac{M}{2}$
H <sub>2</sub> O <sub>2</sub> (R.A.)	O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub> → O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> (O.N. of oxygen in H <sub>2</sub> O <sub>2</sub> is -1 per atom)	2	E = $\frac{M}{2}$
Fe <sup>2+</sup> (R.A.)	Fe <sup>3+</sup>	Fe <sup>2+</sup> → Fe <sup>3+</sup> + e <sup>-</sup>	1	E = $\frac{M}{1}$

**Ex.22** To find the *n*-factor in the following chemical changes.



- Sol.** (i) In this reaction,  $\text{KMnO}_4$  which is an oxidizing agent, itself gets reduced to  $\text{Mn}^{2+}$  under acidic conditions.  
 $n = |1 \times (+7) - 1 \times (+2)| = 5$
- (ii) In this reaction,  $\text{KMnO}_4$  gets reduced to  $\text{Mn}^{4+}$  under neutral or slightly (weakly) basic conditions.  
 $n = |1 \times (+7) - 1 \times (+4)| = 3$
- (iii) In this reaction,  $\text{KMnO}_4$  gets reduced to  $\text{Mn}^{6+}$  under basic conditions.  
 $n = |1 \times (+7) - 1 \times (+6)| = 1$
- (iv) In this reaction,  $\text{K}_2\text{Cr}_2\text{O}_7$  which acts as an oxidizing agent reduced to  $\text{Cr}^{3+}$  under acidic conditions. (It does not react under basic conditions.)  
 $n = |2 \times (+6) - 2 \times (+3)| = 6$
- (v) In this reaction,  $\text{C}_2\text{O}_4^{2-}$  (oxalate ion) gets oxidized to  $\text{CO}_2$  when it is reacted with an oxidizing agent.  
 $n = |2 \times (+3) - 2 \times (+4)| = 2$
- (vi) In this reaction, ferrous ions get oxidized to ferric ions.  
 $n = |1 \times (+2) - 1 \times (+3)| = 1$
- (vi) In this reaction, ferric ions are getting reduced to ferrous ions.  
 $n = |2 \times (+3) - 2 \times (+2)| = 2$

**Ex.23** Calculate the molar ratio in which the following two substances would react ?



**Sol.** *n*-factor of  $\text{Ba}_3(\text{PO}_4)_2 = 3 \times (+2) = 6 = n_1$

While *n*-factor of  $\text{AlCl}_3 = 1 \times (+3) = 3 = n_2$

$$\frac{n_1}{n_2} = \frac{6}{3} \quad \text{If} \quad \frac{n_1}{n_2} = \frac{x}{y}$$

Molar ratio =  $\frac{y}{x}$  (inverse of equivalent ratio)

$\therefore$  Molar ratio in which  $\text{Ba}_3(\text{PO}_4)_2$  and  $\text{AlCl}_3$  will react =  $3 : 6 = 1 : 2$

## 10.4 APPLICATIONS OF THE LAW OF EQUIVALENCE

### 10.4.1 Simple Titration

In this, we can find the concentration of unknown solution by reacting it with solution of known concentration (standard solution).

For example, let there be a solution of substance A of unknown concentration. We are given solution of another substance B whose concentration is known ( $N_1$ ). We take a certain known volume of A in a flask ( $V_2$ ) and then we add B to A slowly till all the A is consumed by B (this can be known with the help of indicators). Let us, assume that the volume of B consumed is  $V_1$ . According to the law of equivalence, the number of g equivalents of B at the end point.

$\therefore N_1 V_1 = N_2 V_2$ , where  $N_2$  is the conc. of A.

From this we can calculate the value of  $N_2$ .

**Ex.24** 1.20 g sample of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  was dissolved in water to form 100 mL of a Solution. 20 mL of this solution required 40 mL of 0.1 N HCl for complete neutralization. Calculate the weight of  $\text{Na}_2\text{CO}_3$  in the mixture. If another 20 mL of this solution is treated with excess of  $\text{BaCl}_2$ , what will be the weight of the precipitate ?

**Sol.** Let, weight of  $\text{Na}_2\text{CO}_3 = x$  g

Weight of  $\text{K}_2\text{CO}_3 = y$  g

$$\therefore x + y = 1.20 \text{ g} \quad \dots\dots\dots(i)$$

For neutralization reaction of 100 mL

Meq. of  $\text{Na}_2\text{CO}_3 + \text{Meq. of } \text{K}_2\text{CO}_3 = \text{Meq. of HCl}$

$$\Rightarrow \frac{x}{106} \times 2 \times 1000 + \frac{y}{138} \times 2 \times 1000 = \frac{40 \times 0.1 \times 100}{20}$$

$$\therefore 69x + 53y = 73.14 \quad \dots\dots\dots(ii)$$

From Eqs. (i) and (ii), we get

$$x = 0.5962 \text{ g}$$

$$y = 0.604 \text{ g}$$

Solution of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  gives ppt. of  $\text{BaCO}_3$  with  $\text{BaCl}_2$

(Meq. of  $\text{Na}_2\text{CO}_3 + \text{Meq. of } \text{K}_2\text{CO}_3$ ) in 20 mL = Meq. of  $\text{BaCO}_3$

$\Rightarrow$  Meq. of HCl for 20 mL mixture = Meq. of  $\text{BaCO}_3$

$\Rightarrow$  Meq. of  $\text{BaCO}_3 = 40 \times 0.1 = 4$

$$\frac{W_{\text{BaCO}_3}}{M_{\text{BaCO}_3}} \times 1000 = 40 \times 0.1 = 4$$

$$\frac{W_{\text{BaCO}_3}}{197} \times 2 \times 1000 = 4$$

$$\therefore W_{\text{BaCO}_3} = 0.394 \text{ g}$$

## 10.4.2 BACK TITRATION

Back titration is used to calculate % purity of a sample. Let us assume that we are given an impure solid substance C weighing  $w$  g and we are asked to calculate the percentage of pure C in the sample. We will assume that the impurities are inert. We are provided with two solutions A and B, where the concentration of B is known ( $N_1$ ) and that of A is not known. This type of titration will work only if the following condition is satisfied, i.e. the nature of compounds A, B and C should be such that A and B can react with each other. A and C can react with each other but the product of A and C should not react with B.

Now, we take a certain volume of A in a flask ( the g equivalents of A taken should be  $\geq$  g equivalents of C in the sample and this can be done by taking A in excess). Now, we perform a simple titration using B. Let us assume that the volume of B used is  $V_1$ . In another beaker, we again take the solution of A in the same volume as taken earlier. Now, C is added to this and after the reaction is completed, the solution is being titrated with B. Let us assume that the volume of B used up is  $V_2$ . Gram equivalents of B used in the first titration =  $N_1 V_1$ .

$\therefore$  gm. equivalents of A initially =  $N_1 V_1$

gm. equivalents of B used in the second titration =  $N_1 V_2$

$\therefore$  gm. equivalents of A left in excess after reacting with C =  $N_1 V_2$

gm. equivalents of A that reacted with C =  $N_1 V_1 - N_1 V_2$

If the n-factor of C is x, then the moles of pure C =  $\frac{N_1 V_1 - N_1 V_2}{x}$

$\therefore$  The weight of C =  $\frac{N_1 V_1 - N_1 V_2}{x} \times \text{Molecular weight of C}$

$\therefore$  Percentage of C =  $\frac{N_1 V_1 - N_1 V_2}{x} \times \frac{\text{Molecular wt. of C}}{w} \times 100$

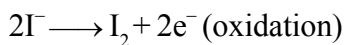
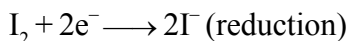
### □ SOME REDOX TITRATIONS (EXCLUDING IODOMETRIC / IODIMETRIC)

Estimation of	By titrating with	Reactions	Relation between O.A. and R.A.
$\text{Fe}^{2+}$	$\text{MnO}_4^-$	$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$ $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$5\text{Fe}^{2+} \equiv \text{MnO}_4^-$ Eq. wt. $\text{Fe}^{2+} = M/1$ Eq. wt. $\text{MnO}_4^- = M/5$
$\text{Fe}^{2+}$	$\text{Cr}_2\text{O}_7^{2-}$	$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$ $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	$6\text{Fe}^{2+} \equiv \text{Cr}_2\text{O}_7^{2-}$ Eq. wt. $\text{Cr}_2\text{O}_7^{2-} = M/6$
$\text{C}_2\text{O}_4^{2-}$	$\text{MnO}_4^-$	$\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2e^-$ $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$5\text{C}_2\text{O}_4^{2-} \equiv 2\text{MnO}_4^-$ Eq. wt. $\text{C}_2\text{O}_4^{2-} = M/2$ Eq. wt. $\text{MnO}_4^- = M/5$
$\text{H}_2\text{O}_2$	$\text{MnO}_4^-$	$\text{H}_2\text{O}_2 \longrightarrow 2\text{H}^+ + \text{O}_2 + 2e^-$ $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$5\text{H}_2\text{O}_2 \equiv 2\text{MnO}_4^-$ Eq. wt. $\text{H}_2\text{O}_2 = M/2$ Eq. wt. $\text{MnO}_4^- = M/5$
$\text{As}_2\text{O}_3$	$\text{MnO}_4^-$	$\text{As}_2\text{O}_3 + 5\text{H}_2\text{O} \longrightarrow 2\text{AsO}_4^{3-} + 10\text{H}^+ + 4e^-$	Eq. wt. $\text{As}_2\text{O}_3 = M/4$
$\text{AsO}_3^{3-}$	$\text{BrO}_3^-$	$\text{AsO}_3^{3-} + \text{H}_2\text{O} \longrightarrow \text{AsO}_4^{3-} + 2\text{H}^+ + 2e^-$ $\text{BrO}_3^- + 6\text{H}^+ + 6e^- \longrightarrow \text{Br}^- + 3\text{H}_2\text{O}$	Eq. wt. $\text{AsO}_3^{3-} = M/2$ Eq. wt. $\text{BrO}_3^- = M/6$



### 10.4.3 Iodometric and Iodimetric Titration :

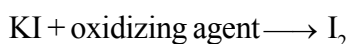
The reduction of free iodine to iodide ions and oxidation of iodide ions to free iodine occurs in these titrations.



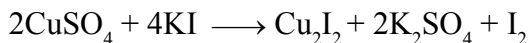
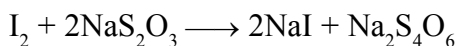
These are divided into two types :

#### (i) Iodometric Titration :

In iodometric titrations, an oxidizing agent is allowed to react in neutral medium or in acidic medium with excess of potassium iodide to liberate free iodine.



Free iodine is titrated against a standard reducing agent usually with sodium thiosulphate. Halogen, dichromates, cupric ion, peroxides etc., can be estimated by this method.



#### (ii) Iodimetric Titration

These are the titrations in which free iodine is used as it is difficult to prepare the solution of iodine (volatile and less soluble in water), it is dissolved in KI solution :



This solution is first standardized before using with the standard solution of substance such as sulphite, thiosulphate, arsenite etc, are estimated.

In iodimetric and iodometric titration, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point, the blue or violet colour disappears when iodine is completely changed to iodide.

□ SOME IODOMETRIC TITRATIONS (TITRATING SOLUTIONS IS  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ )

Estimation of	Reaction	Relation between O.A. and R.A.
$\text{I}_2$	$\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$ or $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$	$\text{I}_2 = 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{Na}_2\text{S}_2\text{O}_3 = \text{M}/1$
$\text{CuSO}_4$	$2\text{CuSO}_4 + 4\text{KI} \longrightarrow 2\text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$ $\text{Cu}^{2+} + 4\text{I}^- \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$ (White ppt.)	$2\text{CuSO}_4 \equiv \text{I}_2 = 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{CuSO}_4 = \text{M}/1$
$\text{CaOCl}_2$	$\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{Cl}_2$ $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$ $\text{CaOCl}_2 \equiv \text{Cl}_2 = \text{I}_2 = 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Cl}_2 + 2\text{I}^- \longrightarrow 2\text{Cl}^- + \text{I}_2$	Eq. wt. of $\text{CaOCl}_2 = \text{M}/2$
$\text{MnO}_2$	$\text{MnO}_2 + 4\text{HCl}(\text{conc}) \xrightarrow{\Delta} \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$ $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$ or $\text{MnO}_2 + 4\text{H}^+ + 2\text{Cl}^- \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} + \text{Cl}_2$ $\text{Cl}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{Cl}^-$	$\text{MnO}_2 \equiv \text{Cl}_2 = \text{I}_2 = 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{MnO}_2 = \text{M}/2$
$\text{IO}_3^-$	$\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$	$\text{IO}_3^- \equiv 3\text{I}_2 \equiv 6\text{I} \equiv 6\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{IO}_3^- = \text{M}/6$
$\text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{I}_2 + 2\text{H}_2\text{O}$	$\text{H}_2\text{O}_2 \equiv \text{I}_2 = 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{H}_2\text{O}_2 = \text{M}/2$
$\text{Cl}_2$	$\text{Cl}_2 + 2\text{I}^- \longrightarrow 2\text{Cl}^- + \text{I}_2$	$\text{Cl}_2 \equiv \text{I}_2 = 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{Cl}_2 = \text{M}/2$
$\text{O}_3$	$\text{O}_3 + 6\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$	$\text{O}_3 \equiv 3\text{I}_2 \equiv 6\text{I} \equiv 6\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{O}_3 = \text{M}/6$
$\text{Cr}_2\text{O}_7^{2-}$	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \longrightarrow 3\text{I}_2 + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	$\text{Cr}_2\text{O}_7^{2-} \equiv 3\text{I}_2 \equiv 6\text{I}$ Eq. wt. of $\text{Cr}_2\text{O}_7^{2-}$
$\text{MnO}_4^-$	$2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \longrightarrow 2\text{MnO}_4^- + 5\text{I}_2 + 8\text{H}_2\text{O}$	$2\text{MnO}_4^- \equiv 5\text{I}_2 \equiv 10\text{I}$ Eq. wt. of $\text{MnO}_4^- = \text{M}/5$
$\text{BrO}_3^-$	$\text{BrO}_3^- + 6\text{I}^- + 6\text{H}^+ \longrightarrow \text{Br}^- + 3\text{I}_2 + 3\text{H}_2\text{O}$	$\text{BrO}_3^- \equiv 3\text{I}_2 \equiv \text{I}_2$ Eq. wt. of $\text{BrO}_3^- = \text{M}/6$
As(V)	$\text{H}_3\text{AsO}_4 + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} + \text{I}_2$	$\text{H}_3\text{AsO}_4 \equiv \text{I}_2 \equiv 2\text{I}$ Eq. wt. of $\text{H}_3\text{AsO}_4 = \text{M}/2$

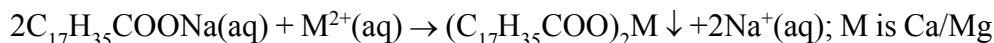
□ SOME IODIMETRIC TITRATION (TITRATING SOLUTIONS IS I<sub>2</sub> IN KI)

Estimation of	Reaction	Relation between O.A. and R.A.
H <sub>2</sub> S (in acidic medium)	$H_2S + I_2 \longrightarrow S + 2I^- + 2H^+$	H <sub>2</sub> S ≡ I <sub>2</sub> ≡ 2I Eq. wt. of H <sub>2</sub> S = M/2
SO <sub>3</sub> <sup>2-</sup> (in acidic medium)	$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_3^{2-} + 2I^- + 2H^+$	SO <sub>3</sub> <sup>2-</sup> ≡ I <sub>2</sub> ≡ 2I Eq. wt. of SO <sub>3</sub> <sup>2-</sup> = M/2
Sn <sup>2+</sup> (in acidic medium)	$Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$	Sn <sup>2+</sup> ≡ I <sub>2</sub> ≡ 2I Eq. wt. of Sn <sup>2+</sup> = M/2
As(III) (at pH = 8)	$H_2AsO_3^- + I_2 + H_2O \longrightarrow$ $HAsO_4^{2-} + 2I^- + 2H^+$	H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup> ≡ I <sub>2</sub> ≡ 2I Eq. wt. of H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup> = M/2
N <sub>2</sub> H <sub>4</sub>	$N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$	N <sub>2</sub> H <sub>4</sub> ≡ 2I <sub>2</sub> ≡ 4I Eq. wt. of N <sub>2</sub> H <sub>4</sub> = M/4

11. Hardness of water :

**Hard water** does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate (C<sub>17</sub>H<sub>35</sub>COONa) reacts with hard water to precipitate out Ca/Mg stearate.



**Hardness of water is of two types**

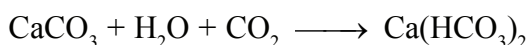
(a) Temporary Hardness

(b) Permanent Hardness

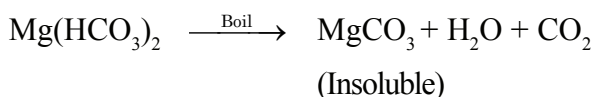
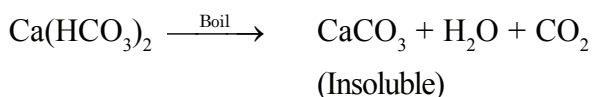
**Temporary Hardness :-**

This is due to presence of bicarbonate of calcium and magnesium. Rain water dissolves a small quantities of CO<sub>2</sub> from the atmosphere forming a very dilute solution of carbonic acid.

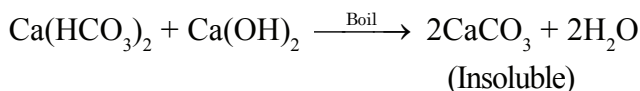
This water attacks Ca and Mg carbonate in any rock



Temporary hardness in water is easily removed by boiling, as the bicarbonates decomposes readily and the insoluble carbonates are precipitated.

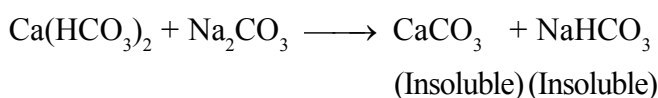
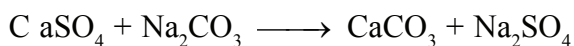
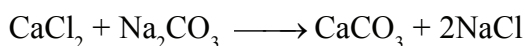


Temporarily hardness can also be removed by Clark's process which involves the addition of slaked lime  $\text{Ca(OH)}$



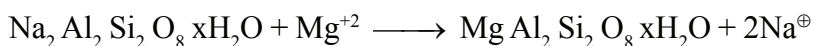
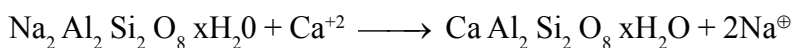
**Permanent Hardness :-** Permanent hardness is due to presence of sulphates and chlorides of both calcium and magnesium. This type of hardness cannot be removed by boiling or by  $\text{Ca(OH)}_2$ . Substance used to remove the hardness of water are known as water softener. This various water softeners are -

- (i) **Washing soda :-** It removes both the temporary and permanent hardness by converting soluble Ca and Mg compounds into insoluble Carbonates.

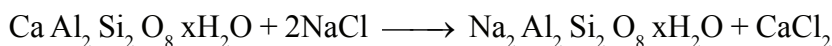


- (ii) **Permutit:** Permutit is technical name given to certain hydrated silicates of aluminium and sodium or sodium aluminium orthosilicate or sodium zeolite.

**Example :**  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$ .

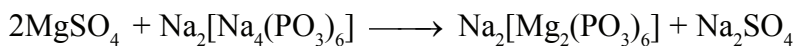
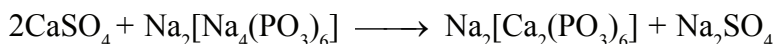


These ions can be re-exchanged by treating it with brine ( $\text{NaCl}$ ) solution.

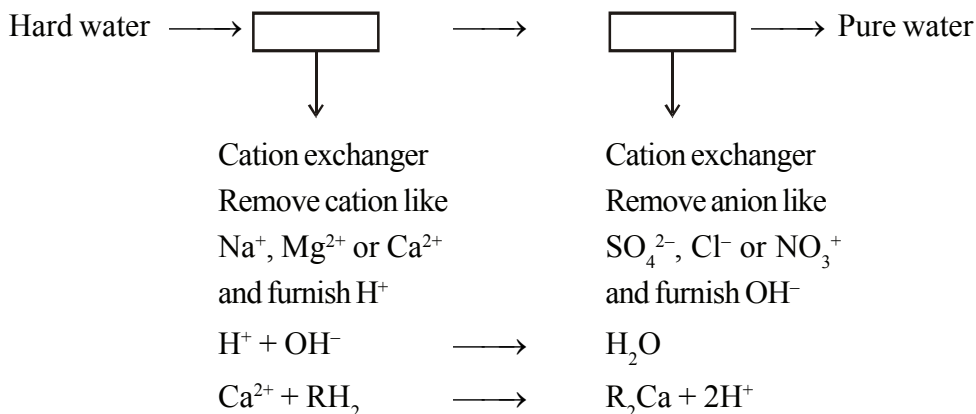


This method is useful for the removal of both temporary and permanent hardness of water.

- (iii) **CALGON:** The complex salt of metaphosphoric acid, sodium hexametaphosphate ( $\text{Na}_4(\text{PO}_3)_6$ ) is called Calgon. It is represented as  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ .

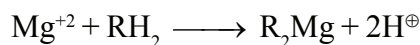
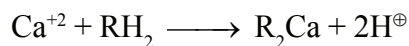


- (iv) **Ion exchange Resins:-** Ion exchange resins are the most popular water softener these days. These resins are synthetic substance. The cation exchanger consists of granular insoluble organic acid resins having giant molecules with  $-\text{SO}_3\text{H}$  or  $-\text{COOH}$  groups while the anion exchanger contains giant organic molecules with basic groups derived from amine. Ion exchange resins remove all soluble mineral from water.

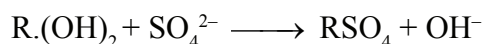
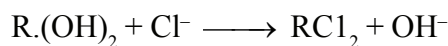


The water coming from cation exchanger is acidic due to  $H^+$ . This water is then passed through another bed containing anion exchanger. This exchanger removes anion like  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$  by exchanging with  $OH^-$  ions.

**Reaction at Cation exchanger :**



**Reaction at Anion exchanger :**



**NOTE :** Degree of Hardness of water is measured in terms of ppm of  $CaCO_3$  which is defined as number of parts of  $CaCO_3$  by mass present in one million parts by mass of water whose equivalent is equal to the gram equivalent of various calcium & magnesium salts.

For **example** consider the sample of hard water which is found to contain 36 mg of  $MgSO_4$  per kg of water.

gm equivalent of  $CaCO_3$  = gm eq. of  $MgSO_4$

$$\frac{W_{CaCO_3}}{100} \times 2 = \frac{36 \times 10^{-3}}{120} \times 2$$

$$W_{CaCO_3} = 3 \times 10^{-2} \text{ gm}$$

$$\text{degree of hardness} = \text{ppm of } CaCO_3 = \frac{3 \times 10^{-2}}{1000} \times 10^6 = 30$$

## 12. GLOSSARY

**Aliquot.** A portion of the whole, usually a simple fraction. A portion of a sample withdraw from a volumetric flask with a pipet is called an aliquot.

**Analytical concentration.** The total number of moles per litre of a solute regardless of any reactions that might occur when the solute dissolves. Used synonymously with formality.

**Equivalent.** The amount of a substance which furnishes or reacts with 1 mol of  $H^+$  (acid-base), 1 mol of electrons (redox), or 1 mol of a univalent cation (precipitation and complex formation).

**Equivalent weight.** The weight in grams of one equivalent of a substance.

**Equivalence point.** The point in a titration where the number of equivalents of titrant is the same as the number of equivalents of analyte.

**End point.** The point in a titration where an indicator changes color.

**Formula weight.** The number of formula weights of all the atoms in the chemical formula of a substance.

**Formality.** The number of formula weights of solute per litre of solution; synonymous with analytical concentration.

**Indicator.** A chemical substance which exhibits different colors in the presence of excess analyte or titrant.

**Normality.** The number of equivalents of solute per litre of solution.

**Primary standard.** A substance available in a pure form or state of known purity which is used in standardizing a solution.

**Standardization.** The process by which the concentration of a solution is accurately ascertained.

**Standard solution.** A solution whose concentration has been accurately determined.

**Titrant.** The reagent (a standard solution) which is added from a buret to react with the analyte.

### SOME MORE SOLVED EXAMPLES

**Ex.25** A 3.00 g sample containing  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and an inert impure substance, is treated with excess of KI solution in presence of dilute  $\text{H}_2\text{SO}_4$ . The entire iron is converted into  $\text{Fe}^{2+}$  along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution require 11 mL of 0.5 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution to reduce the iodine present. A 50 mL of diluted solution after complete extraction of the iodine requires 12.80 mL of 0.25  $\text{KMnO}_4$  solution in dilute  $\text{H}_2\text{SO}_4$  medium for the oxidation of  $\text{Fe}^{2+}$ . Calculate the percentages of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  in the original sample.

**Sol.** Let number of moles of  $\text{Fe}_3\text{O}_4$  is 'a' and no. of moles of  $\text{Fe}_2\text{O}_3$  is 'b' in 3 gram sample.

Now, 'a' moles  $\text{Fe}_3\text{O}_4$  means (a moles  $\text{Fe}_2\text{O}_3$  + a mole of FeO)

So, in sample (a + b) moles  $\text{Fe}_2\text{O}_3$  and 'a' mole FeO present.



No. of gram equivalent of  $\text{Fe}_2\text{O}_3$  = no. of gram equivalent of  $\text{I}_2$

$$n_{\text{Fe}_2\text{O}_3} \times n_{f(\text{Fe}_2\text{O}_3)} = n_{\text{I}_2} \times n_{f(\text{I}_2)}$$

$$(a + b) \times 2 = n_{\text{I}_2} \times 2$$

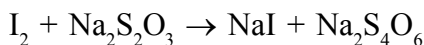
$$n_{\text{I}_2} = (a + b) \text{ moles.}$$

Now, solution is diluted to 100 ml

$$\text{So, } [\text{I}_2] = \frac{n}{V_{\text{litre}}} = \frac{(a + b)}{100/1000} = 10(a + b)$$

$$[\text{Fe}^{2+}] = \left( \frac{n(\text{Fe}^{2+})}{V_{\text{litre}}} \right) = \frac{(3a + 2b)}{100/1000} = 10(3a + 2b)$$

Now 20 ml of this solution titrated with 11 ml, 0.5 M  $\text{Na}_2\text{S}_2\text{O}_3$



No. of gram equivalent of  $\text{I}_2$  = no. of gram equivalent of  $\text{Na}_2\text{S}_2\text{O}_3$

$$(N \times V)_{\text{I}_2} = (N \times V)_{\text{Na}_2\text{S}_2\text{O}_3}$$

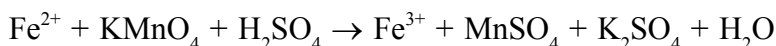
$$(M \times n_f \times V)_{\text{I}_2} = (M \times n_f \times V)_{\text{Na}_2\text{S}_2\text{O}_3}$$

$$10(a + b) \times 2 \times 20 = 0.5 \times 1 \times 11$$

$$a + b = \frac{11}{800} \quad \dots\dots (i)$$

50 ml of solution after extraction of  $I_2$  allowed to oxidation

of  $Fe^{2+}$  by 12.80 ml, 0.25 M  $KMnO_4$ .



no. of gram equivalent of  $Fe^{2+}$  = no. of gram equivalent of  $KMnO_4$ .

$$(M \times n_f \times V)_{Fe^{2+}} = (M \times n_f \times V)_{KMnO_4}$$

$$10(3a + 2b) \times 1 \times 50 = 0.25 \times 5 \times 12.80$$

$$3a + 2b = \frac{16}{500} \dots\dots(ii)$$

By (i) & (ii)

$$a = 0.0045 \text{ moles}$$

$$b = 0.00925 \text{ moles}$$

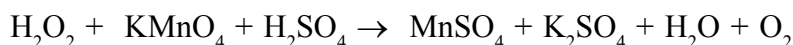
$$\text{so } \% Fe_2O_3 = \frac{Wt(Fe_2O_3)}{\text{Total wt.}} \times 100 = \frac{b \times 160}{3} \times 100 = \frac{0.00925 \times 160}{3} \times 100 = 49.33\%$$

$$\% Fe_2O_3 = \frac{Wt(Fe_2O_3)}{\text{Total wt.}} \times 100 = \frac{a \times 232}{3} \times 100 = \frac{0.0045 \times 232}{3} \times 100 = 34.8\%$$

**Ex.26** Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of  $KMnO_4$  (20 mL) acidified with dilute  $H_2SO_4$ . The same volume of  $KMnO_4$  solution is just decolorized by 10 mL of  $MnSO_4$  in neutral medium simultaneously forming a dark brown precipitate of hydrated  $MnO_2$ . The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute  $H_2SO_4$ . Write the equations involved in the reactions and calculate the molarity of  $H_2O_2$ .

**Sol.** Let molarity of  $H_2O_2$  solution is  $M_1$

20 ml,  $M_1$  molar  $H_2O_2$  react with 20 ml  $KMnO_4$  in  $H_2SO_4$  solution

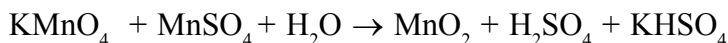


no. of gram equivalent of  $H_2O_2$  = no. of gram equivalent of  $KMnO_4$

$$(M \times n_f \times V)_{H_2O_2} = (M \times n_f \times V)_{KMnO_4}$$

$$M_1 \times 2 \times 20 = M_{KMnO_4} \times 5 \times 20 \dots\dots(i)$$

20 ml  $KMnO_4$  decolourise by 10 ml  $MnSO_4$  in neutral medium.

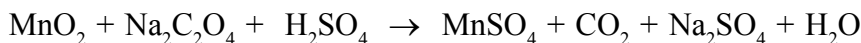


no. of gram equivalent of  $KMnO_4$  = no. of gram equivalent of  $MnO_2$

$$M_{KMnO_4} \times 3 \times 20 \text{ml} = \text{no. of gram equivalent of } MnO_2$$

$$M_{KMnO_4} \times 3 \times 20 \times 10^{-3} = n_{MnO_2} \times 6/5 \dots\dots(ii)$$

and obtained  $MnO_2$  dissolved in 10 ml, 0.2 M  $Na_2C_2O_4$



no. of gram equivalent of  $MnO_2$  = no. of gram equivalent of  $Na_2C_2O_4$

$$n_{MnO_2} \times 2 = 0.2 \times 2 \times 10 \times 10^{-3}$$

$$n_{\text{MnO}_2} = 2 \times 10^{-3} \text{ moles} \quad \dots\dots(\text{iii})$$

From equation (ii)

$$M_{\text{KMnO}_4} \times 3 \times 20 \times 10^{-3} = 2 \times 10^{-3} \times \frac{6}{5}$$

$$M_{\text{KMnO}_4} = \frac{2}{50}$$

From equation (1)

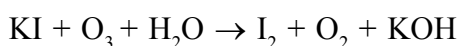
$$M_1 \times 2 \times 20 = \frac{2}{50} \times 5 \times 20$$

$$M_1 = 0.1\text{M}$$

**Ex.27** One litre of a mixture of  $\text{O}_2$  and  $\text{O}_3$  ( $\text{O}_3 \longrightarrow \text{O}_2 + \text{O}^{2-}$ ) at 1 atm and 273 K was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 ml of M/10 sodium thiosulphate solution for titration. What is the percent of ozone in the mixture? Ultraviolet radiation of wave length 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture?

**Sol.** Let in 1 litre mixture x litre is  $\text{O}_2$  and y litre is  $\text{O}_3$  at NTP

excess KI reduce  $\text{O}_3$  into  $\text{O}_2$  and  $\text{O}^{2-}$



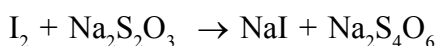
no. of gram equivalent of  $\text{O}_3 =$  no. of gram equivalent of  $\text{I}_2$

$$(n \times n_p)_{\text{O}_3} = (n \times n_p)_{\text{I}_2}$$

$$\frac{y}{22.4} \times 2 = n_{\text{I}_2} \times 2$$

$$n_{\text{I}_2} = \frac{y}{22.4} \quad \dots\dots(1)$$

Now, released  $\text{I}_2$  required 40 ml,  $\frac{1}{10}$  M  $\text{Na}_2\text{S}_2\text{O}_3$



No. of gram equivalent of  $\text{I}_2 =$  no. of gram equivalent of  $\text{Na}_2\text{S}_2\text{O}_3$

$$n_{\text{I}_2} \times 2 = \frac{1}{10} \times 1 \times 40 \times 10^{-3}$$

$$n_{\text{I}_2} = 2 \times 10^{-3} \text{ moles}$$

Now from equation (1)

$$\frac{y}{22.4} = 2 \times 10^{-3}$$

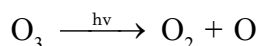


$$y = (44.8 \times 10^{-3}) \text{ litre} = 0.0448 \text{ litre}$$

$$x = 1 - y = 1 - 0.0448 = 0.9552 \text{ litre}$$

$$\begin{aligned} \% \text{ (by wt)} &= \frac{\text{wt}(\text{O}_3)}{\text{wt. (total)}} \times 100 \\ &= \frac{n(\text{O}_3) \times 48}{n(\text{O}_3) \times 48 + n(\text{O}_2) \times 32} \times 100 \\ &= \frac{\frac{y}{22.4} \times 48}{\frac{y}{22.4} \times 48 + \frac{x}{22.4} \times 32} \times 100 \\ &= \frac{3y}{3y + 2x} \times 100 \\ &= \frac{3 \times 0.0448}{3 \times 0.0448 + 2 \times 0.9552} \times 100 \\ &= \frac{0.1344}{2.0448} \times 100 = 6.57 \% \end{aligned}$$

One photon required for breaking of one  $\text{O}_3$  bond in to  $\text{O}_2$  &  $\text{O}$



So, no. of photon required = no. of  $\text{O}_3$  bonds break

= no. of  $\text{O}_3$  molecules

$$\begin{aligned} &= n_{\text{O}_3} \times N_A = \frac{0.0448}{22.4} \times 6 \times 10^{23} \\ &= 1.2 \times 10^{21} \text{ photons.} \end{aligned}$$

**Ex.28** A mixture of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  is reacted with acidified  $\text{KMnO}_4$  solution having a concentration of  $2/5 \text{ M}$ ,  $100 \text{ mL}$  of which was used. The solution was then titrated with  $\text{Zn}$  dust which converted  $\text{Fe}^{3+}$  of the solution to  $\text{Fe}^{2+}$ . The  $\text{Fe}^{2+}$  required  $1000 \text{ mL}$  of  $2/15 \text{ M}$   $\text{K}_2\text{Cr}_2\text{O}_7$  solution. Find the % by mol of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ .

**Sol.** Let no. of moles of  $\text{FeO}$  is  $x$  millimoles &  $\text{Fe}_2\text{O}_3$  is  $y$  millimoles in mixture.



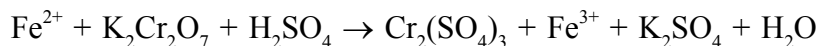
no. of milligram equivalent of  $\text{FeO}$  = no. of milli gram equivalent of  $\text{KMnO}_4$ .

$$x \times 1 = \frac{2}{5} \times 5 \times 100$$

$$x = 200 \text{ m moles.}$$

$\text{Zn}$  - dust convert all  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$

So no. of millimoles of  $\text{Fe}^{2+}$  in solution is =  $(x + 2y)$ .



no. of milli gram equivalent of  $\text{Fe}^{2+}$  = no. of milligram equivalent of  $\text{K}_2\text{Cr}_2\text{O}_7$

$$(x + 2y) \times 1 = \frac{2}{15} \times 6 \times 1000$$

$$(200 + 2y) = \frac{2}{15} \times 1000$$

$$y = 300 \text{ millimoles.}$$

$$\% \text{ FeO (by moles)} = \frac{x}{x + y} \times 100 = \frac{200}{500} \times 100 = 40\%$$

$$\% \text{ Fe}_2\text{O}_3 \text{ (by moles)} = 60\%$$

**Ex.29** A substance of crude copper is boiled in  $\text{H}_2\text{SO}_4$  till all the copper has reacted. The impurities are inert to the acid. The  $\text{SO}_2$  liberated in the action is passed into 100 mL of 0.4 M acidified  $\text{KMnO}_4$  ( $\text{SO}_2 \rightarrow \text{SO}_4^{2-}$ ). The solution of  $\text{KMnO}_4$  after passage of  $\text{SO}_2$  is allowed to react with oxalic acid and requires 25 mL of 1 M oxalic acid. If the purity of copper is 95.25%, what was the weight of the sample.

**Sol.** let given sample is  $w$  gram and no. of moles of Cu in given sample is  $x$  millimoles.



$x$  millimoles                       $x$  millimoles



no. of milligram eq. of  $\text{SO}_2$  = no. of milli gram eq. of  $\text{KMnO}_4$

$$x \times 2 = \text{no. of gram eq. of } \text{KMnO}_4$$

left  $\text{KMnO}_4$  reduced by  $\text{H}_2\text{C}_2\text{O}_4$



no. of milligram eq. of  $\text{KMnO}_4$  (left)

$$= \text{no. of mill gram eq. of } \text{H}_2\text{C}_2\text{O}_4$$

$$= 1 \times 2 \times 25$$

So, total milligram eq. of  $\text{KMnO}_4$  = milligram eq. of  $\text{SO}_2$  + milligram eq. of  $\text{H}_2\text{C}_2\text{O}_4$

$$0.4 \times 5 \times 100 = x \times 2 + 1 \times 2 \times 25$$

$$x = 75 \text{ millimoles}$$

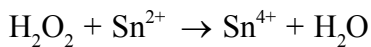
$$\text{wt}(\text{Cu}) = 95.25\% \text{ of } W$$

$$75 \times 10^{-3} \times 63.5 = \frac{95.25}{100} \times W$$

$$\Rightarrow W = 5 \text{ gram.}$$

**Ex.30**  $\text{H}_2\text{O}_2$  is reduced rapidly by  $\text{Sn}^{2+}$ , the products being  $\text{Sn}^{4+}$  and water.  $\text{H}_2\text{O}_2$  decomposes slowly at room temperature to yield  $\text{O}_2$  and water. Calculate the volume of  $\text{O}_2$  produced at 273 K and 1.00 atm when 200 g of 10.0% by mass  $\text{H}_2\text{O}_2$  in water is treated with 88.2 mL of 1 M  $\text{Sn}^{2+}$  and then the mixture is allowed to stand until no further reaction occurs.

**Sol.** Let  $x$  millimoles of  $\text{H}_2\text{O}_2$  react with 1M, 88.2 ml  $\text{Sn}^{2+}$



no. of milligram equivalent of  $\text{H}_2\text{O}_2$

= no. of milligram eq. of  $\text{Sn}^{2+}$

$$x_{\text{millimole}} \times 2 = 1 \times 2 \times 88.2$$

$$x = 88.2 \text{ millimoles}$$

Total given moles of  $\text{H}_2\text{O}_2$  is

$$n_{\text{total}} = \frac{W(\text{H}_2\text{O}_2)}{34} = \frac{10\% \text{ of } 200 \text{ gram}}{34}$$

$$= \frac{20}{34} \text{ moles}$$

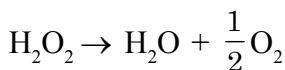
$$= 0.5882 \text{ moles}$$

$$= 588.2 \text{ millimoles.}$$

so. no. of moles of  $\text{H}_2\text{O}_2$  that decomposed to  $\text{O}_2$

$$= 588.2 - 88.2$$

$$= 500 \text{ millimoles}$$

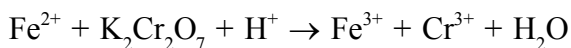


$$n(\text{O}_2) \text{ released} = \frac{1}{2} \times 500 = 250 \text{ millimoles}$$

$$V_{\text{O}_2} \text{ (at 1atm, 273 K)} = 250 \times 10^{-3} \times 22.4 = 5.6 \text{ litre.}$$

**Ex.31** 0.84 g iron ore containing  $x$  percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required  $x$  ml of a dichromic solution for oxidizing the iron content to ferric state. Calculate the normality of dichromic solution.

**Sol.** Let Normality of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is  $N$



no. of gram eq. of  $\text{Fe}^{2+}$  = no. of gram eq. of  $\text{K}_2\text{Cr}_2\text{O}_7$

$$n_{\text{Fe}^{2+}} \times 1 = N \times x \times 10^{-3}$$

$$\frac{W_{\text{Fe}^{2+}}}{56} \times 1 = N \times x \times 10^{-3}$$

$$\frac{x}{100} \times 0.84$$

$$\frac{100}{56} \times 1 = N \times x \times 10^{-3}$$

$$N = 0.15$$

**Ex.32** 5 g of pyrolusite (impure  $\text{MnO}_2$ ) were heated with conc. HCl and  $\text{Cl}_2$  evolved was passed through excess of KI solution. The iodine liberated required 40 mL of N/10 hypo solution. Find the % of  $\text{MnO}_2$  in the pyrolusite.

**Sol.** Let moles of  $\text{MnO}_2$  in 5 gram sample is x.



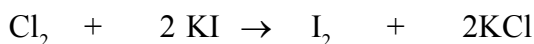
no. of gram eq. of  $\text{MnO}_2$  = no. of gram equivalent of  $\text{Cl}_2$

$$x \times 2 = n_{(\text{Cl}_2)} \times 2$$

$$x = n_{(\text{Cl}_2)}$$

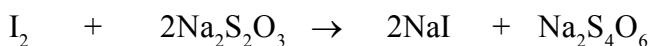
$$\text{so } n_{\text{I}_2} = n_{\text{Cl}_2} = x$$

evolved  $\text{Cl}_2$  passes through KI that released  $\text{I}_2$



x moles                      x moles

Evolved  $\text{I}_2$  required 40 ml,  $\frac{N}{10} \text{Na}_2\text{S}_2\text{O}_3$



no. of gram equivalent of  $\text{I}_2$  = no. of gram equivalent of hypo

$$x \times 2 = \frac{1}{10} \times 40 \times 10^{-3}$$

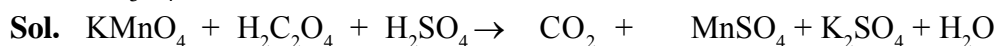
$$x = 2 \times 10^{-3} \text{ moles}$$

$$\% \text{MnO}_2 = \frac{\text{wt.}(\text{MnO}_2)}{\text{total wt.}} \times 100$$

$$= \frac{x \times 87}{5} \times 100 = \frac{2 \times 10^{-3} \times 87}{5} \times 100$$

$$= 3.48 \%$$

**Ex.33** A 458 g sample containing  $\text{Mn}_3\text{O}_4$  was dissolved and all manganese was converted to  $\text{Mn}^{2+}$ . In the presence of fluoride ion,  $\text{Mn}^{2+}$  is titrated with 3 lit of  $\text{KMnO}_4$  solution (which was 1.25 N against oxalate in acidic medium), both reactants being converted to a complex of Mn(III), What was the % of  $\text{Mn}_3\text{O}_4$  in the sample?



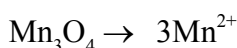
3 litre, M molar

$$\text{Normality}(\text{KMnO}_4) = \text{Molarity} \times n_f$$

$$1.25 = M \times 5$$

$$M = 0.25$$

Let x moles of  $\text{Mn}_3\text{O}_4$  present in 458 gram sample



x mole 3x moles



no. of gram eq. of  $\text{Mn}^{2+}$  = no. of gram eq.  $\text{KMnO}_4$

$$3x \times 1 = (M \times n_f \times V)_{\text{KMnO}_4}$$

$$3x \times 1 = 0.25 \times 4 \times 3$$

$$x = 1 \text{ moles}$$

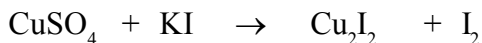
$$\begin{aligned} \% \text{ Mn}_3\text{O}_4 \text{ (by wt)} &= \frac{w(\text{Mn}_3\text{O}_4)}{w_{\text{total}}} \times 100 \\ &= \frac{1 \times 229}{458} \times 100 = 50\% \end{aligned}$$

**Ex.34** 80 gm of a sample of Anhydrous  $\text{CuSO}_4$  was dissolved in water and made to 250 mL. 25 mL of this solution after taking usual precaution was treated with a little excess of KI solution. A white ppt. of  $\text{Cu}_2\text{I}_2$  and iodine was evolved. The iodine so evolved required 40 mL of 1 M hypo solution. What is the approximate purity of  $\text{CuSO}_4$  solution.

**[Mol. wt. of  $\text{CuSO}_4$  = 160]**

**Sol.** Let 80 gram sample contains x moles of  $\text{CuSO}_4$  that dissolve in 250 ml solution

So 25 ml solution contain  $(x/10)$  moles  $\text{CuSO}_4$

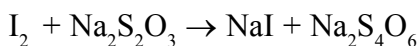


no. of gram eq. of  $\text{CuSO}_4$  = no. of gram eq. of  $\text{I}_2$

$$\frac{x}{10} \times 1 = n_{(\text{I}_2)} \times 2$$

$$n_{(\text{I}_2)} = \frac{x}{20}$$

Evolved  $\text{I}_2$  required 40 ml, 1M hypo solution



no. of gram eq. of  $\text{I}_2$  = no. of gram eq. of hypo

$$n(\text{I}_2) \times 2 = 1 \times 1 \times 40 \times 10^{-3}$$

$$\frac{x}{20} \times 2 = 40 \times 10^{-3}$$

$$x = 40 \times 10^{-2} \text{ moles}$$

$$\begin{aligned} \% \text{ CuSO}_4 \text{ (by mass)} &= \frac{\text{wt}(\text{CuSO}_4)}{\text{wt total}} \times 100 \\ &= \frac{40 \times 10^{-2} \times 160}{80} \times 100 = 80\% \end{aligned}$$

## EXERCISE # S-I

## OXIDATION NUMBER

1. Calculate oxidation number of underlines elements in the following compounds

- (a)  $\text{H}_2\underline{\text{S}}_2\text{O}_7$       (b)  $\text{H}_4\underline{\text{P}}_2\text{O}_7$       (c)  $\underline{\text{S}}_2\text{O}_3^{2-}$       (d)  $\underline{\text{C}}\text{H}_4$   
 (e)  $\underline{\text{C}}\text{Cl}_4$       (f)  $\text{Ca}\underline{\text{O}}_2$       (g)  $\underline{\text{Zn}}\text{O}_2^{2-}$       (h)  $\underline{\text{Cr}}\text{O}_2\text{Cl}_2$   
 (i)  $\text{Ca}(\underline{\text{Cl}}\text{O}_2)_2$

RR0001

2. Classify each of the following unbalanced half-reactions as either an oxidation or a reduction :

- (a)  $\text{O}_2(\text{g}) \longrightarrow \text{OH}^-(\text{aq})$       (b)  $\text{H}_2\text{O}_2(\text{aq}) \longrightarrow \text{O}_2(\text{g})$   
 (c)  $\text{MnO}_4^-(\text{aq}) \longrightarrow \text{MnO}_4^{2-}(\text{aq})$       (d)  $\text{CH}_3\text{OH}(\text{aq}) \longrightarrow \text{CH}_2\text{O}(\text{aq})$

RR0002

3. Identify the oxidant and reductant in the following reactions :

- (a)  $\text{Zn}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{ZnO}(\text{s})$   
 (b)  $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$   
 (c)  $10\text{H}^+(\text{aq}) + 4\text{Zn}(\text{s}) + \text{NO}_3^-(\text{aq}) \longrightarrow 4\text{Zn}^{2+}(\text{aq}) + \text{NH}_4^+(\text{aq}) + 3\text{H}_2\text{O}(\ell)$

RR0003

## BALANCING OF REDOX

4. Balance the following redox reactions by oxidation number method :

- (i)  $\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO}_2 + \text{H}_2\text{O}$  (Acidic medium) RR0004  
 (ii)  $\text{Br}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{BrO}_3^- + \text{H}_2\text{O}$  (Acidic medium) RR0005  
 (iii)  $\text{MnO}_4^- + \text{Fe}^{+2} \longrightarrow \text{Mn}^{+2} + \text{Fe}^{+3}$  (Acidic medium) RR0006  
 (iv)  $\text{MnO}_2 + \text{Cl}^- \longrightarrow \text{Mn}^{+2} + \text{Cl}_2 + \text{H}_2\text{O}$  (Acidic medium) RR0007  
 (v)  $\text{ClO}^- + \text{CrO}_2^- \xrightarrow{\text{OH}^-} \text{Cl}^- + \text{CrO}_4^{2-} + \text{H}_2\text{O}$  (Basic medium) RR0008

5. Balance the following redox reactions by half-reaction method (Ion electron method):

- (i)  $\text{MnO}_4^-(\text{aq}) + \text{I}^-(\text{aq}) \longrightarrow \text{MnO}_2(\text{s}) + \text{I}_2(\text{s})$  (in basic medium) RR0009  
 (ii)  $\text{MnO}_4^-(\text{aq}) + \text{SO}_2(\text{g}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + \text{HSO}_4^-(\text{aq})$  (in acidic solution) RR0010  
 (iii)  $\text{H}_2\text{O}_2(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq}) + \text{H}_2\text{O}(\ell)$  (in acidic solution) RR0011  
 (iv)  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{SO}_2(\text{g}) \longrightarrow \text{Cr}^{3+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$  (in acidic solution) RR0012

6. Find the valence factor for the following acid/bases -

- (1)  $\text{CH}_3\text{COOH}$                       (2)  $\text{NaH}_2\text{PO}_4$                       (3)  $\text{H}_3\text{BO}_3$   
 (4)  $\text{NaOH}$                               (5)  $\text{Ca}(\text{OH})_2$                       (6)  $\text{CsOH}$

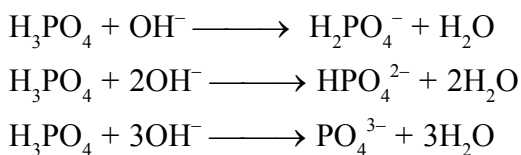
RR0013

7. Find the n-factor of underlined species in the following non redox reaction.

- (1)  $\text{NaOH} + \underline{\text{H}_3\text{PO}_4} \longrightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$   
 (2)  $\text{NaOH} + \underline{\text{H}_2\text{SO}_4} \longrightarrow \text{NaHSO}_4 + \text{H}_2\text{O}$   
 (3)  $\underline{\text{Ca}(\text{OH})_2} + \text{HCl} \longrightarrow \text{Ca}(\text{OH})\text{Cl} + \text{H}_2\text{O}$   
 (4)  $\underline{\text{Na}_2\text{CO}_3} + \text{HCl} \longrightarrow \text{NaHCO}_3 + \text{NaCl}$   
 (5)  $\underline{\text{Na}_2\text{CO}_3} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$

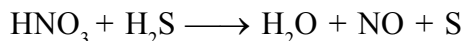
RR0014

8. What will be the equivalent wt. of  $\text{H}_3\text{PO}_4$  in each of the reaction.



RR0015

9. What is the equivalent weight of  $\text{HNO}_3$  in following reaction ?



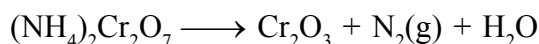
RR0016

10. Find out the equivalent weight of the underlined species in the following reaction :

- (i)  $\underline{\text{ClO}_3^-} + \text{Fe}^{2+} + \text{H}^+ \longrightarrow \text{Cl}^- + \text{Fe}^{3+} + \text{H}_2\text{O}$   
 (ii)  $\text{CuO} + \underline{\text{NH}_3} \longrightarrow \text{Cu} + \text{N}_2 + \text{H}_2\text{O}$

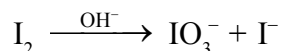
RR0017

11. Find out the  $n_{\text{factor}}$  of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  in the following decomposition reaction.



RR0018

12. Find out the  $n_{\text{factor}}$  of  $\text{IO}_3^-$  in the following disproportionation reaction.



RR0019

### ACID BASE TITRATION

13. How many millilitre of 0.5 M  $\text{H}_2\text{SO}_4$  are needed to dissolve 0.5 g of copper II carbonate ? [JEE 1999]

RR0020

14. An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is : **[JEE 2001]**  
**RR0021**
15. Calculate volume of 1N  $\text{H}_3\text{PO}_4$  required to react with 20 ml 2N  $\text{Ca}(\text{OH})_2$  solution  
**RR0022**
16. Calculate volume of 1N  $\text{H}_2\text{SO}_4$  required to react with 20 ml 1 M  $\text{Al}(\text{OH})_3$  solution  
**RR0023**
17. Calculate volume of 0.4 M NaOH required to react with following mixture  
 $\text{HCl}(1 \text{ mol}) + \text{H}_2\text{SO}_4(2 \text{ mol})$   
**RR0024**
18. Calculate volume of 0.2 M  $\text{H}_2\text{SO}_4$  required to react with following mixture  
 $\text{NaOH}(1 \text{ mol}) + \text{Ca}(\text{OH})_2(2 \text{ mol})$   
**RR0025**
19. How many litre of 0.1N HCl are required to react completely with 19 gm mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  containing equimolar amount of two ?  
**RR0026**
20.  $\text{H}_3\text{PO}_4$  is a tri basic acid and one of its salt is  $\text{NaH}_2\text{PO}_4$ . What volume in ml of 1 M NaOH solution should be added to 12 g of  $\text{NaH}_2\text{PO}_4$  to convert it into  $\text{Na}_3\text{PO}_4$  ?  
**RR0027**

**REDOX TITRATION**

21. Calculate the normality of a solution containing 50 mL of 5 M solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  in acidic medium.  
**RR0028**
22. A 5.0  $\text{cm}^3$  solution of  $\text{H}_2\text{O}_2$  liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of  $\text{H}_2\text{O}_2$  solution in terms of volume strength at STP.  
**[JEE' 1995]**  
**RR0029**
23. Calculate the normality of a solution containing 15.8 g of  $\text{KMnO}_4$  in 50 mL acidic solution.  
**RR0030**
24. 20 mL of  $\text{H}_2\text{O}_2$  after acidification with dil  $\text{H}_2\text{SO}_4$  required 30 mL of  $\frac{\text{N}}{12}$   $\text{KMnO}_4$  for complete oxidation. The strength of  $\text{H}_2\text{O}_2$  solution is [Molar mass of  $\text{H}_2\text{O}_2 = 34$ ]  
**RR0031**
25. It required 40 ml of 1 M  $\text{Ce}^{4+}$  to titrate 20 ml of 1 M  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$ . What is the oxidation state of cerium in the product.  
**RR0032**
26. A volume of 10.0 ml of 1 M  $\text{SeO}_2$  reacted with exactly 20 ml of 2 M  $\text{CrSO}_4$ . In the reaction,  $\text{Cr}^{2+}$  was oxidized to  $\text{Cr}^{3+}$ . To what oxidation state was selenium converted by the reaction.  
**RR0033**



27. Potassium acid oxalate  $K_2C_2O_4 \cdot 3H_2C_2O_4 \cdot 4H_2O$  can be oxidized by  $MnO_4^-$  in acid medium. Calculate the volume of 0.1 M  $KMnO_4$  reacting in acid solution with 5.08 gm of the acid oxalate. **RR0034**
28. A 1 g sample of  $H_2O_2$  solution containing x%  $H_2O_2$  by mass requires x cm<sup>3</sup> of a  $KMnO_4$  solution for complete oxidation under acidic condition. Calculate the normality of  $KMnO_4$  solution. **RR0035**
29. Metallic tin in the presence of HCl is oxidized by  $K_2Cr_2O_7$  to stannic chloride,  $SnCl_4$ . What volume of deci-normal dichromate solution would be reduced by 11.9 gm of tin [Sn = 119] **RR0036**
30. Calculate the number of millimoles of  $K_2Cr_2O_7$  which will completely react with 40 ml 0.1 MKI Solution. **RR0037**
31. Find the number of moles of  $KMnO_4$  needed to oxidise one mole  $Cu_2S$  in acidic medium. The reaction is :  $Cu_2S + KMnO_4 \longrightarrow Cu^{2+} + Mn^{2+} + SO_2$  **RR0038**
32. 0.4 M  $KMnO_4$  solution completely reacts with 0.05 M  $FeSO_4$  solution under acidic conditions. The volume of  $FeSO_4$  used is 50 mL. What volume of  $KMnO_4$  was used ? **RR0039**

**BACK TITRATION**

33. 50 gm of a sample of  $Ca(OH)_2$  is dissolved in 50 ml of 0.5 N HCl solution. The excess of HCl was titrated with 0.3N – NaOH. The volume of NaOH used was 20cc. Calculate % purity of  $Ca(OH)_2$  **RR0040**
34. 10 g  $CaCO_3$  were dissolved in 250 ml of 1 M HCl. What volume of 2 M KOH would be required to neutralise excess HCl. **RR0041**
35. 20 g of a sample of  $Ba(OH)_2$  is dissolved in 10 mL of 0.5 N HCl solution : The excess of HCl was titrated with 0.1 N NaOH. The volume of NaOH used was 20 cc. Calculate the percentage of  $Ba(OH)_2$  in the sample. (Ba = 137) **RR0042**
36. To 50 L of 0.2 N NaOH, 2.5 L of 2N HCl and 15 L of 0.1 N  $FeCl_3$  solutions are added. What weight of  $Fe_2O_3$  can be obtained from the precipitate? Also report the normality of NaOH left in resultant solution : **RR0043**

**Hardness of water**

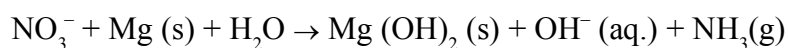
37. Softening of hard water by using sodium aluminium silicate (zeolite) is due to - Adsorption of ..... and .....ions of hard water, replacing ..... ions **RR0044**
38. One litre of a sample of hard water contains 10 mg of  $CaCl_2$  & 9.5 mg of  $MgCl_2$ . What is degree of hardness in terms of ppm of  $CaCO_3$  **RR0045**

## EXERCISE # S-II

1. Find out the oxidation number of the underlined elements in the following compounds:
- (a)  $\text{Na}_2\underline{\text{S}}_4\text{O}_6$       (b)  $\underline{\text{C}}_3\text{O}_2$       (c)  $\text{K}\underline{\text{I}}_3$       (d)  $\underline{\text{Fe}}_3\text{O}_4$  RR0046
- (e)  $\underline{\text{C}}\text{H}_3\underline{\text{C}}\text{H}_2\text{OH}$       (f)  $\underline{\text{C}}\text{H}_3\underline{\text{C}}\text{OOH}$       (g)  $\underline{\text{Br}}_3\text{O}_8$       (h)  $\text{CaO}\underline{\text{Cl}}_2$  RR0047
- (i)  $\underline{\text{Fe}}\underline{\text{S}}_2$       (j)  $\underline{\text{O}}\text{F}_2$       (k)  $\text{H}\underline{\text{O}}\underline{\text{F}}$       (l)  $\underline{\text{O}}_2^+$  RR0048
- (m)  $\underline{\text{O}}_2^-$       (n)  $\text{C}_6\text{H}_5\underline{\text{C}}\text{HO}$       (o)  $\text{C}_6\text{H}_5\underline{\text{N}}\text{O}_2$       (p)  $\text{C}_6\text{H}_5\underline{\text{N}}\text{H}_2$  RR0049
- (q)  $(\underline{\text{C}}\text{N})_2$       (r)  $\underline{\text{C}}\text{N}^-$       (s)  $\underline{\text{C}}\text{NO}^-$  RR0050
2. Calculate oxidation number of underlines elements in the following compounds
- (a)  $\text{K}[\underline{\text{Co}}(\text{C}_2\text{O}_4)_2(\text{NH}_3)_2]$       (b)  $\text{K}\underline{\text{Al}}(\underline{\text{S}}\text{O}_4)_2 \cdot 12\text{H}_2\text{O}$  RR0051
- (c)  $[\underline{\text{Fe}}(\text{CN})_6]^{4-}$       (d)  $\underline{\text{Fe}}_{0.93}\text{O}$
- (e)  $\text{H}_2\underline{\text{S}}_2\text{O}_8$       (f)  $\underline{\text{Cr}}\text{O}_5$  RR0052
- (g)  $\text{H}_2\underline{\text{S}}\text{O}_5$       (h)  $\text{K}_3\underline{\text{Cr}}\text{O}_8$
- (r)  $\text{Na}_2[\underline{\text{Fe}}(\text{CN})_5\text{NO}^+]$       (s)  $\underline{\text{Cr}}(\text{CN})_6^{3-}$  RR0053
3. Balance the following redox reactions by half-reaction method
- (i)  $\text{KMnO}_4(\text{aq.}) + \text{FeC}_2\text{O}_4(\text{aq.}) + \text{H}_2\text{SO}_4(\text{aq.}) \longrightarrow$   
 $\text{MnSO}_4(\text{aq.}) + \text{Fe}_2(\text{SO}_4)_3(\text{aq.}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$  (Acidic medium) RR0054
- (ii)  $\text{P}_4(\text{s}) + \text{OH}^-(\text{aq.}) \longrightarrow \text{PH}_3(\text{aq.}) + \text{HPO}_2^-(\text{aq.})$  (Basic medium) RR0055
- (iii)  $\text{I}_2(\text{s}) + \text{NaOH}(\text{aq.}) \longrightarrow \text{NaI}(\text{aq.}) + \text{NaIO}_3(\text{aq.}) + \text{H}_2\text{O}(\text{l})$  (Basic medium) RR0056
- (iv)  $\text{HNO}_2(\text{aq.}) \rightarrow \text{NO}_3^- + \text{NO}(\text{g})$  (acidic medium) RR0057
- (v)  $\text{IO}_3^- + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O}$  (acidic medium) RR0058
- (vi)  $\text{Cu}_2\text{S} + \text{MnO}_4^- + \text{H}^+ \rightarrow \text{Cu}^{2+} + \text{Mn}^{2+} + \text{SO}_2$  (Acidic medium) RR0059
- (vii)  $\text{HCHO}(\text{l}) + 2[\text{Ag}(\text{NH}_3)_2]^+(\text{aq.}) + 3\text{OH}^-(\text{aq.}) \rightarrow 2\text{Ag}(\text{s}) + \text{HCOO}^-(\text{aq.}) + 4\text{NH}_3(\text{aq.}) + 2\text{H}_2\text{O}(\text{l})$   
 (basic medium) RR0060

4. A solution containing 4.2g of KOH and  $\text{Ca}(\text{OH})_2$  is neutralized by an acid. It consumes 0.1 equivalent of acid, calculate the percentage composition of the sample. **RR0061**
5. Calculate volume of 0.4 M  $\text{KMnO}_4$  required to react with following in acidic medium  
 $\text{KHC}_2\text{O}_4(1 \text{ mol}) + \text{H}_2\text{C}_2\text{O}_4(2 \text{ mol})$  **RR0062**
6. Calculate volume of 0.4 M NaOH required to react with following mixture.  
 $\text{KHC}_2\text{O}_4(1 \text{ mole}) + \text{H}_2\text{C}_2\text{O}_4(2 \text{ mol})$  **RR0063**
7. Calculate volume of 0.2 M  $\text{KMnO}_4$  required to react with following mixture in acidic medium.  
 $\text{KHC}_2\text{O}_4(128 \text{ gm}) + \text{H}_2\text{C}_2\text{O}_4(180 \text{ gm})$  **RR0064**
8. 520 gm mixture of  $\text{Fe}_2\text{O}_3$  and FeO reacts completely with 158 gm  $\text{KMnO}_4$  in acidic medium Calculate the mole % of  $\text{Fe}_2\text{O}_3$  in mixture. **RR0065**
9. Calculate the millimoles of  $\text{Br}_2$  produced when 10 ml of 0.1 M  $\text{BrO}_3^-$  reacts with excess of  $\text{Br}^-$ . **RR0066**
10. One gm of impure sodium carbonate is dissolved in water and the solution is made up to 250 ml. To 50 ml of this made up solution, 50 ml of 0.1N – HCl is added and the mix after shaking well required 10 ml of 0.16 N – NaOH solution for complete titration. Calculate the % purity of the sample. **RR0067**
11. 100 ml sample of hard water containing only  $\text{Ca}^{2+}$  hardness is passed through a column of cation exchange resin ( $\text{H}^+$  – resin). The water coming out the column require 20 ml of 0.02M NaOH for its titration. What is hardness of water as ppm of  $\text{Ca}^{2+}$  **RR0068**
12. 3.55 g sample of bleaching powder suspended in  $\text{H}_2\text{O}$  was treated with enough acetic acid and KI solution. Iodine thus liberated required 80 mL of 0.2 M hypo for titration. Calculate the % of available chlorine. **RR0069**
13. 3.2 g of pyrolusite ( $\text{MnO}_2$ ) was treated with 50 mL of 0.5 M oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 mL in a flask. 25 mL of this solution when treated with 0.02 M  $\text{KMnO}_4$  required 32 mL of the solution : Find the % of  $\text{MnO}_2$  in the sample. **RR0070**

14. Mg can reduce  $\text{NO}_3^-$  to  $\text{NH}_3$  in basic medium.



A 25.0 mL sample of  $\text{NO}_3^-$  solution was treated with Mg. The  $\text{NH}_3$  (g) was passed into 100 mL of 0.15 N HCl. The excess of HCl required 32.10 mL of 0.10 N NaOH for neutralization. What was the molarity of  $\text{NO}_3^-$  ions in the original sample ?

**RR0071**

15. A mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$  (oxalic acid) and some inert impurity weighing 3.185 g was dissolved in water and the solution made up to 1 litre, 10 mL of this solution required 3 mL of 0.1 N NaOH for complete neutralization. In another experiment 100 mL of the same solution in hot condition required 4 mL of 0.02M  $\text{KMnO}_4$  solution for complete reaction. The wt. % of  $\text{H}_2\text{SO}_4$  in the mixture was :-

**RR0072**

16. An aqueous solution containing 0.10 g  $\text{KIO}_3$  (formula wt. 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated  $\text{I}_2$  consumed 45.0 mL of thiosulphate solution to decolourise the blue starch – iodine complex. Calculate the molarity of the sodium thiosulphate solution.

**[JEE 1998]**

**RR0073**

## EXERCISE # O-I

1. The oxidation number of phosphorus in  $\text{Ba}(\text{H}_2\text{PO}_2)_2$  is :  
 (A) +3 (B) +2 (C) +1 (D) -1 RR0074
2. The oxidation states of the most electronegative element in the products of the reaction of  $\text{BaO}_2$  with dilute  $\text{H}_2\text{SO}_4$ .  
 (A) 0 and -1 (B) -1 and -2 (C) -2 and 0 (D) -2 and +2 RR0075
3. In the coordination compound,  $\text{K}_4[\text{Ni}(\text{CN})_6]$ , the oxidation state of nickel is [AIIEEE-03]  
 (A) +1 (B) +2 (C) -1 (D) 0 RR0076
4. The oxidation state of Cr in  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$  is - [AIIEEE-05]  
 (A) +2 (B) +3 (C) 0 (D) +1 RR0077
5. Oxidation number of Cl in  $\text{CaOCl}_2$  (bleaching powder is ) [AIIEEE-02]  
 (A) Zero, since it contains  $\text{Cl}_2$  (B) -1, since it contains  $\text{Cl}^-$   
 (C) +1, since it contains  $\text{ClO}^-$  (D) +1 and -1 since it contains  $\text{ClO}^-$  and  $\text{Cl}^-$  RR0078
6. The oxidation number of sulphur in  $\text{S}_8$ ,  $\text{S}_2\text{F}_2$  and  $\text{H}_2\text{S}$  respectively are :  
 (A) 0, +1 and -2 (B) +2, +1 and -2  
 (C) 0, +1 and +2 (D) -2, +1 and -2 RR0079
7. The incorrect order of decreasing oxidation number of S in compounds is :-  
 (A)  $\text{H}_2\text{S}_2\text{O}_7 > \text{Na}_2\text{S}_4\text{O}_6 > \text{Na}_2\text{S}_2\text{O}_3 > \text{S}_8$  (B)  $\text{H}_2\text{SO}_5 > \text{H}_2\text{SO}_3 > \text{SCl}_2 > \text{H}_2\text{S}$   
 (C)  $\text{SO}_3 > \text{SO}_2 > \text{S}_8 > \text{H}_2\text{S}$  (D)  $\text{H}_2\text{SO}_4 > \text{SO}_2 > \text{H}_2\text{S} > \text{H}_2\text{S}_2\text{O}_8$  RR0080
8. Which of the following is a redox [AIIEEE-02]  
 (A)  $2\text{NaAg}(\text{CN})_2 + \text{Zn} \longrightarrow \text{Na}_2\text{Zn}(\text{CN})_4 + 2\text{Ag}$   
 (B)  $\text{BaO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$   
 (C)  $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_3$   
 (D)  $\text{AgNO}_3 + \text{KI} \longrightarrow \text{AgI} + \text{KNO}_3$  RR0081
9. Which reaction does not represent autoredox or disproportionation :-  
 (A)  $\text{Cl}_2 + \text{OH}^- \longrightarrow \text{Cl}^- + \text{ClO}_3^- + \text{H}_2\text{O}$   
 (B)  $2\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$   
 (C)  $2\text{Cu}^+ \longrightarrow \text{Cu}^{+2} + \text{Cu}$   
 (D)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$  RR0082

10. Which of the following is not a redox reaction?

- (A)  $\text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$       (B)  $2\text{BaO} + \text{O}_2 \rightarrow 2\text{BaO}_2$   
 (C)  $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$       (D)  $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{O} + 3\text{S}$

RR0083

11.  $\text{H}_2\text{O}_2$  acts as a reducing agent in:

- (A)  $\text{FeCl}_2 + \text{HCl} + \text{H}_2\text{O}_2 \longrightarrow \text{FeCl}_3 + \text{H}_2\text{O}$   
 (B)  $\text{Cl}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{HCl} + \text{O}_2$   
 (C)  $\text{HI} + \text{H}_2\text{O}_2 \longrightarrow \text{I}_2 + \text{H}_2\text{O}$   
 (D)  $\text{H}_2\text{SO}_3 + \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$

RR0084

12. Match List-I (Compounds) with List-II (Oxidation states of nitrogen) and select answer using the codes given below the lists :-

List-I		List-II
(a) $\text{NaN}_3$		1. +5
(B) $\text{N}_2\text{H}_2$		2. +2
(C) NO		3. $-1/3$
(D) $\text{N}_2\text{O}_5$		4. -1

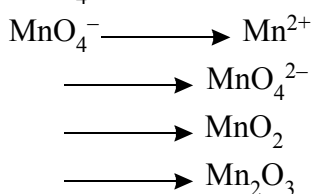
Code :

	(a)	(B)	(C)	(D)
(A)	3	4	2	1
(B)	4	3	2	1
(C)	3	4	1	2
(D)	4	3	1	2

RR0085

13.  $\text{MnO}_4^-$  is good oxidising agent in different medium changing to -

[AIEEE-02]

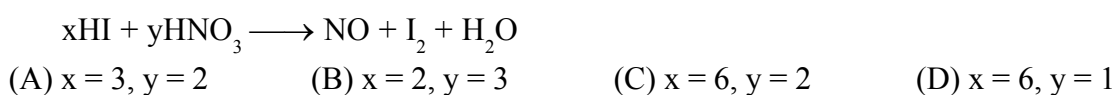


Changes in oxidation number respectively are -

- (A) 1, 3, 4, 5      (B) 5, 4, 3, 2      (C) 5, 1, 3, 4      (D) 2, 6, 4, 3

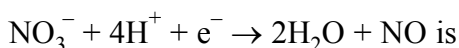
RR0086

14. In the reaction,



RR0087

15. The number of electrons to balance the following equation :-



- (A) 5 (B) 4 (C) 3 (D) 2

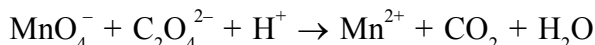
RR0088

16. Number of moles of electrons taken up when 1 mole of  $\text{NO}_3^-$  ions is reduced to 1 mole of  $\text{NH}_2\text{OH}$  is

- (A) 2 (B) 4 (C) 5 (D) 6

RR0089

17. For the redox reaction,



the correct coefficients of the reactants for the balanced reaction are :

- |                  |                             |              |
|------------------|-----------------------------|--------------|
| $\text{MnO}_4^-$ | $\text{C}_2\text{O}_4^{2-}$ | $\text{H}^+$ |
| (A) 2            | 5                           | 16           |
| (B) 16           | 5                           | 2            |
| (C) 5            | 16                          | 2            |
| (D) 2            | 16                          | 5            |

RR0090

18. In a redox reaction, the equivalent weight of  $\text{HNO}_2$  is found to be 23.5. The reaction products might contain

- (A)  $\text{NO}_2$  (B)  $\text{NO}$  (C)  $\text{NH}_3$  (D)  $\text{HNO}_3$

RR0091

19. When  $\text{N}_2$  is converted into  $\text{NH}_3$ , the equivalent weight of nitrogen will be :

- (A) 1.67 (B) 2.67 (C) 3.67 (D) 4.67

RR0092

20. The equivalent mass of  $\text{MnSO}_4$  is half its molecular mass when it is converted to : [JEE 1998]

- (A)  $\text{Mn}_2\text{O}_3$  (B)  $\text{MnO}_2$  (C)  $\text{MnO}_4^-$  (D)  $\text{MnO}_4^{2-}$

RR0093

21. When  $\text{KBrO}_3$  ion reacts with  $\text{Br}^-$  ion in acid solution  $\text{Br}_2$  is liberated. The equivalent weight of  $\text{KBrO}_3$  in this reaction is

- (A)  $M/8$  (B)  $M/3$  (C)  $M/5$  (D)  $M/6$

RR0094

22. In the reaction  $\text{CrO}_5 + \text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} + \text{O}_2$  one mole of  $\text{CrO}_5$  will liberate how many moles of  $\text{O}_2$  :-

- (A)  $5/2$  (B)  $5/4$  (C)  $9/2$  (D)  $7/4$

RR0095

23. A solution of  $\text{KMnO}_4$  is reduced to  $\text{MnO}_2$ . The normality of solution is 0.6. The molarity is :

- (A) 1.8M (B) 0.6M (C) 0.1M (D) 0.2M

RR0096

24. The normality of 0.3 M phosphorus acid ( $\text{H}_3\text{PO}_3$ ) is :  
 (A) 0.1 (B) 0.9 (C) 0.3 (D) 0.6  
**RR0097**
25. 0.52 g of a dibasic acid required 100 mL of 0.2 N NaOH for complete neutralization. The equivalent weight of acid is  
 (A) 26 (B) 52 (C) 104 (D) 156  
**RR0098**
26. What is the equivalent weight of  $\text{H}_2\text{SO}_4$  in the reaction ?  

$$\text{H}_2\text{SO}_4 + \text{NaI} \rightarrow \text{Na}_2\text{SO}_4 + \text{I}_2 + \text{H}_2\text{S} + \text{H}_2\text{O}$$
 (A) 12.25 (B) 49 (C) 61.25 (D) None of these  
**RR0099**
27. 125 mL of 63% (w/v)  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  is made to react with 125 mL of a 40% (w/v) NaOH solution. The resulting solution is :-  
 (A) neutral (B) acidic (C) strongly acidic (D) alkaline  
**RR0100**
28. The mass of oxalic acid crystals ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) required to prepare 50 mL of a 0.2 N solution is :-  
 (A) 4.5 g (B) 6.3 g (C) 0.63 g (D) 0.45 g  
**RR0101**
29. If 25 mL of a  $\text{H}_2\text{SO}_4$  solution reacts completely with 1.06 g of pure  $\text{Na}_2\text{CO}_3$ , what is the normality of this acid solution :  
 (A) 1 N (B) 0.5 N (C) 1.8 N (D) 0.8 N  
**RR0102**
30. The number of moles of  $\text{KMnO}_4$  that will be required to react with 2 mol of ferrous oxalate is  
 (A)  $\frac{6}{5}$  (B)  $\frac{2}{5}$  (C)  $\frac{4}{5}$  (D) 1  
**RR0103**
31. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is -  
 (A) +6 (B) +4 (C) +3 (D) +2  
**[AIIEEE-05]**  
**RR0104**
32. The number of mole of  $\text{KMnO}_4$  that will need to react completely with one mole ferrous oxalate in acidic solution is :  
 (A) 2/5 (B) 3/5 (C) 4/5 (D) 1  
**[JEE 1997]**  
**RR0105**
33. The number of mole of  $\text{KMnO}_4$  that will be needed to react with one mole of sulphite ion in acidic solution is :  
 (A) 2/5 (B) 3/5 (C) 4/5 (D) 1  
**[JEE 1997]**  
**RR0106**



34. What volume of 0.1 M  $\text{KMnO}_4$  is needed to oxidize 100 mg of  $\text{FeC}_2\text{O}_4$  in acid solution ?  
 (A) 4.1 mL (B) 8.2 mL (C) 10.2 mL (D) 4.6 mL **RR0107**
35. What volume of 6 M  $\text{HNO}_3$  is needed to oxidize 8 g of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ,  $\text{HNO}_3$  gets converted to  $\text{NO}$ ?  
 (A) 8 mL (B) 7.936 mL (C) 32 mL (D) 64 mL **RR0108**
36. The minimum quantity of  $\text{H}_2\text{S}$  needed to precipitate 63.5 g of  $\text{Cu}^{2+}$  will be nearly.  
 (A) 63.5 g (B) 31.75 g (C) 34 g (D) 2.0 g **RR0109**
37. The volume of 1.5 M  $\text{H}_3\text{PO}_4$  solution required to neutralize exactly 90 mL of a 0.5 M  $\text{Ba}(\text{OH})_2$  solution is :-  
 (A) 10 mL (B) 30 mL (C) 20 mL (D) 60 mL **RR0110**
38. Hydrogen peroxide in aqueous solution decomposes on warming to give oxygen according to the equation  

$$2\text{H}_2\text{O}_2(\text{aq}) \longrightarrow 2\text{H}_2\text{O}(\ell) + \text{O}_2(\text{g})$$
 Under conditions where 1 mole of gas occupies  $24 \text{ dm}^3$ .  $100 \text{ cm}^3$  of XM solution of  $\text{H}_2\text{O}_2$  produces  $3 \text{ dm}^3$  of  $\text{O}_2$ . Thus X is :-  
 (A) 2.5 (B) 1 (C) 0.5 (D) 0.25 **RR0111**
39. A mixture of  $\text{NaHC}_2\text{O}_4$  and  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$  required equal volumes of 0.2 N  $\text{KMnO}_4$  and 0.12 N  $\text{NaOH}$  separately. What is the molar ratio of  $\text{NaHC}_2\text{O}_4$  and  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$  in the mixture ?  
 (A) 6 : 1 (B) (C) 1 : 3 (D) none **RR0112**
40. Volume  $V_1$  mL of 0.1 M  $\text{K}_2\text{Cr}_2\text{O}_7$  is needed for complete oxidation of 0.678 g  $\text{N}_2\text{H}_4$  in acidic medium. The volume of 0.3 M  $\text{KMnO}_4$  needed for same oxidation in acidic medium will be :-  
 (A)  $\frac{2}{5}V_1$  (B)  $\frac{5}{2}V_1$  (C)  $113 V_1$  (D) can't say **RR0113**
41.  $\text{As}_2\text{O}_3$  is oxidised to  $\text{H}_3\text{AsO}_4$  by  $\text{KMnO}_4$  in acidic medium. Volume of 0.02M  $\text{KMnO}_4$  required for this purpose by 1mmol of  $\text{As}_2\text{O}_3$  will be  
 (A) 10 mL (B) 20 mL (C) 40 mL (D) 80 mL **RR0114**

42. When ozone is passed through dry KOH,  $\text{KO}_3$  is obtained and  $\text{O}_2$  is liberated. In this reaction \_\_\_\_\_ is oxidised and \_\_\_\_\_ is reduced.

- (A) hydrogen, oxygen (B) potassium, oxygen  
(C) oxygen, oxygen (D) oxygen, hydrogen

RR0115

43. 100 ml of 0.1M  $\text{NaAl(OH)}_2\text{CO}_3$  is neutralised by 0.25 N HCl to form NaCl,  $\text{AlCl}_3$  and  $\text{CO}_2$ . Volume of HCl required is

- (A) 10 mL (B) 40 mL (C) 100mL (D) 160 mL

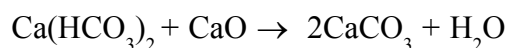
RR0116

44. x mmol of  $\text{XeF}_4$  quantitatively oxidized KI to  $\text{I}_2$  and liberated Xe, alongwith formation of KF. This iodine required 20 ml of decinormal hypo solution for exact titration. The value of x is

- (A) 0.5 (B) 1.0 (C) 2.0 (D) 5.0

RR0117

45. Temporary hardness is due to  $\text{HCO}_3^-$  of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . It is removed by addition of CaO.



Mass of CaO required to precipitate 2 g  $\text{CaCO}_3$  is :-

- (A) 2.00 (B) 0.56 g (C) 0.28 g (D) 1.12 g

RR0118

46. 0.3 g of an oxalate salt was dissolved in 100 mL solution. The solution required 90 mL of N/20  $\text{KMnO}_4$  for complete oxidation. The % of oxalate ion in salt is :-

- (A) 33% (B) 66% (C) 70% (D) 40%

RR0119

## EXERCISE # O-II

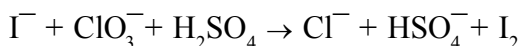
1. If 10 g of  $V_2O_5$  is dissolved in acid and is reduced to  $V^{2+}$  by zinc metal, how many mole  $I_2$  could be reduced by the resulting solution if it is further oxidised to  $VO^{2+}$  ions?  
 [Assume no change in state of  $Zn^{2+}$  ions] ( $V = 51, O = 16, I = 127$ ):  
 (A) 0.11 mole of  $I_2$       (B) 0.22 mole of  $I_2$       (C) 0.055 mole of  $I_2$       (D) 0.44 mole of  $I_2$   
**RR0120**
2. The number of moles of  $Cr_2O_7^{2-}$  needed to oxidize 0.136 equivalents of  $N_2H_5^+$  by the reaction  
 $N_2H_5^+ + Cr_2O_7^{2-} \rightarrow N_2 + Cr^{3+} + H_2O$   
 (A) 0.136      (B) 0.068      (C) 0.0227      (D) 0.272  
**RR0121**
3. Dichloroacetic acid ( $CHCl_2COOH$ ) is oxidized to  $CO_2$ ,  $H_2O$  and  $Cl_2$  by 600 meq of an oxidizing agent. Same amount of acid can neutralize how many moles of ammonia to form ammonium dichloroacetate?  
 (A) 0.0167      (B) 0.1      (C) 0.3      (D) 0.6  
**RR0122**
4.  $HNO_3$  oxidises  $NH_4^+$  ions to nitrogen and itself gets reduced to  $NO_2$ . The moles of  $HNO_3$  required by 1 mol of  $(NH_4)_2SO_4$  is :-  
 (A) 4      (B) 5      (C) 6      (D) 2  
**RR0123**
5. During the disproportionation of iodine to iodide and iodate ions, the ratio of iodate and iodide ions formed in alkaline medium is :-  
 (A) 1 : 5      (B) 5 : 1      (C) 3 : 1      (D) 1 : 3  
**RR0124**
6. When arsenic sulphide is boiled with  $NaOH$ , sodium arsenite and sodium thioarsenite are formed  
 $x As_2S_3 + y NaOH \longrightarrow Na_3AsO_3 + x Na_3AsS_3 + \frac{y}{2} H_2O$ . What are the values of x and y?  
 (A) 1, 6      (B) 2, 8      (C) 2, 6      (D) 1, 4  
**RR0125**
7. 35 mL sample of hydrogen peroxide gives of 500 mL of  $O_2$  at  $27^\circ C$  and 1 atm pressure. Volume strength of  $H_2O_2$  sample will be :-  
 (A) 10 volume      (B) 13 volumes      (C) 11 volume      (D) 12 volume  
**RR0126**
8. An element A in a compound ABD has oxidation number  $A^{n-}$ . It is oxidised by  $Cr_2O_7^{2-}$  in acid medium. In the experiment  $1.68 \times 10^{-3}$  moles of  $K_2Cr_2O_7$  were used for  $3.26 \times 10^{-3}$  moles of ABD. The new oxidation number of A after oxidation is :-  
 (A) 3      (B)  $3 - n$       (C)  $n - 3$       (D)  $+n3$   
**RR0127**

9. 50g of pure  $\text{CaCO}_3$  is heated to liberate  $\text{CO}_2$ . Liberated  $\text{CO}_2$  required 0.4 mol of moist ammonia to yield only  $(\text{NH}_4)_2\text{CO}_3$ . Find the volume of  $\text{CO}_2$  liberated at STP adding excess dil. HCl to this heated residue.

- (A) zero (B) 4.42 L (C) 6.81 L (D) 6.72 L

RR0128

10. For the reaction



The correct statement(s) in the balanced equation is / are :

- (A) Stoichiometric coefficient of  $\text{HSO}_4^-$  is 6  
 (B) Iodide is oxidized  
 (C) Sulphur is reduced  
 (D)  $\text{H}_2\text{O}$  is one of the products

RR0129

11. A sample of  $\text{KMnO}_4$  solution required 50 ml when titrated against 3 mmol of oxalic acid. The normality of same solution in reaction with alkaline  $\text{H}_2\text{O}_2$  is

- (A) 0.120 N (B) 0.060 N (C) 0.072 N (D) 0.036 N

RR0130

### Assertion Reason Type

12. **Statement-1** :- Moles of  $\text{KMnO}_4$  required for oxidation of  $\text{Fe}^{2+}$  in acidic and basic medium will be different.

**Statement-2** :- Final oxidation state to which  $\text{Mn}^{7+}$  will be reduced will be different in case of acidic and basic medium.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

RR0131

13. **Statement-1** :- Mass of a particular substance that combine with 8 gm of oxygen is said to be equivalent weight of substance.

**Statement-2** :- x gm of metal gave y gm of its oxide, so equivalent weight of metal is  $\left(\frac{x}{y-x}\right) \times 8$

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

RR0132

14. **Statement-1** :- Degree of hardness of water is measured in terms of ppm of  $\text{CaCO}_3$ .  
**Statement-2** :- If water contains 120 ppm of  $\text{MgSO}_4$ , and 2ppm  $\text{NaCl}$ , its hardness in terms of  $\text{CaCO}_3 > 100$  ppm.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

RR0133

## MATCH THE COLUMN

- | 15. Column-I  | Column-II                |
|---|--------------------------|
| (A) $\underline{\text{P}_2\text{H}_4} \longrightarrow \text{PH}_3 + \text{P}_4\text{H}_2$                                 | (p) $E = \frac{3M}{4}$   |
| (B) $\underline{\text{I}_2} \longrightarrow \text{I}^- + \text{IO}_3^-$   | (q) $E = \frac{3M}{5}$   |
| (C) $\text{MnO}_4^- + \text{Mn}^{2+} + \text{H}_2\text{O} \longrightarrow \underline{\text{Mn}_3\text{O}_4} + \text{H}^+$ | (r) $E = \frac{15M}{26}$ |
| (D) $\underline{\text{H}_3\text{PO}_2} \longrightarrow \text{PH}_3 + \text{H}_3\text{PO}_3$                               | (s) $E = \frac{5M}{6}$   |

RR0134

## Paragraph for Q.16 to Q.19

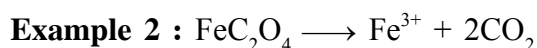
$$\text{Equivalent weight} = \frac{\text{Molecular weight / Atomic weight}}{n - \text{factor}}$$

n-factor is very important in redox as well as non-redox reactions. With the help of n-factor we can predict the molar ratio of the reactant species taking part in reactions. The reciprocal of n-factor's ratio of the reactants is the molar ratio of the reactants.

In general n-factor of acid/base is number of moles of  $\text{H}^+ / \text{OH}^-$  furnished per mole of acid/base. n-factor of a reactant is no. of moles of electrons lost or gained per mole of reactant.

**Example 1 :**

- In acidic medium :  $\text{KMnO}_4 (n = 5) \longrightarrow \text{Mn}^{2+}$
- In neutral medium :  $\text{KMnO}_4 (n = 3) \longrightarrow \text{Mn}^{2+}$
- In basic medium :  $\text{KMnO}_4 (n = 1) \longrightarrow \text{Mn}^{6+}$



Total no. of moles of  $e^-$  lost by 1 mole of  $\text{FeC}_2\text{O}_4 = 1 + 1 \times 2 \Rightarrow 3$

$\therefore$  n-factor of  $\text{FeC}_2\text{O}_4 = 3$

16. n-factor of  $\text{Ba}(\text{MnO}_4)_2$  in acidic medium is :  
 (A) 2 (B) 6 (C) 10 (D) none of these  
**RR0135**
17. For the reaction,  
 $\text{H}_3\text{PO}_2 + \text{NaOH} \longrightarrow \text{NaH}_2\text{PO}_2 + \text{H}_2\text{O}$   
 What is the equivalent weight of  $\text{H}_3\text{PO}_2$  ? (mol. wt. is M)  
 (A) M (B) M/2 (C) M/3 (D) none of these  
**RR0136**
18. For the reaction,  $\text{Fe}_{0.95}\text{O}$  (molar mass : M)  $\longrightarrow$   $\text{Fe}_2\text{O}_3$ . What is the eq. wt. of  $\text{Fe}_{0.95}\text{O}$  ?  
 (A)  $\frac{M}{0.85}$  (B)  $\frac{M}{0.95}$  (C)  $\frac{M}{0.8075}$  (D) none of these  
**RR0137**
19. In the reaction,  $x\text{VO} + y\text{Fe}_2\text{O}_3 \longrightarrow \text{FeO} + \text{V}_2\text{O}_5$ . What is the value of x and y respectively ?  
 (A) 1, 1 (B) 2, 3 (C) 3, 2 (D) none of these  
**RR0138**

**Table type question :**

**Column-I**

(1 mole of each oxidizing agent is taken)

- (A)  $\text{KMnO}_4$  (acidic)  
 (B)  $\text{KMnO}_4$  (neutral)  
 (C)  $\text{MnO}_2$  (acidic)  
 (D)  $\text{K}_2\text{CrO}_4$  (acidic)

**Column-II**

(oxidation number

- (P) O.N of Mn = 4  
 (Q) O.N of Mn = 7  
 (R) O.N of Cr = 6  
 (S) O.N of Cr = 7

**Column-III**

(Reducing agents)

- (1) 3 mole of  $\text{FeSO}_4$   
 (2) 0.5 mole of  $\text{I}_2$  changes to  $\text{HIO}_3$   
 (3) 1 mole of  $\text{K}_2\text{C}_2\text{O}_4$   
 (4) 1.5 mole  $\text{K}_2\text{SO}_3$

20. Which of the following is correct  
 (A) A ; P ; 2 (B) A ; Q ; 4 (C) B ; Q ; 1 (D) B ; Q ; 3  
**RR0139**
21. Which of the following is correct  
 (A) A ; Q ; 3 (B) C ; P ; 3 (C) C ; P ; 4 (D) C ; Q ; 1  
**RR0139**
22. Which of the following is correct  
 (A) D ; R ; 1 (B) D ; R ; 2 (C) D ; S ; 1 (D) D ; R ; 4  
**RR0139**

## EXERCISE # J-MAINS

1. Given : [JEE(Main-online)-2013]  

$$X \text{ Na}_2 \text{ HAsO}_3 + Y \text{ NaBrO}_3 + Z \text{ HCl} \rightarrow \text{NaBr} + \text{H}_3 \text{AsO}_4 + \text{NaCl}$$
 The values of X, Y and Z in the above redox reaction are respectively :  
 (1) 2, 1, 3                      (2) 3, 1, 6                      (3) 2, 1, 2                      (4) 3, 1, 4  
RR0140
2. Consider the following reaction : [JEE(Main)-2013]  

$$x \text{ MnO}_4^- + y \text{ C}_2\text{O}_4^{2-} + z \text{ H}^+ \rightarrow x \text{ Mn}^{2+} + 2y \text{ CO}_2 + \frac{z}{2} \text{ H}_2\text{O}$$
 The values of x, y and z in the reaction are respectively :-  
 (1) 5, 2 and 16                      (2) 2, 5 and 8                      (3) 2, 5 and 16                      (4) 5, 2 and 8  
RR0141
3. How many electrons are involved in the following redox reaction ? [JEE(Main-online)-2014]  

$$\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+} + \text{CO}_2 \text{ (Unbalanced)}$$
 (1) 3                      (2) 4                      (3) 5                      (4) 6  
RR0142
4. Consider the reaction [JEE(Main-online)-2014]  

$$\text{H}_2\text{SO}_3(\text{aq}) + \text{Sn}^{4+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Sn}^{2+}(\text{aq}) + \text{HSO}_4^-(\text{aq}) + 3\text{H}^+(\text{aq})$$
 Which of the following statements is correct?  
 (1)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes oxidation  
 (2)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes reduction  
 (3)  $\text{Sn}^{4+}$  is the reducing agent because it undergoes oxidation  
 (4)  $\text{Sn}^{4+}$  is the oxidizing agent because it undergoes oxidation  
RR0143
5. In which of the following reaction  $\text{H}_2\text{O}_2$  acts as a reducing agent ? [JEE(Main)-2014]  
 (a)  $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$                       (b)  $\text{H}_2\text{O}_2 - 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}^+$   
 (c)  $\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$                       (d)  $\text{H}_2\text{O}_2 + 2\text{OH}^- - 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$   
 (1) (a), (c)                      (2) (b), (d)                      (3) (a), (b)                      (4) (c), (d)  
RR0144
6. The molecular formula of a commercial resin used for exchanging ions in water softening is  $\text{C}_8\text{H}_7\text{SO}_3\text{Na}$  (Mol. wt 206). What would be the maximum uptake of  $\text{Ca}^{2+}$  ions by the resin when expressed in mole per gram resin ? [JEE(Main)-2015]  
 (1)  $\frac{2}{309}$                       (2)  $\frac{1}{412}$                       (3)  $\frac{1}{103}$                       (4)  $\frac{1}{206}$   
RR0145

7. The volume of 0.1N dibasic acid sufficient to neutralize 1 g of a base that furnishes 0.04 mole of  $\text{OH}^-$  in aqueous solution is : [JEE(Main)-OnLine-2016]  
 (1) 400 mL (2) 200 mL (3) 600 mL (4) 800 mL  
**RR0146**
8. Which of the following reactions is an example of a redox reaction ? [JEE(Main)-2017]  
 (1)  $\text{XeF}_4 + \text{O}_2\text{F}_2 \rightarrow \text{XeF}_6 + \text{O}_2$  (2)  $\text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+\text{PF}_6^-$   
 (3)  $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}$  (4)  $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$   
**RR0147**
9. In which of the following reaction, hydrogen peroxide acts as an oxidizing agent ? [JEE(Main)-OnLine-2017]  
 (1)  $\text{I}_2 + \text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow 2\text{I}^- + 2\text{H}_2\text{O} + \text{O}_2$   
 (2)  $\text{HOCl} + \text{H}_2\text{O}_2 \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- + \text{O}_2$   
 (3)  $\text{PbS} + 4\text{H}_2\text{O}_2 \rightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}$   
 (4)  $2\text{MnO}_4^- + 3\text{H}_2\text{O}_2 \rightarrow 2\text{MnO}_2 + 3\text{O}_2 + 2\text{H}_2\text{O} + 2\text{OH}^-$   
**RR0148**
10. In  $\text{KO}_2$ , the nature of oxygen species and the oxidation state of oxygen atom are, respectively [JEE(Main)-OnLine-2018]  
 (1) Superoxide and  $-1/2$  (2) Oxide and  $-2$   
 (3) Peroxide and  $-1/2$  (4) Superoxide and  $-1$   
**RR0150**
11. In the reaction of oxalate with permanganate in acidic medium, the number of electrons involved in producing one molecule of  $\text{CO}_2$  is : [JEE(Main)-(Jan.)-2019]  
 (1) 10 (2) 2 (3) 1 (4) 5  
**RR0151**
12. The chemical nature of hydrogen peroxide is :- [JEE(Main)-(Jan.)-2019]  
 (1) Oxidising and reducing agent in acidic medium, but not in basic medium.  
 (2) Oxidising and reducing agent in both acidic and basic medium  
 (3) Reducing agent in basic medium, but not in acidic medium  
 (4) Oxidising agent in acidic medium, but not in basic medium.  
**RR0152**
13. The hardness of a water sample (in terms of equivalents of  $\text{CaCO}_3$ ) containing  $10^{-3}$  M  $\text{CaSO}_4$  is : [JEE(Main)-(Jan.)-2019]  
 (molar mass of  $\text{CaSO}_4 = 136 \text{ g mol}^{-1}$ )  
 (1) 100 ppm (2) 50 ppm (3) 10 ppm (4) 90 ppm  
**RR0153**



14. 50 mL of 0.5 M oxalic acid is needed to neutralize 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is : **[JEE(Main)-(Jan.)-2019]**  
 (1) 4 g                      (2) 2 g                      (3) 8 g                      (4) 1 g  
**RR0154**
15. In order to oxidise a mixture one mole of each of  $\text{FeC}_2\text{O}_4$ ,  $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ ,  $\text{FeSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$  in acidic medium, the number of moles of  $\text{KMnO}_4$  required is - **[JEE(Main)-(April)-2019]**  
 (1) 3                      (2) 2                      (3) 1                      (4) 1.5  
**RR0155**
16. The correct order of the oxidation states of nitrogen in  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{N}_2\text{O}_3$  is :  
 (1)  $\text{NO}_2 < \text{N}_2\text{O}_3 < \text{NO} < \text{N}_2\text{O}$   
 (2)  $\text{NO}_2 < \text{NO} < \text{N}_2\text{O}_3 < \text{N}_2\text{O}$   
 (3)  $\text{N}_2\text{O} < \text{N}_2\text{O}_3 < \text{NO} < \text{NO}_2$   
 (4)  $\text{N}_2\text{O} < \text{NO} < \text{N}_2\text{O}_3 < \text{NO}_2$  **[JEE(Main)-(April)-2019]**  
**RR0156**
17. An example of a disproportionation reaction is : **[JEE(Main)-(April)-2019]**  
 (1)  $2\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$                       (2)  $2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}$   
 (3)  $2\text{CuBr} \rightarrow \text{CuBr}_2 + \text{Cu}$                       (4)  $2\text{NaBr} + \text{Cl}_2 \rightarrow 2\text{NaCl} + \text{Br}_2$   
**RR0158**
18. 100 mL of a water sample contains 0.81 g of calcium bicarbonate and 0.73 of magnesium bicarbonate. The hardness of this water sample expressed in terms of equivalents of  $\text{CaCO}_3$  is:  
 (molar mass of calcium bicarbonate is  $162 \text{ g mol}^{-1}$  and magnesium bicarbonate is  $146 \text{ g mol}^{-1}$ )  
 (1) 1,000 ppm                      (2) 10,000 ppm                      **[JEE(Main)-(April)-2019]**  
 (3) 100 ppm                      (4) 5,000 ppm  
**RR0159**
19. 25 ml of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution? **[JEE(Main)-(Jan)-2019]**  
 (1) 25 mL                      (2) 50 mL                      (3) 12.5 mL                      (4) 75 mL  
**RR0160**
20. Oxidation number of potassium in  $\text{K}_2\text{O}$ ,  $\text{K}_2\text{O}_2$  and  $\text{KO}_2$ , respectively, is : **[JEE(Main)-(Jan)-2020]**  
 (1) +1, +4 and +2                      (2) +1, +2 and +4  
 (3) +1, +1 and +1                      (4) +2, +1 and  $+\frac{1}{2}$   
**RR0167**

21. The compound that cannot act both as oxidising and reducing agent is :[JEE(Main)-(Jan)-2020]  
(1)  $\text{H}_2\text{O}_2$                       (2)  $\text{H}_2\text{SO}_3$                       (3)  $\text{HNO}_2$                       (4)  $\text{H}_3\text{PO}_4$

RR0168

22. The hardness of a water sample containing  $10^{-3}$  M  $\text{MgSO}_4$  expressed as  $\text{CaCO}_3$  equivalents (in ppm) is \_\_\_\_\_.  
(molar mass of  $\text{MgSO}_4$  is 120.37 g/mol)

[JEE(Main)-(Jan)-2020]

RR0169

## EXERCISE # J-ADVANCED

1. Reduction of the metal centre in aqueous permanganate ion involves - [JEE-2011]  
(A) 3 electrons in neutral medium (B) 5 electrons in neutral medium  
(C) 3 electrons in alkaline medium (D) 5 electrons in acidic medium  
RR0161
2. Reaction of  $\text{Br}_2$  with  $\text{Na}_2\text{CO}_3$  in aqueous solution gives sodium bromide and sodium bromate with evolution of  $\text{CO}_2$  gas. The number of sodium bromide molecules involved in the balanced chemical equation is. [JEE- 2011]  
RR0162
3. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen-  
(A)  $\text{HNO}_3$ ,  $\text{NO}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{N}_2$  (B)  $\text{HNO}_3$ ,  $\text{NO}$ ,  $\text{N}_2$ ,  $\text{NH}_4\text{Cl}$   
(C)  $\text{HNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NO}$ ,  $\text{N}_2$  (D)  $\text{NO}$ ,  $\text{HNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{N}_2$  [JEE- 2012]  
RR0163
4. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N  $\text{Na}_2\text{S}_2\text{O}_3$  was used to reach the end point. The molarity of the household bleach solution is [JEE- 2012]  
(A) 0.48 M (B) 0.96 M (C) 0.24 M (D) 0.024 M  
RR0164
5. In neutral or faintly alkaline solution, 8 moles permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. the magnitude of X is [JEE- 2016]  
RR0165
6. To measure the quantity of  $\text{MnCl}_2$  dissolved in an aqueous solution, it was completely converted to  $\text{KMnO}_4$  using the reaction, [JEE- 2018]  
 $\text{MnCl}_2 + \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{HCl}$  (equation not balanced).  
Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 g) was added in portions till the colour of the permanganate ion disappeared. The quantity of  $\text{MnCl}_2$  (in mg) present in the initial solution is \_\_\_\_\_.  
(Atomic weights in  $\text{g mol}^{-1}$  : Mn = 55, Cl = 35.5)  
RR0166

## ANSWER-KEY

## EXERCISE # S-I

1. (a) +6 (b) +5 (c) +2 (d) -4  
 (e) +4 (f) -1 (g) +2 (h) +6  
 (i) +3
2. (a) Reduction (b) Oxidation  
 (c) Reduction (d) Oxidation
3. (a) Oxidant :  $O_2$  ; Reductant : Zn  
 (b) Oxidant :  $H^+$  ; Reductant : Zn  
 (c) Oxidant :  $NO_3^-$  ; Reductant : Zn
4. (i)  $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$   
 (ii)  $Br_2 + 5H_2O_2 \longrightarrow 2BrO_3^- + 4H_2O + 2H^+$   
 (iii)  $MnO_4^- + 5Fe^{+2} + 8H^+ \longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$   
 (iv)  $MnO_2 + 2Cl^- + 4H^+ \longrightarrow Mn^{+2} + Cl_2 + 2H_2O$   
 (v)  $3ClO^- + 2CrO_2^- + 2OH^- \longrightarrow 3Cl^- + 2CrO_4^{2-} + H_2O$
5. (i)  $2MnO_4^- + 6I^- + 4H_2O \longrightarrow 2MnO_2 + 3I_2 + 8OH^-$   
 (ii)  $H^+ + 2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5HSO_4^-$   
 (iii)  $2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$   
 (iv)  $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$
6. Ans. (1) 1 (2) 2, 1 (3) 1  
 (4) 1 (5) 2 (6) 1
7. (1) 1 (2) 1 (3) 1 (4) 1 (5) 2
8. 98, 49, 32.67 9. Ans.21 10. Ans. (i)  $\frac{83.5}{6}$  ; (ii)  $\frac{17}{3}$
11. Ans. 6 12. Ans.5 13. Ans.(8.097 mL)
14. Ans.(40) 15. Ans.40 ml 16. Ans.60 ml 17. Ans.12.5 L
18. Ans.12.5 L 19. Ans. V = 3 lit. 20. Ans. 200 mL 21. Ans. 30 N
22. Ans.(4.48) 23. Ans. 10 N 24. Ans.2.12 g/L 25. Ans.+ 3
26. Ans.Zero 27. Ans.V = 160 ml 28. Ans.0.588 N 29. Ans.4 lit.
30. Ans.  $\frac{2}{3}$  31. Ans. 8/5 32. Ans. 1.25 mL 33. Ans.1.406 %
34. Ans.V = 25 mL 35. Ans.1.28 % 36. Ans.40 g , 0.0518N
37. Ans.( $Ca^{2+}$  ,  $Mg^{2+}$  ,  $Na^+$ )
38. Ans.(19.09)

## EXERCISE # S-II

1. (a) +2.5 (b) +4/3 (c) -1/3 (d) +8/3  
 (e) -3, -1 (f) -2, +2 (g) +16/3 (h) 0  
 (i) +2, -1 (j) +2 (k) 0 (l) +1/2  
 (m) -1/2 (n) +1 (o) +3 (p) -3  
 (q) +3 (r) +2 (s) +4
2. (a) +3 (b) +3, +6 (c) +2 (d)  $+\frac{200}{93}$   
 (e) +6 (f) +6 (g) +6 (h) +5  
 (r) +2 (s) +3
3. (i)  $6\text{KMnO}_4(\text{aq.}) + 10\text{FeC}_2\text{O}_4(\text{aq.}) + 24\text{H}_2\text{SO}_4(\text{aq.}) \longrightarrow$   
 $6\text{MnSO}_4(\text{aq.}) + 5\text{Fe}_2(\text{SO}_4)_3(\text{aq.}) + 20\text{CO}_2(\text{g}) + 3\text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}(\text{l})$   
 (ii)  $5\text{P}_4(\text{s}) + 12\text{OH}^-(\text{aq.}) + 12\text{H}_2\text{O} \longrightarrow 8\text{PH}_3(\text{aq}) + 12\text{HPO}_2^-(\text{aq.})$   
 (iii)  $3\text{I}_2(\text{s}) + 6\text{NaOH}(\text{aq.}) \longrightarrow 5\text{NaI}(\text{aq.}) + \text{NaIO}_3(\text{aq.}) + 3\text{H}_2\text{O}(\text{l})$   
 (iv)  $3\text{HNO}_2(\text{aq.}) \rightarrow \text{NO}_3^- + \text{H}^+ + 2\text{NO}(\text{g}) + \text{H}_2\text{O}$   
 (v)  $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$   
 (vi)  $5\text{Cu}_2\text{S} + 8\text{MnO}_4^- + 44\text{H}^+ \rightarrow 10\text{Cu}^{2+} + 5\text{O}_2 + 8\text{Mn}^{2+} + 22\text{H}_2\text{O}$   
 (vii)  $\text{HCHO}(\text{l}) + [\text{Ag}(\text{NH}_3)_2]^+(\text{aq.}) + 2\text{OH}^-(\text{aq.}) \rightarrow \text{Ag}(\text{s}) + 2\text{NH}_3(\text{aq.}) + \text{HCOO}^-(\text{aq.}) + \text{H}_2\text{O}(\text{l})$
4.  $\text{KOH} = 35\%$ ,  $\text{Ca}(\text{OH})_2 = 65\%$
5. Ans. 3 l 6. Ans. 12.5 l  
 7. Ans. 6 l 8. Ans. 16.66 %  
 9. Ans. 3 10. Ans. 90.1 %  
 11. Ans. (80) 12. Ans. 16 %  
 13. Ans. 24.46 % 14. Ans. 0.47  
 15. Ans. (40) 16. Ans. (0.0626 M)

## EXERCISE # O-I

1. Ans. (C) 2. Ans. (B) 3. Ans. (B) 4. Ans. (B)  
 5. Ans. (D) 6. Ans. (A) 7. Ans. (D) 8. Ans. (A)  
 9. Ans. (D) 10. Ans. (A) 11. Ans. (B) 12. Ans. (A)  
 13. Ans. (C) 14. Ans. (C) 15. Ans. (C) 16. Ans. (D)  
 17. Ans. (A) 18. Ans. (D) 19. Ans. (D) 20. Ans. (B)  
 21. Ans. (C) 22. Ans. (D) 23. Ans. (D) 24. Ans. (D)  
 25. Ans. (A) 26. Ans. (C) 27. Ans. (D) 28. Ans. (C)  
 29. Ans. (D) 30. Ans. (A) 31. Ans. (C) 32. Ans. (B)  
 33. Ans. (A) 34. Ans. (A) 35. Ans. (B) 36. Ans. (C)  
 37. Ans. (C) 38. Ans. (A) 39. Ans. (D) 40. Ans. (A)  
 41. Ans. (C) 42. Ans. (C) 43. Ans. (D) 44. Ans. (A)  
 45. Ans. (B) 46. Ans. (B)

**EXERCISE # O-II**

- 
- |              |                  |   |              |
|--------------|------------------|---|--------------|
| 1. Ans. (A)  | 2. Ans. (C)      | 3. Ans. (B)   | 4. Ans. (C)  |
| 5. Ans. (A)  | 6. Ans. (A)      | 7. Ans. (B)   | 8. Ans. (B)  |
| 9. Ans. (C)  | 10. Ans. (A,B,D) | 11. Ans. (C)  | 12. Ans. (A) |
| 13. Ans. (B) | 14. Ans. (C)     | 15. (A) $\rightarrow$ s ; (B) $\rightarrow$ q ; (C) $\rightarrow$ r ; (D) $\rightarrow$ p |              |
| 16. Ans. (C) | 17. Ans. (A)     | 18. Ans. (A)  | 19. Ans. (B) |
| 20. Ans. (C) | 21. Ans. (B)     | 22. Ans. (A,D)  |              |

**EXERCISE # J-MAINS**

- 
- |              |                |              |              |
|--------------|----------------|--------------|--------------|
| 1. Ans. (2)  | 2. Ans. (3)    | 3. Ans. (4)  | 4. Ans. (1)  |
| 5. Ans. (2)  | 6. Ans. (2)    | 7. Ans. (1)  | 8. Ans. (1)  |
| 9. Ans. (3)  | 10. Ans. (1)   | 11. Ans. (3) | 12. Ans. (2) |
| 13. Ans. (1) | 14. Ans. (1)   | 15. Ans. (2) | 16. Ans. (4) |
| 17. Ans. (3) | 18. Ans. (2)   | 19. Ans. (1) | 20. Ans. (3) |
| 21. Ans. (4) | 22. Ans. (100) |              |              |

**EXERCISE # J-ADVANCED**

- 
- |                 |               |             |             |
|-----------------|---------------|-------------|-------------|
| 1. Ans. (A,C,D) | 2. Ans. (5)   | 3. Ans. (B) | 4. Ans. (C) |
| 5. Ans. (6)     | 6. Ans. (126) |             |             |



## LIQUID SOLUTION

### 1. SOLUTION

It is the homogeneous mixture of two or more components.

The substance which dissolve other substance is **solvent** & the substance which is dissolved is **solute**, independent of their quantity. If both are soluble in each other then the substance present in larger amount by mole is solvent.

\* A solution may exist in any physical state.

#### Types of Solution :

	Solvent	Solute	Examples
1.	Gas	Gas	Mixture of gases, eg. air.
2.	Gas	Liquid	$\text{CHCl}_3(\ell) + \text{N}_2(\text{g})$
3.	Gas	Solid	Camphor (s) + $\text{N}_2(\text{g})$ .
4.	Liquid	Gas	$\text{CO}_2$ gas dissolve in water (aerated drink), soda water.
5.	Liquid	Liquid	Mixture of miscible liquids e.g. alcohol in water.
6.	Liquid	Solid	Salt in water, sugar in water.
7.	Solid	Gas	hydrogen over palladium.
8.	Solid	Liquid	Mercury in zinc, mercury in gold, i.e. all amalgams.
9.	Solid	Solid	Alloys e.g. copper in gold, zinc in copper.

### 2. SOLUBILITY

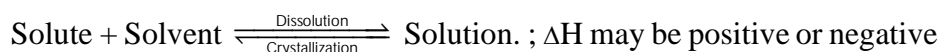
Maximum amount of solute which can be dissolved in a specified amount of solvent at constant temperature is its solubility. Solubility is affected by

1. nature of solute and solvent
2. temperature and
3. pressure

### 3. SOLUBILITY OF SOLID IN A LIQUID

Polar solutes are soluble in polar solvent and non polar solutes are soluble in non polar solvent due to similar intermolecular forces.

When solid solutes are dissolved in solvent, then following equilibrium exist.

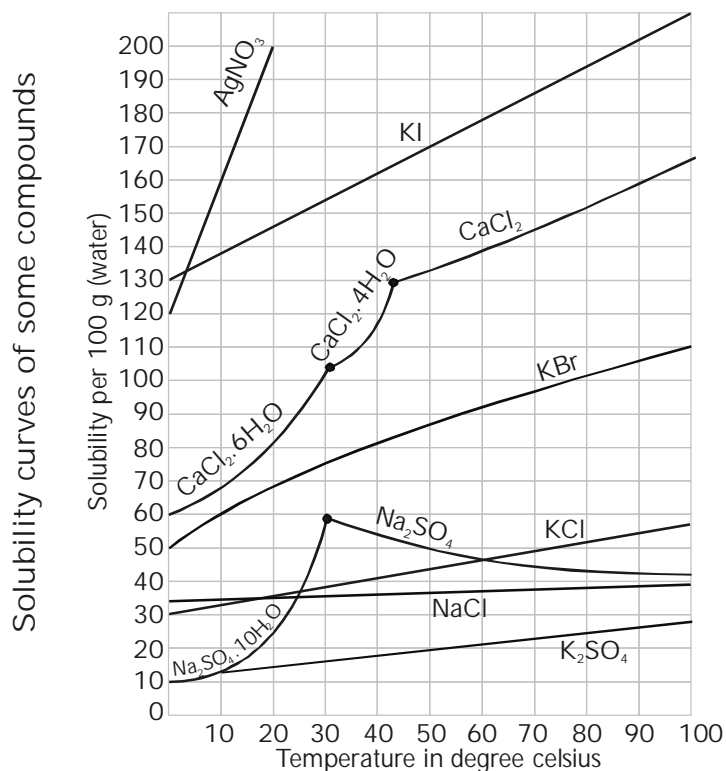


Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution**. An unsaturated solution is one in which more solute can be dissolved at the same temperature. The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent.

#### 3.1 Effect of temperature :

The solubility of a solid in a liquid is significantly affected by temperature changes, obeying **Le Chateliers Principle**. In general, if in a nearly saturated solution, the dissolution process is endothermic ( $\Delta_{\text{sol}}H > 0$ ), the solubility should increase with rise in temperature and if it is exothermic ( $\Delta_{\text{sol}}H < 0$ ) the solubility should decrease. These trends are also observed experimentally.





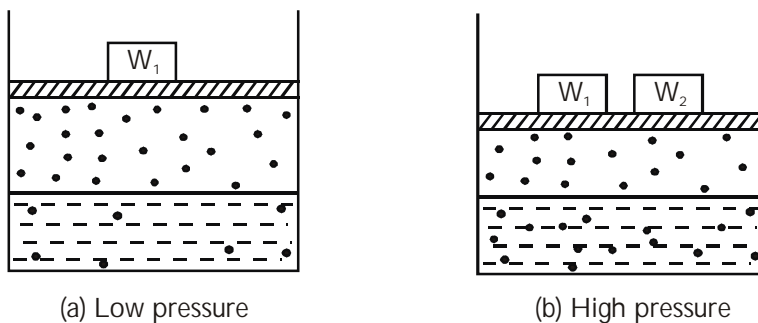
### 3.2 Effect of pressure :

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

## 4. SOLUBILITY OF GASES IN LIQUID

Certain gases are highly soluble in water like  $\text{NH}_3$ ,  $\text{HCl}$ , etc, and certain gases are less soluble in water like  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{He}$ , etc. Solubility of gases is greatly effected by pressure and temperature. Increasing pressure increases solubility and increase in temperature decreases solubility since dissolution of any gas in any liquid is exothermic in nature.

### 4.1 Henry' Law :



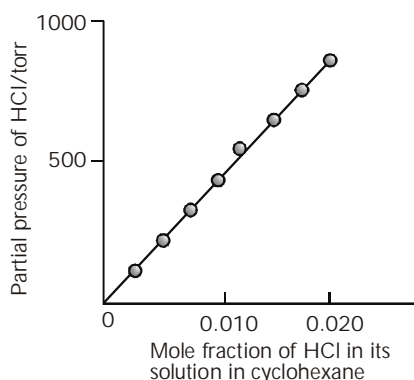
*Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure on the gas above the solution.*

The partial pressure of the gas in vapour phase ( $p$ ) is proportional to the mole fraction of the gas ( $x$ ) in the solution, at constant temperature

$$P = K_H X$$

$K_H$  = Henry's Law Constant

- \* Henry's Law Constant depends on nature of gas and liquid as well as temperature.
- \*  $K_H$  increases with increases in temperature.
- \* Greater  $K_H$  means low solubility.



Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant  $K_H$ .

#### Values of Henry's Law Constant for Some Selected Gases in Water

Gas	Temperature/K	$K_H$ /kbar
He	293	144.97
H <sub>2</sub>	293	69.16
N <sub>2</sub>	293	76.48
N <sub>2</sub>	303	88.84
O <sub>2</sub>	293	34.86
O <sub>2</sub>	303	46.82
Argon	298	40.3
CO <sub>2</sub>	298	1.67
Formaldehyde	298	$1.83 \times 10^{-5}$
Methane	298	0.413
Vinyl chloride	298	0.611

#### 4.2 Limitations of Henry' Law :

- (1) It is valid only for ideal behaviour of gas. As none of the gas is ideal, this law may be applied at low pressure and high temperature.
- (2) It gives better result when the solubility of gas in the liquid is low.
- (3) The gas should neither dissociate nor associate in the liquid.

### 4.3 Henry' Law application :

- (1) To increase the solubility of  $\text{CO}_2$  in soft drinks and soda water, the bottle is sealed under high pressure.
- (2) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
- (3) At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

### 4.4 Effect of Temperature :

Solubility of any gas in any liquid decreases with rise in temperature as dissolution is an exothermic process.

At constant pressure, 
$$\ln \frac{C_2}{C_1} = \frac{\Delta H_{\text{sol}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

where C = molar concentration of gas in solution

**Ex.1.** If  $\text{N}_2$  gas is bubbled through water at 293 K, how many millimoles of  $\text{N}_2$  gas would dissolve in 1 litre of water? Assume that  $\text{N}_2$  exerts a partial pressure of 0.987 bar. Given that Henry's law constant for  $\text{N}_2$  at 293 K is 76.48 kbar.

**Sol:** 
$$x(\text{Nitrogen}) = \frac{p(\text{nitrogen})}{K_H} = \frac{0.98 \text{ bar}}{76,480 \text{ bar}} = 1.29 \times 10^{-5}$$

As 1 litre of water contains 55.5 mol of it, therefore if  $n$  represents number of moles of  $\text{N}_2$  in solution,

$$x(\text{Nitrogen}) = \frac{n \text{ mol}}{n \text{ mol} + 55.5 \text{ mol}} = \frac{n}{55.5} = 1.29 \times 10^{-5}$$

( $n$  in denominator is neglected as it is  $\ll 55.5$ )

$$\text{Thus } n = 1.29 \times 10^{-5} \times 55.5 \text{ mol} = 7.16 \times 10^{-4} \text{ mol} = 0.716 \text{ m mol}$$

**Ex.2** The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K, if the Henry's law constants for oxygen and nitrogen are  $3.30 \times 10^7$  mm and  $6.51 \times 10^7$  mm respectively, calculate the composition of these gases in water.

**Sol:** Percentage of oxygen ( $O_2$ ) in air = 20%

Percentage of nitrogen ( $N_2$ ) in air = 79%

Also, it is given that water is in equilibrium with air at a total pressure of 10 atm, that is,  $(10 \times 760)$  mm Hg = 7600 mm Hg

Partial pressure of oxygen,  $p_{O_2} = \frac{20}{100} \times 7600 \text{ mm Hg} = 1520 \text{ mm Hg}$

Partial pressure of nitrogen,  $p_{N_2} = \frac{79}{100} \times 7600 \text{ mm Hg} = 6004 \text{ mm of Hg}$

Now, according to Henry's law :

$$p = K_H x$$

For oxygen :

$$p_{O_2} = K_H \cdot x_{O_2}$$

$$\Rightarrow x_{O_2} = \frac{p_{O_2}}{K_H} = \frac{1520 \text{ mm of Hg}}{3.30 \times 10^7 \text{ mm of Hg}} \quad (\text{Given } K_H = 3.30 \times 10^7 \text{ mm of Hg} = 4.61 \times 10^{-5})$$

For nitrogen,

$$p_{N_2} = K_H \cdot x_{N_2}$$

$$\Rightarrow x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{6004 \text{ mm Hg}}{6.51 \times 10^7 \text{ mm Hg}} = 9.22 \times 10^{-5}$$

Hence, the mole fractions of oxygen and nitrogen in water are  $4.61 \times 10^{-5}$  and  $9.22 \times 10^{-5}$  respectively.

**5. Vapour pressure :**

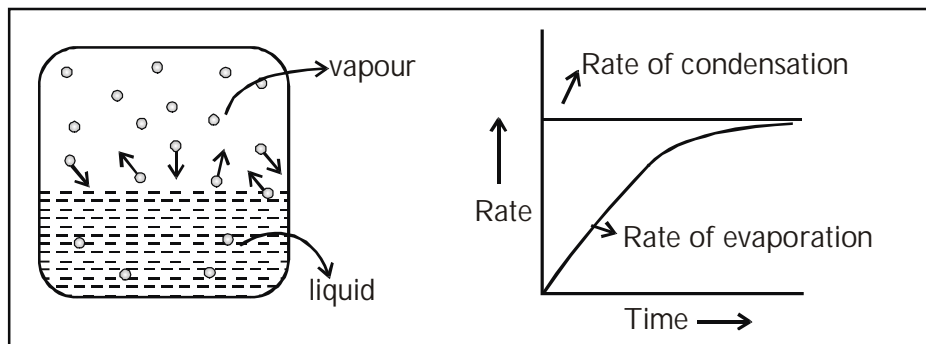
**The Evaporation of a Liquid in a Closed Container**

When a liquid is taken in a closed vessel at constant temperature, then there are two process which takes place.

- (i) Evaporation
- (ii) Condensation

In the constant evaporation from the surface particles continue to break away from the surface of the liquid.

As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and will be trapped there. This is called condensation. The rate of condensation increases with time, but rate of evaporation remain constant. There will rapidly be an equilibrium set up in which the number of particles leaving the surface is exactly balanced by the number rejoining it.



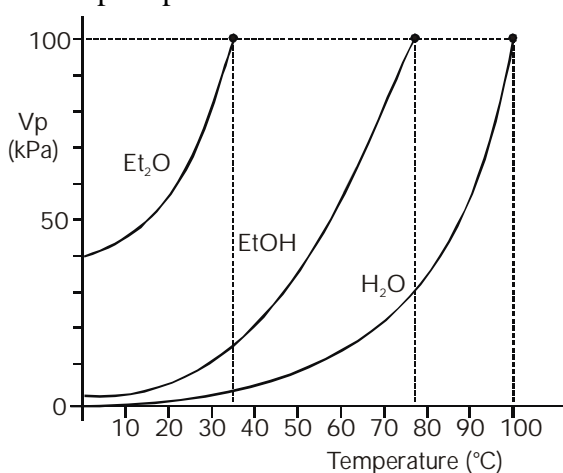
This pressure at equilibrium is called the **vapour pressure** (also known as **saturation vapour pressure**) **of the liquid at that temperature.**

### 5.1 Effect of Temperature on vapour pressure

When the space above the liquid is saturated with vapour particles, you have this equilibrium occurring on the surface of the liquid :

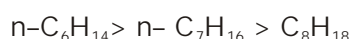


The forward change (liquid to vapour) is endothermic. It needs heat to convert the liquid into the vapour. According to Le Chatelier, increasing the temperature of a system in a dynamic equilibrium favours the endothermic change. That means increasing the temperature increase the amount of vapour present, and so increases the vapour pressure.



**Effect of nature :**

$$V.p \propto \frac{1}{\text{Inter molecular attraction force (I.M.A.F.)}}$$



The dependence of vapour pressure of a liquid on temperature is given by clausius-clapeyron equation : In

$$\frac{P_2}{P_1} = \frac{\Delta H_{\text{vap.}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

5.2 Nature of liquid : Weaker the intermolecular attraction , higher will be the vapour pressure.

## 6. VAPOUR PRESSURE OF LIQUID SOLUTION

### 6.1 Raoult's law :

The partial pressure of any volatile constituents of a solution at a constant temperature is equal to the vapour pressure of pure constituents multiplied by the mole fraction of that constituent in the solution, at equilibrium.

### 6.2 Vapour pressure of liquid – liquid solution :

Let  $P_A$  and  $P_B$  be the partial vapour pressures of two constituents A and B in solution and  $P_A^0$  and  $P_B^0$  the vapour pressures in pure state respectively.

Thus, according Raoult's law

$$P_A = \frac{n_A}{n_A + n_B} P_A^0 = X_A P_A^0 \quad \dots(1)$$

and  $P_B = \frac{n_B}{n_A + n_B} P_B^0 = X_B P_B^0 \quad \dots(2)$

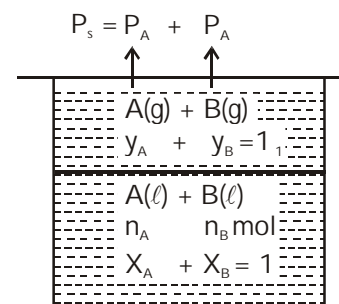
If total pressure be  $P_S$ , then

$$P_S = P_A + P_B = X_A P_A^0 + X_B P_B^0$$

$$P_S = X_A P_A^0 + (1 - X_A) P_B^0 \quad [\because X_A + X_B = 1]$$

$$P_S = X_A P_A^0 - X_A P_B^0 + P_B^0$$

$$P_S = X_A [P_A^0 - P_B^0] + P_B^0$$



#### 6.2.1 Relation between Dalton's Law and Raoult's Law :

The composition of the vapour in equilibrium with the solution can be calculated applying Dalton's law of partial pressures. Let the mole fraction of A and B in vapours be  $Y_A$  and  $Y_B$  respectively.

$$p_A = Y_A P_S = X_A P_A^0 \quad \dots\dots(1)$$

$$p_B = Y_B P_S = X_B P_B^0 \quad \dots\dots(2)$$

Now,  $X_A = \frac{Y_A \cdot P_S}{P_A^0}$  and  $X_B = \frac{Y_B \cdot P_S}{P_B^0}$

As,  $X_A + X_B = 1$ ,  $\frac{Y_A \cdot P_S}{P_A^0} + \frac{Y_B \cdot P_S}{P_B^0} = 1$

$$\therefore \frac{1}{P_S} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0}$$

Hence, the total vapour pressure of solution may be calculated from liquid composition at equilibrium as

$$P_S = X_A \cdot P_A^0 + X_B \cdot P_B^0$$

and from vapour composition at equilibrium at

$$\frac{1}{P_S} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0}$$

### 6.2.2 Comparison between liquid and vapour composition :

$$\frac{Y_A}{Y_B} = \frac{P_A/P_S}{P_B/P_S} = \frac{P_A}{P_B} = \frac{X_A \cdot P_A^0}{X_B \cdot P_B^0}$$

If A is more volatile than B ( $P_A^0 > P_B^0$ ), then  $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$

It means that the mole-fraction of A in vapour form is relatively greater than that in liquid form, relative to B. Hence, in any ideal solution, vapour is always more richer in the more volatile component, relative to liquid.

### 6.2.3 Raoult's law as a special case of Henry's law :

From Raoult's law, the vapour pressure of volatile component in the solution is  $P = P^0 \cdot X$ .

In the solution of gas in liquid, one component is so volatile that it exists as gas and its pressure is given by Henry's law as  $P = K_H \cdot X$

In both laws, the partial pressure of volatile component is directly proportional to its mole-fraction in solution. Only the proportionality constant  $K_H$  differs from  $P^0$ . Hence, Raoult's law becomes a special case of Henry's law in which  $K_H$  becomes  $P^0$ .

### 6.3 Vapour pressure of solution of solids in liquid :

Let us assume A = non volatile solid & B = volatile liquid

According to Raoult's law –

$$\therefore P_S = X_A P_A^0 + X_B P_B^0$$

for A,  $P_A^0 = 0$

$$\therefore P_S = X_B P_B^0 \quad \dots(5)$$

Let  $P_B^0 = P^0 =$  Vapour pressure of pure state of solvent.

here  $X_B$  is mole fraction of solvent

$$P_s = \frac{n_B}{n_A + n_B} P^0 \quad \dots(6)$$

$$P_s \propto \frac{n_B}{n_A + n_B} \quad \text{i.e. vapour pressure of solution} \propto \text{mole fraction of solvent}$$

$$\Rightarrow P_s = X_B P_B^0 \Rightarrow P_s = (1 - X_A) P_B^0$$

$$\Rightarrow P_s = P_B^0 - X_A P_B^0$$

$$\Rightarrow \frac{P_B^0 - P_s}{P_B^0} = X_A$$

$$\text{or } \frac{P^0 - P_s}{P^0} = X_A \quad \dots(7);$$

$$\boxed{\frac{P^0 - P_s}{P^0} = \frac{n_A}{n_A + n_B}} \quad \dots(8)$$

$$\text{or } \frac{P^0}{P^0 - P_s} = \frac{n_A + n_B}{n_A}$$

$$\text{or } \frac{P^0}{P^0 - P_s} = 1 + \frac{n_B}{n_A} \quad \text{or } \frac{P^0}{P^0 - P_s} - 1 = \frac{n_B}{n_A}$$

$$\frac{P_s}{P^0 - P_s} = \frac{n_B}{n_A}$$

$$\boxed{\frac{P^0 - P_s}{P_s} = \frac{n_A}{n_B} = \frac{w_A \cdot m_B}{m_A \cdot w_B}} \quad \dots(9)$$

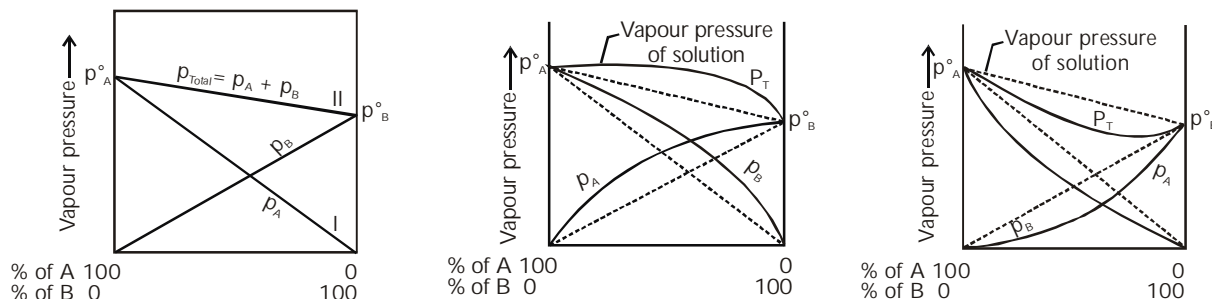


### 6.4 Ideal and Non ideal solutions :

The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions.

**Table : Comparison between Ideal and Non-ideal solutions**

Ideal solutions	Non-ideal solutions	
	+ve deviation from Raoult's law	- deviation from Raoult's law
1. Obeys Raoult's law at every concentrations.	Do not obey Raoult's law.	Do not obey Raoult's law.
2. $\Delta H_{\text{mix}} = 0$ ; Neither heat is evolved nor absorbed during dissolution.	$\Delta H_{\text{mix}} > 0$ . Endothermic dissolution; heat is absorbed.	$\Delta H_{\text{mix}} < 0$ ; exothermic dissolution heat is evolved.
3. $\Delta V_{\text{mix}} = 0$ ; total volume of solution is equal to sum of volumes of the components.	$\Delta V_{\text{mix}} > 0$ . Volume is increased after dissolution.	$\Delta V_{\text{mix}} < 0$ ; volume is decreased during dissolution.
4. $P = p_A + p_B = p_A^0 X_A + p_B^0 X_B$ i.e., $P_A = p_A^0 X_A$ ; $p_B = p_B^0 X_B$	$P_A > p_A^0 X_A$ ; $p_B > p_B^0 X_B$ $\therefore (P_A + p_B) > (p_A^0 X_A + p_B^0 X_B)$	$P_A < p_A^0 X_A$ ; $p_B < p_B^0 X_B$ $\therefore (P_A + p_B) < (p_A^0 X_A + p_B^0 X_B)$
5. A—A, A—B, B—B interactions should be same, i.e., 'A' and 'B' are identical in shape, size and character.	A—B, attraction force should be weaker than A—A and B—B attractive forces. 'A' and 'B' have different shape, size and character.	A—B, attraction force should be greater than A—A and B—B attractive forces. 'A' and 'B' have different shape, size and character.
6. Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.	'A' and 'B' escape easily showing high vapour pressure than the expected value.	Escaping tendency of both components A and B is lowered showing lower vapour pressure than expected ideally.
<b>Example :</b> dilute solutions ; benzene + toluene ; n-hexane + n-heptane ; chlorobenzene + bromobenzene ; ethyl bromide + ethyl iodide ; n-butyl chloride + n-butyl bromide $\text{CCl}_4 + \text{SiCl}_4$ ; $\text{C}_2\text{H}_4\text{Br}_2 + \text{C}_2\text{H}_4\text{Cl}_2$ $\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{Cl}$	<b>Example :</b> acetone + ethanol ; acetone + $\text{CS}_2$ ; water + methanol ; water + ethanol ; $\text{CCl}_4 + \text{CHCl}_3$ ; $\text{CCl}_4 + \text{toluene}$ ; acetone + benzene $\text{CCl}_4 + \text{CH}_3\text{OH}$ ; cyclohexane + ethanol	<b>Example :</b> acetone + aniline ; acetone + chloroform ; $\text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$ ; $\text{H}_2\text{O} + \text{HNO}_3$ ; water + HCl ; acetic acid + pyridine ; $\text{HNO}_3 + \text{CHCl}_3$



**Ex.3.** 1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mole Octane (V.P. = 31 mm of Hg), form an ideal solution. Find out the vapour pressure of solution.

**Sol.** Total mole = 1 + 4 = 5

Mole fraction of heptane =  $X_A = 1/5$

Mole fraction of octane =  $X_B = 4/5$

$$P_s = X_A P_A^0 + X_B P_B^0 = \frac{1}{5} \times 92 + \frac{4}{5} \times 31 = 43.2 \text{ mm of Hg.}$$

**Ex.4.** At 88°C, benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will be boil at 88°C at 1 atm pressure, benzene – toluene form an ideal solution.

**Sol.**  $P_s = 760$  torr, because solution boils at 88°C

$$\therefore 760 = 900x + 360(1-x)$$

$$x = 0.74 \text{ where 'x' is mole fraction } C_6H_6.$$

**Ex.5.** The vapour pressure of benzene at 90°C is 1020 torr. A solution of 5 g of a solute in 58.5 g benzene has vapour pressure 990 torr. What is the molecular weight of solute ?

$$\text{Sol. } \frac{P^0 - P_s}{P_s} = \frac{w \times M}{m \times W} \Rightarrow \frac{1020 - 990}{990} = \frac{5 \times 78}{m \times 58.5} \Rightarrow m = 220$$

**Ex.6.** Two liquids A and B form an ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 mole of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.

**Sol.** Let the vapour pressure of pure A be =  $p_A^0$ ; and the vapour pressure of pure B be =  $p_B^0$ .

Total vapour pressure of solution (1 mole A + 3 mole B)

$$= X_A \cdot p_A^0 + X_B \cdot p_B^0 \quad [X_A \text{ is mole fraction of A and } X_B \text{ is mole fraction of B}]$$

$$550 = \frac{1}{4} p_A^0 + \frac{3}{4} p_B^0 \quad \text{or} \quad 2200 = p_A^0 + 3p_B^0 \quad \dots\dots(i)$$

$$\text{Total vapour pressure of solution (1 mole A + 4 mole B)} = \frac{1}{5} p_A^0 + \frac{4}{5} p_B^0$$

$$560 = \frac{1}{5} p_A^0 + \frac{4}{5} p_B^0$$

$$2800 = p_A^0 + p_B^0 \quad \dots\dots(ii)$$

Solving eqs. (i) and (ii)

$$p_B^0 = 600 \text{ mm of Hg} = \text{vapour pressure of pure B}$$

$$p_A^0 = 400 \text{ mm of Hg} = \text{vapour pressure of pure A}$$

**Ex.7.** Liquids 'A' and 'B' form an ideal solution. Calculate the vapour pressure of solution having 40 mole-percent of A in the vapour at equilibrium. ( $P_A^0 = 80\text{cmHg}$ ,  $P_B^0 = 30\text{cmHg}$ )

$$\text{Sol.} \quad \frac{1}{P_{\text{total}}} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0} = \frac{0.4}{80} + \frac{0.6}{30} = \frac{1}{40}$$

$$P_{\text{total}} = 40 \text{ cm Hg}$$

**Ex.8.** Liquids 'A' and 'B' form an ideal solution. Calculate the molar-fraction of 'A' in vapour form above the liquid solution containing 25 mole-percent of 'A' at equilibrium ( $P_A^0 = 0.2\text{atm}$ ,  $P_B^0 = 0.5\text{atm}$ )

$$\text{Sol.} \quad Y_A = \frac{P_A}{P_{\text{total}}} = \frac{X_A \cdot P_A^0}{X_A \cdot P_A^0 + X_B \cdot P_B^0} = \frac{0.25 \times 0.2}{0.25 \times 0.2 + 0.75 \times 0.5} = \frac{2}{17}$$

**Ex.9.** Liquids 'A' and 'B' form an ideal solution. At  $80^\circ\text{C}$ ,  $P_A^0 = 0.4\text{bar}$  and  $P_B^0 = 0.8\text{bar}$ . All the vapour above the liquid solution containing equal moles of both the liquids at equilibrium is collected in another empty vessel and condensed. Now, the condensate is heated to  $80^\circ\text{C}$  and all the vapours above the liquid solution at equilibrium is again collected in another empty vessel and condensed. What is the mole-fraction of 'B' in new condensate ?

**Sol.** For the first condensate,

$$\frac{n_B'}{n_A'} = \frac{X_B'}{X_A'} = \frac{Y_B}{Y_A} = \frac{X_B \cdot P_B^0}{X_A \cdot P_A^0} = \frac{n_B}{n_A} \times \frac{P_B^0}{P_A^0}$$

For second condensate,

$$\frac{n_B''}{n_A''} = \frac{X_B''}{X_A''} = \frac{Y_B'}{Y_A'} = \frac{X_B' \cdot P_B^0}{X_A' \cdot P_A^0} = \frac{n_B'}{n_A'} \times \left(\frac{P_B^0}{P_A^0}\right)^2 = \frac{n_B}{n_A} \times \left(\frac{0.8}{0.4}\right)^2 = \frac{4}{1}$$

$$\therefore \text{Mole fraction of B} = \frac{4}{5} = 0.8$$

**Note :** For multi-step condensation at constant temperature,

$$\boxed{\frac{n_B^f}{n_A^f} = \frac{n_B^i}{n_A^i} \cdot \left(\frac{P_B^0}{P_A^0}\right)^n} \quad n : \text{number of steps}$$

**Ex.10.** *Liquid A & B form an ideal solution. In a cylinder piston arrangement, 2 moles of vapours of liquid A & 3 moles of vapours of liquid B are taken at 0.3 atm.  $P_A^0 = 0.4 \text{ atm}$ ,  $P_B^0 = 0.6 \text{ atm}$ .*

- (i) *Predict whether vapours will condense or not ?*
- (ii) *If the vapours are compressed slowly & isothermally, at what pressure  $P^{\text{st}}$  drop of liquid will form*
- (iii) *If the initial volume of vapours was 10L, at what volume  $P^{\text{st}}$  drop of liquid will form ?*
- (iv) *What is the composition of  $P^{\text{st}}$  drop of liquid formed ?*
- (v) *If the vapours are further compressed slowly & isothermally, at what  $P$  almost complete condensation will occur ?*
- (vi) *What is the composition of last traces of vapours remained ?*
- (vii) *What is the composition of system at 0.58 atm ?*
- (viii) *What is the composition of system at 0.51 atm ? Also calculate moles of A & B in liquid & vapour form.*
- (ix) *At what  $P$ , half of the total amount of vapours will condense ?*

**Sol.** (i) 
$$\frac{1}{P_T} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0} = \frac{2/5}{0.4} + \frac{3/5}{0.6} \Rightarrow P_{\text{total}} = 0.5 \text{ atm} > 0.3 \text{ atm}$$

$\therefore$  100% gas, no condensation

(ii) 0.5 atm.

(iii)  $P_i V_i = P_f V_f$

$$V_f = \frac{0.3 \times 10}{0.5} = 6 \text{ L}$$

(iv)  $P_{\text{total}} = X_A \cdot P_A^0 + X_B \cdot P_B^0$

or  $0.5 = X_A \times 0.4 + (1 - X_A) \times 0.6 \Rightarrow X_A = 0.5$

(v)  $P_T = 0.4 \times 0.4 + 0.6 \times 0.6 = 0.52 \text{ atm}$

**Note :** For a pure liquid, there is a fixed  $P(V.P.)$  below & above which, the system will be 100% gas & 100% liquid, respectively but for a solution, a pressure range exist in which both physical states will be present.

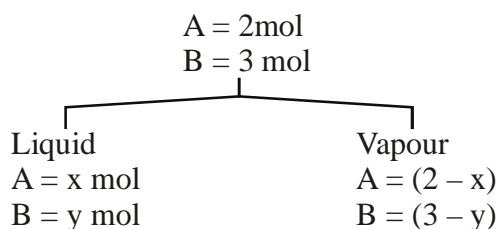
$$(vi) \quad Y_A = \frac{X_A \cdot P_A^0}{P_{total}} = \frac{0.4 \times 0.4}{0.52} = \frac{4}{13}$$

(vii) 100% liquid,  $A = 2 \text{ mole}$  and  $B = 3 \text{ mole}$

$$(viii) \quad P_{total} = X_A P_A^0 + X_B P_B^0$$

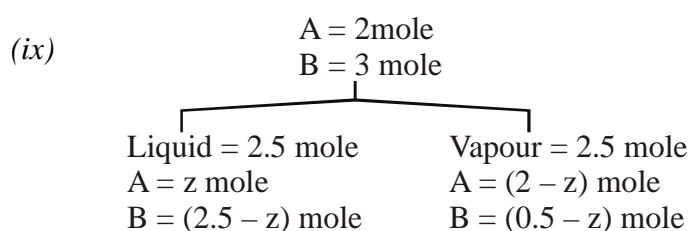
$$0.51 = X_A \times (0.4) + (1 - X_A) \times 0.6 \quad \& \quad Y_A = \frac{X_A P_A^0}{P_{total}} = \frac{0.45 \times 0.4}{0.51} = 0.35$$

$$X_A = 0.45$$



$$X_A = \frac{9}{20} = \frac{x}{x+y} \quad \text{and} \quad Y_A = \frac{18}{51} = \frac{2-x}{(2-x)+(3-y)}$$

$$\therefore x = 1.09; \quad y = 1.33$$



$$P_T = \frac{z}{2.5} \times 0.4 + \frac{2.5-z}{2.5} \times 0.6$$

$$\frac{2-z}{2.5} = \frac{z \times 0.4}{2.5 \times P_T}$$

On solving,  $z = 1.12$ ,  $P_T = 0.5104 \text{ atm}$

6.5 Graphs for ideal Binary solution of liquid A & liquid B :

(Assume  $P_A^0 < P_B^0$ )

I. Vapour pressure V/s liquid composition

$$P_A = X_A P_A^0 = (1 - X_B) P_A^0$$

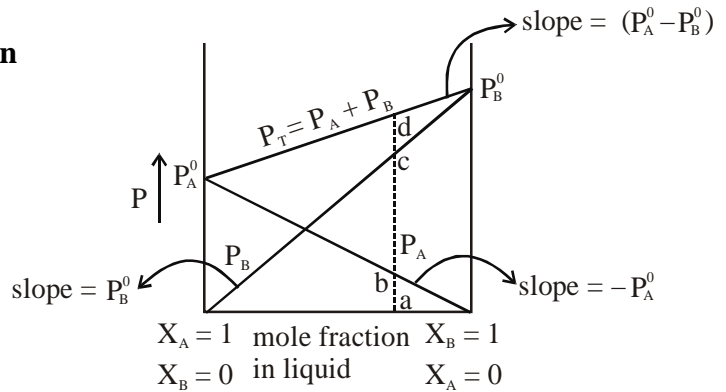
$$P_A = P_A^0 - X_B P_A^0$$

$$P_B = X_B P_B^0$$

$$P_T = X_A P_A^0 + X_B P_B^0 = (1 - X_B) P_A^0 + X_B P_B^0$$

$$\therefore P_T = P_A^0 + X_B (P_B^0 - P_A^0)$$

As  $P_T = P_A + P_B$ ,  $ad = ab + ac$



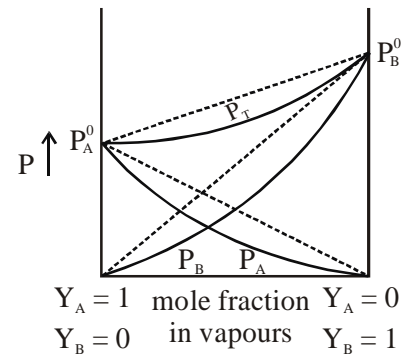
II. Vapour pressure V/s vapour composition

$$\frac{1}{P_T} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0}$$

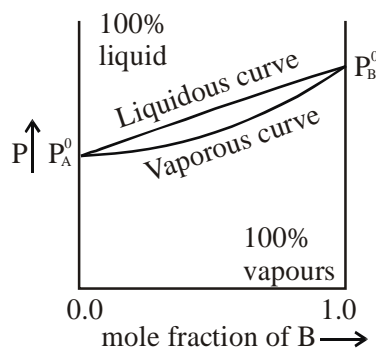
$$\frac{1}{P_T} = \frac{1}{P_A^0} + Y_B \left( \frac{1}{P_B^0} - \frac{1}{P_A^0} \right)$$

$$\frac{1}{y} = c + mx$$

So curve will be rectangular hyperbola.



III. Vapour pressure V/s composition



- (i) The V.P. of ideal solution always lie in between the V.P. of pure components.
- (ii) Below vapourous curve, the system will be 100% vapour & above liquidous and curve, 100% liquid. Both the physical states exist only in between the curves.
- (iii) At any composition, the physical state of system may be changed by changing the pressure.
- (iv) At any pressure in between  $P_A^0$  and  $P_B^0$ , the physical state of system may be changed by changing the composition.

### 6.6 Boiling point :

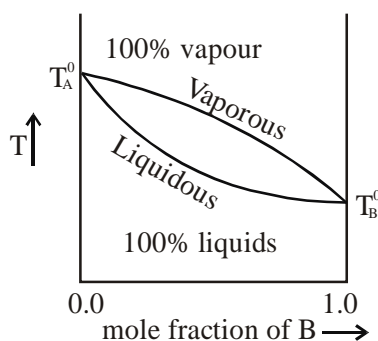
Boiling point of a liquid is the temperature at which the vapour pressure of the liquid become equal to the atmospheric pressure.

**Ex.11** Liquid 'A' and 'B' form an ideal solution. At 27°C, the vapour pressure of pure liquids 'A' and 'B' are 0.6 atm and 1.2 atm, respectively. What the composition of liquid solution boiling at 27°C?

**Sol.**  $P_T = X_A \cdot P_A^0 + X_B \cdot P_B^0$

$$\text{or } 1 = X_A \times 0.6 + (1 - X_A) \times 1.2 \Rightarrow X_A = \frac{1}{3}$$

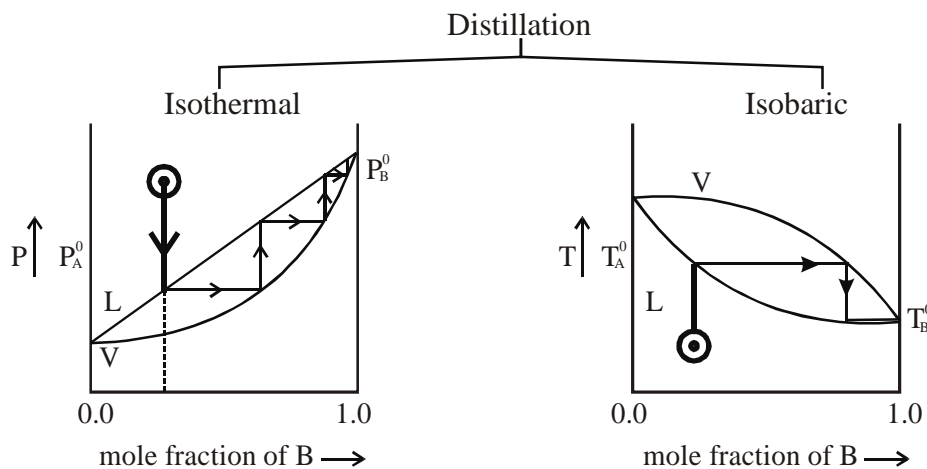
### 6.7 Boiling point curves for ideal binary solution :



- (i) The boiling point of ideal solution always lie in between the boiling points of pure liquids.
- (ii) Below liquidus curve, the system is 100% liquid and above vaporous curve, the system is 100% vapour. Both the physical states exist only in between the curves.
- (iii) At any composition, the physical state of system may be changed by changing the temperature.
- (iv) At any temperature in between  $T_A^0$  and  $T_B^0$ , the physical state of system may be changed by changing the composition.

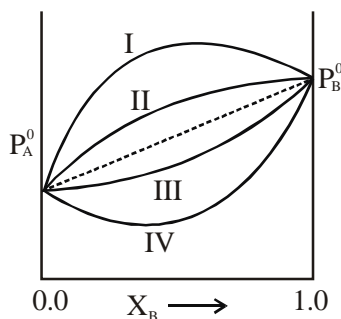
### 6.8 Distillation

It is the method of separation of liquids by converting them into vapours (boiling).



- (i) The separation of liquid by distillation occurs because at any T or P, the composition of distillate or condensate is different than the composition of original liquid.
- (ii) With the elimination of vapour above the liquid, the boiling point of residual liquid increases.
- (iii) The boiling point of distillate is less than that of original liquid.

### 6.9 Graphs for Non-ideal solutions and azeotropic mixture



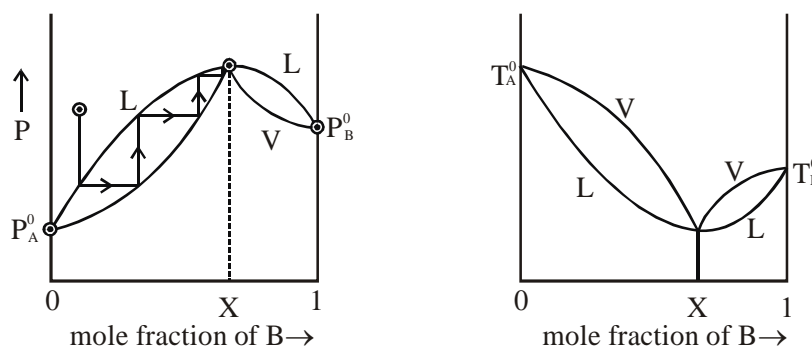
- (I) Large positive deviation :  $(V.P.)_{\text{solution}} > P_B^0$  at some composition
- (II) Small positive deviation :  $P_A^0 < (V.P.)_{\text{solution}} < P_B^0$
- (III) Small negative deviation :  $P_A^0 < (V.P.)_{\text{solution}} < P_B^0$
- (IV) Large negative deviation :  $(V.P.)_{\text{solution}} < P_A^0$  at some composition



### 6.9.1 Konowaloff's rule :

In ideal or non-ideal solution the vapour is always more rich in the component, addition of which in liquid, increase the vapour pressure of solution.

### 6.9.2 Large (+)ve deviation (Minimum boiling azeotrope)



The solution of large positive deviation can not be separated by distillation because at composition 'x', the liquid & vapour composition becomes identical.

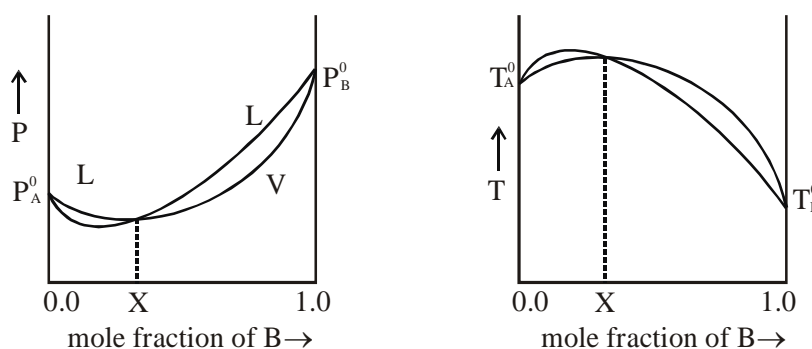
Such solution which can not be separated by distillation are called **azeotropic mixture or constant boiling solution**.

At any composition less than X, traces of pure A may be obtained but not pure B. Similarly at composition greater than X, traces of pure B may be obtained but not pure A.

Minimum boiling point Azeotropic

Mixture	% Composition of azeotrope	Boiling point (pressure = 1atm)
1. Water-Ethanol	96 Ethanol	78.15°C
2. Pyridine-Water	57.00 Pyridine	92.60°C
3. Ethanol-Benzene	32.4 Ethanol	67.80°C
4. Acetic acid-Toluene	28.0 Acetic acid	105.40°C

### 5.9.3 Large (-)ve deviation (Maximum boiling azeotrope)



## Maximum boiling point Azeotropic

Mixture	% Composition of azeotrope	Boiling point (pressure = 1atm)
1. Nitric acid-Water	68% Nitric acid	125.5°C
2. Acetic acid-Pyridine	65% Pyridine	139.0°C
3. Chloroform-Acetone	80% Chloroform	65.0°C
4. Hydrogen chloride-Water	79.8 Water	108.6°C

**Note :** Azeotrope is not formed in ideal solution or solution of small deviations.

## 7. COLLIGATIVE PROPERTIES

Properties of a solution which depends on the number of solute particles irrespective of their nature, relative to the total number of particles present in solution are called colligative properties.

The following properties are colligative properties of solution :

- (i) Relative lowering of vapour pressure.
- (ii) Elevation in boiling point.
- (iii) Depression in freezing point.
- (iv) Osmotic pressure.

### 7.1 Lowering of vapour pressure :

When a non-volatile solute 'A' is dissolved in a pure solvent 'B', the vapour pressure of the solvent is lowered i.e. the vapour pressure of a solution is always lower than that of pure solvent, because the escaping tendency of solvent molecules decreases.

If at a certain temperature  $P^{\circ}$  is the vapour pressure of pure solvent, and  $P_s$  is the vapour pressure of solution then

$$\text{Lowering of vapour pressure} = P^{\circ} - P_s$$

$$\text{Relative lowering of vapour pressure} = \frac{P^{\circ} - P_s}{P^{\circ}}$$

from equation (8)

$$\frac{P^{\circ} - P_s}{P^{\circ}} = \frac{\Delta P}{P^{\circ}} = \frac{n_A}{n_A + n_B} = X_A$$

For a very dilute solution  $n_A \ll n_B$

$$\text{so } \frac{P^{\circ} - P_s}{P^{\circ}} = \frac{n_A}{n_B} = \frac{w_A}{m_A} \times \frac{m_B}{w_B}$$

**Ex.12.** Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25 °C is 23.8 mm Hg.

**Sol.** According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{n+N} \quad \text{or} \quad \Delta p = \frac{n}{n+N} \cdot p_0$$

$$\text{Given : } n = \frac{50}{342} = 0.146 ; N = \frac{500}{18} = 27.78 \text{ and } p_0 = 23.8 \text{ mmHg}$$

Substituting the values in the above equation,

$$\Delta p = \frac{0.146}{0.146 + 27.78} \times 23.8 = 0.124 \text{ mm Hg}$$

### 7.1.1 Measurement of Lowering in Vapour Pressure by Dynamic Method

#### (Ostwald and Walker Method)

The apparatus used is shown in Fig. It consists of two sets of bulbs. The first set of three bulbs is filled with solution to half of their capacity and second set of another three bulbs is filled with the pure solvent.

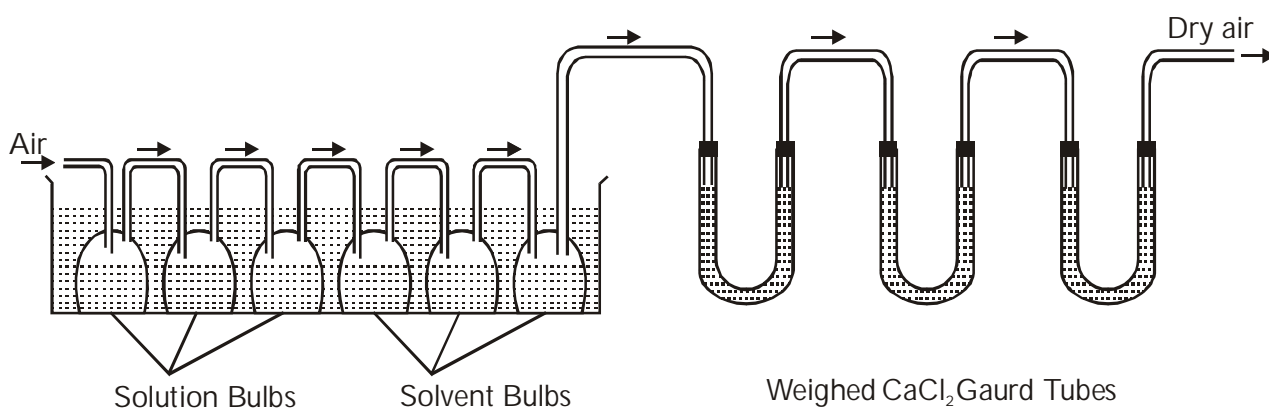


Fig. Ostwald and Walker method

Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents like  $P_2O_5$ , conc.  $H_2SO_4$  etc. The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature.

A current of pure dry air is bubbled through the series of bulbs as shown in fig. The air gets saturated with the vapour in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapours from the solvent which is proportional to the difference in the vapour pressure of the solvent and the vapour pressure of solution, i.e.,  $p_0 - p_s$ .

The two sets of bulbs are weighed again. The guard tubes are also weighed.

$$\text{Loss in mass in the solution bulbs} \propto p_s$$

$$\text{Loss in mass in the solvent bulbs} \propto (p_0 - p_s)$$

$$\text{Total loss in both sets of bulbs} \propto [p_s + (p_0 - p_s)] \propto p_0$$

Total loss in mass of both sets of bulbs is equal to gain in mass of guard tubes.

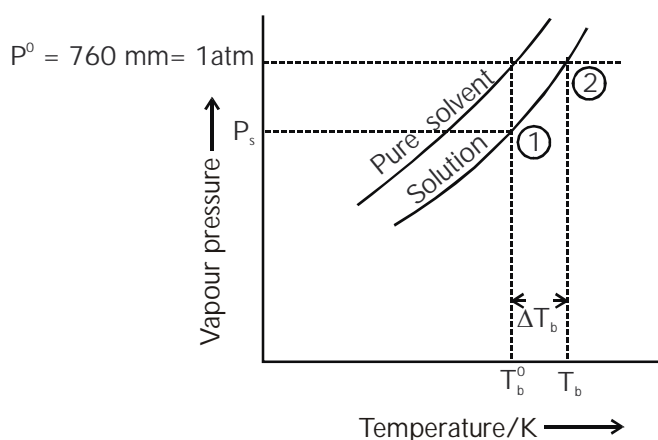
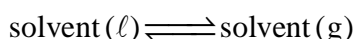
$$\text{Thus, } \frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}}$$

Further, we know from Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{w_A / m_A}{w_A / m_A + w_B / m_B}$$

$$\therefore \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of gaurd tubes}} = \frac{w_A / m_A}{w_A / m_A + w_B / m_B}$$

## 6.2 Elevation in boiling point (Ebullioscopy) :



The vapour pressure curve for solution lies below the curve for pure solvent .

$\Delta T_b$  denotes the elevation of boiling point of a solution.

When a non-volatile solute A is dissolved in a pure solvent B, its vapour pressure decreases and hence the boiling point increases. The difference  $\Delta T_b$  of boiling points of the solution and pure solvent is called elevation in boiling point.

If  $T_b^0$  is the boiling point of pure solvent and  $T_b$  is the boiling point of the solution then,  $T_b > T_b^0$

and the elevation in boiling point  $\Delta T_b = T_b - T_b^0$

Experiments have shown that for dilute solutions, the elevation of boiling point ( $\Delta T_b$ ) is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m$$

or 
$$\Delta T_b = K_b \cdot m$$

where  $K_b$  = boiling point elevation constant or molal elevation constant or ebullioscopic constant.

Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_b = \frac{RT_b^2 \cdot M}{1000 \Delta H_{\text{vap}}}$$

Where,  $R$  is molar gas constant =  $2 \text{ cal/mol-K}$ ,  $M$  = molar mass of solvent

$T_b$  is the boiling point of the pure solvent (in K)

and  $\Delta H_{\text{vap}}$  is the latent heat of vaporisation of pure solvent

$$\text{For water} \quad K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515 \text{ K-kg/mol}$$

The molal elevation constant for some common solvents are given in the following table

Solvent	B.P. ( $^{\circ}\text{C}$ )	Molal elevation constant
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.63
Carbon tetrachloride	76.8	5.03
Benzene	80.0	2.53
Ethyl alcohol	78.4	1.20

**Ex.13.** *0.15 g of a substance dissolved in 15 g of solvent boiled at a temperature higher by  $0.216^{\circ}\text{C}$  than that of the pure solvent. What is the molecular weight of the substance. [ $K_b$  for solvent =  $2.16 \text{ K-kg/mol}$ ]*

**Sol.** *Given :  $K_b = 2.16^{\circ}\text{C}$ ,  $w = 0.15 \text{ g}$ ,  $\Delta T_b = 0.216^{\circ}\text{C}$ ,  $W = 15 \text{ g}$*

$$\Delta T_b = \text{molality} \times K_b$$

$$\Delta T_b = \frac{w}{m \times W} \times 1000 \times K_b$$

$$0.216 = \frac{0.15}{m \times 15} \times 1000 \times 2.16$$

$$m = \frac{0.15 \times 1000 \times 2.16}{0.216 \times 15} = 100$$

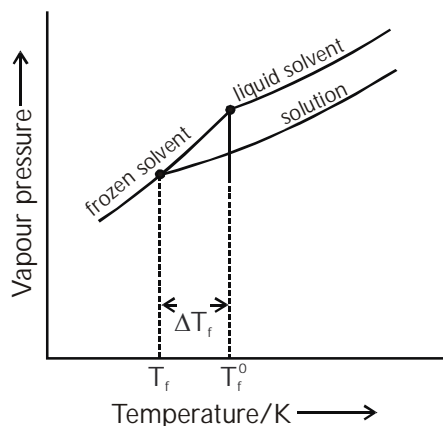
**Ex.14** *The rise in boiling point of a solution containing 1.8 g glucose in 100 g of a solvent is  $0.1^{\circ}\text{C}$ . The molal elevation constant of the liquid is :-*

**Sol.**  *$\Delta T_b = 0.1^{\circ}\text{C}$ ,  $m = 180$ ,  $W = 100$ ,  $w = 1.8$*

$$K_b = \frac{\Delta T_b \times m \times W}{1000 \times w} = \frac{180 \times 0.1 \times 100}{1000 \times 1.8} = 1.0$$

### 7.3 Depression in freezing point (Cryoscopy) :

The freezing point of a liquid is that temperature at which the liquid and its solid state exist in equilibrium with each other. It may also be defined as the temperature at which the liquid and solid states of a substance have the same vapour pressure.



When a non-volatile non-electrolyte is dissolved in a pure solvent, the vapour pressure of the solvent is lowered and it become equal to that of solid solvent at lower temperature.

If  $T_f^0$  is the freezing point of pure solvent and ( $T_f$ ) is the freezing point of its solution then,

$$T_f < T_f^0$$

The difference in the freezing point of pure solvent and solution is the depression of freezing point ( $\Delta T_f$ ) Thus,

$$T_f^0 - T_f = \Delta T_f$$

Similar to elevation in boiling point, depression in freezing point for dilute solution is directly proportional to its molality,

$$\Delta T_f \propto m$$

or 
$$\Delta T_f = K_f \cdot m$$

where  $K_f$  is called freezing point depression constant or molal depression constant or cryoscopic constant.

$K_f$  is characteristic of a particular solvent and can be calculated from the thermodynamical relationship

$$K_f = \frac{R \cdot T_f^{02} \cdot M}{1000 \cdot \Delta H_{fus}}$$

where,  $T_f^0$  is the freezing point of pure solvent in (Kelvin) and  $\Delta H_{fus}$  is the latent heat of fusion pure solvent.

For water,

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86 \text{ K}\cdot\text{kg/mol}$$

The molal depression constant for some common solvents are given in the following table

Solvent	F.P.(°C)	Molal depression solvents
Water	0.0	1.86
Ethyl alcohol	- 114.6	1.99
Chloroform	- 63.5	4.79
Carbon tetrachloride	- 22.8	31.8
Benzene	5.5	5.12
Camphor	179.0	39.70

**Ex.15.** If freezing point of a solution prepared from 1.25 g of a non electrolyte and 20 g of water is 271.9 K, the molar mass of the solute will be – ( $K_f$  of water = 1.86 K-kg/mol)

**Solution :** Given  $T_f = 271.9$  K

$$w = 1.25 \text{ g} \quad W = 20 \text{ g} \quad K_f = 1.86$$

$$\Delta T_f = T_f^0 - T_f = 273 - 271.9 = 1.1 \text{ K}$$

$$\Delta T_f = \text{molality} \times K_f$$

$$\Rightarrow \Delta T_f = \frac{w}{m \times W} \times 1000 \times K_f$$

$$\text{or } m = \frac{w \times 1000 \times K_f}{\Delta T_f \times W} = \frac{1.25 \times 1000 \times 1.86}{1.1 \times 20} = 105.68 \text{ mol/kg}$$

**Ex.16.** Molal depression constant for water is 1.86. What is freezing point of a 0.05 molal solution of a non electrolyte in water ?

( $K_f$  of water = 1.86 K-kg/mol)

**Solution :**  $\Delta T_f = \text{molality} \times K_f$

$$= 0.05 \times 1.86 = 0.093^\circ\text{C}$$

$$T_f = T_f^0 - 0.093 = 0 - 0.093$$

$$T_f = -0.093^\circ\text{C}$$

**Ex.17.** 2m aqueous urea solution is cooled to  $-7.44^\circ\text{C}$ . Calculate the mass percent of water present in solution, which will separate as ice, ( $K_f$  of water = 1.86 K-kg/mol)

**Sol.** Let the initial mass of water in the solution = 1kg

$$\therefore \text{Moles of solute} = 2$$

$$\text{Now, } \Delta T_f = K_f \cdot m = K_f \cdot \frac{n_{\text{solute}}}{\text{Kg}_{\text{solvent}}} \text{ or } 7.44 = 1.86 \times \frac{2}{\text{Kg}_{\text{solvent}}}$$

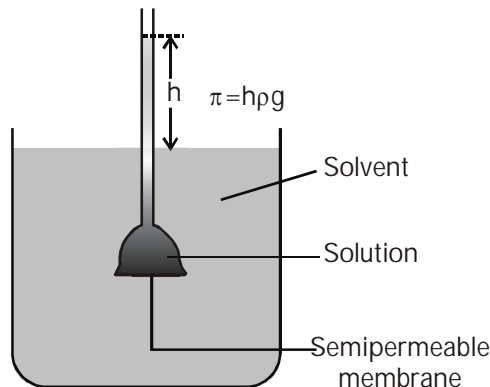
$$\therefore \text{Kg}_{\text{solvent}} \text{ left in the solution} = 0.5$$

$$\therefore \text{Mass percent of water separated as ice} = \frac{0.5}{1} \times 100 = 50\%$$

7.4 Osmosis and osmotic pressure :

7.4.1 Osmosis :

Osmosis is defined as the spontaneous flow of solvent molecules through semipermeable membrane from a pure solvent to solution.



Level of solution rises in the funnel due to osmosis of solvent

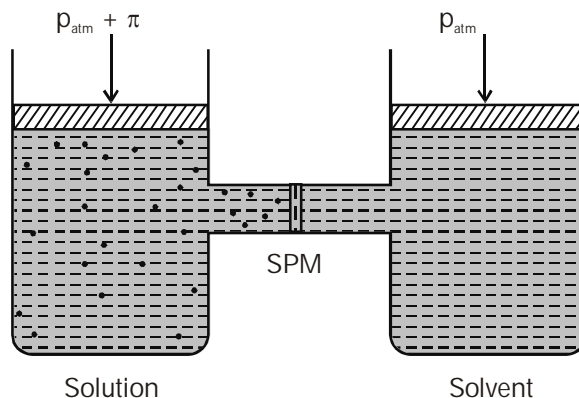
7.4.2 Semi-permeable membrane (SPM) :

There are the membranes (substances) which allow selective movement of particles across them. For a solution of solid solute in a liquid solvent, ideal SPM allow free movement of solvent particles across it, but not solute particles. These membranes contain a network of submicroscopic holes or pores through which small solvent molecules may pass but not the bigger solute particle.

7.4.3 Osmotic pressure ( $\pi$ ) : It is the pressure which should be applied on the solution to just prevent osmosis or The hydrostatic pressure built up on the solution which just stops the osmosis.

osmotic pressure = hydrostatic pressure

$$\pi = \rho gh$$



The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis



#### 7.4.4 Van't Hoff laws :

(i) The osmotic pressure ( $\pi$ ) of a solution is directly proportional to its molar concentration ( $C$ ), when the temperature is kept constant. (Van't Hoff-Boyle's law)

thus  $\pi \propto C$  (when temperature is constant)

(ii) Concentration remaining same, the osmotic pressure of a dilute solution is directly proportional to its absolute temperature ( $T$ ). (Van't Hoff-Charle's law)

$\pi \propto T$  (when  $C$  is constant)

Combining the two laws, i.e., when concentration and temperature both are changing, the osmotic pressure will be given by :

$\pi \propto C.T$  or  $\pi = CRT$

Where  $R$  = Universal gas constant.

#### 7.4.5 Isotonic or iso-osmotic solution :

Solutions which have the same osmotic pressures at a given temperature are called isotonic or iso-osmotic solutions

When isotonic solutions are separated by semipermeable membrane, no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously. On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called **hypertonic**. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be **hypotonic**. In this case, water will flow into the cells if placed in this solution and they would swell.

**Ex.18.** A cane sugar solution has an osmotic pressure of 2.46 atm at 300 K. What is the strength of the solution.

**Sol.**  $\pi = CRT$  or  $C = \frac{\pi}{RT} = \frac{2.46}{300 \times 0.0821} = 0.1 \text{ M}$

**Ex.19** A solution containing 8.6 g urea in one litre was found to be isotonic with 0.5% (wt./vol.) solution of an organic, non-volatile solution. The molecular weight of latter is

**Sol.** Solutions are isotonic

so  $\pi_1 = \pi_2$

$\frac{n_1}{V_1} RT = \frac{n_2}{V_2} RT$  { $R$  &  $T$  are constant}

so,  $\frac{n_1}{V_1} = \frac{n_2}{V_2}$

or  $\left( \frac{w_1}{m_1 \times v_1} \right)_{\text{urea}} = \left( \frac{w_2}{m_2 \times v_2} \right)_{\text{organic}}$

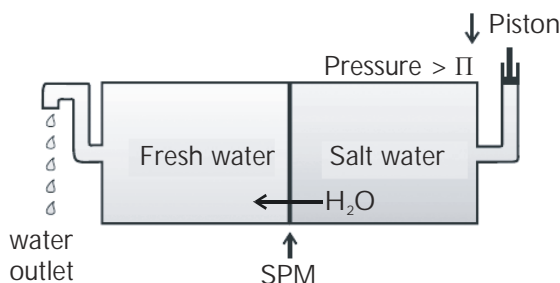
or  $\frac{8.6}{60 \times 1000} = \frac{0.5}{m_2 \times 100}$

$m_2 = 34.89 \text{ gm/mol}$

### 7.5 Reverse Osmosis and water purification :

If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis.

Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.



Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

### 8 Abnormal colligative properties :

It has been observed that difference in the observed and calculated molecular masses of solute is due to association or dissociation of solute molecules in solution. It results in a change in the number of particles in solution.

Van't Hoff in 1880, introduced a factor, called Van't Hoff factor (*i*). The factor '*i*' is defined as

$$i = \frac{\text{observed colligative property}}{\text{Calculated colligative property}} = \frac{\text{Normal molecular mass}}{\text{observed molecular mass.}}$$

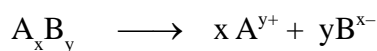
$$= \frac{\text{total number of particles after dissociation / association}}{\text{Number of particles initially taken}}$$

In case of association of solute particles in solution, the observed molecular weight of solute being more than the normal, the value of factor '*i*' is less than unity (i.e.  $i < 1$ ), while for dissociation the value of *i* is greater than unity (i.e.  $i > 1$ ), because the observed molecular weight has lesser value than normal molecular weight.

Values of van't Hoff factor, *i*, at Various Concentrations for NaCl, KCl, MgSO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>

Salt	*Values of <i>i</i>			Van't Hoff factor <i>i</i> for complete dissociation of solute
	0.1 m	0.1 m	0.001 m	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
MgSO <sub>4</sub>	1.21	1.53	1.82	2.00
K <sub>2</sub> SO <sub>4</sub>	2.32	2.70	2.84	3.00

## 8.1 Calculation of 'i' in case of dissociation



Initial mol            1                    0            0

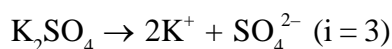
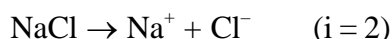
after dissociation     $1 - \alpha$                      $x\alpha$              $y\alpha$

Total no. of solute particles =  $1 - \alpha + x\alpha + y\alpha = 1 - \alpha + \alpha(x + y)$

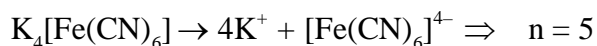
or  $i = 1 - \alpha + n\alpha$  [where  $x + y = n$  (total ions.)]

or  $i = 1 + \alpha(n - 1)$

For strong electrolytes :  $\alpha = 1$  or 100%, so  $i = n$  (total no. of ions)



For complex compound



S. No.	Solute type	Example	Ionisation	No. of particles in the solution from 1 mole solute (n)	van't Hoff factor ('i')	Abnormal molecular mass
1.	Non-electrolyte	Urea, sucrose, glucose, fructose	—	1	1	$m_{\text{normal}}$
2.	Binary electrolyte AB type	NaCl, KCl, HCl CH <sub>3</sub> COOH NH <sub>4</sub> OH, NaOH etc.	$AB \rightleftharpoons A^+ + B^-$ $1 - \alpha \quad \alpha \quad \alpha$	2	$1 + \alpha$	$\frac{m_{\text{normal}}}{1 + \alpha}$
3.	Ternary electrolyte AB <sub>2</sub> type or A <sub>2</sub> B type	CaCl <sub>2</sub> , BaCl <sub>2</sub> H <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> [PtCl <sub>6</sub> ]	$AB_2 \rightleftharpoons A^{2+} + 2B^-$ $1 - \alpha \quad \alpha \quad 2\alpha$ $A_2B \rightleftharpoons 2A^+ + B^-$ $1 - \alpha \quad 2\alpha \quad \alpha$	3 3	$1 + 2\alpha$ $1 + 2\alpha$	$\frac{m_{\text{normal}}}{1 + 2\alpha}$ $\frac{m_{\text{normal}}}{1 + 2\alpha}$
4.	Quaternary electrolyte AB <sub>3</sub> or A <sub>3</sub> B type	AlCl <sub>3</sub> , K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	$AB_3 \rightleftharpoons A^{3+} + 3B^-$ $1 - \alpha \quad \alpha \quad 3\alpha$ $A_3B \rightleftharpoons 3A^+ + B^{3-}$ $1 - \alpha \quad 3\alpha \quad \alpha$	4 4	$1 + 3\alpha$ $1 + 3\alpha$	$\frac{m_{\text{normal}}}{1 + 3\alpha}$ $\frac{m_{\text{normal}}}{1 + 3\alpha}$
5.	General electrolyte AB <sub>n-1</sub>	One mole of solute giving 'n' ions in the solution	$AB_{n-1} \rightleftharpoons A^{+(n-1)} + (n-1)B^-$ $1 - \alpha \quad \alpha \quad (n-1)\alpha$	n	$1 + (n-1)\alpha$	$\frac{m_{\text{normal}}}{[1 + (n-1)\alpha]}$

8.2 Calculation of 'i' in case of association

$$\begin{array}{ccc}
 nA & \longrightarrow & (A)_n \\
 \text{Initial mol} & & 1 \qquad 0 \\
 \text{after dissociation} & & 1 - \alpha \qquad \alpha/n \\
 \\ 
 & & i = \frac{1 - \alpha + \frac{\alpha}{n}}{n}, \quad \alpha = \text{degree of association} \\
 & & i = 1 + \alpha \left( \frac{1}{n} - 1 \right)
 \end{array}$$

**Ex.20.** Determine the amount of  $\text{CaCl}_2$  ( $i = 2.47$ ) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at  $27^\circ\text{C}$ .

**Sol.** We know that,

$$\pi = i \frac{n}{V} RT \Rightarrow \pi = i \frac{w}{MV} RT \Rightarrow w = \frac{\pi MV}{iRT} = \frac{0.75 \times 111 \times 2.5}{2.47 \times 0.0821 \times 300} = 3.42 \text{ g}$$

Hence, the required amount of  $\text{CaCl}_2$  is 3.42 g.

**Ex.21** 19.5 g of  $\text{CH}_2\text{FCOOH}$  is dissolved in 500 g of water. The depression in the freezing point of water observed is  $1.0^\circ\text{C}$ . Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

**Sol.** It is given that :

$$w_1 = 500 \text{ g}$$

$$w_2 = 19.5 \text{ g}$$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

$$\Delta T_f = 1 \text{ K}$$

We know that :

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1} = \frac{1.86 \text{ K kg mol}^{-1} \times 19.5 \text{ g} \times 1000 \text{ g kg}^{-1}}{500 \text{ g} \times 1 \text{ K}} = 72.54 \text{ mol}^{-1}$$

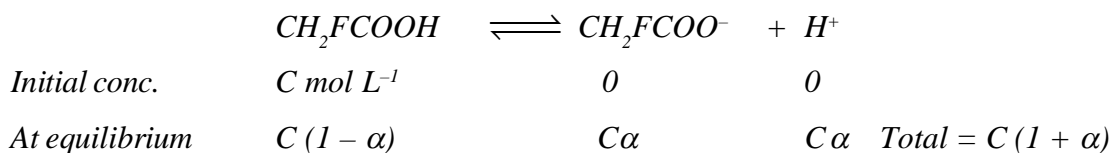
Therefore, observed molar mass of  $\text{CH}_2\text{FCOOH}$ ,  $(M_2)_{\text{obs}} = 72.54 \text{ mol}$

The calculated molar mass of  $\text{CH}_2\text{FCOOH}$  is :

$$(M_2)_{\text{cal}} = 14 + 19 + 12 + 16 + 16 + 1 = 78 \text{ g mol}^{-1}$$

$$\text{Therefore, van't Hoff factor, } i = \frac{(M_2)_{\text{cal}}}{(M_2)_{\text{obs}}} = \frac{78 \text{ g mol}^{-1}}{72.54 \text{ g mol}^{-1}} = 1.0753$$

Let  $\alpha$  be the degree of dissociation of  $\text{CH}_2\text{FCOOH}$



$$\therefore i = \frac{C(1+\alpha)}{C}$$

$$\Rightarrow i = 1 + \alpha \Rightarrow \alpha = i - 1$$

$$= 1.0753 - 1 = 0.0753$$

Now, the value of  $K_a$  is given as :

$$K_a = \frac{[\text{CH}_2\text{FCOO}^-][\text{H}^+]}{[\text{CH}_2\text{FCOOH}]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Taking the volume of the solution as 500 mL. We have the concentration : 19.5 M

$$C = \frac{78}{500} \times 1000 \text{ M} = 0.5 \text{ M}$$

$$\text{Therefore, } K_a = \frac{C\alpha^2}{1-\alpha}$$

$$= \frac{0.5 \times (0.0753)^2}{1 - 0.0753} = \frac{0.5 \times 0.00567}{0.9247} = 0.00307 \text{ (approximately)} = 3.07 \times 10^{-3}$$

MISCELLANEOUS PREVIOUS YEAR QUESTIONS

1. To 500 cm<sup>3</sup> of water, 3×10<sup>-3</sup> kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point ? K<sub>f</sub> and density of water are 1.86 K kg<sup>-1</sup> mol<sup>-1</sup> and 0.997 g cm<sup>-3</sup> respectively. [JEE 2000]

Ans. 0.23 K

2. Match the boiling point with K<sub>b</sub> for x, y and z, if molecular weight of x, y and z are same. [JEE 2003]

	b.pt.	K <sub>b</sub>
x	100	0.68
y	27	0.53
z	253	0.98

Ans. K<sub>b</sub>(x) = 0.68, K<sub>b</sub>(y) = 0.53, K<sub>b</sub>(z) = 0.98

3. During depression of freezing point in a solution, the following are in equilibrium [JEE 2003]

- (A) liquid solvent-solid solvent (B) liquid solvent-solid solute  
(C) liquid solute-solid solute (D) liquid solute-solid solvent

Ans. (A)

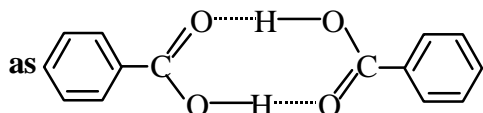
Sol. Equilibrium exists between liquid solvent & solid solvent.

4. 1.22 g of benzoic acid is dissolved in (i) 100 g acetone (K<sub>b</sub> for acetone = 1.7) and (ii) 100 g benzene (K<sub>b</sub> for benzene = 2.6). The elevation in boiling points T<sub>b</sub> is 0.17°C and 0.13°C respectively.

- (a) What are the molecular weights of benzoic acid in both the solutions?  
(b) What do you deduce out of it in terms of structure of benzoic acid?

[JEE 2004]

Ans. (a) 122, (b) It means that benzoic acid remains as it is in acetone while it dimerises in benzene



Sol. (a)

(i)  $\Delta T_b = i K_b \cdot m$

$$0.17 = i \times 1.7 \times \frac{1.22/122}{0.1}$$

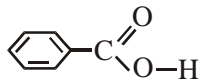
$$i = 1 = \frac{(\text{mol wt})_{\text{Th}}}{(\text{mol wt})_{\text{Acet}}}$$

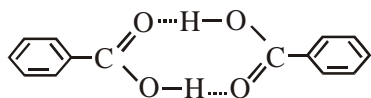
$$(\text{mol wt})_{\text{Acet}} = \frac{122}{1} \text{ gm/mol}$$

(ii)  $\Delta T_b = i \times K_b \cdot m$

$$0.13 = i \times 2.6 \times \frac{1.22/122}{0.1}$$

$$i = 0.5 = \frac{(\text{mol wt})_{\text{Th}}}{(\text{mol wt})_{\text{Acet}}} \Rightarrow (\text{mol wt})_{\text{Acet}} = \frac{122}{0.5} = 244 \text{ gm/mol}$$

- (b) In Acetone its normal i.e.   
but in benzene it is in dimeric form



5. A 0.004 M solution of  $\text{Na}_2\text{SO}_4$  is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of  $\text{Na}_2\text{SO}_4$  is  
(A) 25% (B) 50% (C) 75% (D) 85% [JEE 2004]

Ans. (C)

Sol.  $\pi_{\text{Na}_2\text{SO}_4} = \pi_{\text{glucose}}$

$$i \times 0.004 = 0.010$$

$$i = 2.5 = 1 + 2\alpha \Rightarrow \alpha = 0.75 \text{ or } 75\%$$

6. The elevation in boiling point, when 13.44 g of freshly prepared  $\text{CuCl}_2$  are added to one kilogram of water, is [Some useful data,  $K_b(\text{H}_2\text{O}) = 0.52 \text{ kg K mol}^{-1}$ , mol. wt. of  $\text{CuCl}_2 = 134.4 \text{ gm}$ ]  
(A) 0.05 (B) 0.1 (C) 0.16 (D) 0.21 [JEE 2005]

Ans.(C)

Sol.  $\Delta T_b = i K_b \cdot m$

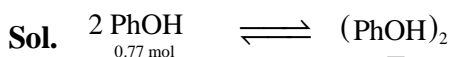
$$= 3 \times 0.52 \times \frac{13.44/134.4}{1}$$

$$= 0.156 \text{ K}$$

$$\approx 0.16 \text{ K}$$

7. 72.5 g of phenol is dissolved in 1 kg of a solvent ( $k_f = 14$ ) which leads to dimerization of phenol and freezing point is lowered by 7 kelvin. What percent of total phenol is present in dimeric form? [JEE 2006]

Ans. 35% (degree of asso = 70%)



$$0.77(1-\alpha) \quad 0.77 \alpha / 2$$

$$i = 1 - \alpha / 2$$

$$\Delta T_f = i K_f \cdot m$$

$$7 = (1 - \alpha) \times 14 \times \frac{72.5/94}{1}$$

$$0.649 = 1 - \alpha / 2$$

$$\alpha / 2 = 0.35$$

$$\alpha = 0.70$$

% of phenol in dimeric form

$$= \frac{0.77 \alpha / 2}{0.77} \times 100 = \frac{\alpha}{2} \times 100 = 35\%$$

8. When 20 g of naphtholic acid ( $C_{11}H_8O_2$ ) is dissolved in 50 g of benzene ( $K_f = 1.72 \text{ K kg mol}^{-1}$ ), a freezing point depression of 2 K is observed. The van't Hoff factor ( $i$ ) is [JEE 2007]  
 (A) 0.5 (B) 1 (C) 2 (D) 3

Ans. (A)

Sol.  $\Delta T_f = i K_f \cdot \frac{n}{W/1000}$   
 $2 = i \times 1.72 \times \frac{20/172}{50/1000}$   
 $i = 0.5$

**Paragraph for Question No. Q.9 to Q.11**

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution **M** is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

- Given :
- Freezing point depression constant of water ( $K_f^{\text{water}}$ ) = 1.86 K kg mol<sup>-1</sup>
  - Freezing point depression constant of ethanol ( $K_f^{\text{ethanol}}$ ) = 2.0 K kg mol<sup>-1</sup>
  - Boiling point elevation constant of water ( $K_b^{\text{water}}$ ) = 0.52 K kg mol<sup>-1</sup>
  - Boiling point elevation constant of ethanol ( $K_b^{\text{ethanol}}$ ) = 1.2 K kg mol<sup>-1</sup>
  - Standard freezing point of water = 273 K
  - Standard freezing point of ethanol = 155.7 K
  - Standard boiling point of water = 373 K
  - Standard boiling point of ethanol = 351.5 K
  - Vapour pressure of pure water = 32.8 mm Hg
  - Vapour pressure of pure ethanol = 40 mm Hg
  - Molecular weight of water = 18 g mol<sup>-1</sup>
  - Molecular weight of ethanol = 46 g mol<sup>-1</sup>

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

9. The freezing point of the solution **M** is [JEE 2008]  
 (A) 268.7 K (B) 268.5 K (C) 234.2 K (D) 150.9 K

Ans. (D)

$$\begin{aligned} (T_f')_{\text{Alc.sol}^n} &= (T_f)_{\text{EtOH}} - (K_f)_{\text{etoh}} \cdot m \\ &= 155.7 - 2 \times \frac{0.1}{0.9 \times 46/1000} \\ &= 155.7 - 2 \times 2.415 \\ &= 150.9 \text{ K} \end{aligned}$$



10. The vapour pressure of the solution **M** is

[JEE 2008]

- (A) 39.3 mm Hg      (B) 36.0 mm Hg      (C) 29.5 mm Hg      (D) 28.8 mm Hg

Ans. (B)

$$\begin{aligned}\text{Sol. } P^s &= (P^\circ)_{\text{solvent}} \cdot X_{\text{solvent}} \\ &= 40 \times 0.9 \\ &= 36.0 \text{ mm Hg}\end{aligned}$$

11. Water is added to the solution **M** such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is

[JEE 2008]

- (A) 380.4 K      (B) 376.2 K      (C) 375.5 K      (D) 354.7 K

Ans. (B)

$$\begin{aligned}\text{Sol. } (T_b')_{\text{Aqsol}^n} &= (T_b)_{\text{solventH}_2\text{O}} + K_b \cdot m \\ &= 373 + 0.52 \times \frac{0.1}{0.9 \times 18/1000} \\ &= 373 + 0.52 \times 6.173 \\ &= 376.2 \text{ K}\end{aligned}$$

12. The Henry's law constant for the solubility of  $\text{N}_2$  gas in water at 298 K is  $1.0 \times 10^5$  atm. The mole fraction of  $\text{N}_2$  in air is 0.8. The number of moles of  $\text{N}_2$  from air dissolved in 10 moles of water at 298 K and 5 atm pressure is-

[JEE 2009]

- (A)  $4.0 \times 10^{-4}$       (B)  $4.0 \times 10^{-5}$       (C)  $5.0 \times 10^{-4}$       (D)  $4.0 \times 10^{-5}$

Ans. (A)

$$\text{Sol. } P_{\text{N}_2} = K_H X_{\text{N}_2}$$

$$Y_{\text{N}_2} \cdot P_T = K_H \times N_2$$

$$0.8 \times 5 = 1 \times 10^5 \times \frac{n}{n+10}$$

$$4 = 10^5 \times \frac{n}{10}$$

$$n = 4 \times 10^{-4}$$

## EXERCISE # S-I

*(Raoult's law)*

- At 25°C, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of CH<sub>3</sub>OH in a solution in which the (partial) vapor pressure of CH<sub>3</sub>OH is 24.0 torr at 25°C?  
**LS0001**
- The vapour pressure of ethanol and methanol are 44.0 mm and 88.0 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 69 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.  
**LS0002**
- Liquide 'A' and 'B' form an ideal solution. The vapour pressure of solution containing equal moles of both liquids is 80 cm Hg. At the same temperature, the vapour pressure of solution containing 25 mole percent of liquid 'A' is 70 cm Hg. Calculate  $P_A^0$  and  $P_B^0$ .  
**LS0003**
- Liquids 'A' and 'B' form an ideal solution. Calculate the mole-fraction of 'A' in the vapours above the liquid solution containing the liquids 'A' and 'B' in 2 : 3 mole ratio, at equilibrium.  
[Given :  $P_A^0 = 0.4 \text{ atm}$ ,  $P_B^0 = 0.8 \text{ atm}$ ]  
**LS0004**
- Liquids 'P' and 'Q' form an ideal solution. At equilibrium, the vapours contain 40% molecules of 'P'. Calculate the vapour pressure of solution.  
[Given :  $P_P^0 = 0.4 \text{ bar}$ ,  $P_Q^0 = 0.6 \text{ bar}$ ]  
**LS0005**
- Liquids 'X' and 'Y' form an ideal solution. The vapour pressure of solution may be expressed as :  $P[\text{cmHg}] = (80 - 25x)$ , where 'x' is the mole-fraction of liquid 'X' in the liquid solution at equilibrium. Calculate the vapour pressures of pure liquids 'X' and 'Y'.  
**LS0006**
- Liquid 'R' and 'S' form an ideal solution. The mole-fraction of 'R' in liquid and vapour phases at equilibrium are 0.25 and 0.40, respectively. If the vapour pressure of solution is 0.50 bar, calculate  $P_R^0$  and  $P_S^0$ .  
**LS0007**

*Colligative properties*

- The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?  
**LS0008**
- Calculate the relative lowering in vapour pressure if 100 g of a nonvolatile solute (mol. wt. 100) are dissolved in 432 g water.  
**LS0009**
- The vapour pressure of pure benzene at 30° C is 640 mm of Hg and the vapour pressure of a solution of a solute in C<sub>6</sub>H<sub>6</sub> at the same temperature is 624 mm of Hg. Calculate molality of solution.  
**LS0010**

11. The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A nonvolatile nonelectrolyte solid weighing 2.175 g is added to 39.0 of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance?  
**LS0011**
12. The vapour pressure of water is 17.54 mm Hg at 293 K. Calculate vapour pressure of 0.5 molal solution of a solute in it.  
**LS0012**
13. When 10.5 g of a nonvolatile substance is dissolved in 742 g of ether, its boiling point is raised 0.25°C. What is the molecular weight of the substance? Molal boiling point constant for ether is 2.12°C·kg/mol.  
**LS0013**
14. Calculate the molal elevation constant,  $K_b$  for water and the boiling point of 0.1 molal urea solution. Latent heat of vaporisation of water is 9.72 kcal mol<sup>-1</sup> at 373.15 K. [(373.15)<sup>2</sup> = 258 × 540]  
**LS0014**
15. Pure benzene freeze at 5.45°C. A solution containing 6.72 g of C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> in 120 g of benzene was observed to freeze at 3.75°C. What is the molal freezing point constant of benzene?  
**LS0015**
16. The freezing point of a solution containing 2.40 g of a compound in 60.0 g of benzene is 0.10°C lower than that of pure benzene. What is the molecular weight of the compound? ( $K_f$  is 5.12°C/m for benzene)  
**LS0016**
17. Normal boiling point of diethyl ether is 327° and at 190 mmHg boiling points in 27°C. What is the value of  $\Delta H_{\text{vap}}^\circ$  in kJ/mole.  
(Use : R = 8.3 J/K-mole, ln2 = 0.7)  
**LS0017**
18. A 6.84% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.8% (w/v) solution of non-volatile solute. Find molecular weight of solute.  
**LS0018**
19. Calculate the osmotic pressure of 12% (w/v) aq. urea solution at 27°C.  
**LS0019**
20. Calculate the osmotic pressure of a solution containing 18 gm glucose and 17.1 gm canesugar (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) per litre, at 27°C.  
**LS0020**
21. A storage battery contains a solution of H<sub>2</sub>SO<sub>4</sub> 38% by weight. What will be the Van't Hoff factor if the  $\Delta T_{f(\text{experiment})}$  is 22.8K. [Given  $K_f = 1.86 \text{ mol}^{-1} \text{ Kg}$ ]  
**LS0021**

22. A certain mass of a substance, when dissolved in 100 g  $C_6H_6$ , lowers the freezing point by  $1.28^\circ C$ . The same mass of solute dissolved in 100g water lowers the freezing point by  $1.40^\circ C$ . If the substance has normal molecular weight in benzene and is completely ionized in water, into how many ions does it dissociate in water?  $K_f$  for  $H_2O$  and  $C_6H_6$  are 1.86 and  $5.12 K kg mol^{-1}$ .

LS0022

23. 2.0 g of benzoic acid dissolved in 25.0g of benzene shows a depression in freezing point equal to  $1.96 K$ . Molal depression constant ( $K_f$ ) of benzene is  $4.9 K.kg.mol^{-1}$ . What is the percentage association of the acid?

LS0023

24. A decimolar solution of potassium ferrocyanide is 50% (w/v) dissociated at 300K. Calculate the osmotic pressure of the solution. ( $R=8.314 JK^{-1} mol^{-1}$ )

LS0024

25. A 1.2% solution (w/v) of NaCl is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl.

LS0025

#### Henry's law

26. How many gm  $O_2$  gas will dissolve in 100 gm water at 9 bar and  $27^\circ C$ ? ( $K_H = 40 Kbar$ )

LS0026

27. The Henry law constant for dissolution of a gas in aqueous medium is  $3 \times 10^2 atm$ . At what partial pressure of the gas (in atm), the molality of gas in aqueous solution will be  $\frac{5}{9} m$ .

LS0027

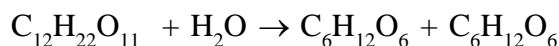
## EXERCISE # S-II

- At  $90^{\circ}\text{C}$ , the vapour pressure of toluene is 400 torr and that of  $\sigma$ -xylene is 150 torr. What is the composition of the liquid mixture that boils at  $90^{\circ}\text{C}$ , when the pressure is 0.50 atm? What is the composition of vapour produced?  
**LS0028**
- The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calculate molality and mole fraction of solute.  
**LS0029**
- Calculate the amount of ice that will separate out of cooling a solution containing 50g of ethylene glycol in 200 g water to  $-9.3^{\circ}\text{C}$ . ( $K_f$  for water =  $1.86 \text{ K mol}^{-1} \text{ kg}$ )  
**LS0030**
- A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in  $125 \text{ cm}^3$  of an aqueous medium. At  $4^{\circ}\text{C}$  an osmotic pressure rise of 2.77 mm of the solution was observed. The solution had a density of  $1.013 \text{ g/cm}^3$ . Determine the molecular weight of the protein. ( $g = 10 \text{ m/s}^2$ ), ( $R = 0.08 \text{ l-atm/K-mol}$ )  
**LS0031**
- The vapour pressure of an aqueous solution is found to be 750 torr at certain temperature 'T'. If 'T' is the temperature at which pure water boils under atmospheric pressure, calculate the atmospheric pressure. The boiling point of solution is  $101.04^{\circ}\text{C}$ . ( $K_b = 0.52 \text{ K kg mol}^{-1}$ ).  
**LS0032**
- How many grams of sucrose (mol.wt. = 342) should be dissolved in 100 gm water in order to produce a solution with  $105^{\circ}\text{C}$  difference between the freezing point & boiling point temperature at 1 atm? (Unit:  $K_f = 2 \text{ K.kg mol}^{-1}$ ;  $k_b = 0.5 \text{ K.kg mol}^{-1}$ )  
**LS0033**
- An aqueous solution containing 288 gm of a non-volatile compound having the stoichiometric composition  $\text{C}_x\text{H}_{2x}\text{O}_x$  in 90 gm water boils at  $101.38^{\circ}\text{C}$  at 1.00 atmospheric pressure. What is the molecular formula?  $K_b(\text{H}_2\text{O}) = 0.52 \text{ K mol}^{-1} \text{ kg}$   
**LS0034**
- A complex is represented as  $\text{CoCl}_3 \cdot x\text{NH}_3$ . It's 0.1 molal solution in a solution shows  $\Delta T_f = 0.558^{\circ}\text{C}$ .  $K_f$  for  $\text{H}_2\text{O}$  is  $1.86 \text{ K mol}^{-1} \text{ kg}$ . Assuming 100% ionisation of complex and coordination no. of Co is six, calculate formula of complex.  
**LS0035**
- Phenol associates in benzene to a certain extent to form a dimer. A solution containing  $18.8 \times 10^{-3} \text{ kg}$  phenol in 1 kg of benzene has its freezing point depressed by 0.768 K. Calculate the fraction of phenol that has dimerised.  $K_f$  for benzene =  $5.12 \text{ kg mol}^{-1} \text{ K}$ .  
**LS0036**
- The molar volume of liquid benzene (density =  $0.877 \text{ g ml}^{-1}$ ) increases by a factor of 2750 as it vaporizes at  $20^{\circ}\text{C}$  and that of liquid toluene (density =  $0.867 \text{ gml}^{-1}$ ) increases by a factor of 7720 at  $20^{\circ}\text{C}$ . A Solution of benzene & toluene has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.  
**LS0037**

11. The cryoscopic constant for acetic acid is  $3.6 \text{ K kg/mol}$ . A solution of  $1 \text{ g}$  of a hydrocarbon in  $100 \text{ g}$  of acetic acid freezes at  $16.14^\circ\text{C}$  instead of the usual  $16.60^\circ\text{C}$ . The hydrocarbon contains  $92.3\%$  carbon. What is the molecular formula?

LS0038

12. Cane sugar undergoes the inversion as follow



If solution of  $0.025$  moles of sugar in  $200 \text{ gm}$  of water show depression in freezing point  $0.372^\circ\text{C}$ , then what % sucrose has inverted. ( $K_f(\text{H}_2\text{O}) = 1.86 \text{ K kg mol}^{-1}$ )

LS0039

13. When  $0.1 \text{ M Pb}(\text{NO}_3)_2$  solution is titrated with  $0.1 \text{ M KI}$  solution then what will be the osmotic pressure (in atm) of solution when equivalence point is reached at  $300 \text{ K}$ .

(Take :  $R = 0.08 \text{ atm L/mol-k}$ )

LS0040

14. Using the following information determine the boiling point of a mixture contains  $1560 \text{ gm}$  benzene and  $1125 \text{ gm}$  chlorobenzene, when the external pressure is  $1000 \text{ torr}$ . Assume the solution is ideal.

Temperature ( $0^\circ\text{C}$ )	Vapour pressure of benzene(torr)	Vapour pressure of chlorobenzene(torr)
80	750	120
90	1000	200
100	1350	300
110	1800	400
120	2200	540

LS0041

## EXERCISE # O-I

## Single correct :

1. The boiling point of  $C_6H_6$ ,  $CH_3OH$ ,  $C_6H_5NH_2$  and  $C_6H_5NO_2$  are  $80^\circ C$ ,  $65^\circ C$ ,  $184^\circ C$  and  $212^\circ C$  respectively which will show highest vapour pressure at room temperature :  
 (A)  $C_6H_6$  (B)  $CH_3OH$  (C)  $C_6H_5NH_2$  (D)  $C_6H_5NO_2$  **LS0042**
2. Mole fraction of A vapours above the solution in mixture of A and B ( $X_A = 0.4$ ) will be  
 [Given :  $P_A^\circ = 100$  mm Hg and  $P_B^\circ = 200$  mm Hg]  
 (A) 0.4 (B) 0.8 (C) 0.25 (D) none of these **LS0043**
3. At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by  

$$P_{\text{Total}} = 120 - 75 X_B$$
 hence, vapour pressure of pure A and B respectively (in Torr) are  
 (A) 120, 75 (B) 120, 195 (C) 120, 45 (D) 75, 45 **LS0044**
4. Two liquids A & B form an ideal solution. What is the vapour pressure of solution containing 2 moles of A and 3 moles of B at 300 K? [Given : At 300 K, Vapour pr. of pure liquid A ( $P_A^\circ$ ) = 100 torr, Vapour pr. of pure liquid B ( $P_B^\circ$ ) = 300 torr ]  
 (A) 200 torr (B) 140 torr (C) 180 torr (D) None of these **LS0045**
5. If Raoult's law is obeyed, the vapour pressure of the solvent in a solution is directly proportional to  
 (A) Mole fraction of the solvent (B) Mole fraction of the solute  
 (C) Mole fraction of the solvent and solute (D) The volume of the solution **LS0046**
6. 1 mole of heptane (V. P. = 92 mm of Hg) was mixed with 4 moles of octane (V. P. = 31 mm of Hg). The vapour pressure of resulting ideal solution is :  
 (A) 46.2 mm of Hg (B) 40.0 mm of Hg (C) 43.2 mm of Hg (D) 38.4 mm of Hg **LS0047**
7. Mole fraction of A vapours above solution in mixture of A and B ( $X_A = 0.4$ ) will be :-  
 ( $P_A^\circ = 100$  mm,  $P_B^\circ = 200$  mm)  
 (A) 0.4 (B) 0.8 (C) 0.25 (D) None **LS0048**
8. The vapour pressure of a pure liquid 'A' is 70 torr at  $27^\circ C$ . It forms an ideal solution with another liquid B. The mole fraction of B is 0.2 and total vapour pressure of the solution is 84 torr at  $27^\circ C$ . The vapour pressure of pure liquid B at  $27^\circ C$  is  
 (A) 14 (B) 56 (C) 140 (D) 70 **LS0049**

9. At 88 °C benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will boil at 88 °C at 1 atm. pressure, benzene - toluene form an ideal solution:

(A) 0.416 (B) 0.588 (C) 0.688 (D) 0.740

LS0050

10. The exact mathematical expression of Raoult's law is ( $n$  = moles of solute ;  $N$  = moles of solvent)

(A)  $\frac{P^0 - P_s}{P^0} = \frac{n}{N}$  (B)  $\frac{P^0 - P_s}{P^0} = \frac{N}{n}$  (C)  $\frac{P^0 - P_s}{P_s} = \frac{n}{N}$  (D)  $\frac{P^0 - P_s}{P^0} = n \times N$

LS0051

11. The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg

(A) 0.2 (B) 0.4 (C) 0.6 (D) 0.8

LS0052

12. The vapour pressure of a solution having solid as solute and liquid as solvent is :

(A) Directly proportional to mole fraction of the solvent  
 (B) Inversely proportional to mole fraction of the solvent  
 (C) Directly proportional to mole fraction of the solute  
 (D) Inversely proportional to mole fraction of the solute

LS0053

13. One mole of non volatile solute is dissolved in two moles of water. The vapour pressure of the solution relative to that of water is

(A)  $\frac{2}{3}$  (B)  $\frac{1}{3}$  (C)  $\frac{1}{2}$  (D)  $\frac{3}{2}$

LS0054

14. The vapour pressure of pure A is 10 torr and at the same temperature when 1 g of B is dissolved in 20 gm of A, its vapour pressure is reduced to 9.0 torr. If the molecular mass of A is 200 amu, then the molecular mass of B is :

(A) 100 amu (B) 90 amu (C) 75 amu (D) 120 amu

LS0055

15. The vapour pressure of a pure liquid solvent (X) is decreased to 0.60 atm. from 0.80 atm on addition of a non volatile substance (Y). The mole fraction of (Y) in the solution is:-

(A) 0.20 (B) 0.25 (C) 0.5 (D) 0.75

LS0056

16. Among the following, that does not form an ideal solution is :

(A)  $C_6H_6$  and  $C_6H_5CH_3$  (B)  $C_2H_5Cl$  and  $C_6H_5OH$   
 (C)  $C_6H_5Cl$  and  $C_6H_5Br$  (D)  $C_2H_5Br$  and  $C_2H_5I$

LS0057



17. Colligative properties of the solution depend upon  
 (A) Nature of the solution (B) Nature of the solvent  
 (C) Number of solute particles (D) Number of moles of solvent  
**LS0058**
18. Elevation of boiling point of 1 molar aqueous glucose solution (density = 1.2 g/ml) is  
 (A)  $K_b$  (B)  $1.20 K_b$  (C)  $1.02 K_b$  (D)  $0.98 K_b$   
**LS0059**
19. When common salt is dissolved in water  
 (A) Melting point of the solution increases (B) Boiling point of the solution increases  
 (C) Boiling point of the solution decreases (D) Both Melting point and Boiling point is decreases  
**LS0060**
20. What should be the freezing point of aqueous solution containing 17 gm of  $C_2H_5OH$  in 1000 gm of water (water  $K_f = 1.86 \text{ deg} - \text{kg mol}^{-1}$ )  
 (A)  $-0.69^\circ\text{C}$  (B)  $-0.34^\circ\text{C}$  (C)  $0.0^\circ\text{C}$  (D)  $0.34^\circ\text{C}$   
**LS0061**
21. If mole fraction of the solvent in solution decreases then :  
 (A) Vapour pressure of solution increases (B) B. P. decreases  
 (C) Osmotic pressure increases (D) All are correct  
**LS0062**
22. 5% (w/v) solution of sucrose is isotonic with 1% (w/v) solution of a compound 'A' then the molecular weight of compound 'A' is -  
 (A) 32.4 (B) 68.4 (C) 121.6 (D) 34.2  
**LS0063**
23. Osmotic pressure of a sugar solution at  $24^\circ\text{C}$  is 2.5 atmosphere. The concentration of the solution in mole per litre is :  
 (A) 10.25 (B) 1.025 (C) 1025 (D) 0.1025  
**LS0064**
24. A solution containing 4 g of a non volatile organic solute per 100 ml was found to have an osmotic pressure equal to 500 cm of mercury at  $27^\circ\text{C}$ . The molecular weight of solute is :  
 (A) 14.97 (B) 149.7 (C) 1697 (D) 1.497  
**LS0065**
25. If a 6.84% (wt. / vol.) solution of cane-sugar (mol. wt. 342) is isotonic with 1.52% (wt./vol.) solution of thiocarbamide, then the molecular wight of thiocarbamide is :  
 (A) 152 (B) 76 (C) 60 (D) 180  
**LS0066**
26. Which of the following aqueous solution will show maximum vapour pressure at 300 K?  
 (A) 1 M NaCl (B) 1 M  $CaCl_2$  (C) 1 M  $AlCl_3$  (D) 1 M  $C_{12}H_{22}O_{11}$   
**LS0067**
27. The correct relationship between the boiling points of very dilute solution of  $AlCl_3$  ( $T_1K$ ) and  $CaCl_2$  ( $T_2K$ ) having the same molar concentration is  
 (A)  $T_1 = T_2$  (B)  $T_1 > T_2$  (C)  $T_2 > T_1$  (D)  $T_2 \leq T_1$   
**LS0068**

28. 1.0 molal aqueous solution of an electrolyte  $A_2B_3$  is 60% ionised. The boiling point of the solution at 1 atm is ( $K_{b(H_2O)} = 0.52 \text{ K kg mol}^{-1}$ )  
 (A) 274.76 K (B) 377 K (C) 376.4 K (D) 374.76 K **LS0069**
29. The freezing point depression of a 0.1 M a solution of weak acid (HX) is  $-0.20^\circ\text{C}$ . What is the value of equilibrium constant for the reaction?  

$$\text{HX (aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{X}^-(\text{aq})$$
**[Given :  $K_f$  for water =  $1.8 \text{ kg mol}^{-1} \text{ K}$ . & Molality = Molarity]**  
 (A)  $1.46 \times 10^{-4}$  (B)  $1.35 \times 10^{-3}$  (C)  $1.21 \times 10^{-2}$  (D)  $1.35 \times 10^{-4}$  **LS0070**
30. The Vant Hoff factor (i) for a dilute solution of  $K_3[Fe(CN)_6]$  is (Assuming 100% ionisation) :  
 (A) 10 (B) 4 (C) 5 (D) 0.25 **LS0071**
31. The substance A when dissolved in solvent B shows the molecular mass corresponding to  $A_3$ . The vant Hoff's factor will be -  
 (A) 1 (B) 2 (C) 3 (D) 1/3 **LS0072**
32. The value of observed and calculated molecular weight of silver nitrate are 92.64 and 170 respectively. The degree of dissociation of silver nitrate is :  
 (A) 60% (B) 83.5 % (C) 46.7% (D) 60.23% **LS0073**
33. The freezing point of 1 molal NaCl solution assuming NaCl to be 100% dissociated in water is : ( $K_f = 1.86 \text{ K Molality}^{-1}$ )  
 (A)  $-1.86^\circ\text{C}$  (B)  $-3.72^\circ\text{C}$  (C)  $+1.86^\circ\text{C}$  (D)  $+3.72^\circ\text{C}$  **LS0074**
34. What is the freezing point of a solution containing 8.1 gm. of HBr in 100gm. water assuming the acid to be 90% ionised ( $K_f$  for water =  $1.86 \text{ K molality}^{-1}$ ) :-  
 (A)  $0.85^\circ\text{C}$  (B)  $-3.53^\circ\text{C}$  (C)  $0^\circ\text{C}$  (D)  $-0.35^\circ\text{C}$  **LS0075**
35. If a ground water contains  $H_2S$  at concentration of 2 mg/l, determine the pressure of  $H_2S$  in head space of a closed tank containing the ground water at  $20^\circ\text{C}$ . Given that for  $H_2S$ , Henry's constant is equal to  $6.8 \times 10^3 \text{ bar}$  at  $20^\circ\text{C}$ .  
 (A) 720 Pa (B)  $77 \times 10^2 \text{ Pa}$  (C) 553 Pa (D)  $55 \times 10^2 \text{ Pa}$  **LS0076**
36. A pressure cooker reduces cooking time for food because -  
 (A) The higher pressure inside the cooker crushes the food material  
 (B) Cooking involves chemical changes helped by a rise in temperature  
 (C) Heat is more evenly distributed in the cooking space  
 (D) Boiling point of water involved in cooking is increased **LS0077**

## EXERCISE # O-II

**Single correct :**

1. An ideal solution was obtained by mixing (MeOH) methanol and (EtOH) ethanol. If the partial vapour pressure of methanol and ethanol are 2.619 K Pa and 4.556 K Pa respectively, the composition of vapour (in terms of mole fraction) will be -
- (A) 0.635 MeOH, 0.365 EtOH                      (B) 0.365 MeOH, 0.635 EtOH  
(C) 0.574 MeOH, 0.326 EtOH                      (D) 0.173 MeOH, 0.827 EtOH

LS0078

2. Molar volume of liquid A ( $d = 0.8 \text{ gm/ml}$ ) increase by factor of 2000 when it vapourises at 200K. Vapour pressure of liquid A at 200K is [ $R = 0.08 \text{ L-atm/mol-K}$ ]  
(Molar mass of A = 80g/mol)

(A) 0.4 atm                      (B) 8 atm                      (C) 0.8 atm                      (D) 0.08 atm

LS0079

3. Assuming each salt to be 90 % dissociated, which of the following will have highest boiling point?
- (A) Decimolar  $\text{Al}_2(\text{SO}_4)_3$   
(B) Decimolar  $\text{BaCl}_2$   
(C) Decimolar  $\text{Na}_2\text{SO}_4$   
(D) A solution obtained by mixing equal volumes of (B) and (C)

LS0080

4. The vapour pressure of a saturated solution of sparingly soluble salt ( $\text{XCl}_3$ ) was 17.20 mm Hg at 27°C. If the vapour pressure of pure  $\text{H}_2\text{O}$  is 17.25 mm Hg at 300 K, what is the solubility of sparingly soluble salt  $\text{XCl}_3$  in mole/Litre.
- (A)  $4.04 \times 10^{-2}$                       (B)  $8.08 \times 10^{-2}$                       (C)  $2.02 \times 10^{-2}$                       (D)  $4.04 \times 10^{-3}$

LS0081

5. A solution has a 1 : 4 mole ratio of pentane to hexane. The vapour pressures of the pure hydrocarbons at 20°C are 440 mmHg for pentane and 120 mmHg for hexane. The mole fraction of pentane in the vapour phase would be :-
- (A) 0.200                      (B) 0.478                      (C) 0.549                      (D) 0.786

LS0082

6. For which of the following vant' Hoff's factor is not correctly matched -

Salt	Degree of dissociation ( $\alpha$ )	$i$
(A) $\text{Na}_2\text{SO}_4$	50 %	2
(B) $\text{K}_3[\text{Fe}(\text{CN})_6]$	75%	3.25
(C) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	80 %	1.8
(D) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$	90 %	2.8

LS0083

7. In the depression of freezing point experiment, it is found that
- (I) The vapour pressure of the solution is less than that of pure solvent.
  - (II) The vapour pressure of the solution is more than that of pure solvent.
  - (III) Only solute molecules solidify at the freezing point.
  - (IV) Only solvent molecules solidify at the freezing point.
- (A) I, II                      (B) II, III                      (C) I, IV                      (D) I, II, III

LS0084

8. **Statement-1** : Addition of ethylene glycol (non-volatile) to water lowers the freezing point of water hence used as antifreeze.

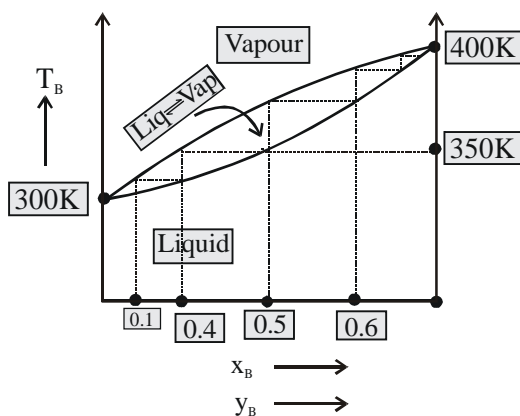
**Statement-2** : Addition of any substance to water lowers its freezing point of water.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

LS0085

*More than one may be correct*

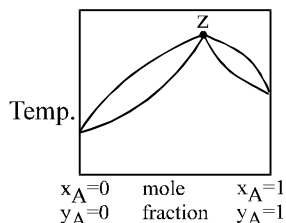
9. For an ideal solution having two liquid A ( $P_A^0$ ) and liquid B ( $P_B^0$ ) boiling point versus composition graph is given below, then select incorrect statement (s) :



- (A) B is less volatile than A
- (B) If mole percent of A in liquid phase is 40% then mole percent of A in vapour phase is 50%
- (C) If mole percent of B in liquid phase is 10% then mole percent of B in vapour phase is 40%
- (D) If the mole percent of A in solution is 50% then its boiling point is 350K

LS0086

- 10 A liquid mixture having composition corresponding to point z in the figure shown is subjected to distillation at constant pressure.



Which of the following statement is correct about the process

- (A) The composition of distillate differs from the mixture  
 (B) The boiling point goes on changing  
 (C) The mixture has lowest vapour pressure than for any other composition.  
 (D) Composition of an azeotrope alters on changing the external pressure.

LS0087

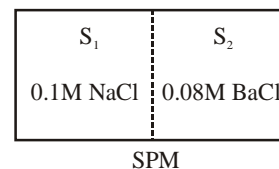
11. Which of the following is correct for a non-ideal solution of liquids A and B, showing negative deviation?

- (A)  $\Delta H_{\text{mix}} = -ve$  (B)  $\Delta V_{\text{mix}} = -ve$   
 (C)  $\Delta S_{\text{mix}} = +ve$  (D)  $\Delta G_{\text{mix}} = -ve$

LS0088

12. Two solutions  $S_1$  and  $S_2$  containing 0.1M NaCl(aq.) and 0.08M BaCl<sub>2</sub>(aq.) are separated by semipermeable membrane. Which among the following statement(s) is/are correct -

- (A)  $S_1$  and  $S_2$  are isotonic  
 (B)  $S_1$  is hypertonic and  $S_2$  is hypotonic  
 (C)  $S_1$  is hypotonic and  $S_2$  is hypertonic  
 (D) Osmosis will take place to from  $S_1$  to  $S_2$



LS0089

13. For an ideal binary liquid solution with  $P_A^\circ > P_B^\circ$ , which relation between  $X_A$  (mole fraction of A in liquid phase) and  $Y_A$  (mole fraction of A in vapour phase) is correct?

- (A)  $Y_A < Y_B$  (B)  $X_A > X_B$  (C)  $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$  (D)  $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

LS0090

14. Which of the following plots represents an ideal binary mixture?
- (A) Plot of  $P_{\text{total}}$  v/s  $1/X_B$  is linear ( $X_B$  = mole fraction of 'B' in liquid phase).
- (B) Plot of  $P_{\text{total}}$  v/s  $Y_A$  is linear ( $Y_B$  = mole fraction of 'A' in vapour phase)
- (C) Plot of  $\frac{1}{P_{\text{total}}}$  v/s  $Y_A$  is linear
- (D) Plot of  $\frac{1}{P_{\text{total}}}$  v/s  $Y_B$  is non linear

LS0091

**Paragraph for Q.15 to Q.17**

An ideal solution is obtained by mixing a non-volatile solute B with a volatile solvent A (molar mass = 60). If the mass ratio of A : B in solution is 10 : 1 and vapour pressure of pure A is 400 mm and vapour pressure decreases by 4% on forming the above solution at 300K.

15. The mole fraction of solute in the solution is -
- (A) 0.96                      (B) 0.04                      (C) 0.16                      (D) 0.84

LS0092

16. The molality the solution is -
- (A) 1                              (B)  $\frac{36}{25}$                       (C)  $\frac{25}{36}$                       (D)  $\frac{36}{25}$

LS0092

17. The molar mass of B in the solution is -
- (A) 1440                      (B) 14400                      (C) 4                              (D) 144

LS0092

**Table type question :**

Column-I	Column-II	Column-III
(1) $C_6H_6 + C_6H_5-CH_3$	(a) $DH = 0$	(P) $DG = -ve$
(2) $CHCl_3 + CH_3COCH_3$	(b) $DH = +ve$	(Q) Form minimum boiling azerotrope
(3) $CCl_4 + CH_3COCH_3$	(c) $DH = -ve$	(R) Form maximum boiling azerotrope
(4) $C_2H_5OH + H_2O$	(d) $DS = +ve$	(S) No azeotrope

18. Select the correct match -
- (A) 1 , a, R                      (B) 2, b, P                      (C) 3, b, Q                      (D) 4, d, R

LS0093

19. Select the correct match -

- (A) 1, d, S                      (B) 3, b, S                      (C) 2, b, S                      (D) 4, c, P

LS0093

20. Select the incorrect match -

- (A) 1, d, P                      (B) 2, c, R                      (C) 3, d, S                      (D) 3, b, P

LS0093

Match the column :

21.

Column-I

(Colligative properties)

(A)  $\Delta T_f = 0.3 \times K_f$

(B)  $\Delta T_b = 0.28 \times K_b$

(C)  $\pi = 0.19 \times RT$

(D) 
$$\frac{P^0 - P}{P^0} = \frac{\left(\frac{\Delta T_f}{K_f}\right)}{\left(\frac{1000}{18}\right) + \left(\frac{\Delta T_f}{K_f}\right)}$$

Column-II

(Aqueous solution)

(Assume  $m = M$ )

(P) 0.1 m -  $\text{Ca}(\text{NO}_3)_2$

(Q) 0.14 m - NaBr

(R) 0.1 m -  $\text{MgCl}_2$  ( $\alpha = 0.9$ )

(S) 0.28 m - Urea

(T) 0.1 m - HA (monobasic acid,  $K_a = 0.81$ )

LS0094

## EXERCISE # (J-MAIN)

1. The degree of dissociation ( $\alpha$ ) of a weak electrolyte,  $A_xB_y$  is related to van't Hoff factor ( $i$ ) by the expression :- [AIEEE-2011]
- (1)  $\alpha = \frac{x+y-1}{i-1}$       (2)  $\alpha = \frac{x+y+1}{i-1}$       (3)  $\alpha = \frac{i-1}{(x+y-1)}$       (4)  $\alpha = \frac{i-1}{x+y+1}$
- LS0095**
2.  $K_f$  for water is  $1.86 \text{ K kg mol}^{-1}$ . If your automobile radiator holds  $1.0 \text{ kg}$  of water, how many grams of ethylene glycol ( $C_2H_6O_2$ ) must you add to get the freezing point of the solution lowered to  $-2.8^\circ\text{C}$  ? [AIEEE-2012]
- (1)  $27 \text{ g}$       (2)  $72 \text{ g}$       (3)  $93 \text{ g}$       (4)  $39 \text{ g}$
- LS0096**
3. A solution containing  $0.85 \text{ g}$  of  $ZnCl_2$  in  $125.0 \text{ g}$  of water freezes at  $-0.23^\circ\text{C}$ . The apparent degree of dissociation of the salt is : [JEE (MAIN)-2012 ONLINE]
- ( $k_f$  for water =  $1.86 \text{ K kg mol}^{-1}$ , atomic mass ;  $Zn = 65.3$  and  $Cl = 35.5$ )
- (1)  $1.36\%$       (2)  $2.47\%$       (3)  $73.5\%$       (4)  $7.35\%$
- LS0097**
4. Liquids A and B form an ideal solution. At  $30^\circ\text{C}$ , the total vapour pressure of a solution containing  $1 \text{ mol}$  of A and  $2 \text{ moles}$  of B is  $250 \text{ mm Hg}$ . The total vapour pressure becomes  $300 \text{ mm Hg}$  when  $1 \text{ more mol}$  of A is added to the first solution. The vapour pressures of pure A and B at the same temperature are :- [JEE (MAIN)-2012 ONLINE]
- (1)  $450, 150 \text{ mm Hg}$       (2)  $250, 300 \text{ mm Hg}$       (3)  $125, 150 \text{ mm Hg}$       (4)  $150, 450 \text{ mm Hg}$
- LS0098**
5. The freezing point of a  $1.00 \text{ m}$  aqueous solution of HF is found to be  $-1.91^\circ\text{C}$ . The freezing point constant of water,  $K_f$ , is  $1.86 \text{ K kg mol}^{-1}$ . The percentage dissociation of HF at this concentration is [JEE (MAIN)-2012 ONLINE]
- (1)  $2.7\%$       (2)  $30\%$       (3)  $10\%$       (4)  $5.2\%$
- LS0099**
6. How many grams of methyl alcohol should be added to  $10 \text{ litre}$  tank of water to prevent its freezing at  $268 \text{ K}$  ? [JEE (MAIN)-2013 ONLINE]
- ( $K_f$  for water is  $1.86 \text{ K kg mol}^{-1}$ , Normal freezing point of water =  $273.15\text{K}$ )
- (1)  $899.04 \text{ g}$       (2)  $886.02 \text{ g}$       (3)  $868.06 \text{ g}$       (4)  $880.07 \text{ g}$
- LS0100**
7. Vapour pressure of pure benzene is  $119 \text{ torr}$  and that of toluene is  $37.0 \text{ torr}$  at the same temperature. Mole fraction of toluene in vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene  $0.50$ , will be : [JEE (MAIN)-2013 ONLINE]
- (1)  $0.137$       (2)  $0.205$       (3)  $0.237$       (4)  $0.435$
- LS0101**



8. A molecule M associates in a given solvent according to the equation  $M \rightleftharpoons (M)_n$ . For a certain concentration of M, the van't Hoff factor was found to be 0.9 and the fraction of associated molecules was 0.2. The value of n is : **[JEE (MAIN)-2013 ONLINE]**  
 (1) 2 (2) 4 (3) 5 (4) 3 **LS0102**
9. 12g of a nonvolatile solute dissolved in 108g of water produces the relative lowering of vapour pressure of 0.1. The molecular mass of the solute is : **[JEE (MAIN)-2013 ONLINE]**  
 (1) 60 (2) 80 (3) 40 (4) 20 **LS0103**
10. The molarity of a solution obtained by mixing 750 mL of 0.5(M)HCl with 250 mL of 2(M)HCl will be :- **[JEE (MAIN)-2013]**  
 (1) 0.875 M (2) 1.00 M (3) 1.75 M (4) 0.975 M **LS0104**
11. The observed osmotic pressure for a 0.10 M solution of  $Fe(NH_4)_2(SO_4)_2$  at 25°C is 10.8 atm. The expected and experimental (observed) values of Van't Hoff factor (i) will be respectively : **[JEE (MAIN)-2014 ONLINE]**  
 (R= 0.082 L atm k<sup>-1</sup> mol<sup>-1</sup>)  
 (1) 3 and 5.42 (2) 5 and 3.42 (3) 4 and 4.00 (4) 5 and 4.42 **LS0105**
12. For an ideal Solution of two components A and B, which of the following is true ? **[JEE(MAIN)-2014 ONLINE]**  
 (1)  $\Delta H_{\text{mixing}} < 0$  (zero)  
 (2) A – A, B – B and A – B interactions are identical  
 (3) A – B interaction is stronger than A – A and B – B interactions  
 (4)  $\Delta H_{\text{mixing}} > 0$  (zero) **LS0106**
13. Consider separate solution of 0.500 M  $C_2H_5OH(aq)$ , 0.100 M  $Mg_3(PO_4)_2(aq)$ , 0.250 M  $KBr(aq)$  and 0.125 M  $Na_3PO_4(aq)$  at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes ? **[JEE (MAIN)-2014]**  
 (1) 0.125 M  $Na_3PO_4(aq)$  has the highest osmotic pressure.  
 (2) 0.500 M  $C_2H_5OH(aq)$  has the highest osmotic pressure.  
 (3) They all have the same osmotic pressure.  
 (4) 0.100 M  $Mg_3(PO_4)_2(aq)$  has the highest osmotic pressure. **LS0107**
14. Determination of the molar mass of acetic acid in benzene using freezing point depression is affected by : **[JEE (MAIN)-2015 ONLINE]**  
 (1) association (2) dissociation (3) complex formation (4) partial ionization **LS0108**

15. A solution at 20°C is composed of 1.5 mol of benzene and 3.5 mol of toluene. If the vapour pressure of pure benzene and pure toluene at this temperature are 74.7 torr and 22.3 torr, respectively, then the total vapour pressure of the solution and the benzene mole fraction in equilibrium with it will be, respectively : [JEE (MAIN)-2015 ONLINE]
- (1) 38.0 torr and 0.589 (2) 30.5 torr and 0.389  
 (3) 35.8 torr and 0.280 (4) 35.0 torr and 0.480
- LS0109**
16. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol<sup>-1</sup>) of the substance is : [JEE (MAIN)-2015]
- (1) 128 (2) 488 (3) 32 (4) 64
- LS0110**
17. An aqueous solution of a salt MX<sub>2</sub> at certain temperature has a van't Hoff factor of 2. The degree of dissociation for this solution of the salt is : [JEE (MAIN--2016-ONLINE)]
- (1) 0.50 (2) 0.80 (3) 0.67 (4) 0.33
- LS0111**
18. The solubility of N<sub>2</sub> in water at 300 K and 500 torr partial pressure is 0.01 g L<sup>-1</sup>. The solubility (in g L<sup>-1</sup>) at 750 torr partial pressure is : [JEE (MAIN--2016-ONLINE)]
- (1) 0.02 (2) 0.005 (3) 0.015 (4) 0.0075
- LS0112**
19. 18 g glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) is added to 178.2g at 100°C water. The vapour pressure of water (in torr) for this aqueous solution is : [JEE (MAIN)-2016]
- (1) 759.0 (2) 7.6 (3) 76.0 (4) 752.4
- LS0113**
20. The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be :- [JEE (MAIN)-2017]
- (K<sub>f</sub> for benzene = 5.12 K kg mol<sup>-1</sup>)**
- (1) 64.6% (2) 80.4% (3) 74.6% (4) 94.6%
- LS0114**
21. 5 g of Na<sub>2</sub>SO<sub>4</sub> was dissolved in x g of H<sub>2</sub>O. The change in freezing point was found to be 3.82°C. If Na<sub>2</sub>SO<sub>4</sub> is 81.5% ionised, the value of x [JEE (MAIN--2017-ONLINE)]
- (K<sub>f</sub> for water = 1.86°C kg mol<sup>-1</sup>) is approximately.**
- (Molar mass of S = 32 g mol<sup>-1</sup> and that of Na = 23 g mol<sup>-1</sup>)**
- (1) 45 g (2) 65 g (3) 15 g (4) 25 g

**LS0115**

22. A solution is prepared by mixing 8.5 g of  $\text{CH}_2\text{Cl}_2$  and 11.95 g of  $\text{CHCl}_3$ . If vapour pressure of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  at 298 K are 415 and 200 mmHg respectively, the mole fraction of  $\text{CHCl}_3$  in vapour form is: (Molar mass of Cl = 35.5 g mol<sup>-1</sup>) [JEE (MAIN-2017-ONLINE)]

(1) 0.486                      (2) 0.325                      (3) 0.162                      (4) 0.675

LS0116

23. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point ? [JEE (MAIN)-2018]

(1)  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$                       (2)  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$   
 (3)  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$                       (4)  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$

LS0117

24. Two 5 molal solutions are prepared by dissolving a non-electrolyte non-volatile solute separately in the solvents X and Y. The molecular weights of the solvents are  $M_x$  and  $M_y$ , respectively where  $M_x = \frac{3}{4} M_y$ . The relative lowering of vapour pressure of the solution in X is "m" times that of the solution in Y. Given that the number of moles of solute is very small in comparison to that of solvent, the value of "m" is - [JEE (MAIN-2018-ONLINE)]

(1)  $\frac{3}{4}$                       (2)  $\frac{4}{3}$                       (3)  $\frac{1}{2}$                       (4)  $\frac{1}{4}$

LS0118

25. The mass of a non-volatile, non-electrolyte solute (molar mass = 50 g mol<sup>-1</sup>) needed to be dissolved in 114 g octane to reduce its vapour pressure by 75%, is :- [JEE (MAIN-2018-ONLINE)]

(1) 50 g                      (2) 37.5 g                      (3) 75 g                      (4) 150 g

LS0119

26. Freezing point of a 4% aqueous solution of X is equal to freezing point of 12% aqueous solution of Y. If molecular weight of X is A, then molecular weight of Y is :- [JEE (MAIN-2019-(JAN.)ONLINE)]

(1) A                      (2) 3A                      (3) 4A                      (4) 2A

LS0120

27. Molecules of benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ) dimerise in benzene. 'w' g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2K. If the percentage association of the acid to form dimer in the solution is 80, then w is : [JEE (MAIN-2019-(JAN.)ONLINE)]

(Given that  $K_f = 5 \text{ K kg mol}^{-1}$ , Molar mass of benzoic acid = 122 g mol<sup>-1</sup>)

(1) 1.8 g                      (2) 2.4 g                      (3) 1.0 g                      (4) 1.5 g

LS0121

28. The freezing point of a diluted milk sample is found to be  $-0.2^{\circ}\text{C}$ , while it should have been  $-0.5^{\circ}\text{C}$  for pure milk. How much water has been added to pure milk to make the diluted sample ?

- (1) 2 cups of water to 3 cups of pure milk  
(2) 1 cup of water to 3 cups of pure milk  
(3) 3 cups of water to 2 cups of pure milk  
(4) 1 cup of water to 2 cups of pure milk

[JEE (MAIN-2019-(JAN.)ONLINE]

LS0122

29.  $\text{K}_2\text{HgI}_4$  is 40% ionised in aqueous solution. The value of its van't Hoff factor (i) is :-

- (1) 1.8  
(2) 2.2  
(3) 2.0  
(4) 1.6

[JEE (MAIN-2019-(JAN.)ONLINE]

LS0123

30. Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapor pressures of pure A and pure B are  $7 \times 10^3$  Pa and  $12 \times 10^3$  Pa, respectively. The composition of the vapor in equilibrium with a solution containing 40 mole percent of A at this temperature is :

- (1)  $y_A = 0.37$ ;  $y_B = 0.63$   
(2)  $y_A = 0.28$ ;  $y_B = 0.72$   
(3)  $y_A = 0.76$ ;  $y_B = 0.24$   
(4)  $y_A = 0.4$ ;  $y_B = 0.6$

[JEE (MAIN-2019-(JAN.)ONLINE]

LS0124

31. A solution containing 62 g ethylene glycol in 250 g water is cooled to  $-10^{\circ}\text{C}$ . If  $K_f$  for water is  $1.86 \text{ K kg mol}^{-1}$ , the amount of water (in g) separated as ice is : [JEE (MAIN-2019-(JAN.)ONLINE]

- (1) 32  
(2) 48  
(3) 16  
(4) 64

LS0125

32. Which one of the following statements regarding Henry's law is not correct ?

- (1) The value of  $K_H$  increases with increase of temperature and  $K_H$  is function of the nature of the gas  
(2) Higher the value of  $K_H$  at a given pressure, higher is the solubility of the gas in the liquids.  
(3) The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution.  
(4) Different gases have different  $K_H$  (Henry's law constant) values at the same temperature.

[JEE (MAIN-2019-(JAN.)ONLINE]

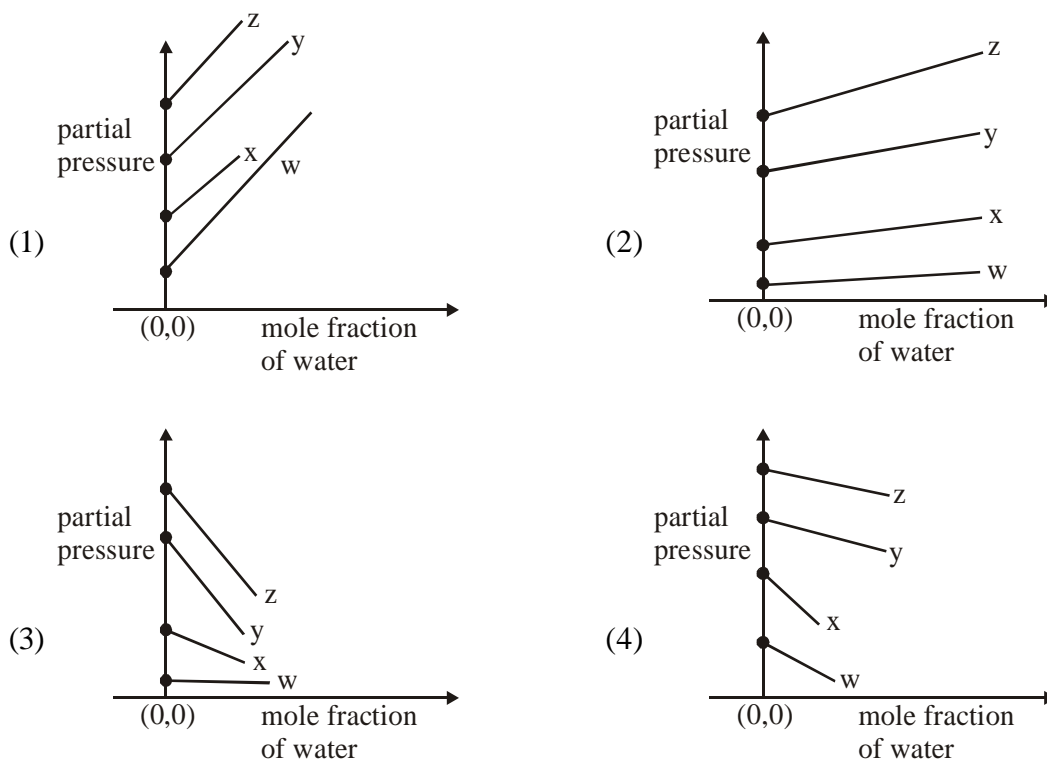
LS0126

33. Elevation in the boiling point for 1 molal solution of glucose is 2 K. The depression in the freezing point of 2 molal solutions of glucose in the same solvent is 2 K. The relation between  $K_b$  and  $K_f$  is:
- (1)  $K_b = 0.5 K_f$  (2)  $K_b = 2 K_f$  [JEE(MAIN-2019-(JAN.)ONLINE]  
 (3)  $K_b = 1.5 K_f$  (4)  $K_b = K_f$

LS0127

34. For the solution of the gases w, x, y and z in water at 298K, the Henry's law constants ( $K_H$ ) are 0.5, 2, 35 and 40 kbar, respectively. The correct plot for the given data is :-

[JEE (MAIN-2019-(APRIL)ONLINE]



LS0128

35. The vapour pressures of pure liquids A and B are 400 and 600 mmHg, respectively at 298K. On mixing the two liquids, the sum of their initial volumes is equal to the volume of the final mixture. The mole fraction of liquid B is 0.5 in the mixture. The vapour pressure of the final solution, the mole fraction of components A and B in vapour phase, respectively are

[JEE (MAIN-2019-(APRIL)ONLINE]

- (1) 500 mmHg, 0.5, 0.5 (2) 450 mmHg, 0.4, 0.6  
 (3) 450 mmHg, 0.5, 0.5 (4) 500 mmHg, 0.4, 0.6

LS0129

36. Molal depression constant for a solvent is  $4.0 \text{ kg mol}^{-1}$ . The depression in the freezing point of the solvent for  $0.03 \text{ mol kg}^{-1}$  solution of  $\text{K}_2\text{SO}_4$  is :

[JEE (MAIN-2019-(APRIL)ONLINE]

(Assume complete dissociation of the electrolyte)

- (1) 0.12 K (2) 0.36 K (3) 0.18 K (4) 0.24 K

LS0130

37. The osmotic pressure of a dilute solution of an ionic compound XY in water is four times that of a solution of 0.01 M BaCl<sub>2</sub> in water. Assuming complete dissociation of the given ionic compounds in water, the concentration of XY (in mol L<sup>-1</sup>) in solution is : [JEE (MAIN-2019-(APRIL)ONLINE]
- (1)  $6 \times 10^{-2}$                       (2)  $4 \times 10^{-4}$                       (3)  $16 \times 10^{-4}$                       (4)  $4 \times 10^{-2}$

LS0131

38. Liquid 'M' and liquid 'N' form an ideal solution. The vapour pressures of pure liquids 'M' and 'N' are 450 and 700 mmHg, respectively, at the same temperature. Then correct statement is:

$x_M$  = Mole fraction of 'M' in solution ;

[JEE (MAIN-2019-(APRIL)ONLINE]

$x_N$  = Mole fraction of 'N' in solution ;

$y_M$  = Mole fraction of 'M' in vapour phase ;

$y_N$  = Mole fraction of 'N' in vapour phase)

(1)  $(x_M - y_M) < (x_N - y_N)$

(2)  $\frac{x_M}{x_N} < \frac{y_M}{y_N}$

(3)  $\frac{x_M}{x_N} > \frac{y_M}{y_N}$

(4)  $\frac{x_M}{x_N} = \frac{y_M}{y_N}$

LS0132

39. A solution is prepared by dissolving 0.6 g of urea (molar mass = 60 g mol<sup>-1</sup>) and 1.8 g of glucose (molar mass = 180 g mol<sup>-1</sup>) in 100 mL of water at 27°C. The osmotic pressure of the solution is :

(R = 0.08206 L atm K<sup>-1</sup> mol<sup>-1</sup>)

[JEE (MAIN-2019-(APRIL)ONLINE]

(1) 4.92 atm

(2) 1.64 atm

(3) 2.46 atm

(4) 8.2 atm

LS0133

40. At room temperature, a dilute solution of urea is prepared by dissolving 0.60 g of urea in 360 g of water. If the vapour pressure of pure water at this temperature is 35 mmHg, lowering of vapour pressure will be (molar mass of urea = 60 g mol<sup>-1</sup>):-

[[JEE (MAIN-2019-(APRIL)ONLINE]

(1) 0.027 mmHg

(2) 0.028 mmHg

(3) 0.017 mmHg

(4) 0.031 mmHg

LS0134

41. 1 g of non-volatile non-electrolyte solute is dissolved in 100g of two different solvents A and B whose ebullioscopic constants are in the ratio of 1 : 5. The ratio of the elevation in their boiling points,  $\frac{\Delta T_b(A)}{\Delta T_b(B)}$ , is :

[JEE (MAIN-2019-(APRIL)ONLINE]

(1) 5 : 1

(2) 10 : 1

(3) 1 : 5

(4) 1 : 0.2

LS0135

## EXERCISE # (J-ADVANCED)

1. The freezing point (in °C) of a solution containing 0.1 g of  $K_3[Fe(CN)_6]$  (Mol. Wt. 329) in 100 g of water ( $K_f = 1.86 \text{ K kg mol}^{-1}$ ) is - [JEE 2011]  
 (A)  $-2.3 \times 10^{-2}$       (B)  $-5.7 \times 10^{-2}$       (C)  $-5.7 \times 10^{-3}$       (D)  $-1.2 \times 10^{-2}$

LS0136

2. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is  $2^\circ\text{C}$ . Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is  
 (take  $K_b = 0.76 \text{ K kg mol}^{-1}$ ) [JEE 2012]  
 (A) 724      (B) 740      (C) 736      (D) 718

LS0137

3. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are) [J-Adv. 2013]  
 (A)  $\Delta G$  is positive      (B)  $\Delta S_{\text{system}}$  is positive      (C)  $\Delta S_{\text{surroundings}} = 0$       (D)  $\Delta H = 0$

LS0138

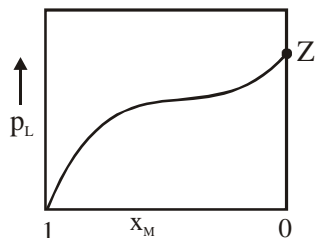
4. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong electrolyte) is  $-0.0558^\circ\text{C}$ , the number of chloride (s) in the coordination sphere of the complex is- [ $K_f$  of water =  $1.86 \text{ K kg mol}^{-1}$ ] [JEE-Adv. 2015]

LS0139

5. Mixture(s) showing positive deviation from Raoult's law at  $35^\circ\text{C}$  is (are) [JEE-Adv. 2016]  
 (A) carbon tetrachloride + methanol      (B) carbon disulphide + acetone  
 (C) benzene + toluene      (D) phenol + aniline

LS0140

6. For a solution formed by mixing liquids L and M, the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure, Here  $x_L$  and  $x_M$  represent mole fractions of L and M, respectively, in the solution. the correct statement(s) applicable to this system is(are)

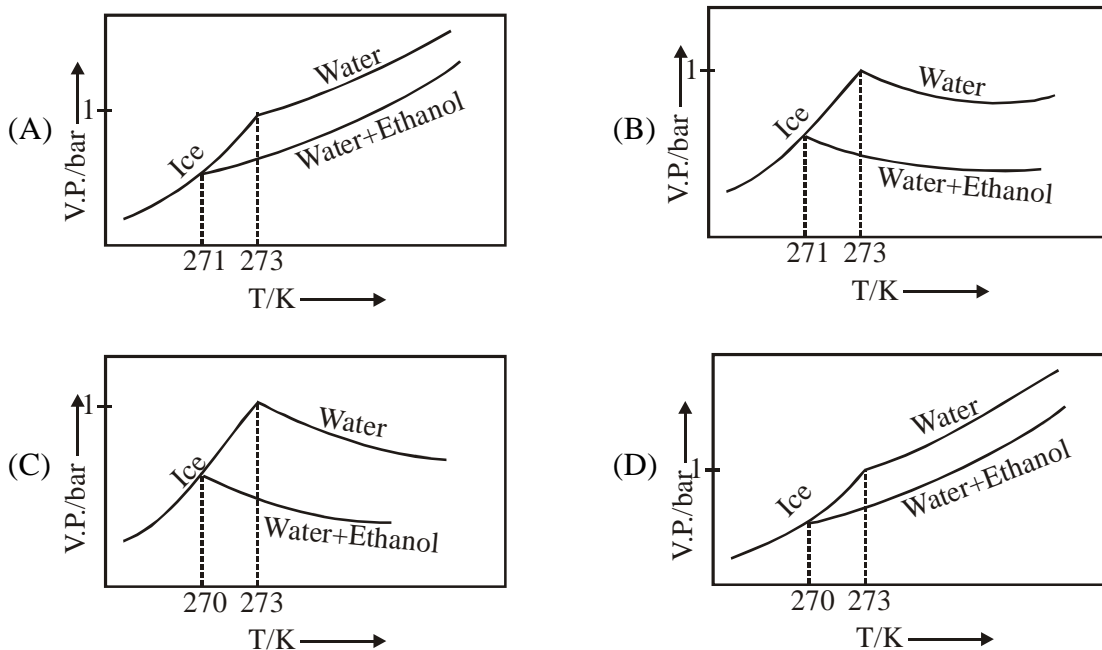


- (A) Attractive intramolecular interactions between L–L in pure liquid L and M–M in pure liquid M are stronger than those between L–M when mixed in solution [JEE-Adv. 2017]  
 (B) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when  $x_L \rightarrow 0$   
 (C) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when  $x_L \rightarrow 1$   
 (D) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from  $x_L = 0$  to  $x_L = 1$

LS0141

7. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as  $2 \text{ K kg mol}^{-1}$ . The figures shown below represents plots of vapour pressure (V.P.) versus temperature (T). [Molecular weight of ethanol is  $46 \text{ g mol}^{-1}$ ]

Among the following, the option representing change in the freezing point is -[JEE-Adv. 2017]



LS0142



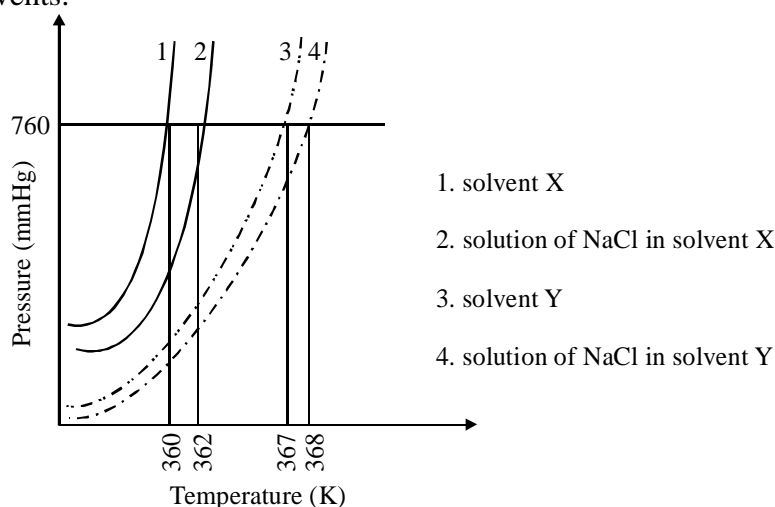
8. Liquids A and B form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids A and B has vapour pressure 45 Torr. At the same temperature, a new solution of A and B having mole fractions  $x_A$  and  $x_B$ , respectively, has vapour pressure of 22.5 Torr. The value of  $x_A/x_B$  in the new solution is \_\_\_\_.

[JEE-Adv. 2018]

(Given that the vapour pressure of pure liquid A is 20 Torr at temperature T)

LS0143

9. The plot given below shows P–T curves (where P is the pressure and T is the temperature) for two solvents X and Y and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, the degree of dimerization in solvent X is \_\_\_\_.

[JEE-Adv. 2018]

LS0144

10. On dissolving 0.5 g of a non-volatile non-ionic solute to 39 g of benzene, its vapor pressure decreases from 650 mm Hg to 640 mm Hg. The depression of freezing point of benzene (in K) upon addition of the solute is \_\_\_\_.

(Given data : Molar mass and the molal freezing point depression constant of benzene are  $78 \text{ g mol}^{-1}$  and  $5.12 \text{ K kg mol}^{-1}$ , respectively)

[JEE-Adv. 2019]

LS0145

## ANSWER-KEY

## EXERCISE # S-I

- |  |   |
|--|---|
| 1. Ans.0.25  | 2. Ans. 64.0 mm Hg  |
| 3. Ans. $P_A^0 = 100 \text{ cmHg}$ , $P_B^0 = 60 \text{ cmHg}$ . | 4. Ans. 0.25  |
| 5. Ans. 0.5 bar  | 6. Ans. $P_X^0 = 55 \text{ cmHg}$ , $P_Y^0 = 80 \text{ cmHg}$           |
| 7. Ans. $P_R^0 = 0.8 \text{ bar}$ , $P_S^0 = 0.4 \text{ bar}$    | 8. Ans.0.25   |
| 9. Ans.0.04  | 10. Ans.0.32 m  |
| 11. Ans.65.25  | 12. Ans.17.38 mm Hg   |
| 13. Ans.120 g/mol  | 14. Ans. $K_b = 0.516 \text{ kg mol K}^{-1}$ , $T_b = 373.20 \text{ K}$ |
| 15. Ans.5.1 K-kg/mol   | 16. Ans.2048 g/mol  |
| 17. Ans.(6.972)  | 18. Ans.40 g/mol  |
| 19. Ans. 49.26 atm   | 20. Ans.3.69 atm  |
| 21. Ans.1.96   | 22. Ans.3 ions  |
| 23. Ans.78 %   | 24. Ans. $7.482 \times 10^5 \text{ Nm}^{-2}$                            |
| 25. Ans.0.95; 1.95   | 26. Ans. 0.04   |
| 27. Ans.(3)  |   |

## EXERCISE # S-II

- |  |  |
|--|--|
| 1. Ans.92 mol% toluene; 96.8 mol % toluene | 2. Ans.0.741 m, 0.0136                                   |
| 3. Ans.38.71 g                             | 4. Ans. $4.8 \times 10^5 \text{ g/mol}$                  |
| 5. Ans.(777)                               | 6. Ans(68.4)   |
| 7. Ans. $C_{40}H_{80}O_{40}$               | 8. Ans. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ |
| 9. Ans.a = 0.50                            | 10. Ans.0.73   |
| 11. Ans. $C_6H_6$                          | 12. Ans (60%)  |
| 13. Ans.(3.2)                              | 14. Ans. (100°C)   |

## EXERCISE # O-I

- |             |             |             |             |
|-------------|-------------|-------------|-------------|
| 1. Ans.(B)  | 2. Ans.(C)  | 3. Ans.(C)  | 4. Ans.(D)  |
| 5. Ans.(A)  | 6. Ans.(C)  | 7. Ans.(C)  | 8. Ans.(C)  |
| 9. Ans.(D)  | 10. Ans.(C) | 11. Ans.(C) | 12. Ans.(A) |
| 13. Ans.(A) | 14. Ans.(B) | 15. Ans.(B) | 16. Ans.(B) |
| 17. Ans.(C) | 18. Ans.(D) | 19. Ans.(B) | 20. Ans.(A) |
| 21. Ans.(C) | 22. Ans.(B) | 23. Ans.(D) | 24. Ans.(B) |
| 25. Ans.(B) | 26. Ans.(D) | 27. Ans.B   | 28. Ans.(D) |
| 29. Ans.(B) | 30. Ans.(B) | 31. Ans.(D) | 32. Ans.(B) |
| 33. Ans.(B) | 34. Ans.(B) | 35. Ans.(A) | 36. Ans.(D) |

## EXERCISE # O-II

- |   |                |                      |                |
|---|----------------|----------------------|----------------|
| 1. Ans.(B)  | 2. Ans.(D)     | 3. Ans.(A)           | 4. Ans.(A)     |
| 5. Ans.(B)  | 6. Ans.(D)     | 7. Ans.(C)           | 8. Ans.(C)     |
| 9. Ans.(C)  | 10. Ans.(C, D) | 11. Ans.(A, B, C, D) | 12. Ans.(C, D) |
| 13. Ans.(C)   | 14. Ans.(C)    | 15. Ans.(B)          | 16. Ans. (C)   |
| 17. Ans.(D)   | 18. Ans.(C)    | 19. Ans.(A)          | 20. Ans.(C)    |
| 21. Ans.(A) $\rightarrow$ P ; (B) $\rightarrow$ Q, R, S ; (C) $\rightarrow$ T ; (D) $\rightarrow$ P, Q, R, S, T |                |                      |                |

## EXERCISE # J-MAIN

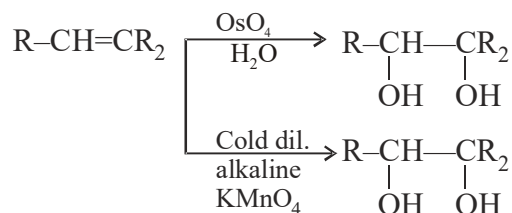
- |              |             |             |              |
|--------------|-------------|-------------|--------------|
| 1. Ans.(3)   | 2. Ans.(3)  | 3. Ans.(3)  | 4. Ans.(1)   |
| 5. Ans.(1)   | 6. Ans.(2)  | 7. Ans.(3)  | 8. Ans.(1)   |
| 9. Ans.(4)   | 10. Ans.(1) | 11. Ans.(4) | 12. Ans.(2)  |
| 13. Ans.(3)  | 14. Ans.(1) | 15. Ans.(1) | 16. Ans. (4) |
| 17. Ans. (1) | 18. Ans.(3) | 19. Ans.(4) | 20. Ans.(4)  |
| 21. Ans.(1)  | 22. Ans.(2) | 23. Ans.(3) | 24. Ans.(1)  |
| 25. Ans.(4)  | 26. Ans.(2) | 27. Ans.(2) | 28. Ans.(3)  |
| 29. Ans.(1)  | 30. Ans.(2) | 31. Ans.(4) | 32. Ans.(2)  |
| 33. Ans.(2)  | 34. Ans.(3) | 35. Ans.(4) | 36. Ans.(2)  |
| 37. Ans.(1)  | 38. Ans.(3) | 39. Ans.(1) | 40. Ans.(3)  |
| 41. Ans.(3)  |             |             |              |

## EXERCISE # J-ADVANCED

- |               |                        |                |             |
|---------------|------------------------|----------------|-------------|
| 1. Ans.(A)    | 2. Ans.(A)             | 3. Ans.(B,C,D) | 4. Ans.(1)  |
| 5. Ans.(A,B)  | 6. Ans.(A,C)           | 7. Ans.(D)     | 8. Ans.(19) |
| 9. Ans.(0.05) | 10. Ans.(1.02 or 1.03) |                |             |

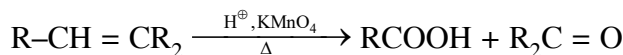
## OXIDATION

### (I) OXIDATION OF ALKENES



- \* Cold dil. alkaline  $\text{KMnO}_4$  is called as Bayer's reagent, use as a test of unsaturation.
- \* Overall syn addition
- \* Given by alkenes & alkynes
- \* Benzene & Cyclopropane can not give this reaction.

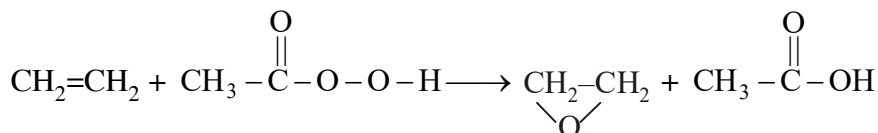
If we use acidic  $\text{KMnO}_4$  or warm  $\text{KMnO}_4$  or concentrated  $\text{KMnO}_4$  the oxidative cleavage of Glycol occurs resulting in mixture of Carboxylic acids & Ketones.



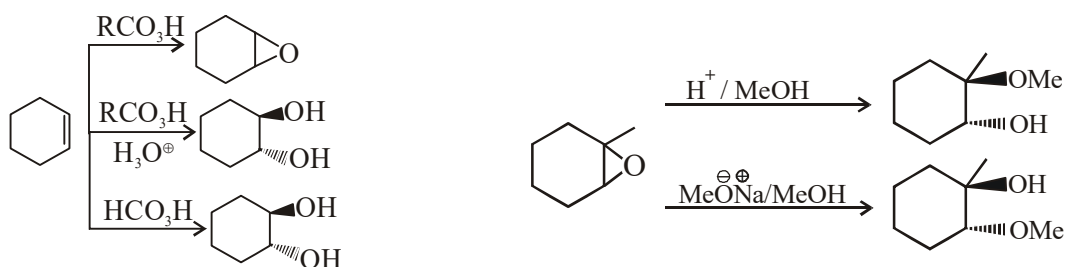
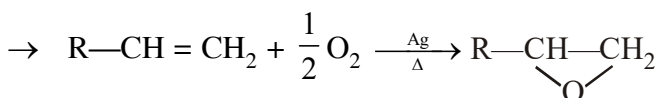
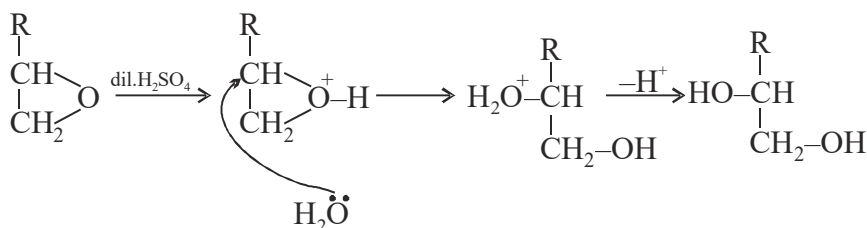
Hot acidic  $\text{KMnO}_4$ , Hot acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  & hot acidic  $\text{NaIO}_4$  gives same result with alkene. The effect is similar to that of oxidative ozonolysis on alkenes.

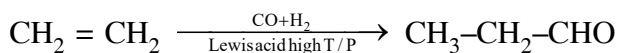
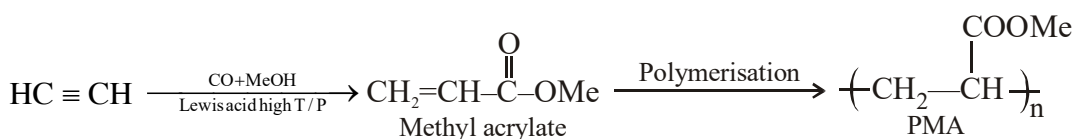
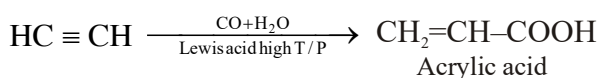
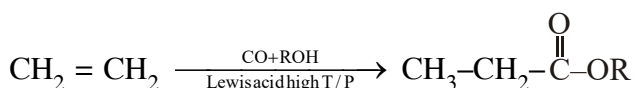
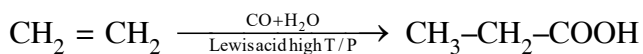
#### Preilschaive reaction :

Epoxidation of alkenes is reaction of alkenes with peroxyacids.

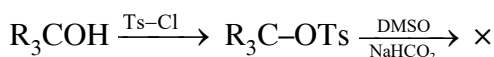
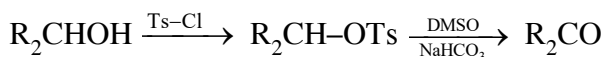
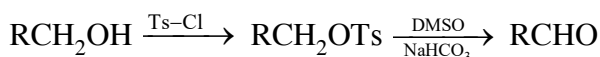
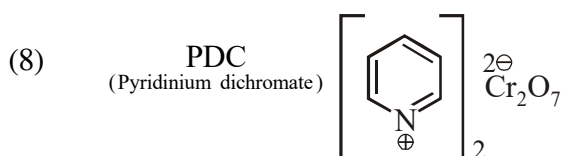
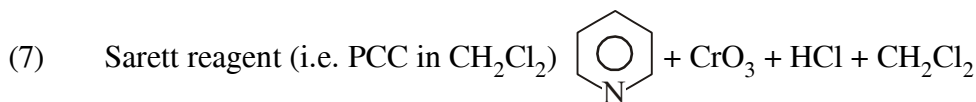
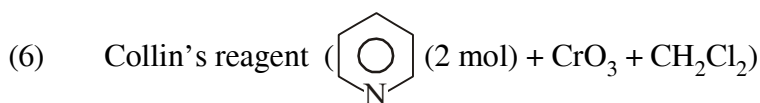
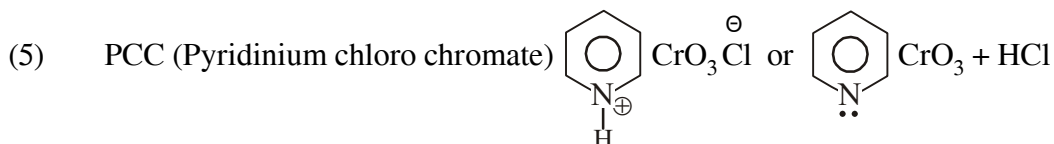


- Rate  $\propto$  nucleophilicity of alkene.
- With the increase in  $e^-$  withdrawing substituents in leaving group, rate increases.
- Hydrolysis of epoxides form anti diols.



**OXO PROCESS :****Hydroformylation/rolyen synthesis :****Carbonylation / Koch's reaction :****(II) OXIDATION OF ALCOHOLS****Oxidising agents**

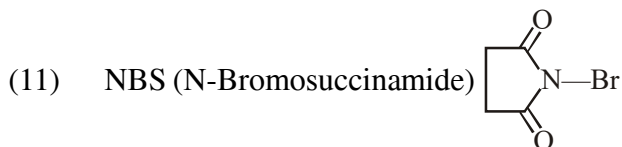
- (1)  $\text{H}^\oplus / \text{K}_2\text{Cr}_2\text{O}_7, \Delta$  (Strong oxidising agent)
- (2)  $\text{H}^\oplus / \text{KMnO}_4, \Delta$  (Strong oxidising agent)
- (3) **Jones reagent** :  $\text{CrO}_3 / \text{H}_2\text{SO}_4$  treated with alcohol usually taken in acetone (strong oxidising agent)
- (4)  $\text{Cu} / 300^\circ\text{C}$  (or Red hot Cu tube)



(10)  $\text{MnO}_2$ -Oxidises only allylic or benzylic-OH.  $1^\circ$  Allylic or benzylic OH  $\xrightarrow{\text{MnO}_2}$  Aldehyde

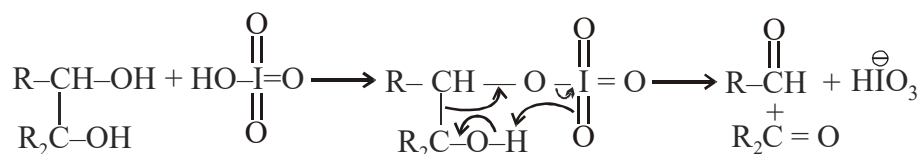
$2^\circ$  Allylic or benzylic OH  $\xrightarrow{\text{MnO}_2}$  Ketone

No effect on  $3^\circ$  ROH and on Carbon-Carbon multiple bond.



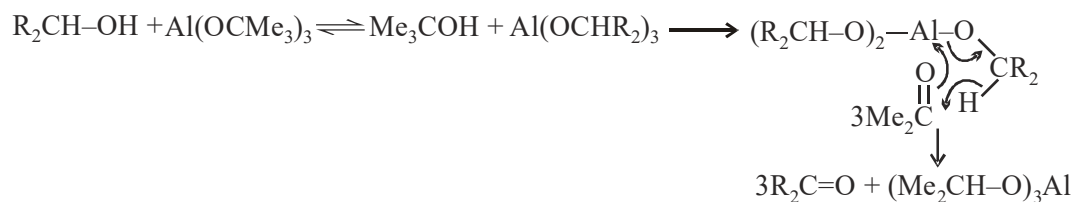
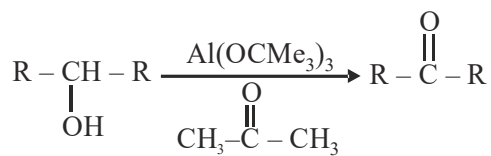
(12) **Periodic cleavage**

A similar oxidation is obtained in case of  $\text{HIO}_4$  known as periodic cleavage.



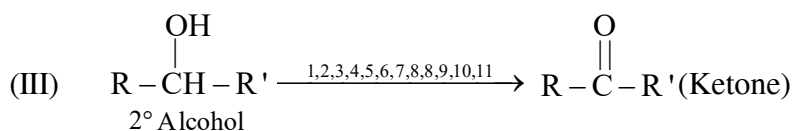
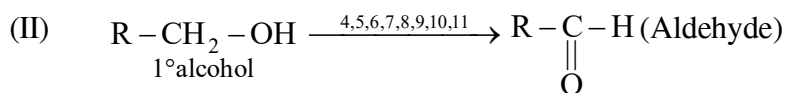
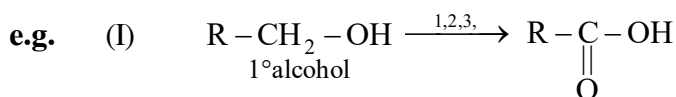
Reaction is observed for Vic-diols.

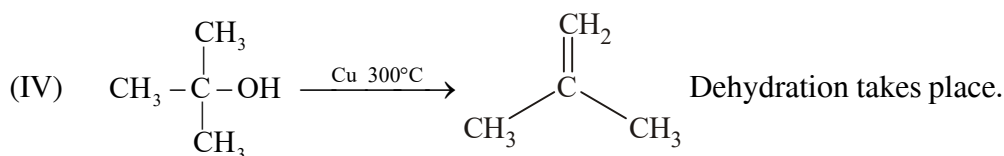
(13) **Openaur oxidation**



Oxidation of alcohol with aluminium tertiary butoxide is Openaur oxidation.

**Ex.** Different oxidising agents are used to oxidise alcohols in corresponding carbonyl compounds and carboxylic acids.



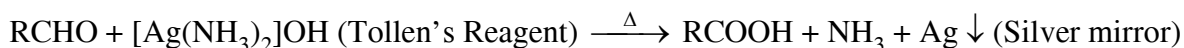


(V) Double bond or Tripple bond is not affected by 4,5,6,7,8,9,10

(VI) No effect on 3° alcohol by 1,2,3,5,6,7,8,9,10,12,13

### (III) OXIDATION OF CARBONYL COMPOUNDS

#### 1. Tollen's Test (Silver mirror test)



Aldehyde acts as reducing agent, they can reduce mild oxidizing agents like Tollen's Reagent.

Tollen's test gentle Heating for 20 to 25 mins.

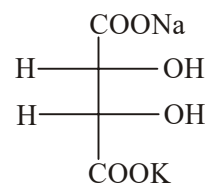
#### 2. Fehling's Solutions

Fehling's A

aq.  $\text{CuSO}_4$

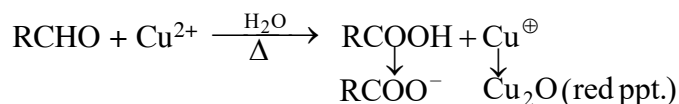
Fehling's B

Alkaline solution of Roschelye salt (sodium potassium tartrate)



It act's a carrier for  $\text{Cu}^{2+}$  as it make reversible complex with  $\text{Cu}^{2+}$

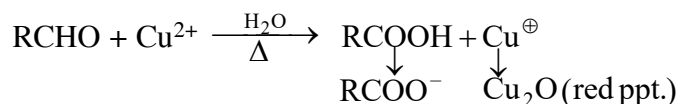
This test is also used is Blood and Urine test.



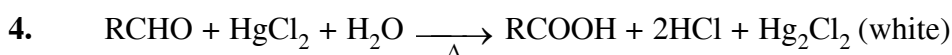
**Note :** Aromatic aldehyde shows negative test with fehling reagent.

#### 3. Benedict's solution

Sodium Citrate + NaOH +  $\text{NaHCO}_3$  +  $\text{CuSO}_4$



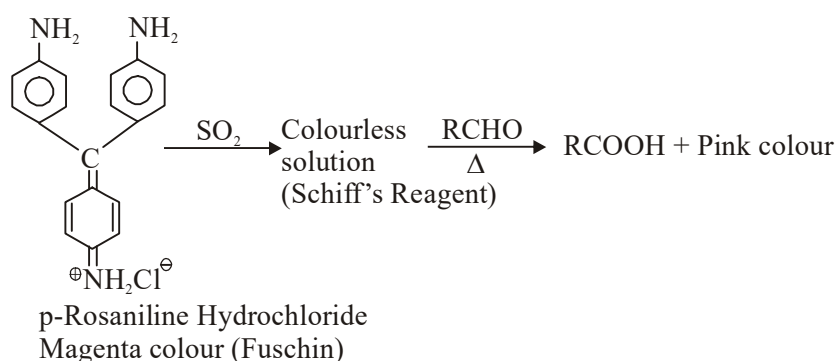
It is similar to Fehling test



#### 5. Schiff's Reagent

Schiff's Reagent is aq. solution of following base decolourised by passing  $\text{SO}_2$ .

Aldehyde restore pink colour of Schiff's reagent.

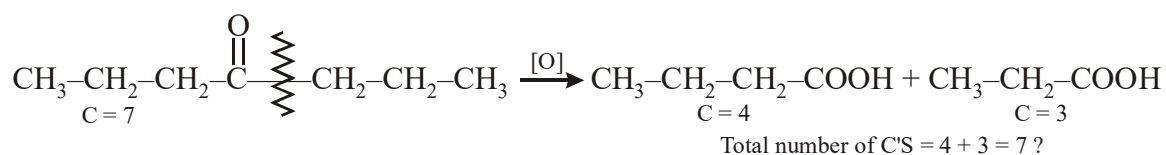


Ketons are not easy to oxidize so they do not give these 5 tests. These five tests can be used to distinguish aldehyde and ketones. Both gives 2,4 DNP test

**Oxidation of ketones :** Ketones undergo oxidation only in drastic conditions.

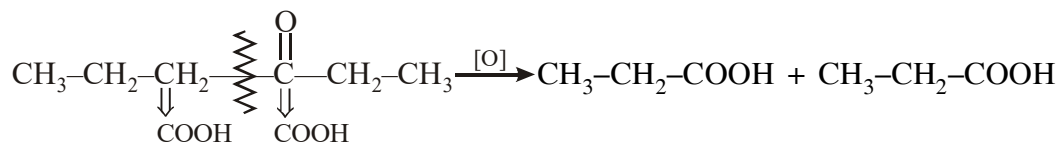
During the oxidation of ketones there is breaking of carbon-carbon bond between  $\alpha$ -carbon and carbonyl carbon. In this process both carbons convert into carboxylic groups. This leads to the formation of two moles of monocarboxylic acids.

**Case - I : Oxidation of Symmetrical ketones :**

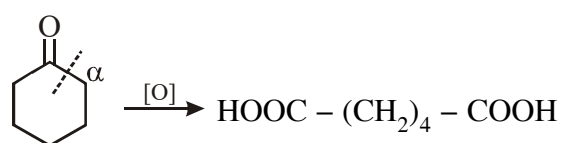


Thus number of carbons in any product is less than the number of carbons in ketone.

**Case - II : Oxidation of unsymmetrical ketones :** In case of unsymmetrical ketones, those  $\text{---C(=O)---R}$  bond break in which alkyl group has more number of carbons. This rule is known as **Poff's rule**.

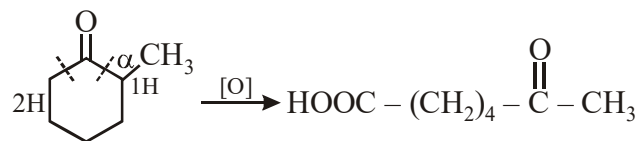


**Case - III : Oxidation of cyclic ketones :** Formation of dibasic acid takes place from cyclic ketones. In this case number of carbons in ketone and dibasic carboxylic acid is always same.



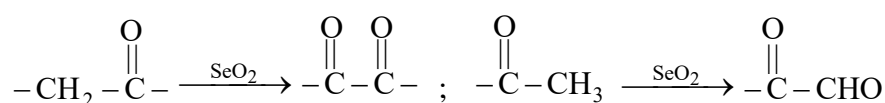


**Note :** If both  $\alpha$ -carbons are not identical then ;

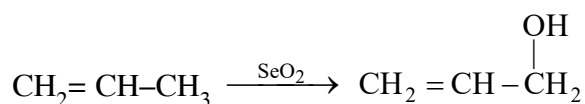


### Allylic oxidation

$\text{SeO}_2$  is a selective oxidizing agent which converts  $-\text{CH}_2-$  group adjacent to carbonyl group into carbonyl group. The reagent, in general, oxidises active methylene and methyl groups to ketonic and aldehydic groups respectively.

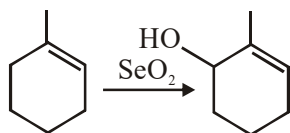
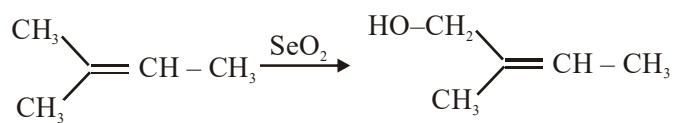
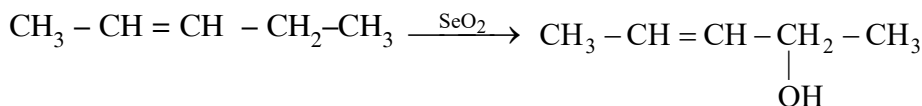


Double bonds, triple bonds and aromatic rings may also activate the methylene group. The methylene or methyl group  $\alpha$  to the most highly substituted end of the double bond is hydroxylated according to the order of preference of oxidation  $\text{CH}_2 > \text{CH}_3 > \text{CH}$  groups.

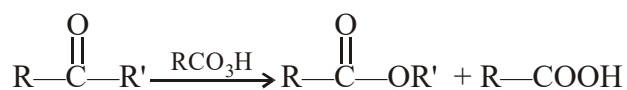


$2^\circ \text{C} - \text{H} > 1^\circ \text{C} - \text{H} > 3^\circ \text{C} - \text{H}$

Rate of reactivity order



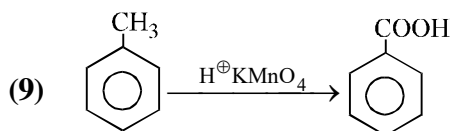
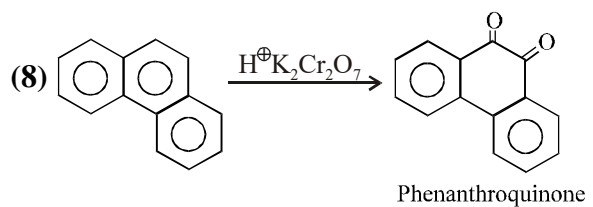
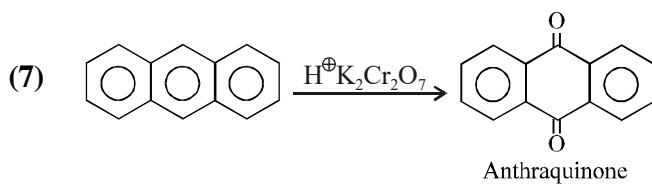
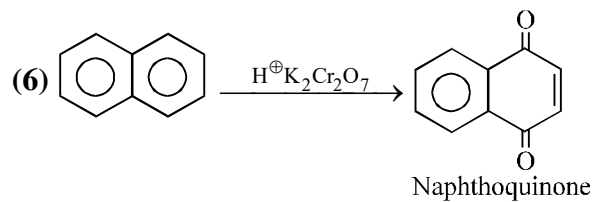
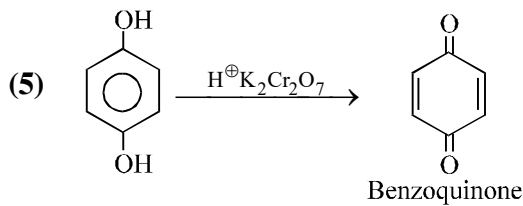
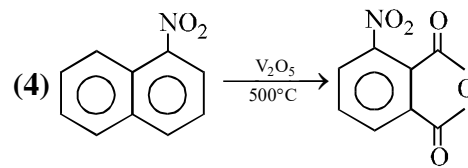
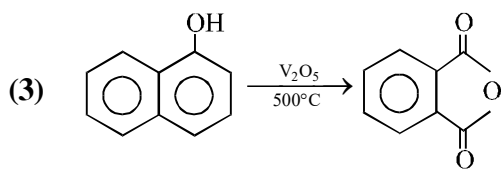
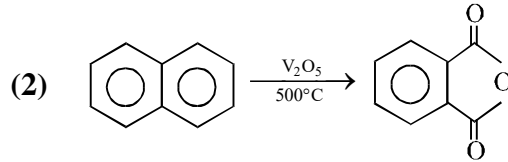
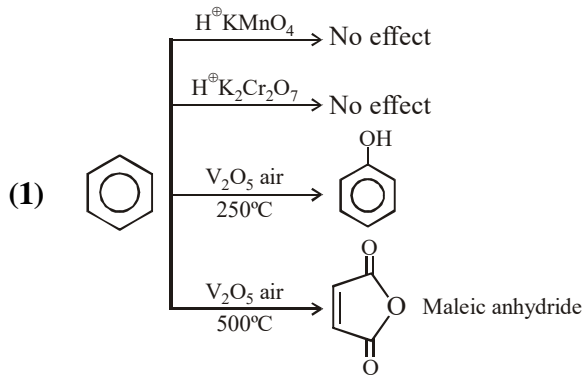
### Baeyer villiger oxidation




Migratory order for above reaction

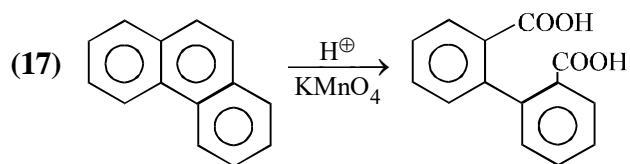
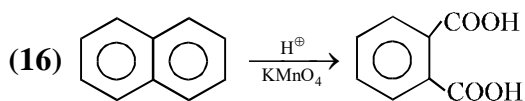
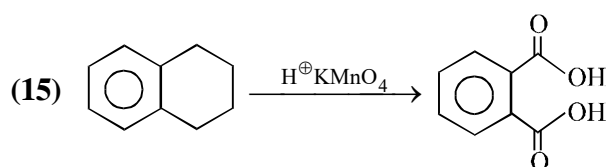
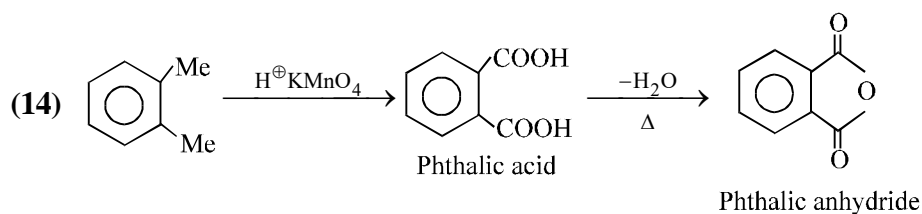
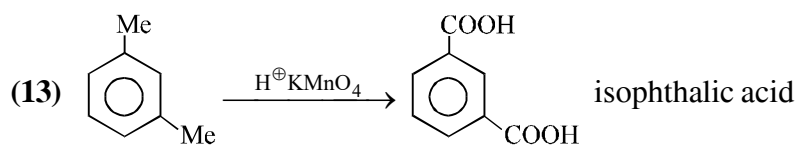
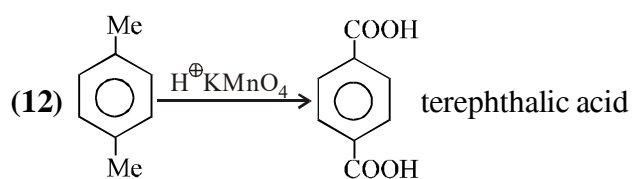
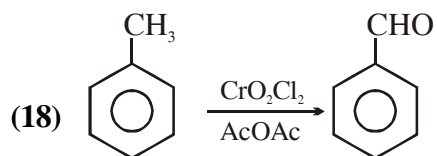
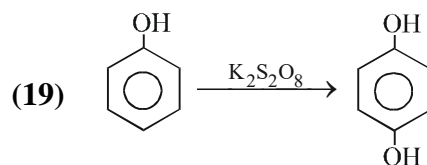
$-\text{H} > 3^\circ > 2^\circ > -\text{Ph} > 1^\circ > -\text{Me}$

Oxidation of Aromatic Compounds.



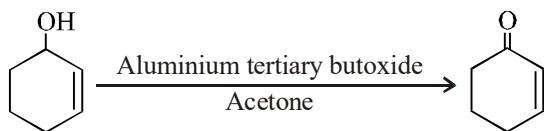
(10)  $Ph-(CH_2)_n-CH_3$ ,  $PhCHMe_2$ ,  $Ph-CH_2OH$ ,  $Ph-CH_2Br$ ,  $PhCHCl_2$ ,  $PhCHO$ ,  $Ph-$   & all the compounds having at least one  $\alpha$  H give  $PhCOOH$ .



**Etard oxidation****Elb's persulphate oxidation:**

## EXERCISE#O-I

1. The given reaction

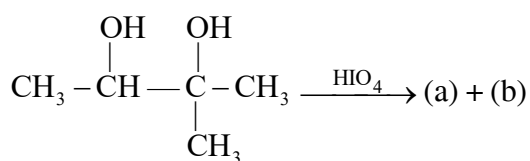


is known as :

- (A) Kolbe reaction      (B) Tischenko reaction      (C) MPV reaction      (D) Oppenauer oxidation

**OX0001**

2. In the given reaction :



(a) and (b) respectively be :

- (A)  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{CHO}$       (B)  $\text{CH}_3\text{COCH}_3$  and  $\text{CH}_3\text{CHO}$   
 (C)  $\text{CH}_3\text{COCH}_3$  and  $\text{CH}_3\text{COCH}_3$       (D)  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COCH}_3$

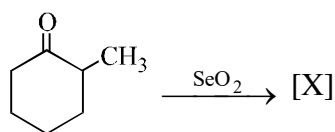
**OX0002**

3.  $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{H}$  and  $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$  is differentiated by

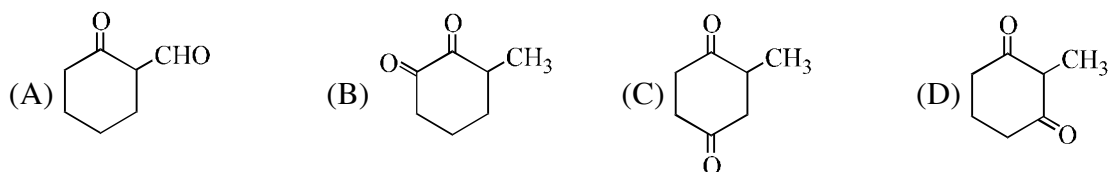
- (A) Tollen's reagent      (B) Lucas test      (C) Iodoform test      (D)  $\text{NaHSO}_3$  test

**OX0003**

4. In the given reaction



[X] will be:



**OX0004**

5. Which will give silver mirror test with Tollens reagent :

- (A)  $\text{C}_6\text{H}_5\text{CHO}$       (B)  $\text{CH}_3 - \text{CHO}$       (C)  $\text{HCOOH}$       (D) All of these

**OX0005**

6. Which one of the following compounds will give dimethyl glyoxal with  $\text{SeO}_2$ :

- (A) Acetone (B) Acetophenone  
(C) Ethyl methyl ketone (D) Propanaldehyde

OX0006

7. Which one of the following alcohols can be oxidised by  $\text{K}_2\text{CrO}_4$ ?

- (A) Ethanol (B) Tert butyl alcohol  
(C) Isopropyl alcohol (D) Allyl alcohol

OX0007

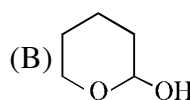
8. Fehling solution gives red precipitate with:

- (A) Aromatic aldehyde (B) Aliphatic aldehyde (C) Ketones (D)  $\begin{array}{c} \text{CH}_2 - \text{C} - \text{CH}_3 \\ | \quad || \\ \text{OH} \quad \text{O} \end{array}$

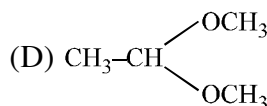
OX0008

9. Which of the following compound will give positive Tollens test

(A)  $\text{CH}_3\text{CHO}$



(C)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\underset{\text{OH}}{\text{CH}}-\text{OCH}_3$



OX0009

10. Schiff's reagent gives pink colour with :

- (A) Acetaldehyde (B) Formic acid (C) Acetic acid (D) Methyl acetate

OX0010

11. Which one of the following alcohols are oxidised by  $\text{MnO}_2$ ?

(A)  $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH}_2 - \text{OH}$

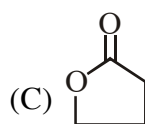
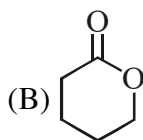
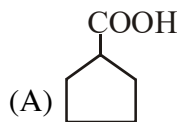
(B)  $\text{CH}_2 = \text{CH} - \text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \text{CH}_3$

(C)  $\text{CH}_3 - \text{CH} = \underset{\text{OH}}{\text{CH}} - \text{CH}_3$

(D)  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$

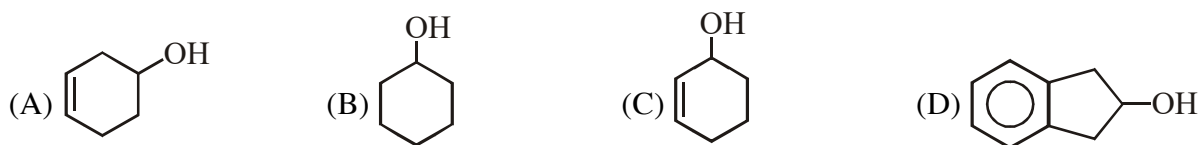
OX0011

12. Major product is :

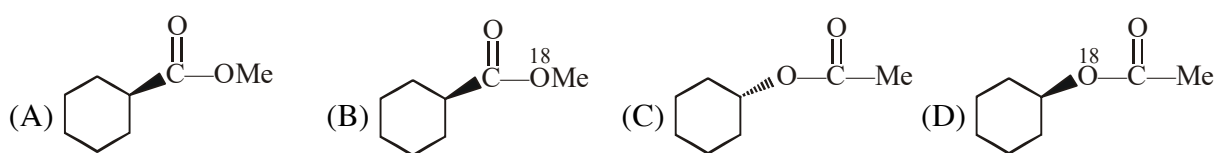
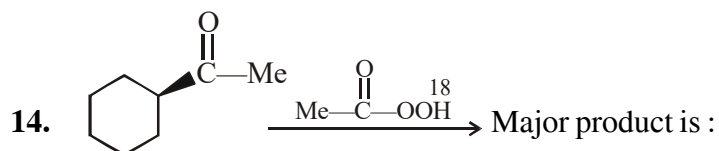


OX0012

13. Which of the following can be oxidised by  $MnO_2$ :

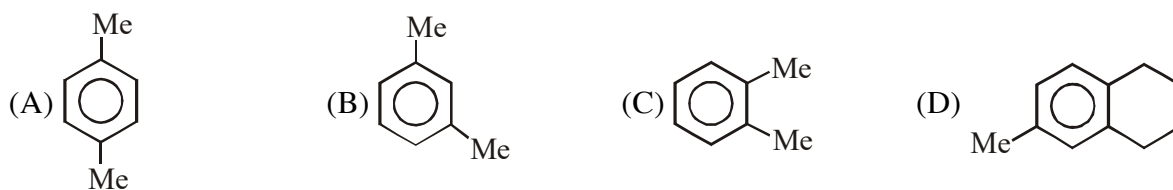


OX0013



OX0014

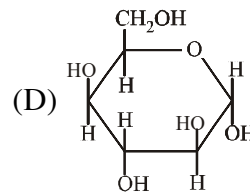
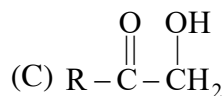
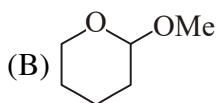
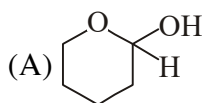
15.  $A \xrightarrow{H^+ / KMnO_4} B \xrightarrow{\Delta} \text{Phthalic Anhydride}$  ; A is :



OX0015

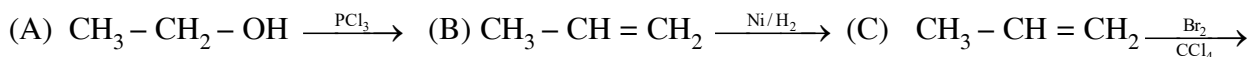
## EXERCISE#O-II

1. Which will give the Tollen test.

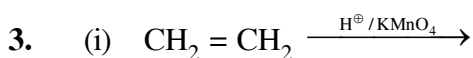


OX0016

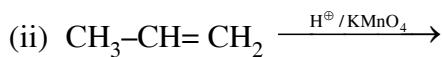
2. Which of the following is an example of oxidation reaction :



OX0017



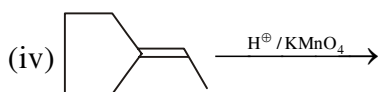
OX0018



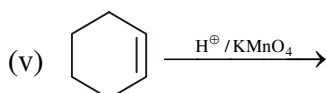
OX0019



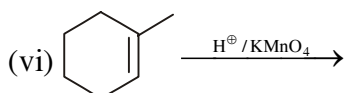
OX0020



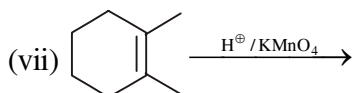
OX0020



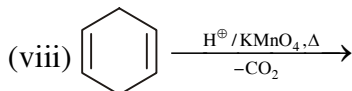
OX0021



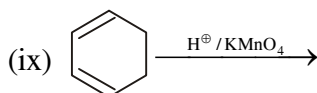
OX0021



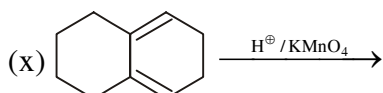
OX0022



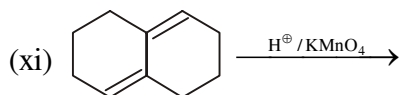
OX0022



OX0023



OX0023

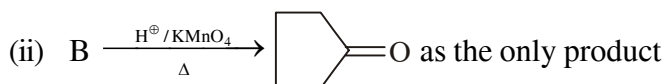


OX0023

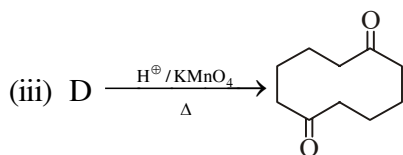
4. A to F alkenes with minimum possible carbon.



OX0024



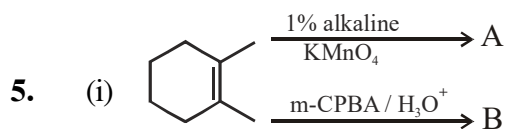
OX0024



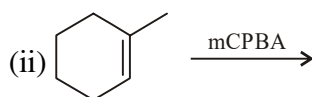
OX0025



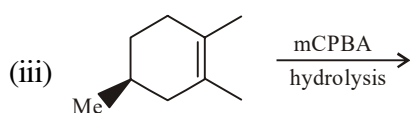
OX0025



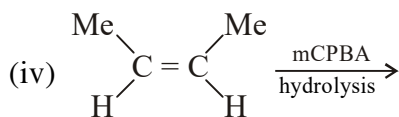
OX0026



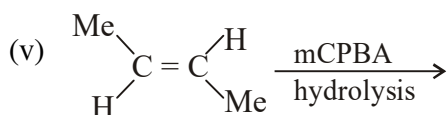
OX0026



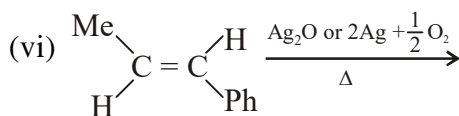
OX0027



OX0027

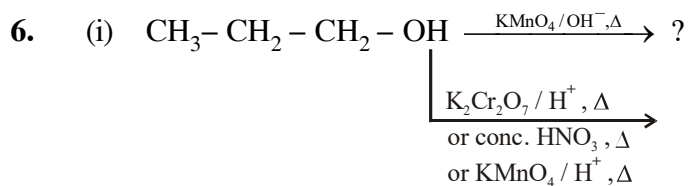


OX0028

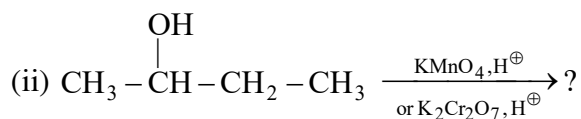


OX0028

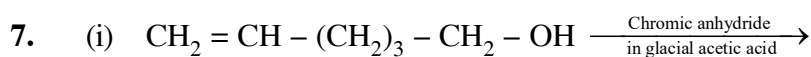




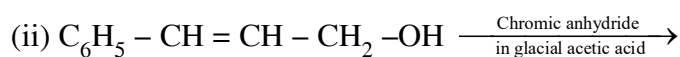
OX0029



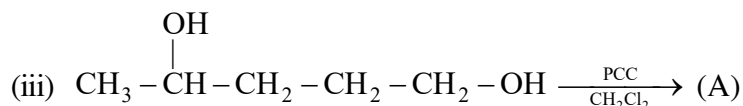
OX0029



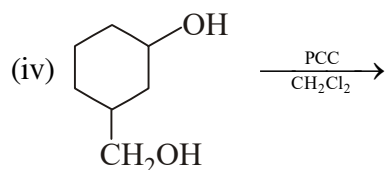
OX0030



OX0030



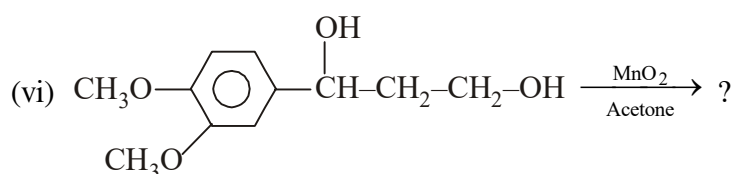
OX0030



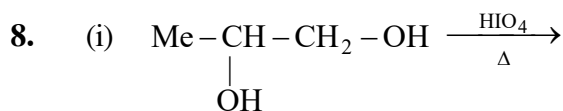
OX0031



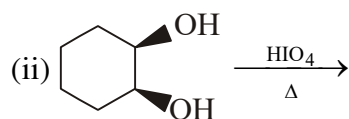
OX0031



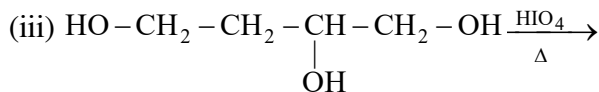
OX0031



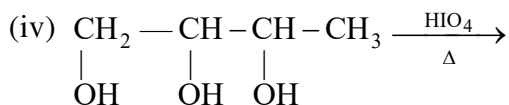
OX0032



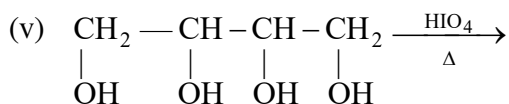
OX0032



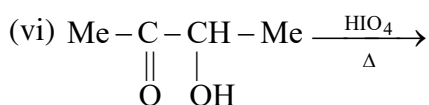
OX0032



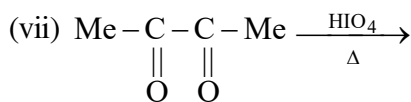
OX0032



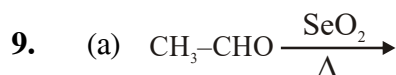
OX0033



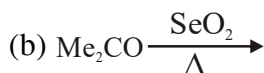
OX0033



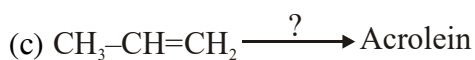
OX0033



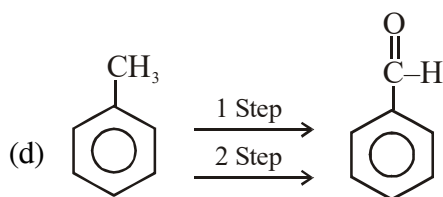
OX0034



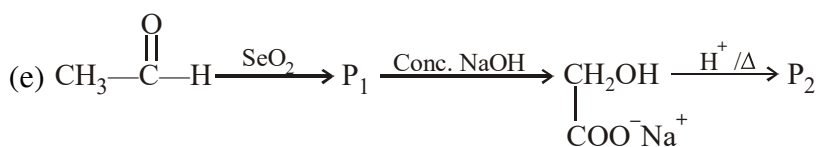
OX0034



OX0034



OX0035



OX0036

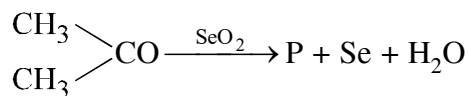
10. (a) How will you differentiate HCHO and PhCHO ?  
 (b) How will you differentiate HCHO and MeCHO ?

OX0037

## EXERCISE# (MAIN &amp; ADVANCE)

1. In the reaction, P is

[IIT 1995]



- (A)  $\text{CH}_3\text{COCHO}$       (B)  $\text{CH}_3\text{COOCH}_3$       (C)  $\text{CH}_3\text{COCH}_2\text{OH}$       (D) None

OX0038

2. The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is -

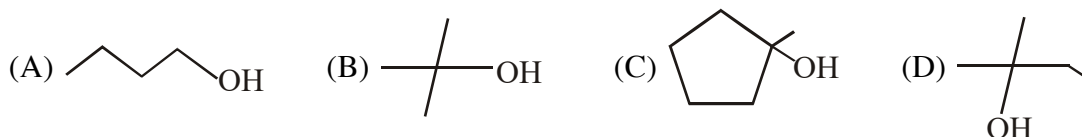
[AIIEEE-2005]

- (A) Acidic dichromate      (B) Acidic permanganate  
(C) Pyridinium chloro-chromate      (D) Chromic anhydride in glacial acetic acid

OX0039

3. Which of the following will change the colour of acidic dichromate solution.

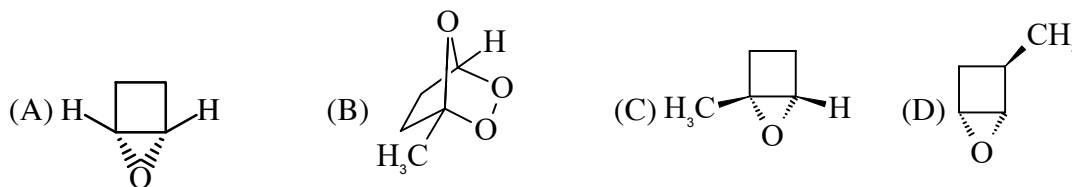
[JEE-MAINS 2013]



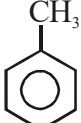
OX0040

4.   $\xrightarrow{\text{MCPBA}}$  Product

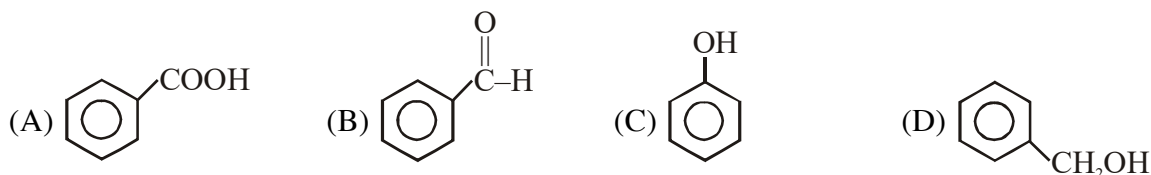
[JEE-MAINS 2013]



OX0041

5.   $\xrightarrow[\Delta]{\text{KMnO}_4}$  Major product of reaction is?

[JEE-MAINS 2013]



OX0042

6. The most suitable reagent for the conversion of  $\text{R-CH}_2\text{-OH} \rightarrow \text{R-CHO}$  is :-

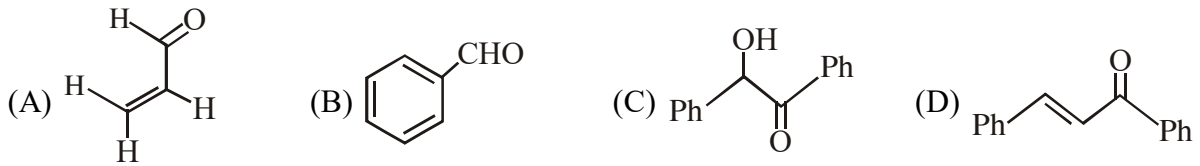
[JEE-MAINS 2014]

- (A)  $\text{CrO}_3$       (B) PCC (Pyridinium chlorochromate)  
(C)  $\text{KMnO}_4$       (D)  $\text{K}_2\text{Cr}_2\text{O}_7$

OX0043

7. Positive Tollen's test is observed for

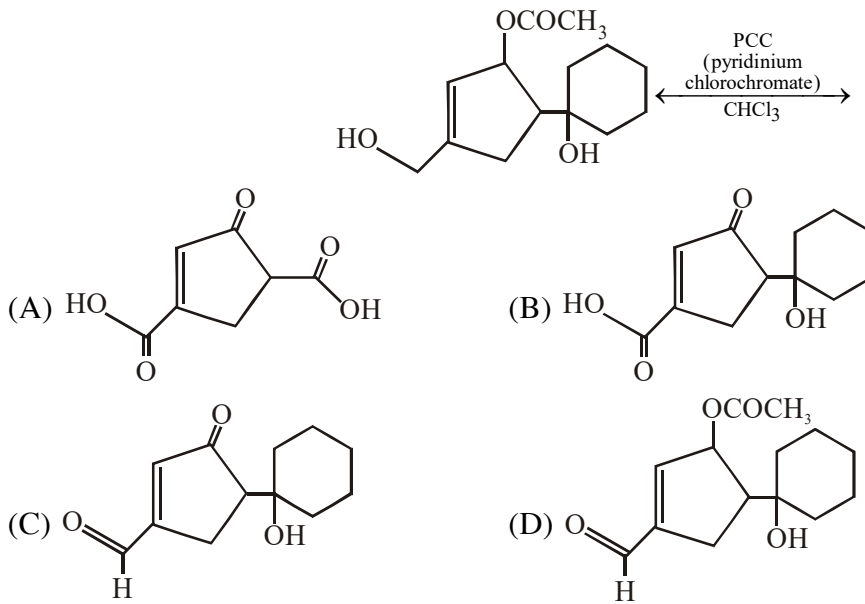
[JEE-Advance 2016]



OX0044

8. The major product formed in the following reaction is :-

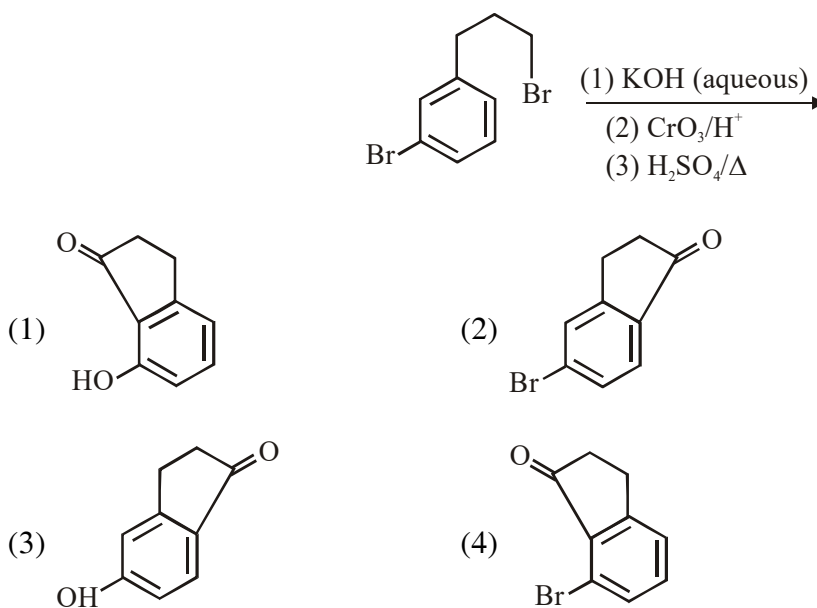
[Jee Main - Onl\_line Evening 2018]



OX0045

9. The major product of the following reaction is:

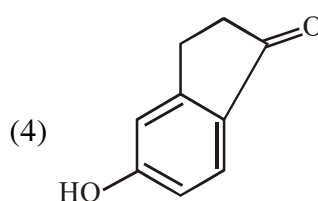
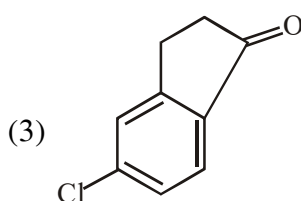
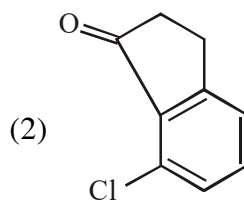
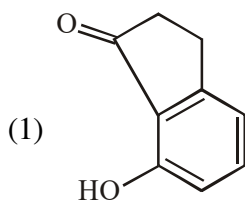
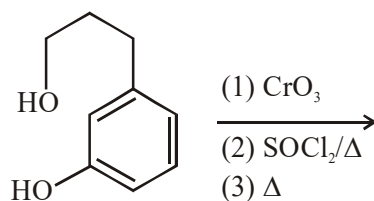
[JEE-MAIN-On-line-(Jan)-2019]



OX0046

10. The major product of the following reaction

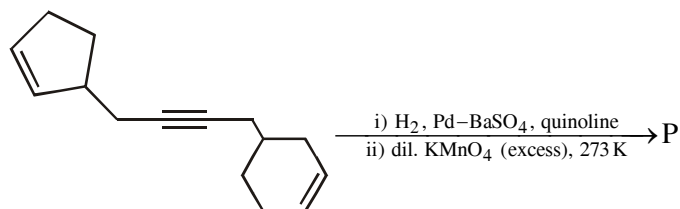
[JEE-MAIN-On-line-(April)-2019]



OX0047

11. Total number of hydroxyl groups present in a molecule of the major product P is \_\_\_\_

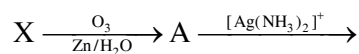
[JEE-Advance 2019]



OX0048

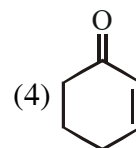
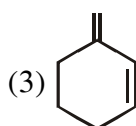
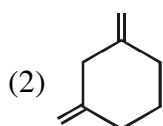
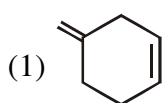
12. An unsaturated hydrocarbon X absorbs two hydrogen molecules on catalytic hydrogenation, and also gives following reaction :

[JEE-MAIN-On-line-(Jan)-2020]



B(3-oxo-hexanedicarboxylic acid)

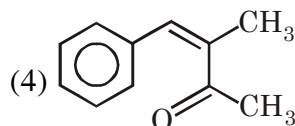
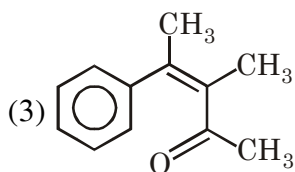
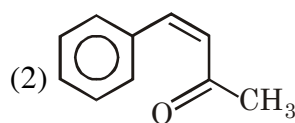
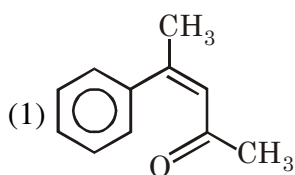
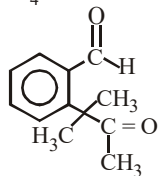
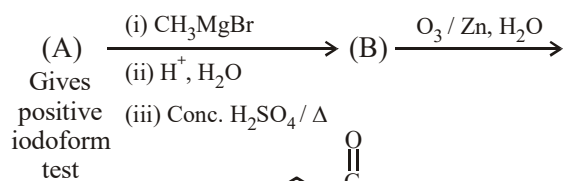
X will be :-



OX0049

13. Identify (A) in the following reaction sequence :

[JEE-MAIN-On-line-(Jan)-2020]



OX0050

## ANSWER-KEY

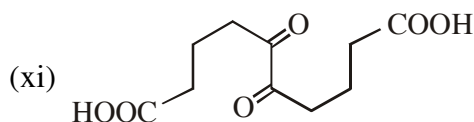
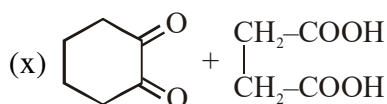
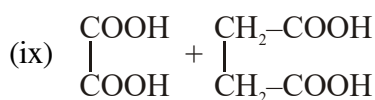
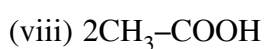
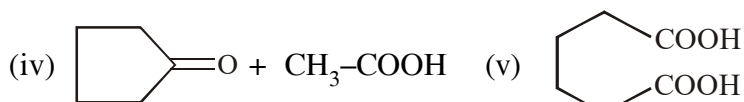
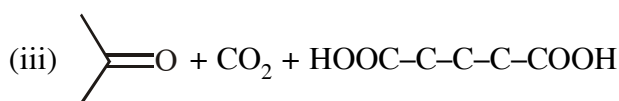
## EXERCISE#O-I

- |                 |                |                 |               |
|-----------------|----------------|-----------------|---------------|
| 1. Ans. (D)     | 2. Ans. (B)    | 3. Ans. (A)     | 4. Ans. (B)   |
| 5. Ans. (D)     | 6. Ans. (C)    | 7. Ans. (A,C,D) | 8. Ans. (B,D) |
| 9. Ans. (A,B,C) | 10. Ans. (A,B) | 11. Ans. (C)    | 12. Ans. (B)  |
| 13. Ans. (C)    | 14. Ans. (D)   | 15. Ans. (C)    |               |

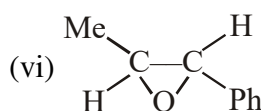
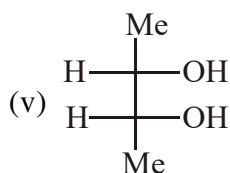
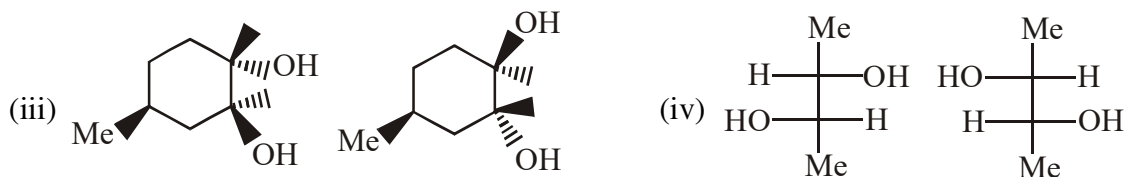
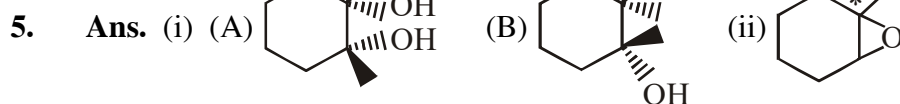
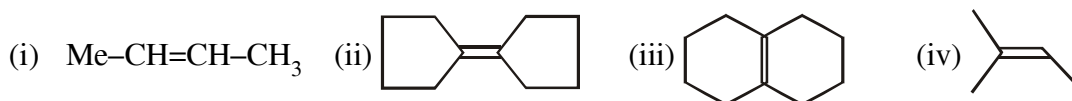
## EXERCISE#O-II

1. Ans. (A,C,D)      2. Ans. (C)

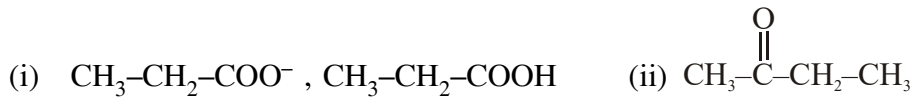
3. Ans.



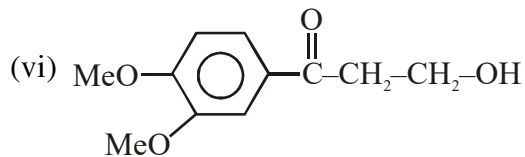
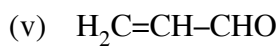
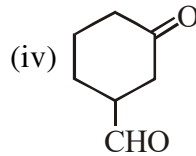
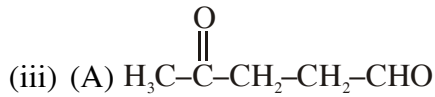
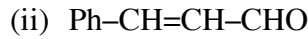
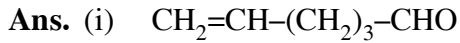
4. Ans.



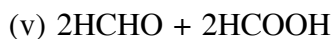
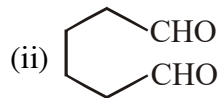
6. Ans.



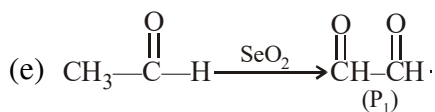
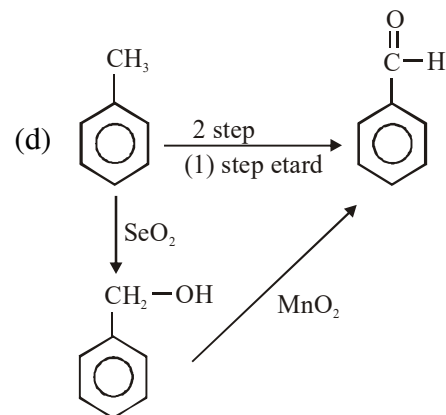
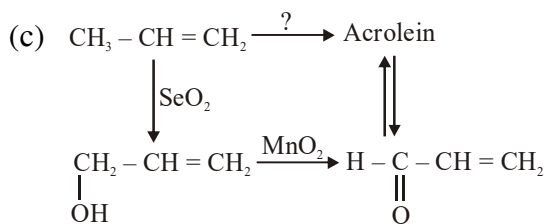
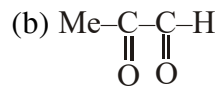
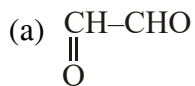
7.



8. Ans.



9. Ans.



10. (a) Ans. F and B test

(b) Ans. Iodoform test

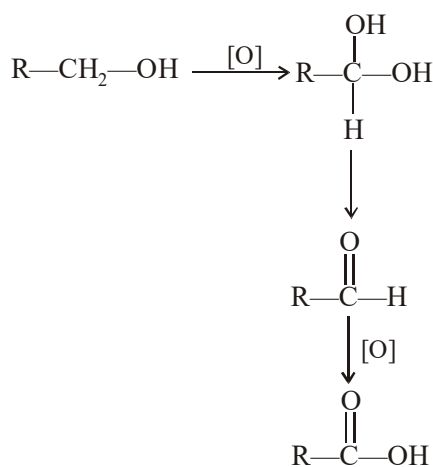


## EXERCISE# (MAIN &amp; ADVANCE)

1. Ans. (A)

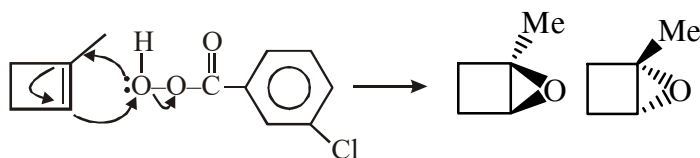
2. Ans. (D)

3. Ans. (A)



3° alcohols do not oxidize  
they undergo dehydration

4. Ans. (C)

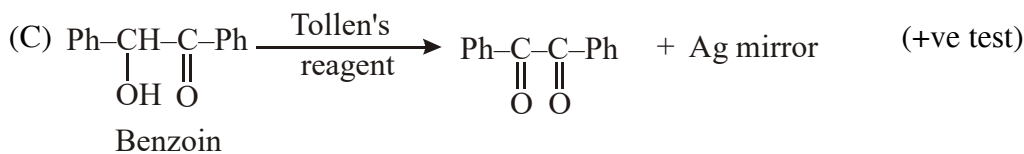
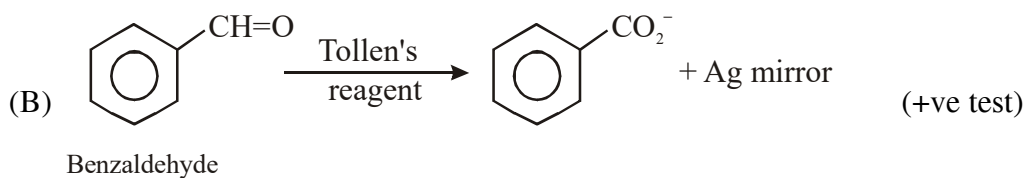
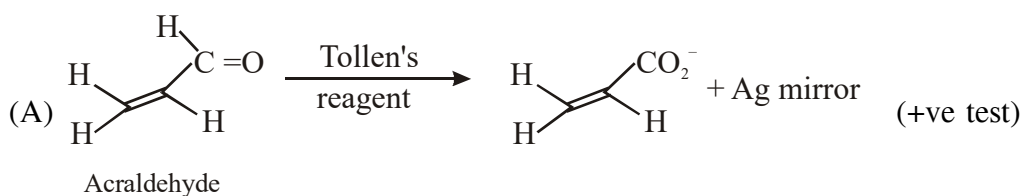


5. Ans. (A)

6. Ans. (B)

7. Ans. (A,B,C)

**Sol.** Tollens's test is given by compounds having aldehyde group. Also  $\alpha$ -hydroxy carbonyl gives positive tollen's test.



8. Ans. (D)

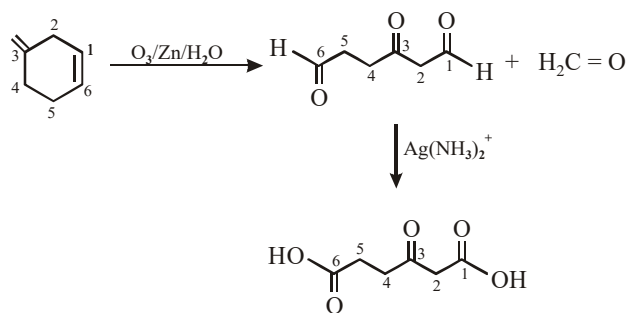
9. Ans. (2)

10. Ans. (4)

11. Ans. (6.00)

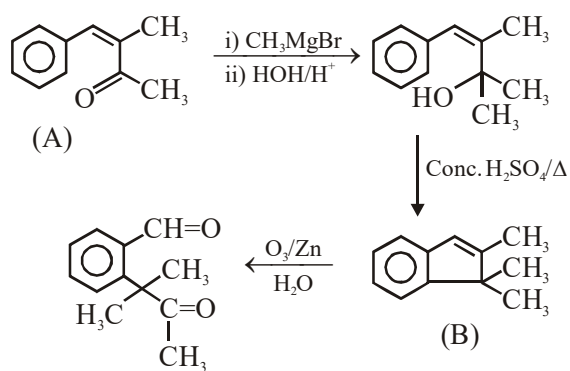
12. Ans. (1)

Sol.



13. Ans. (4)

Sol.

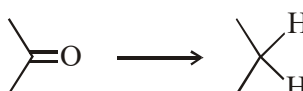
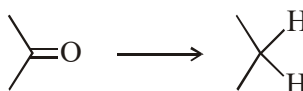
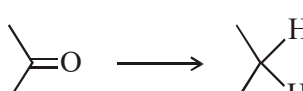
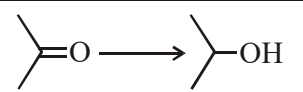
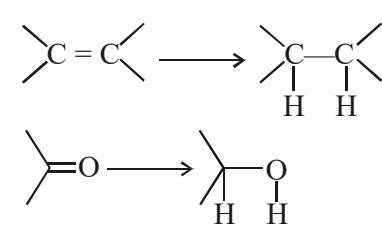
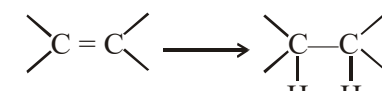


REDUCING AGENTS AND THEIR ROLE

Group	Product	LAH in Ether	NaBH <sub>4</sub> in H <sub>2</sub> O	B <sub>2</sub> H <sub>6</sub> in THF	H <sub>2</sub> / Catalyst Δ
-CHO	-CH <sub>2</sub> OH	+	+	+	+
>C = O	>CH - OH	+	+	+	+
-CO <sub>2</sub> H	-CH <sub>2</sub> OH	+	-	+	-
-CO <sub>2</sub> R	-CH <sub>2</sub> OH	+	-	+	+
-COCl	-CH <sub>2</sub> OH	+	+	-	+
-CONH <sub>2</sub>	-CH <sub>2</sub> NH <sub>2</sub>	+	-	+	+
(RCO) <sub>2</sub> O	RCH <sub>2</sub> OH	+	-	+	+
-CN	-CH <sub>2</sub> NH <sub>2</sub>	+	-	+	+
>C = NOH	-CH <sub>2</sub> NH <sub>2</sub>	+	-	-	+
>C = C<	>CH - CH<	-	-	+	+
-C ≡ C-	-CH = CH-	-	-	+	+
1° RX	RH	+	-	-	+

Note :

1. B<sub>2</sub>H<sub>6</sub> in THF not able to reduce cyclic ester.
2. NaBH<sub>4</sub> can also reduce imine group ( >C = NH ).
3. Reactivity order towards Ni / H<sub>2</sub> , Δ ⇒ -C ≡ N >  $\begin{matrix} -C \\ || \\ O \end{matrix}$  - O - R

Name	Reagent	Function
Wolf Kishner Reduction	(i) $N_2H_4$ / (ii) $KOH, \Delta$	
Clemenson Reduction	$Zn-Hg / HCl$	
Mozingo Reduction	$\begin{matrix} \text{SH} \\   \\ \text{---} \\   \\ \text{SH} \end{matrix}$ Dry $HCl$ , followed by Raney $Ni$	
Stephen's Reduction	$SnCl_2 / HCl$ followed by $H_3O^+$	$R-C \equiv N \longrightarrow R-CH=O$
MPV Reduction	$Al \left( \begin{matrix} \text{CH}_3 \\   \\ \text{---} \\   \\ \text{CH}_3 \end{matrix} \right)_3 / HO-CH \left( \begin{matrix} \text{CH}_3 \\   \\ \text{---} \\   \\ \text{CH}_3 \end{matrix} \right)$	
Hydroboration Reduction	$B_2H_6 / AcOH, H_2O$	
Bouvault Blank Reduction	$Na / EtOH$	$R-COO-R \longrightarrow RCH_2OH + ROH$
Transfer Hydrogenation	$N_2H_4 / H_2O_2$	
Rosenmund Reduction	$H_2, Pd-BaSO_4$	$R-\overset{O}{\parallel}C-Cl \longrightarrow R-\overset{O}{\parallel}C-H$ * $-C \equiv C- \longrightarrow \begin{matrix} \text{H} & \text{H} \\   &   \\ -C & = & C- \\   &   \\ \text{H} & \text{H} \end{matrix}$
Birch Reduction	$Na / Liq. NH_3$	$-C \equiv C- \longrightarrow \begin{matrix} \text{H} \\   \\ -C = C- \\   \\ \text{H} \end{matrix}$
DIBAL-H ( $-78^\circ C$ )	$H-Al \left( \begin{matrix} \text{---} & \text{CH} & \text{---} \\   &   & \\ \text{CH}_2 & \text{---} & \text{CH}_3 \\ &   & \\ & \text{CH}_3 & \end{matrix} \right)_2$ followed by $H_3O^+$	$\left. \begin{matrix} -COOR \\ -C \equiv N \\ -COCl \\ -\overset{O}{\parallel}C-O-\overset{O}{\parallel}C- \end{matrix} \right\} \longrightarrow -CHO$ $-CHO \left. \right\} \longrightarrow -CH_2OH$
Red phosphorus in presence of $HI$	Red $P + HI$	$R-CO_2H \longrightarrow RCH_3$ $R-CH=O \longrightarrow RCH_3$ $R-\overset{O}{\parallel}C-R \longrightarrow RCH_2R$ $R-\overset{O}{\parallel}O \longrightarrow R-H$

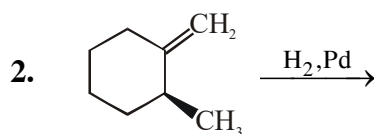
EXERCISE # O-I



The end products of the reaction are :

- (A)  $\text{CH}_3\text{C}(\text{CH}_3)\text{-SH}$  and  $\text{HS-CH}_2\text{-CH}_2\text{-SH}$  (B)  $\text{CH}_3\text{C}(\text{CH}_3)\text{-S-CH}_2\text{-CH}_2\text{-SH}$   
 (C)  $\text{CH}_3\text{C}(\text{CH}_3)\text{-S}_2\text{-CH}_2\text{-CH}_2\text{-SH}$  and  $\text{H}_2\text{O}$  (D)  $\text{CH}_3\text{C}(\text{CH}_3)=\text{O}$  and  $\text{HS-CH}_2\text{-CH}_2\text{-SH}$

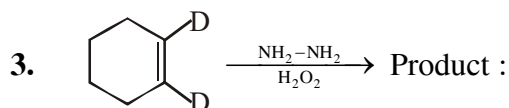
RD0001



Products of the above reaction will be :

- (A) Racemic mixture (B) Diastereomers (C) Meso (D) Structural isomer

RD0002



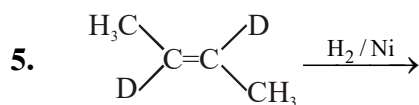
- (A)  $\text{Cyclohexane}$  (B)  $\text{Cyclohexane ring with D and H at } 1 \text{ and } 2$  (C)  $\text{Cyclohexane ring with D and H at } 1 \text{ and } 2$  (D) Both (B) and (C)

RD0003

4. On catalytic reduction with  $\text{H}_2/\text{Pt}$  how many alkenes will give n-butane ?

- (A) 1 (B) 2 (C) 3 (D) 4

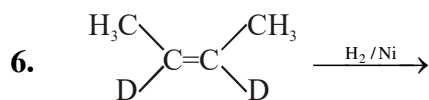
RD0004



Product of above reaction will be :

- (A) Racemic mixture (B) Diastereomers (C) Meso (D) Constitutional isomers

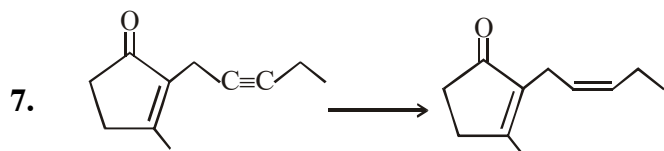
RD0005



Product of above reaction will be :

- (A) Racemic mixture (B) Diastereomers (C) Meso (D) Constitutional isomers

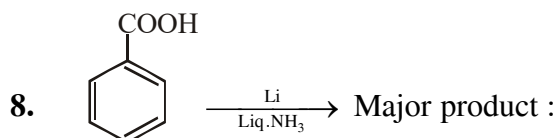
RD0006

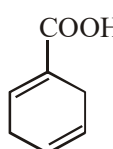
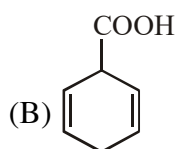
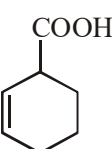
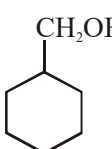


Which reagent will be used for the above conversion ?

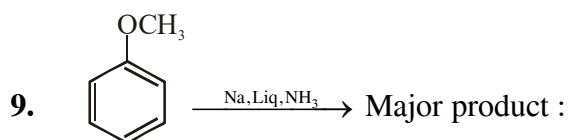
- (A) Na/Liq.  $\text{NH}_3$       (B)  $\text{H}_2$ , Pd- $\text{CaCO}_3$       (C) Li, Ph- $\text{NH}_2$       (D)  $\text{H}_2$ , Pt

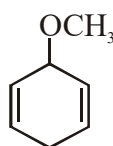
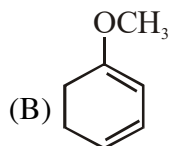
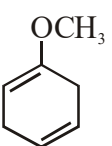
RD0007



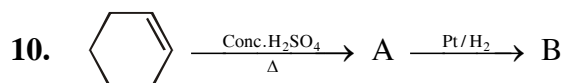
- (A)       (B)       (C)       (D) 

RD0008

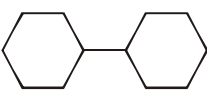





- (A)       (B)       (C)       (D) None of these

RD0009

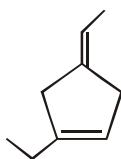


A and B respectively are :

- (A) Both       (B)   
 (C)       (D) 

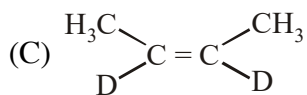
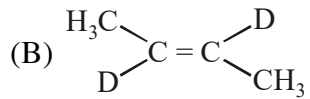
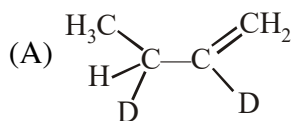
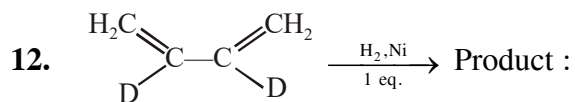
RD0010

11. If the following compound is treated with Pd in excess of  $\text{H}_2$  gas, how many stereoisomers of the product will be obtained ?



- (A) 1      (B) 2      (C) 3      (D) 4

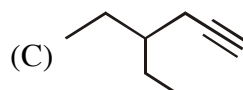
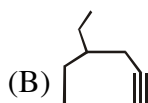
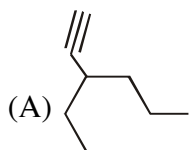
RD0011



(D) All of these

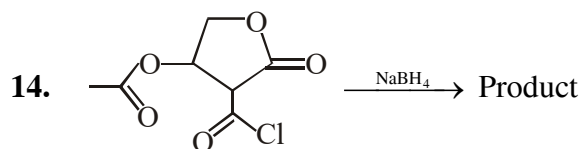
RD0012

13. Which alkyne gives 3-ethylhexane on catalytic hydrogenation ?

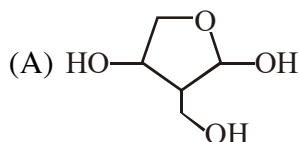


(D) All of these

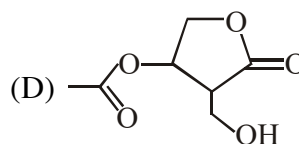
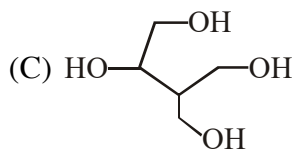
RD0013



The product is :



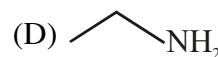
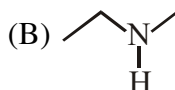
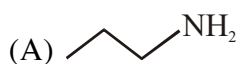
(B)  $\text{CH}_3-\text{CH}_2-\text{OH}$



RD0014

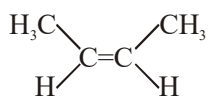
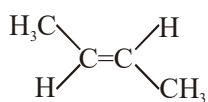
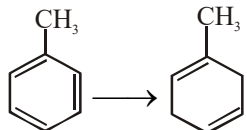


The final product (B) is :

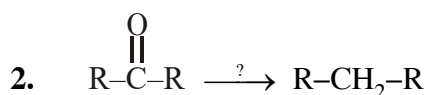


RD0015

## EXERCISE # O-II

1. Column-I (Conversion)	Column-II (Required Reagent)
(A) $\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{CH}_3 \longrightarrow$ 	(P) $\text{H}_2$ , Pd-BaSO <sub>4</sub>
(B) $\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{CH}_3 \longrightarrow$ 	(Q) Li, Liq.NH <sub>3</sub>
(C) $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_3 \longrightarrow \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	(R) N <sub>2</sub> H <sub>4</sub> / H <sub>2</sub> O <sub>2</sub> (1 eq.)
(D) 	(S) B <sub>2</sub> H <sub>6</sub> , CH <sub>3</sub> COOH

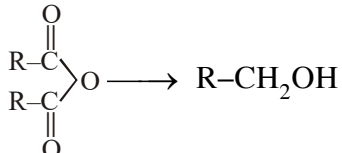
RD0016



Identify numbers of reagent that can be used for above conversion.

- (a) Zn-Hg / HCl      (b) LiAlH<sub>4</sub>      (c) N<sub>2</sub>H<sub>4</sub> /  $\overset{\ominus}{\text{O}}\text{H}$       (d)  $\begin{array}{c} \text{CH}_2-\text{SH} \\ | \\ \text{CH}_2-\text{SH} \end{array}$ , H<sub>2</sub> / Ni

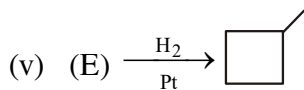
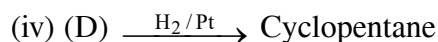
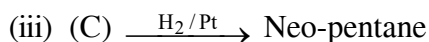
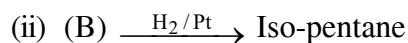
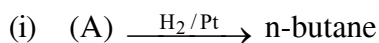
RD0017

3. Column-I (Conversion)	Column-II (Required Reagent)
(A) $-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \longrightarrow -\text{CH}_2\text{OH}$	(P) LiAlH <sub>4</sub>
(B) $-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl} \longrightarrow -\text{CH}_2\text{OH}$	(Q) NaBH <sub>4</sub>
(C) $-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}' \longrightarrow -\text{CH}_2\text{OH}$	(R) B <sub>2</sub> H <sub>6</sub> / THF
(D) 	(S) H <sub>2</sub> / Catalyst, Δ

RD0018

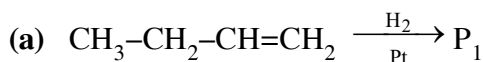


4. How many alkene on catalytic reduction gives following product.

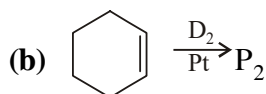


RD0019

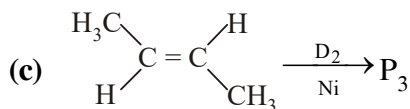
5. Give the expected major product for each reaction, including stereochemistry where applicable.



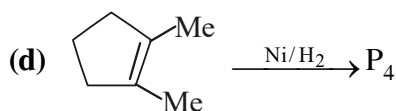
RD0020



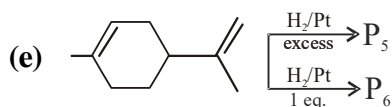
RD0021



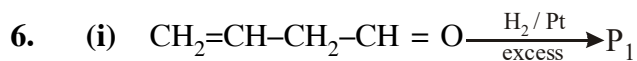
RD0022



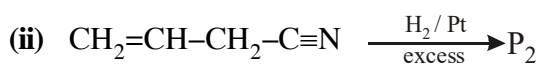
RD0023



RD0024

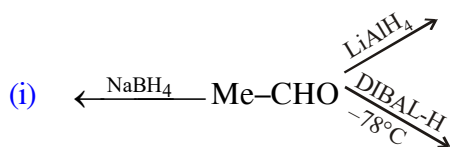


RD0025

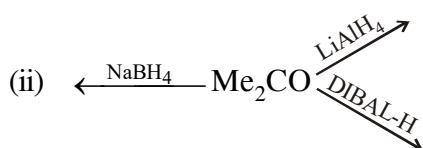


RD0026

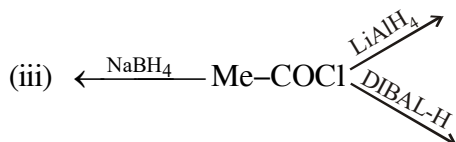
7. (a) Identify the product ?



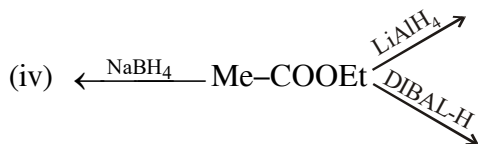
RD0027



RD0028



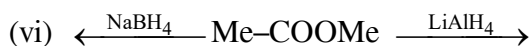
RD0029



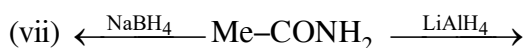
RD0030

**(b) Identify the product ?**

RD0031



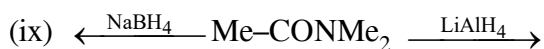
RD0031



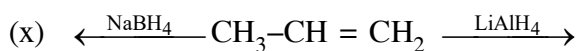
RD0031



RD0032



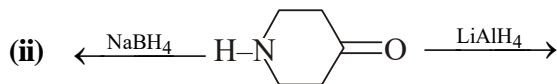
RD0032



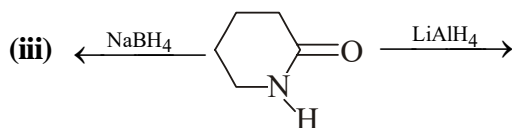
RD0032

**8. Give product in following reactions.**

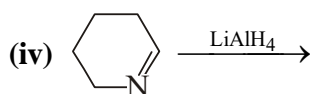
RD0033



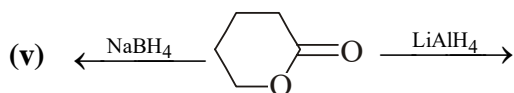
RD0034



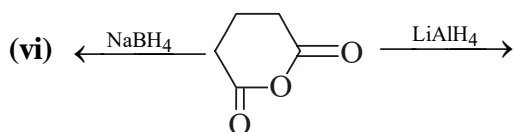
RD0033



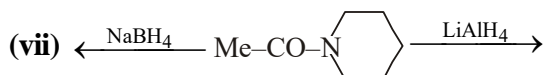
RD0034



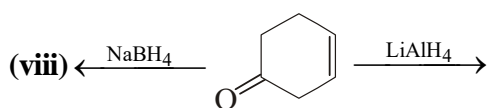
RD0033



RD0034

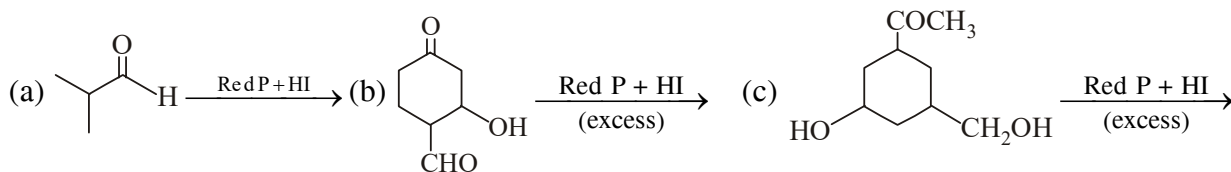


RD0033



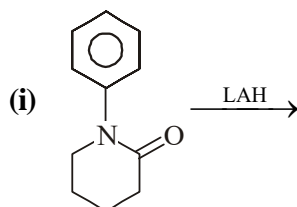
RD0034

9. Give product in following reactions.

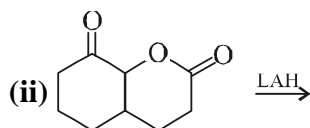


RD0035

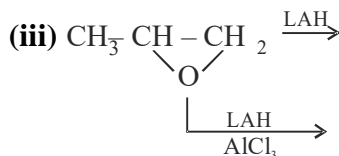
10. Give product in following reactions.



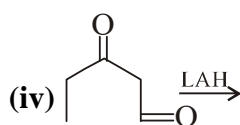
RD0036



RD0037

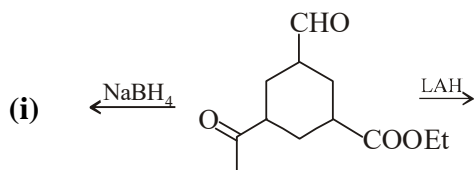


RD0038

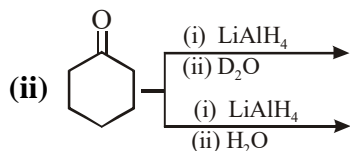


RD0039

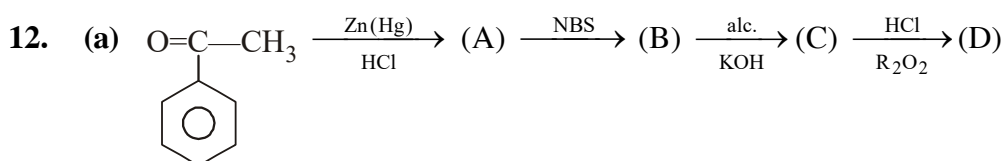
11. Give product in following reactions.



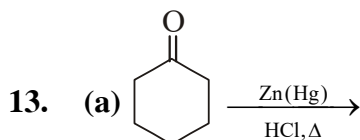
RD0040



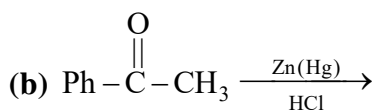
RD0041



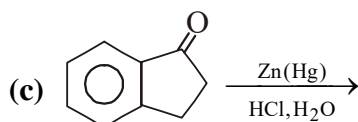
RD0042



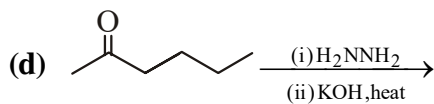
RD0043



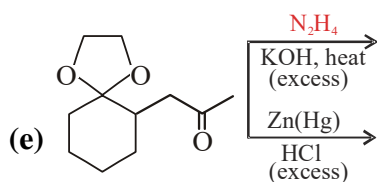
RD0043



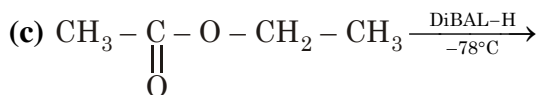
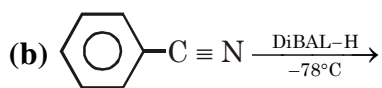
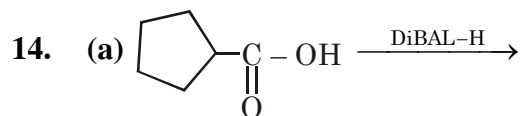
RD0043



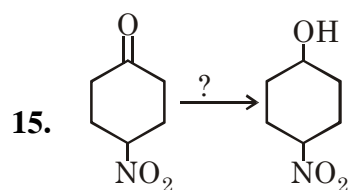
RD0044



RD0045



RD0046



above conversion can be achieved by

- (A)  $\text{LiAlH}_4$       (B)  $\text{H}_2 / \text{Ni}, \Delta$       (C)  $\text{NaBH}_4$       (D) All

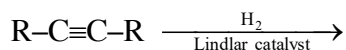
RD0047

## EXERCISE # (MAIN &amp; ADVANCE)

1. Hydrogenation of benzoyl chloride in the presence of Pd and BaSO<sub>4</sub> gives : [IIT 1992]  
 (A) Benzyl alcohol (B) Benzaldehyde (C) Benzoic acid (D) Phenol

RD0048

2. Draw the stereochemical structure of the product in the following reactions. [IIT 1994]

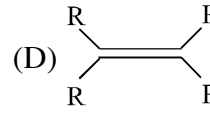
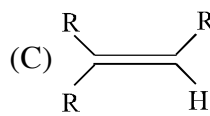
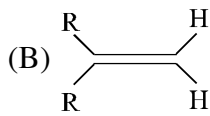
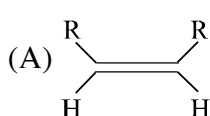


RD0049

3. Under Wolff Kishner reduction conditions, the conversions which may be brought about is?  
 (A) Benzaldehyde into Benzyl alcohol (B) Cyclohexanol into Cyclohexane  
 (C) Cyclohexanone into Cyclohexanol (D) Benzophenone into Diphenylmethane [IIT 1995]

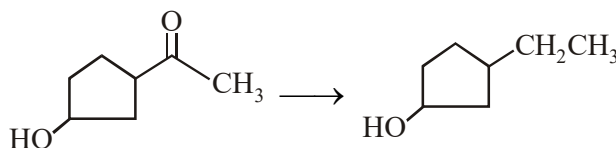
RD0050

4. Which one of the following alkenes will react fastest with H<sub>2</sub> under catalytic hydrogenation condition [IIT 2000]



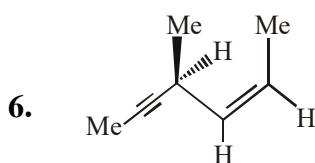
RD0051

5. The appropriate reagent for the following transformation: [IIT-2000]



- (A) Zn(Hg), HCl (B) NH<sub>2</sub>NH<sub>2</sub>, OH<sup>-</sup> (C) H<sub>2</sub>/Ni (D) NaBH<sub>4</sub>

RD0052



Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives-

- (A) An optically active compound (B) An optically inactive compound [IIT-2001]  
 (C) A racemic mixture (D) A diastereomeric mixture

RD0053

7. When CH<sub>2</sub>=CH-COOH is reduced with LiAlH<sub>4</sub>, the compound obtained will be -[AIIEEE-2003]  
 (A) CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>OH (B) CH<sub>3</sub>-CH<sub>2</sub>-CHO  
 (C) CH<sub>3</sub>-CH<sub>2</sub>-COOH (D) CH<sub>2</sub>=CH-CH<sub>2</sub>OH

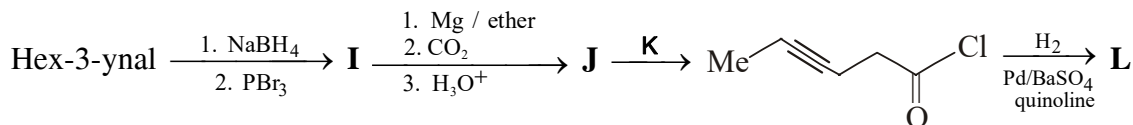
RD0054

8. 2-hexyne can be converted into trans-2-hexene by the action of : [IIT-2004]  
 (A) H<sub>2</sub>-Pd-BaSO<sub>4</sub> (B) Li in liq. NH<sub>3</sub> (C) H<sub>2</sub>-PtO<sub>2</sub> (D) NaBH<sub>4</sub>

RD0055

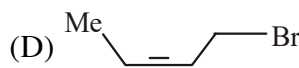
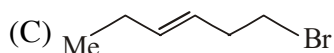
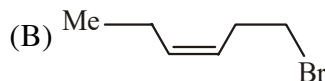
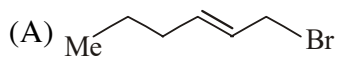
Paragraph for Question No. 09 to 11

In the following reaction sequence, products I, J and L are formed. K represents a reagent.



9. The structure of the product I is

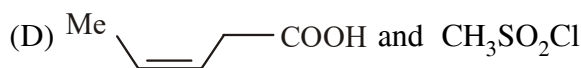
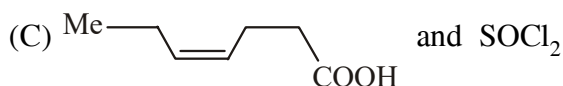
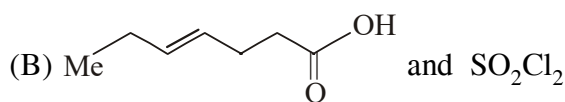
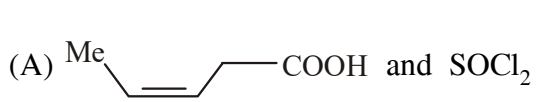
[JEE-2008]



RD0056

10. The structures of compounds J and K, respectively, are

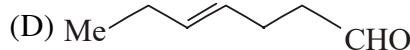
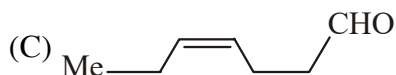
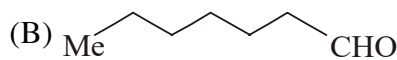
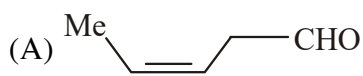
[JEE-2008]



RD0056

11. The structure of product L is :

[JEE-2008]



RD0056

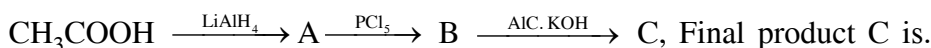
12. Consider all possible isomeric ketones including stereoisomers of MW = 100, All these isomers are independently reacted with NaBH<sub>4</sub> (NOTE : stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are.

[JEE-2014]

RD0057

13. In the reaction,

[JEE-2014]

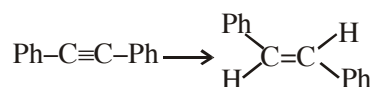


(A) Ethylene (B) Acetyl chloride (C) Acetaldehyde (D) Acetylene

RD0058

14. The reagent needed for converting is :

[JEE-2014]



(A) H<sub>2</sub> / Lindlar Cat.

(B) Cat. hydrogenation

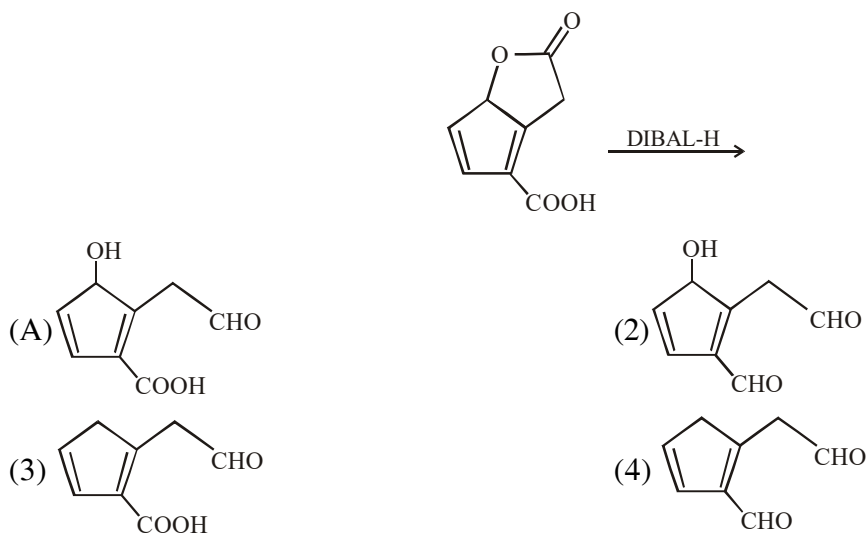
(C) LiAlH<sub>4</sub>

(D) Li / NH<sub>3</sub>

RD0059

15. The major product obtained in the following reaction is :

[JEE MAIN-2017]



RD0060

16. Glucose on prolonged heating with HI gives :

[Jee Main - 2018]

- (1) 1-Hexene                      (2) Hexanoic acid                      (3) 6-iodohexanal                      (4) n-Hexane

RD0061

17. The *trans*-alkenes are formed by the reduction of alkynes with :

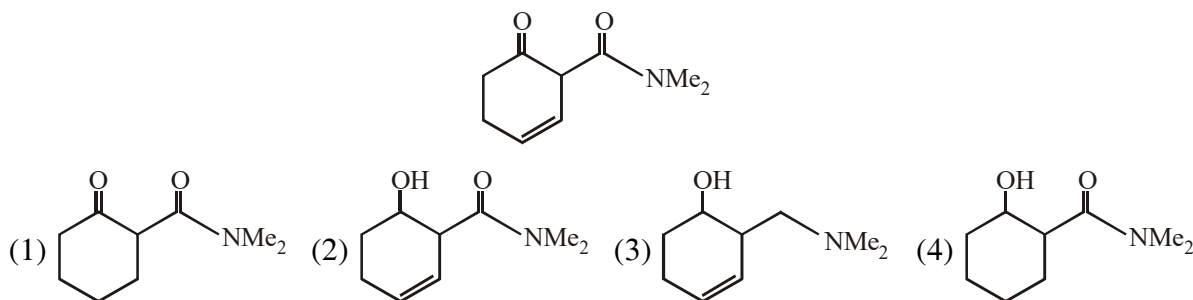
[Jee Main - 2018]

- (1)  $\text{NaBH}_4$                       (2)  $\text{Na/liq.NH}_3$                       (3)  $\text{Sn-HCl}$                       (4)  $\text{H}_2\text{-Pd/C, BaSO}_4$

RD0062

18. The main reduction product of the following compound with  $\text{NaBH}_4$  in methanol is :-

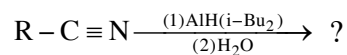
[Jee Main - Onl\_line Morning 2018]



RD0063

19. The major product of following reaction is :

[JEE-MAIN-On-line-(Jan)-2019]



- (1)  $\text{RCHO}$                       (2)  $\text{RCOOH}$                       (3)  $\text{RCH}_2\text{NH}_2$                       (4)  $\text{RCONH}_2$

RD0064

20. Wilkinson catalyst is :

[JEE-MAIN-On-line-(Jan)-2019]

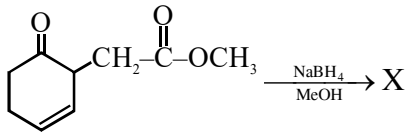
- (1)  $[(\text{Ph}_3\text{P})_3\text{RhCl}]$  ( $\text{Et} = \text{C}_2\text{H}_5$ )                      (2)  $[\text{Et}_3\text{P}]_3\text{IrCl}]$   
 (3)  $[\text{Et}_3\text{P}]_3\text{RhCl}]$                       (4)  $[\text{Ph}_3\text{P}]_3\text{IrCl}]$

RD0065



21. The major product 'X' formed in the following reaction is :

[JEE-MAIN-On-line-(Jan)-2019]

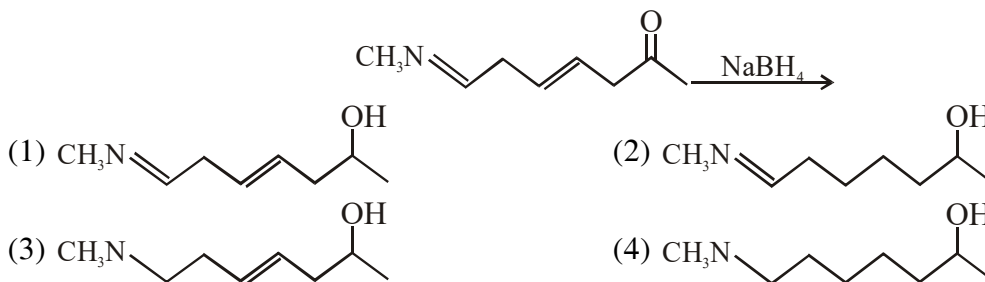


- (1) (2) (3) (4)

RD0066

22. The major product of the following reaction is:

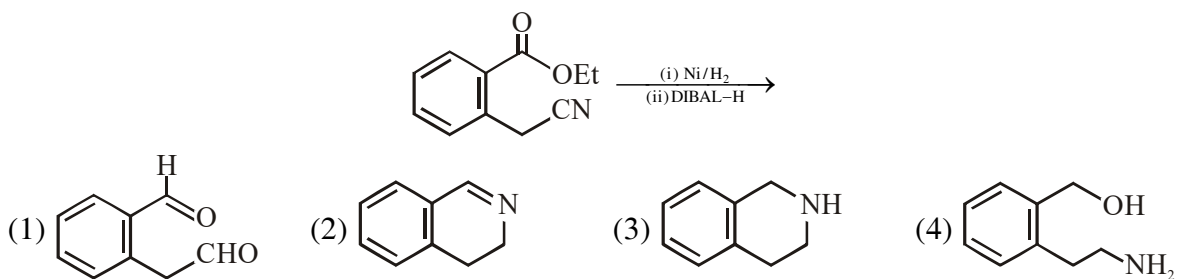
[JEE-MAIN-On-line-(Jan)-2019]



RD0067

23. The major product of the following reaction is:

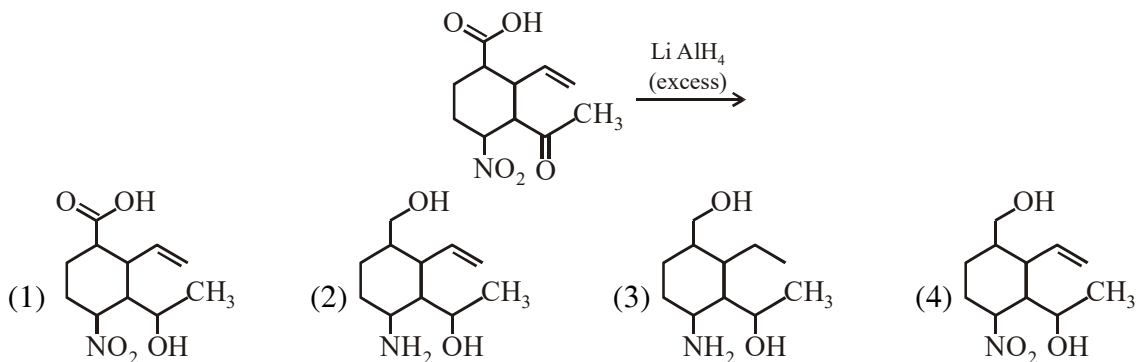
[JEE-MAIN-On-line-(Jan)-2019]



RD0068

24. The major product obtained in the following reaction is :-

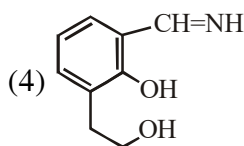
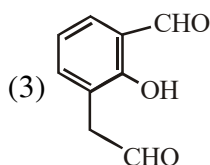
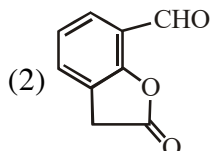
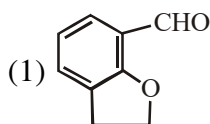
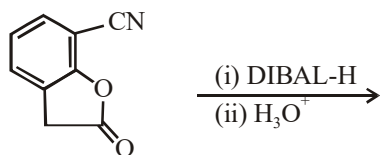
[JEE-MAIN-On-line-(Jan)-2019]



RD0069

25. The major product of the following reaction is:

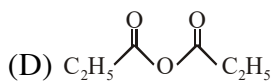
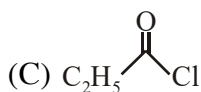
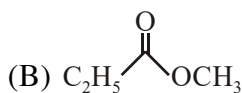
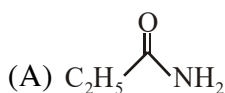
[JEE-MAIN-On-line-(Jan)-2019]



RD0070

26. The increasing order of the reactivity of the following with  $\text{LiAlH}_4$  is :

[JEE-MAIN-On-line-(Jan)-2019]



(1) (A) < (B) < (D) < (C)

(2) (A) < (B) < (C) < (D)

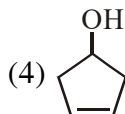
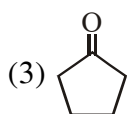
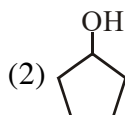
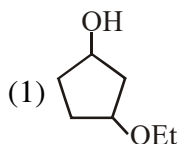
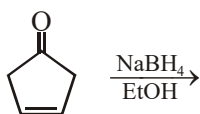
(3) (B) < (A) < (D) < (C)

(4) (B) < (A) < (C) < (D)

RD0071

27. The major product of the following reaction is:

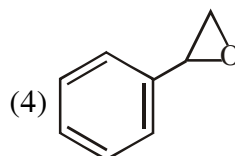
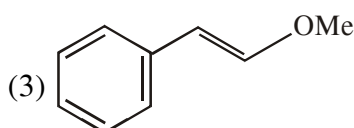
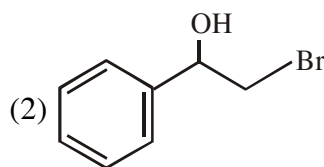
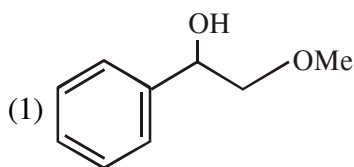
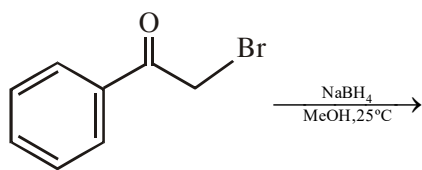
[JEE-MAIN-On-line-(Jan)-2019]



RD0072

28. The major product of the following reaction is:

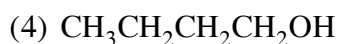
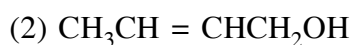
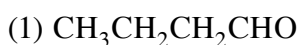
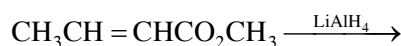
[JEE-MAIN-On-line-(April)-2019]



RD0073

29. The major product of the following reaction is :

[JEE-MAIN-On-line-(April)-2019]

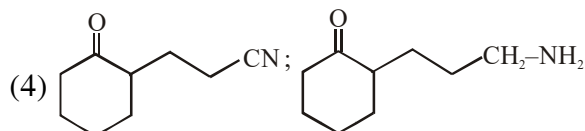
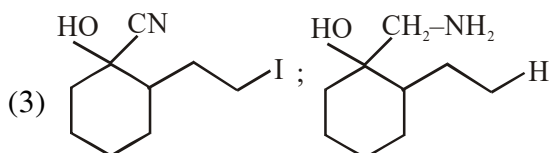
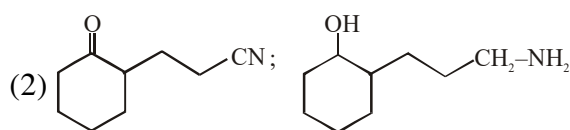
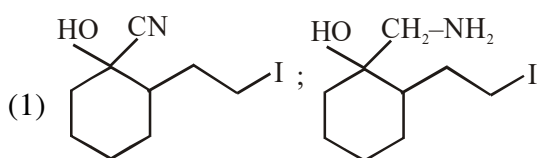


RD0074

30. The major products A and B for the following reactions are, respectively:



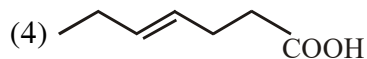
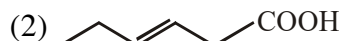
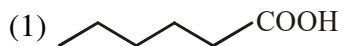
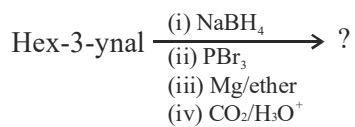
[JEE-MAIN-On-line-(April)-2019]



RD0075

31. What is the product of following reaction ?

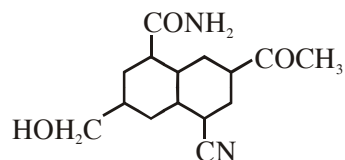
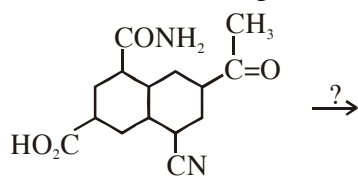
[JEE-MAIN-On-line-(Jan)-2020]



RD0076

32. The most suitable reagent for the given conversion is :

[JEE-MAIN-On-line-(Jan)-2020]




RD0077

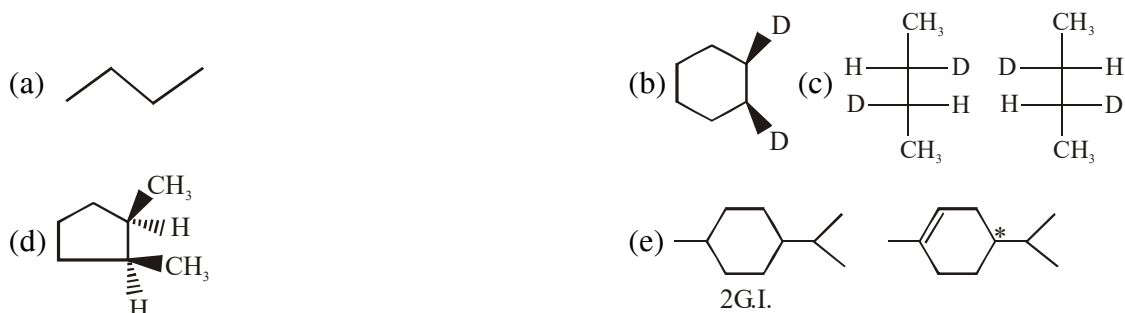
ANSWER KEY  
EXERCISE # O-I

- |              |              |              |              |              |
|--------------|--------------|--------------|--------------|--------------|
| 1. Ans. (D)  | 2. Ans. (B)  | 3. Ans. (C)  | 4. Ans. (C)  | 5. Ans. (A)  |
| 6. Ans. (C)  | 7. Ans. (B)  | 8. Ans. (B)  | 9. Ans. (C)  | 10. Ans. (B) |
| 11. Ans. (C) | 12. Ans. (C) | 13. Ans. (D) | 14. Ans. (D) | 15. Ans. (B) |

EXERCISE # O-II

1. Ans. (A)→P, R, S; (B)→Q; (C)→R, S; (D)→Q      2. Ans. (3)
3. Ans. (A)→P, R, S; (B)→P, Q, S; (C)→P, R, S; (D)→P, R, S
4. Ans.  
 (i) Cis & trans 2-butene & 1-butene ;      (ii)  $\begin{matrix} \text{C}-\text{C}-\text{C}=\text{C} & \text{C}-\text{C}=\text{C}-\text{C} & \text{C}-\text{C}-\text{C}-\text{C} \\ | & | & || \\ \text{C} & \text{C} & \text{C} \end{matrix}$   
 (iii) Zero (Neo-pentane can not be prepared by catalytic hydrogenation of alkene) ;      (iv) One  
 (v) Including optical = 4  , Excluding optical = 3.

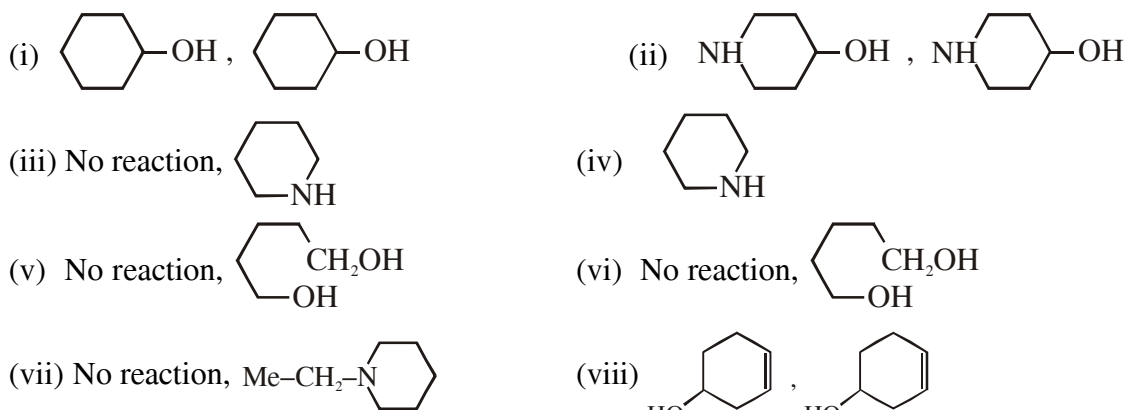
5. Ans.




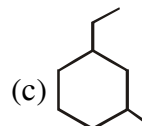
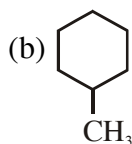
6. Ans. (i)  $P_1 = \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$

(ii)  $P_2 = \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$

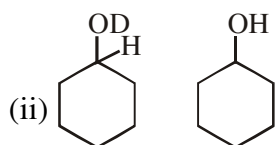
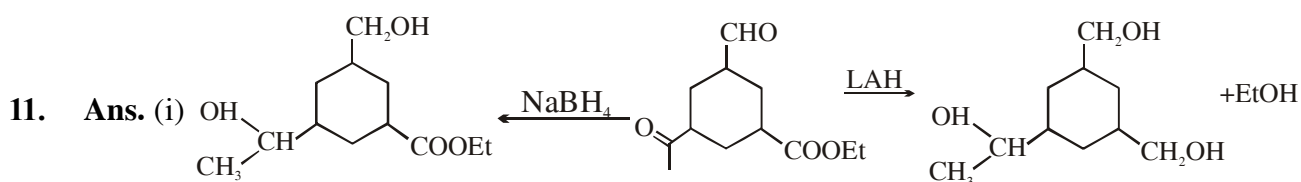
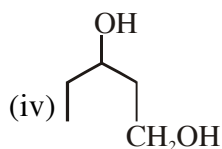
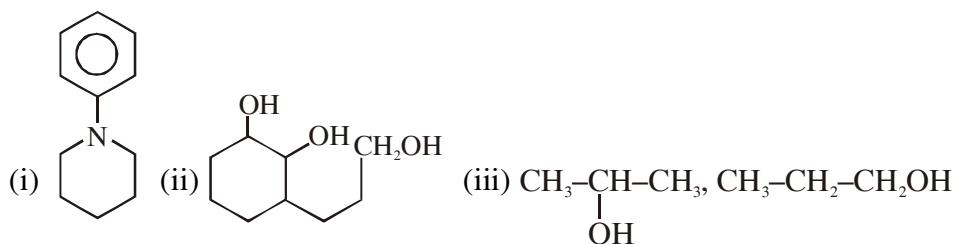
8. Ans.



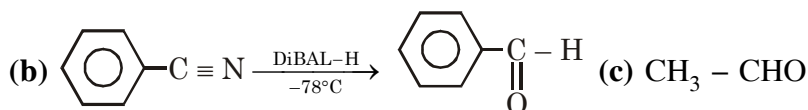
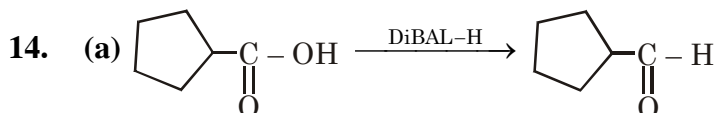
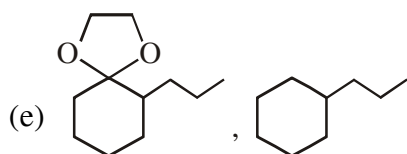
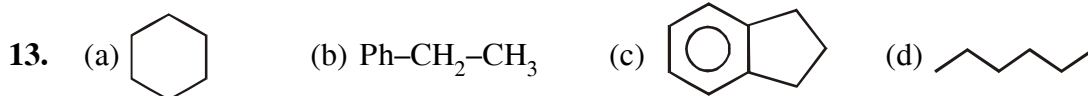
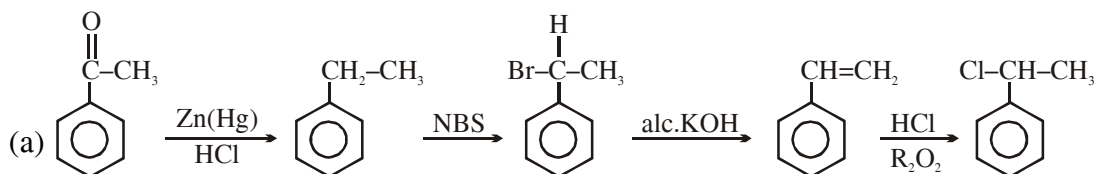
9. Ans. (a) 



10. Ans.



12. Ans.



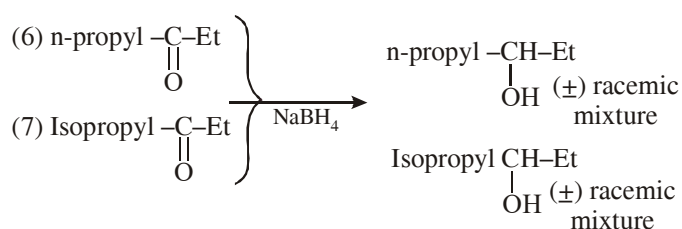
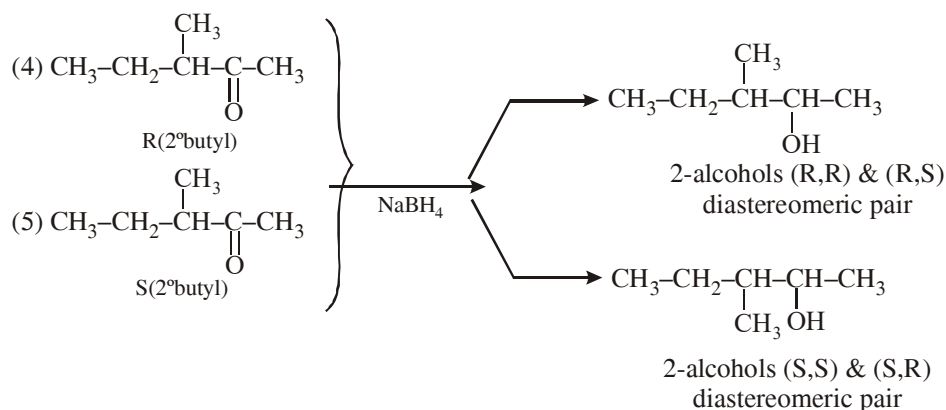
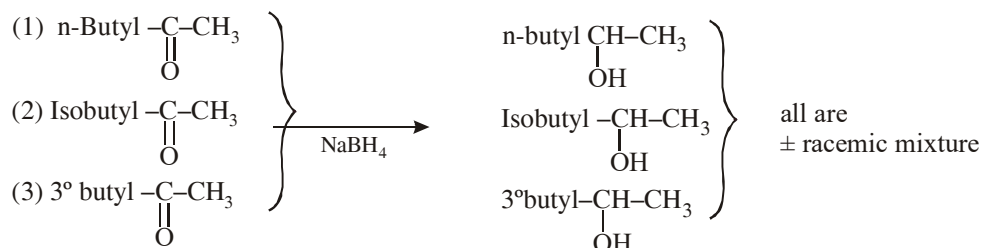
15. Ans.(C)

## EXERCISE # (MAIN &amp; ADVANCE)

1. Ans. (B)      2. Ans.  $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \text{R} \\ \diagup \\ \text{C} = \text{C} \\ \diagdown \\ \text{H} \end{array}$       3. Ans. (D)      4. Ans. (A)
5. Ans. (B)      6. Ans. (B)      7. Ans. (D)      8. Ans. (B)
9. Ans. (D)      10. Ans. (A)      11. Ans. (C)
12. Ans. (5)

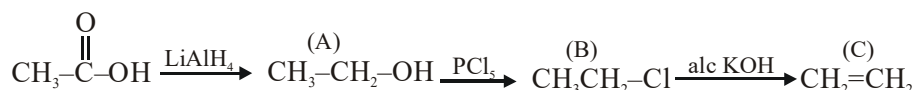
M. wt 100 of ketone

So m. formula =  $\text{C}_6\text{H}_{12}\text{O}$



(1 ; 2 ; 3 ; 6 ; 7)

13. Ans. (A)



Reduction of  $\text{CH}_3\text{COOH}$  will produce  $\text{CH}_3\text{---CH}_2\text{---OH(A)}$

Now reaction of  $\text{CH}_3\text{---CH}_2\text{---OH(A)}$  with  $\text{PCl}_5$  will produce  $\text{CH}_3\text{---CH}_2\text{---Cl(B)}$ .

Now alcoholic KOH with  $\text{Et---Cl}$  will produce  $\text{CH}_2=\text{CH}_2(\text{C})$  Ethylene by  $\text{E}_2$  elimination.

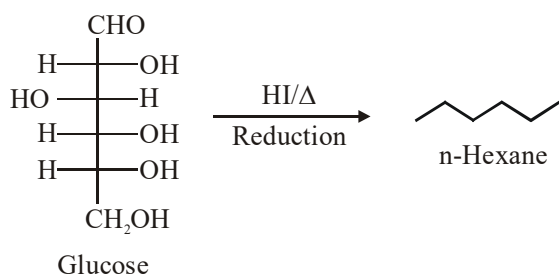
Thus Ans. is (1) Ethylene.

14. Ans. (D)

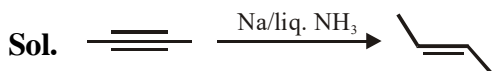
15. Ans. (1)

16. Ans. (4)

Sol.



17. Ans. (2)



Birch reduction is anti addition. So trans alkene will be produced.

18. Ans. (4)

19. Ans. (1)

20. Ans. (1)

21. Ans. (4)

22. Ans. (3)

23. Ans. (2)

24. Ans. (2)

25. Ans. (3)

26. Ans. (1)

27. Ans. (4)

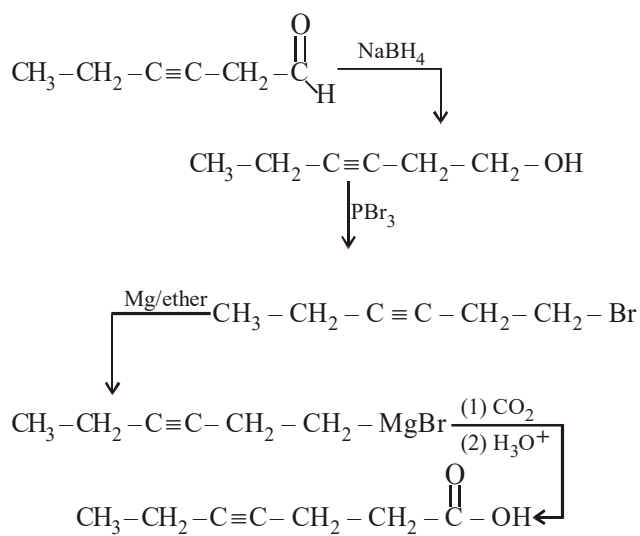
28. Ans. (4)

29. Ans. (2)

30. Ans. (2)

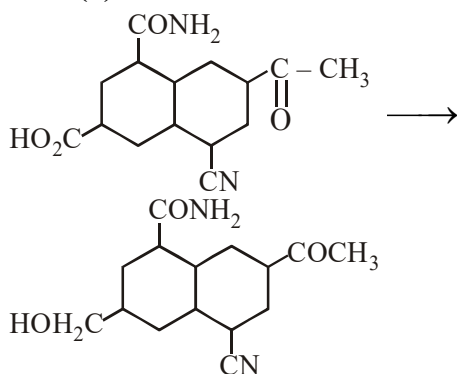
31. Ans. (3)

Sol.



32. Ans. (4)

Sol.



Most suitable reagent for given conversion is  $\text{B}_2\text{H}_6$  (electrophilic reducing agent)



## ELECTROCHEMISTRY

### 1. INTRODUCTION :

Electrochemistry deals with the study of electrical properties of solutions of electrolytes and the inter-relation of chemical phenomenon and electrical energies.

❖ **Electric Conductors are of two types :**

- (i) Metallic conductors (ii) Electrolytic conductors or electrolytes.

(i) **Metallic conductors :**

The conductors which conduct electric current by movement of free electrons without undergoing any chemical change are known as metallic conductors.

eg. Metals : Cu, Ag, Fe, Al etc., non metals : graphite and various alloys.

(ii) **Electrolytic conductors :**

Those substances whose aqueous solution conducts the electric current and which are decomposed by the passage of DC current are called electrolytes. In this case, conduction takes place by movement of ions.

Electrolytes also conduct electricity in fused state and undergo decomposition by passage the electric current.

❖ **Strong electrolyte :**

Electrolytes which are completely ionized in aqueous solution or in their molten state, are called *strong electrolytes*. Their aqueous solutions are strongly conducting.

*Ex : All salts, strong acids and strong bases.*

❖ **Weak electrolyte :**

Electrolytes which are not completely ionized in aqueous solution are called *Weak electrolytes*. Their aqueous solutions are weakly conducting.

*Ex : Organic acids  $CH_3COOH$ ,  $HCN$  (Except : Alkyl sulphonic acids,  $RSO_3H$ )*

*Organic base : Amines, Aniline etc.*

**Note :** Ostwald's dilution law is only applicable for weak electrolytes according to which degree of dissociation ( $\alpha$ ) increases on dilution.

- For weak electrolyte :  $\alpha \ll 1 \Rightarrow$  lesser ions  $\Rightarrow$  weakly conducting
- For strong electrolyte :  $\alpha = 1$  (always)  $\Rightarrow$  more ions  $\Rightarrow$  strongly conducting

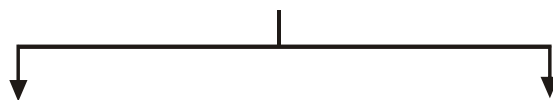
❖ **Difference between metallic and electrolytic conduction :**

Metallic conduction	Electrolytic conduction
(i) Flow of electricity takes place due to free electrons without the decomposition of the substance.	Flow of electricity takes place by ions.
(ii) No transfer of matter takes place.	Transfer of matter takes place.
(iii) The resistance to the flow of current increases with the increase in temperature and hence the increase in temperature decreases the conduction.	The resistance to the flow of current decreases with the increase in temperature and hence increase in temperature increases the conduction.

## 2. ELECTROCHEMICAL CELL :

It is device for inter-converting chemical energy in to electrical energy or vice versa.

**Electrochemical cells are of two types**

**Galvanic cell or Voltaic cell**

- A spontaneous chemical reaction generates an electric current | EMF
- Chemical energy converted into electrical energy.

**Electrolytic cell.**

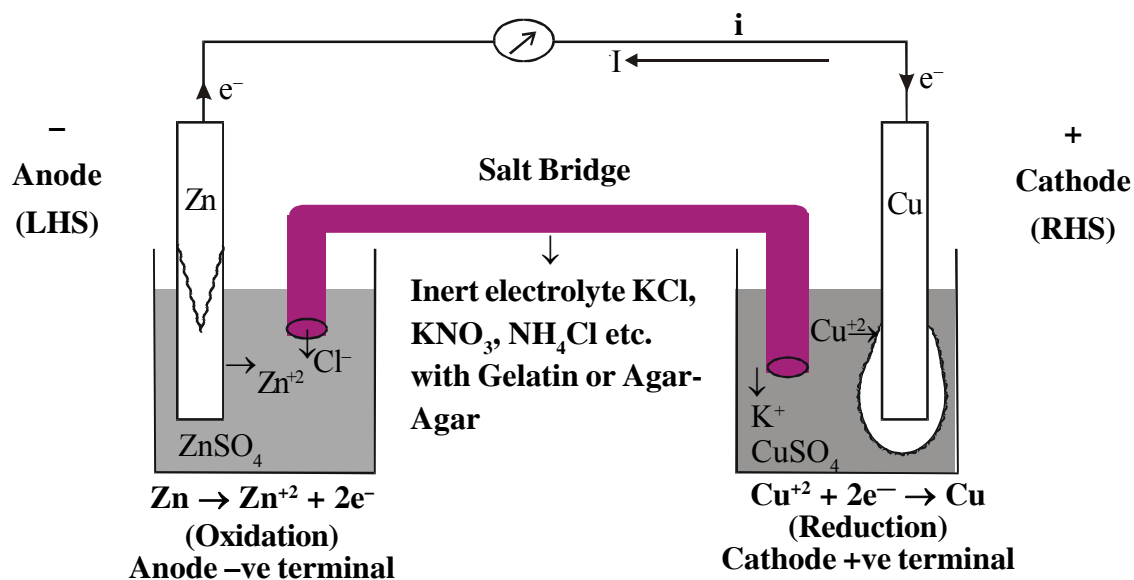
- An electric current drives a non-spontaneous reaction.
- Electrical energy converted into chemical energy.

## 3. GALVANIC CELL | VOLTAIC CELL

- A cell in which the chemical energy is transformed into electrical energy.
- The chemical reaction occurring in a galvanic cell is a spontaneous redox reaction.
- During the chemical process, the reduction in Gibbs free energy is converted in the form of electrical energy.

$$(\Delta G)_{T,P} = w_{\text{Useful}}|_{\text{max.}} = -nF E_{\text{cell}}$$

Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It may be represented by Daniel cell which is a type of Galvanic cell. Zinc rod immersed in  $\text{ZnSO}_4$  behaves as anode and copper rod immersed in  $\text{CuSO}_4$  behaves as cathode.



## ❖ Oxidation takes place at anode :



## ❖ Reduction takes place at cathode :

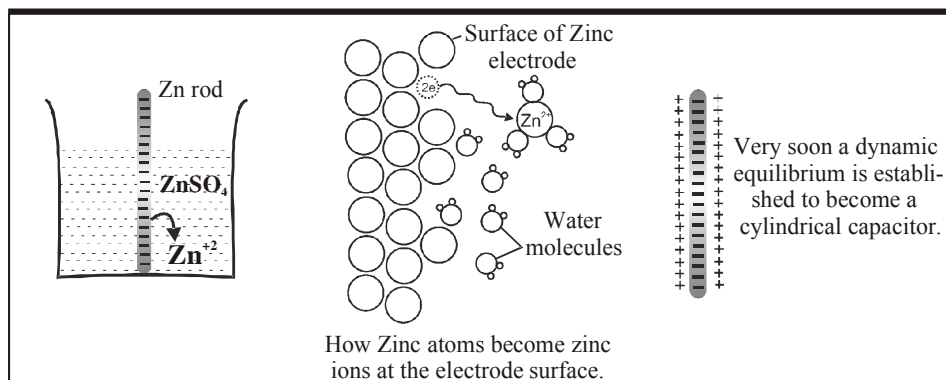


3.1 Construction of Cell :

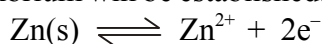
- It has two half-cells, each having a beaker containing a metal strip that dips in its aqueous solution.
- The metal strips are called *electrodes* and are connected by a conducting wire.
- Two solutions are connected by a *salt bridge*.

3.2 Construction | Working principle of Daniel cell :

I. **Anode of Daniel cell :** Zn rod is placed in ZnSO<sub>4</sub> solution are found to have tendency to go into the solution phase when these are placed in contact with their ions or their salt solutions.



The Zn atom or metal atoms will move in the solution to form Zn<sup>2+</sup>. After some time following equilibrium will be established.



There will be accumulation of sufficient negative charge on the rod which will not allow extra zinc ions to move in the solution. i.e. solution will be saturated with Zn<sup>2+</sup> ions.

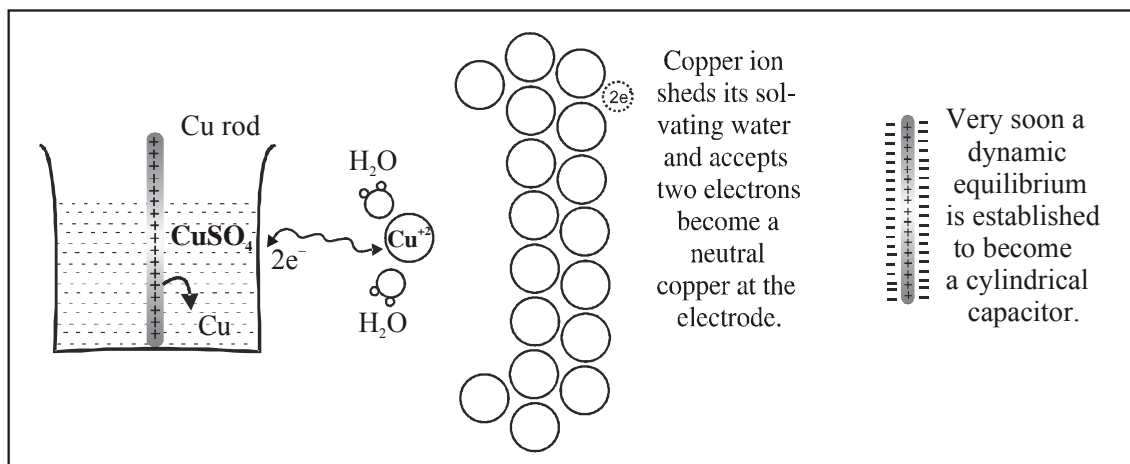
The positive charge will be more concentrated near the rod.

The extra positive charge of the solution will be more concentrated around the negatively charged rod. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as electrode potential

This particular electrode is known as anode :

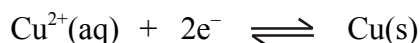
- At anode oxidation will take place. (Release of electron).
- To act as source of electrons.
- It is of negative polarity.
- The electrode oxidation potential is represented by  $E_{\text{Zn(s)}/\text{Zn}^{2+}_{\text{(aq)}}}$  & reduction potential by  $E_{\text{Zn}^{2+}/\text{Zn}}$ .

II. Cathode of Daniel cell :



Cu, when placed in contact with their aqueous ions, the ions ( $\text{Cu}^{2+}$ ) from the solution will get deposited on the metal rod.

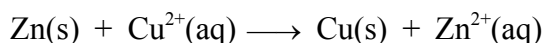
The following equilibrium will be established :



So rod will have deficiency of electron (positive charge). Extra negative charge will surround this positively charged rod and form double layer. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as electrode potential. This will be known as cathode.

- At cathode reduction will take place. (Gain of  $\text{e}^{-}$  will take place)
- Cathode acts as sink of electron.
- Positive polarity will be developed.
- Their electrode reduction potential can be represented by :  $E_{\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})}$ .
- **Anode :**  $\begin{cases} \text{Is where oxidation occurs} \\ \text{Has a negative sign} \end{cases}$  • **Cathode :**  $\begin{cases} \text{Is where reduction occurs} \\ \text{Has a positive sign} \end{cases}$

#### ❖ Overall process :



In Galvanic cell like Daniel cell ; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit ; zinc dissolves as  $\text{Zn}^{2+}$  ;  $\text{Cu}^{2+}$  ion in the cathode cell picks up two electron and is deposited at cathode.

**Note:** The electrode potential will keep on decreasing with time as  $\text{Zn}^{2+}$  ions increase &  $\text{Cu}^{2+}$  ions decrease in solution therefore tendency of cell reaction decreases and cell attains equilibrium.

### 3.3 Functions of Salt Bridge :

- A **salt bridge** is a U-shaped inverted tube that contains a gel permeated with an inert electrolyte.
- It connects the solution of two half cell to complete the circuit.
- It minimise the liquid junction potential, the potential difference between the junction of two liquids)
- It maintains the electrical neutrality of the solution in order to give continuous flow or generation of current " The simultaneous electrical neutrality of the anodic oxidation chamber and cathodic reduction chamber is due to almost same mobility or velocity of  $\text{K}^{+}$  and  $\text{NO}_3^{-}$  ions taken into salt bridge.
- If the salt bridge is removed then voltage drops to zero & cell stops working.
- The ions of the inert electrolyte should not react with other ions in the solution and the ions are not oxidised or reduced at the electrodes.
- Generally tube is filled with a paste of agar-agar powder with neutral electrolyte generally not common to anodic|cathodic compartment with porous plugs at each mouth of tube.
- It prevents mechanical mixing of two electrolytic solutions.

❖ **Liquid Junction Potential :**

The potential difference which arises between two solutions when in contact with each other. Salt bridge removes effects of junction potential by providing appropriate migration of ions.

❖ **Characteristics of electrolyte used in salt bridge :**

1. The electrolyte should be inert.
2. The cations and anions of the electrolyte used should be of ionic mobility.
3. Ions of electrolyte should not react with ions involved in cell reaction.

**3.4 Representation of galvanic cell (IUPAC)**

The anode is written on the LHS & cathode on the RHS.

we denote salt bridge by two vertical parallel lines (||), if used, in between anode & cathode.

- **Ex.**  $\text{Pt(s)} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq.}) || \text{H}^+(\text{aq.}) | \text{H}_2(\text{g}) | \text{Pt(s)}$
- **Ex.** Daniel cell :  $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq.}) || \text{Cu}^{2+}(\text{aq.}) | \text{Cu(s)}$
- **Ex.** For cell reaction :  $\text{H}_2(\text{g}) + \text{Cu}^{+2}(\text{aq.}) \longrightarrow 2\text{H}^+(\text{aq.}) + \text{Cu(s)}$   
 $\text{Pt} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq.}) || \text{Cu}^{2+}(\text{aq.}) | \text{Cu(s)}$ .

**3.5 Electrode potential :**

When a strip of metal is brought in contact with the solution containing its own ions then the strip of metal gets positively charged or negatively charged and results into a potential being developed between the metallic strip and its solution which is known as electrode potential.

- **At anode :**  $\text{M} \rightarrow \text{M}^{+n} + n\text{e}^-$  (Oxidation Potential)
- **At cathode :**  $\text{M}^{+n} + n\text{e}^- \rightarrow \text{M}$  (Reduction Potential)
- The value of electrode potential depends upon :
  - (i) the nature of electrode
  - (ii) the concentration of solution
  - (iii) the temperature

**3.6 Standard electrode potential ( $E^\circ$ ) :**

If the concentration of ions is unity, temperature is  $25^\circ\text{C}$  (or any constant temperature) and pressure is 1 bar (standard conditions), the potential of the electrode is called **standard electrode potential**.

- The given value of electrode potential is regarded as reduction potential unless it is specifically mentioned that it is an oxidation potential.

**3.7 Electromotive force of cell or cell voltage :**

The difference in the electrode potentials of the two electrodes of the cell is termed as electro motive force [EMF] or cell voltage which causes current to flow.

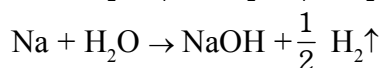
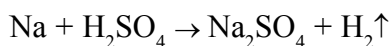
$$E_{\text{cell}} = E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode}) = E_{\text{oxi.}}(\text{anode}) - E_{\text{oxi.}}(\text{cathode}) = E_{\text{oxi.}}(\text{anode}) + E_{\text{red}}(\text{cathode})$$

## 3.8 Electro chemical series: Standard aqueous electrode potentials at 298 K

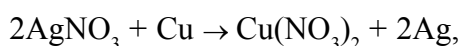
Electrode Reduction Reaction	Standard electrode Reduction potential $E^\circ$ , Volts
$\text{Li}^+ + e^- \rightarrow \text{Li}$	- 3.05
$\text{K}^+ + e^- \rightarrow \text{K}$	- 2.93
$\text{Ba}^{+2} + 2e^- \rightarrow \text{Ba}$	- 2.90
$\text{Ca}^{+2} + 2e^- \rightarrow \text{Ca}$	- 2.87
$\text{Na}^+ + e^- \rightarrow \text{Na}$	- 2.71
$\text{Mg}^{+2} + 2e^- \rightarrow \text{Mg}$	- 2.37
$\text{Al}^{+3} + 3e^- \rightarrow \text{Al}$	- 1.66
$\text{Mn}^{+2} + 2e^- \rightarrow \text{Mn}$	- 1.18
$\text{H}_2\text{O} + e^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^-$	- 0.83
$\text{Zn}^{+2} + 2e^- \rightarrow \text{Zn}$	- 0.76
$\text{Cr}^{+3} + 3e^- \rightarrow \text{Cr}$	- 0.74
$\text{Fe}^{+2} + 2e^- \rightarrow \text{Fe}$	- 0.44
$\text{Cd}^{+2} + 2e^- \rightarrow \text{Cd}$	- 0.40
$\text{Ni}^{+2} + 2e^- \rightarrow \text{Ni}$	- 0.25
$\text{Sn}^{+2} + 2e^- \rightarrow \text{Sn}$	- 0.14
$\text{Pb}^{+2} + 2e^- \rightarrow \text{Pb}$	- 0.13
$2\text{D}^+ + e^- \rightarrow \text{D}_2$	- 0.01 V
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0
$\text{AgBr(s)} + e^- \rightarrow \text{Ag(s)} + \text{Br}^-$	+0.09 V
$\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$	0.22 V
$\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu}$	+ 0.34
$\frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} + e^- \rightarrow \text{OH}^-$	+0.401 V
$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	+ 0.54
$\text{Q} + 2\text{H}^+ + 1e^- \rightarrow \text{H}_2\text{Q}$	+ 0.70
$\text{Hg}_2^{+2} + 2e^- \rightarrow 2\text{Hg}$	+ 0.79
$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+ 0.80
$\text{Hg}^{+2} + 2e^- \rightarrow \text{Hg}$	+ 0.85
$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	+ 1.08
$\frac{1}{4} \text{O}_2 + \text{H}^+ + e^- \rightarrow \frac{1}{2} \text{H}_2\text{O}$	+1.23 V
$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+ 1.36
$\text{Pt}^{+2} + 2e^- \rightarrow \text{Pt}$	+ 1.20
$\text{Au}^{+3} + 3e^- \rightarrow \text{Au}$	+ 1.50
$\text{Au}^+ + e^- \rightarrow \text{Au}$	+ 1.69
$\text{S}_2\text{O}_8^{--} + 2e^- \rightarrow 2\text{SO}_4^{--}$	+2.0 V
$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	+ 2.87

• **Application of electrochemical series :**

- (i) **Activity of metal :** From electrochemical series, the activity of any metal can easily be determined. All the metals which are placed above hydrogen are stronger reducing agents & can easily evolve H<sub>2</sub> gas whereas metals lying below hydrogen are weaker reducing agents cannot lose electrons to H<sup>+</sup> ions & hence can't evolve H<sub>2</sub> gas. For e.g. Na, K, Zn etc. can easily evolve H<sub>2</sub> whereas Cu, Hg, Ag etc. do not have tendency to evolve H<sub>2</sub> gas.

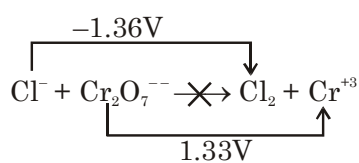
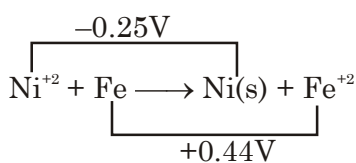


- (ii) **Displacement reaction :** The active metal can easily displace less active metal from their aq. salt solution for e.g. Zn can replace Cu<sup>2+</sup> from an aq. solution of CuSO<sub>4</sub>. But Cu cannot displace Zn<sup>2+</sup> from solution similarly,

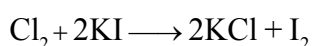
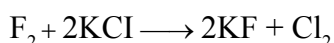


- (iii) **Feasibility of redox reaction :** The feasibility of particular redox reaction can be easily find out from electrochemical series. The metal placed higher or have more reducing property can easily lose electrons to the metal ion present below in series, hence redox reaction become feasible i.e. cell will serve as source of electrical energy. For e.g. NiSO<sub>4</sub> solution cannot be placed in Fe vessel because, the redox reaction between them is feasible.

**Note:** If emf of the cell for redox reaction comes out to be positive, it suggests the redox reaction is spontaneous or feasible. Negative value indicates that redox reaction is not feasible.



- (iv) **Oxidising & reducing powers :** The metals placed above hydrogen in the electrochemical series are strong reducing agents whereas non-metals placed after hydrogen, are strong oxidising agents.
- (v) **Displacement of one non-metal from its salt solution by another non-metal :** A non metal lower in the series will have more reduction potential and will displace another non-metal with lower reduction potential. e.g. F<sub>2</sub> can displace all halide ion from solution.



## EXERCISE # 1

1. A standard reduction electrode potentials of four metal cations are -  
 $A^+ = -0.250 \text{ V}$ ,  $B^+ = -0.140 \text{ V}$   $C^+ = -0.126 \text{ V}$ ,  $D^+ = -0.402 \text{ V}$   
 The metal that displaces  $A^+$  from its aqueous solution is :-  
 (A) B (B) C (C) D (D) None of the above
2. The standard reduction potentials for two half-cell reactions are given below,  
 $Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$ ,  $E^\circ = -0.40 \text{ V}$   
 $Ag^+(aq) + e^- \rightarrow Ag(s)$ ,  $E^\circ = 0.80 \text{ V}$   
 The standard free energy change for the reaction  
 $2Ag^+(aq) + Cd(s) \rightarrow 2Ag(s) + Cd^{2+}(aq)$  is given by :  
 (A) 115.8 KJ (B) -115.8 KJ (C) -231.6 KJ (D) 231.6KJ
3. The reduction potential values are given below:  
 $Al^{3+} | Al = -1.67 \text{ volt}$ ,  $Mg^{2+} | Mg = -2.34 \text{ volt}$   
 $Cu^{2+} | Cu = +0.34 \text{ volt}$ ,  $I_2 | 2I^- = +0.53 \text{ volt}$   
 Which one is the best reducing agent ?  
 (A) Al (B) Mg (C) Cu (D)  $I_2$
4.  $E^\circ$  for  $F_2 + 2e^- = 2F^-$  is 2.8 V,  $E^\circ$  for  $\frac{1}{2}F_2 + e^- = F^-$  is ?  
 (A) 2.8 V (B) 1.4 V (C) -2.8 V (D) -1.4 V
5. If  $\Delta G^\circ$  of the cell reaction,  
 $AgCl(s) + \frac{1}{2}H_2(g) \rightarrow Ag(s) + H^+ + Cl^-$  is -21.52 KJ  
 then  $\Delta G^\circ$  of  $2AgCl(s) + H_2(g) \rightarrow 2Ag(s) + 2H^+ + 2Cl^-$  is :  
 (A) -21.52 KJ (B) -10.76 KJ (C) -43.04 KJ (D) 43.04 KJ
6. Given electrode potentials :  
 $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$ ;  $E^\circ = 0.771 \text{ volts}$   $I_{2(g)} + 2e^- \longrightarrow 2I^-_{(aq)}$ ;  $E^\circ = 0.536 \text{ volts}$   
 $E^\circ_{\text{cell}}$  for the cell reaction,  
 $2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(g)}$  is -  
 (A)  $(2 \times 0.771 - 0.536) = 1.006 \text{ volts}$  (B)  $(0.771 - 0.5 \times 0.536) = 0.503 \text{ volts}$   
 (C)  $0.771 - 0.536 = 0.235 \text{ volts}$  (D)  $0.536 - 0.771 = -0.235 \text{ volts}$

## 3.9 NERNST EQUATION :

For a reaction  $aA + bB = cC + dD$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$-nFE = -nFE^\circ + RT \ln Q$$

With the help of Nernst equation, we can calculate the non-standard electrode potential of electrode or EMF of cell. *Nernst equation predicts effects of concentration, pressure or temperature changes on cell EMF.* Nernst equation can be applied on half-cell as well as complete Galvanic cells reaction.

$$E_{\text{cell}} = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{2.303RT}{nF} \log Q$$



- Where -
- $E^0$  = Standard electrode potential
  - $R$  = Gas constant
  - $T$  = Temperature (in K)
  - $F$  = Faraday (96500 coulomb  $\text{mol}^{-1}$ )
  - $n$  = No. of  $e^-$  gained or lost in balanced equation.
  - $Q$  = Reaction quotient

$$\frac{2.303 \times 8.314 \times 298}{96500} = 0.059 \text{ volt (At 298 K)}$$

- Note:** (i) For writing Nernst equation, first write balanced cell reaction.  
(ii) Nernst equation can be applied on half-cell as well as complete Galvanic cells.

### 3.10 THERMODYNAMIC TREATMENT OF CELL :

- (i) **Determination of equilibrium constant** : We know, that

$$E = E^0 - \frac{0.0591}{n} \log Q \quad \dots(i)$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e.  $E = 0$  &  $Q = K_{\text{eq}}$ .  
 $\therefore$  From E (i), we have

$$0 = E^0 - \frac{0.0591}{n} \log K_{\text{eq}} \quad \text{or} \quad K_{\text{eq}} = \text{anti log} \left[ \frac{nE^0}{0.0591} \right] = 10^{\frac{nE^0}{0.0591}}$$

- (ii) **Heat of Reaction inside the cell:** Let  $n$  Faraday charge flows out of a cell of e.m.f.  $E$ , then

$$-\Delta G = nFE \quad (i)$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T \left[ \frac{\partial \Delta G}{\partial T} \right]_p \quad (ii)$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T \left[ \frac{\partial (-nFE)}{\partial T} \right]_p = \Delta H - nFT \left[ \frac{\partial E}{\partial T} \right]_p$$

$$\therefore \Delta H = -nFE + nFT \left[ \frac{\partial E}{\partial T} \right]_p$$

- (iii) **Entropy change inside the cell** : We know that  $G = H - TS$  or  $\Delta G = \Delta H - T\Delta S$  ... (i)

where  $\Delta G$  = Free energy change ;  $\Delta H$  = Enthalpy change and  $\Delta S$  = entropy change.

According to Gibbs Helmholtz equation,

$$\Delta G = \Delta H + T \left[ \frac{\partial \Delta G}{\partial T} \right]_p \quad \dots(ii)$$

From Eqs. (i) and (ii), we have

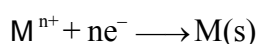
$$-T\Delta S = T \left[ \frac{\partial \Delta G}{\partial T} \right]_p \quad \text{or} \quad \Delta S = - \left[ \frac{\partial \Delta G}{\partial T} \right]_p$$

$$\text{or} \quad \Delta S = nF \left[ \frac{\partial E}{\partial T} \right]_p$$

where  $\left[ \frac{\partial E}{\partial T} \right]_p$  is called temperature coefficient of cell.

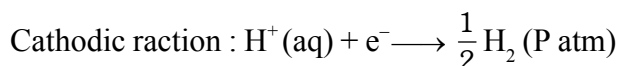
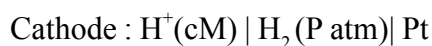
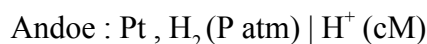
### 3.11 DIFFERENT TYPES OF ELECTRODES

#### I. Metal - Metal ion electrode : Ex. - $M^{n+} | M$



$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

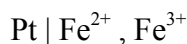
#### II. Gas - ion Electrode :



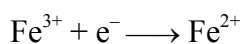
$$E = E^\circ - 0.0591 \log \frac{P_{H_2}^{\frac{1}{2}}}{[H^+]} = -0.0591 \text{ pH} \left[ \because E_{H^+/H_2}^0 = 0 \text{ \& } pH_2 = 1 \text{ bar} \right]$$

#### III. Oxidation - reduction Electrode (or redox electrode) :

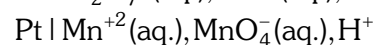
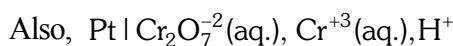
It has same metal (or element) in two different oxidation states in same solution.



As a reduction electrode



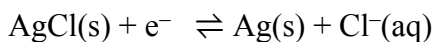
$$E = E^\circ - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$



#### IV. Metal - metal insoluble salt-anion electrode :

In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell:

This half cell is represented as  $\text{Cl}^-|\text{AgCl}|\text{Ag}$ . The equilibrium reaction that occurs at the electrode is



$$E_{\text{Cl}^-/\text{AgCl}/\text{Ag}}^0 = E_{\text{Ag}^+/\text{Ag}}^0 + \frac{0.0591}{1} \log K_{\text{sp}}$$

$$E_{\text{Cl}^-/\text{AgCl}/\text{Ag}} = E_{\text{Cl}^-/\text{AgCl}/\text{Ag}}^0 - \frac{0.0591}{1} \log [\text{Cl}^-]$$

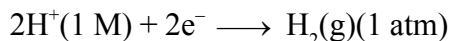
potential of such cells depends upon the concentration of anions. Such cells can be used as **Reference Electrode**.

### 3.12 Reference Electrode :

Absolute values of electrode potentials can not be measured. Reference electrodes is an electrode used to measure the electrode potential of other electrodes.

#### (a) Standard Hydrogen Electrode (SHE) :

It consist of a platinum electrode over which  $\text{H}_2$  gas (1 bar pressure) is bubbled and the electrode is immersed in a solution that is 1 M in  $\text{H}^+$  at any specified temperature.

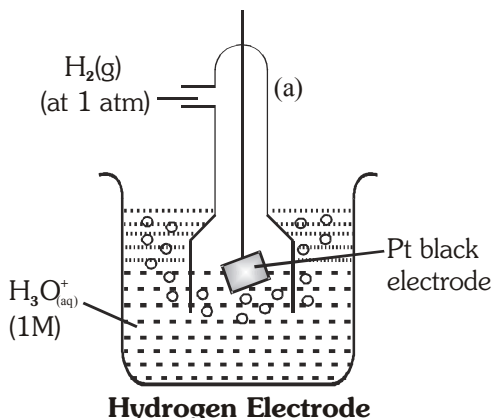


The potential of this electrode at all temperature is taken as Zero volt.

[IUPAC convention :  $E_{\text{H}^+/\text{H}_2}^\circ = E_{\text{H}_2/\text{H}^+}^\circ = 0$  ]

#### Calculation of electrode potential :

<p><b>At Anode</b></p> $\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}^+ + 2e^-$ <ul style="list-style-type: none"> <li>• Oxidation potential O.P. = <math>E_{\text{H}_2(\text{g})/\text{H}^+(\text{aq})}</math></li> <li>• <math>E_{\text{H}_2(\text{g})/\text{H}^+(\text{aq})}^0 = \text{SOP} = 0</math></li> <li>• <math>E_{\text{H}_2/\text{H}^+} \neq 0</math></li> </ul>	<p><b>At Cathode</b></p> $2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(\text{g})$ <ul style="list-style-type: none"> <li>• Reduction Potential (R.P.)</li> <li><math>E_{\text{H}^+/\text{H}_2(\text{g})} = \text{RP}</math></li> <li>• <math>E_{\text{H}^+/\text{H}_2(\text{g})}^0 = \text{SRP} = 0</math></li> <li>• <math>E_{\text{H}^+/\text{H}_2} \neq 0</math></li> </ul>
---	--



- To calculate standard potential of any other electrode a cell is coupled with standard hydrogen electrode (SHE) and its potential is measured that gives the value of electrode potential of that electrode.

**Ex. Anode :** Zinc electrode

**Cathode :** SHE

**Cell :** Zinc electrode || SHE

$$E_{\text{cell}} = E_{\text{H}^+/\text{H}_2(\text{g})} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

$$= 0.76 \text{ V} \quad (\text{at } 298 \text{ K experimentally})$$

So,  $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$  (SRP)

$E_{\text{Zn}|\text{Zn}^{2+}(\text{aq})}^{\circ} = 0.76 \text{ V}$  (SOP)

**(b) Calomel Electrode :**

Cathode :  $\text{Cl}^-(\text{c M}) | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}(\text{l}) | \text{Pt}(\text{s})$

It is prepared by a Pt wire in contact with a paste of Hg and  $\text{Hg}_2\text{Cl}_2$  present in a KCl solution.

reaction  $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{Hg}(\text{l}) + 2\text{Cl}^-$ ;  $E^{\circ} = +0.27 \text{ V}$

$$\Rightarrow \boxed{E_{\text{Cl}^-/\text{Hg}_2\text{Cl}_2/\text{Hg}} = E_{\text{Cl}^-/\text{Hg}_2\text{Cl}_2/\text{Hg}}^{\circ} - \frac{0.059}{2} \log[\text{Cl}^-]^2}$$

#### 4. CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cells.

##### 4.1 Electrode concentration cell :

Pt,  $\text{H}_2(\text{P}_1) | \text{H}^+(\text{C}) | \text{H}_2(\text{P}_2), \text{Pt}$

Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

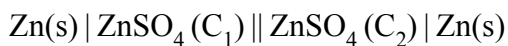
Cell process :  $1/2\text{H}_2(\text{p}_1) \rightarrow \text{H}^+(\text{c}) + \text{e}^-$  (Anode process)

$$\frac{\text{H}^+(\text{c}) + \text{e}^- \rightarrow 1/2\text{H}_2(\text{p}_2)}{1/2\text{H}_2(\text{p}_1) \rightleftharpoons 1/2\text{H}_2(\text{p}_2)} \quad \therefore \quad E = -\frac{2.303RT}{F} \log \left[ \frac{\text{p}_2}{\text{p}_1} \right]^{1/2}$$

$$\text{or} \quad E = \left[ \frac{2.303RT}{2F} \right] \log \left[ \frac{\text{p}_2}{\text{p}_1} \right], \text{ At } 25^{\circ}\text{C}, \quad E = \frac{0.059}{2F} \log \left[ \frac{\text{p}_1}{\text{p}_2} \right]$$

For spontaneity of such cell reaction,  $\text{p}_1 > \text{p}_2$

#### 4.2 Electrolyte concentration cells:



In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,



∴ From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F} \log \left[ \frac{C_1}{C_2} \right] \quad \text{or} \quad E = \frac{2.303RT}{2F} \log \left[ \frac{C_2}{C_1} \right]$$

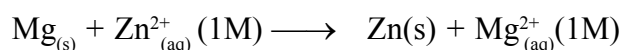
For spontaneity of such cell reaction,  $C_2 > C_1$

## EXERCISE # 2

## Representation of Cell diagrams, complete and half cell reactions :

- The reduction potential of hydrogen electrode ( $P_{H_2} = 1 \text{ atm}$ ;  $[H^+] = 0.1 \text{ M}$ ) at  $25^\circ\text{C}$  will be -  
(A) 0.00 V            (B)  $-0.059 \text{ V}$             (C)  $0.118 \text{ V}$             (D)  $0.059 \text{ V}$
- Which of the following represents the reduction potential of silver wire dipped into  $0.1 \text{ M AgNO}_3$  solution at  $25^\circ\text{C}$  ?  
(A)  $E_{\text{red}}^\circ$             (B)  $(E_{\text{red}}^\circ + 0.059)$             (C)  $(E_{\text{oxi}}^\circ - 0.059)$             (D)  $(E_{\text{red}}^\circ - 0.059)$
- For a reaction -  $A(s) + 2B_{(\text{aq})}^+ \rightarrow A_{(\text{aq})}^{2+} + 2B_{(s)}$   $K_c$  has been found to be  $10^{12}$ . The  $E^\circ_{\text{cell}}$  is:  
(A)  $0.354 \text{ V}$             (B)  $0.708 \text{ V}$             (C)  $0.0098 \text{ V}$             (D)  $1.36 \text{ V}$

- For the cell reaction

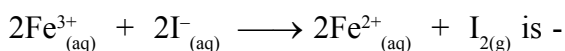


The emf has been found to be  $1.60 \text{ V}$ ,  $E^\circ$  of the cell is :

- (A)  $-1.60 \text{ V}$             (B)  $1.60 \text{ V}$             (C)  $0.0 \text{ V}$             (D)  $0.16 \text{ V}$
- The emf of the cell in which the following reaction,  
 $\text{Zn}_{(s)} + \text{Ni}_{(\text{aq})}^{2+} (a = 0.1) \rightarrow \text{Zn}_{(\text{aq})}^{2+} (a = 1.0) + \text{Ni}_{(s)}$   
occurs, is found to be  $0.5105 \text{ V}$  at  $298 \text{ K}$ . The standard e.m.f. of the cell is :-  
(A)  $-0.5105 \text{ V}$             (B)  $0.5400 \text{ V}$             (C)  $0.4810 \text{ V}$             (D)  $0.5696 \text{ V}$
  - Given electrode potentials :



$E^\circ_{\text{cell}}$  for the cell reaction,



- (A)  $(2 \times 0.771 - 0.536) = 1.006 \text{ volts}$   
(B)  $(0.771 - 0.5 \times 0.536) = 0.503 \text{ volts}$   
(C)  $0.771 - 0.536 = 0.235 \text{ volts}$   
(D)  $0.536 - 0.771 = -0.235 \text{ volts}$

### 5. SOME COMMERCIAL BATTERIES

Any battery or cell that we use as a source of electrical energy is basically an electrochemical cell where oxidising and reducing agents are made to react by using a suitable device. In principle, any redox reaction can be used as the basis of an electrochemical cell, but there are limitations to the use of most reactions as the basis of practical batteries. A battery should be reasonably light and compact and its voltage should not vary appreciably during the use.

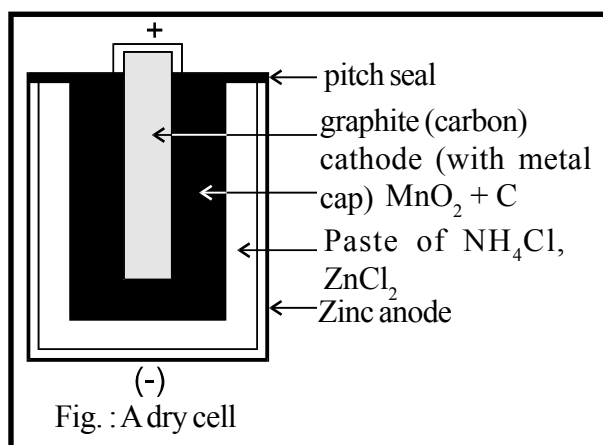
There are mainly two types of cells :

(i) primary cells and (ii) secondary cells. In primary cells, the reaction occurs only once and the battery then becomes dead over a period of time and cannot be used again. (For example, dry cell, mercury cell.) Contrary to this, secondary cells can be recharged by passing a current through them so that they can be used again and again. (For example, lead storage battery, nickel- cadmium storage cell.)

## 5.1 Primary Batteries

### 5.1.1 Dry cell or Laclanche cell :

The most familiar type of battery is the dry cell which is a compact of Leclanche cell known after its discoverer Leclanche (fig.) : In this cell, the anode consists of a zinc container and the cathode is a graphite rod surrounded by powdered  $\text{MnO}_2$  and carbon. The space between the electrodes is filled with a moist paste of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$ . The electrode reactions are complex, but they can be written approximately as follows.

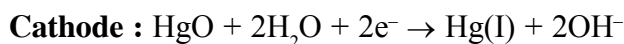
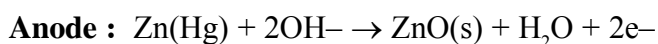


- **Anode**  $\text{Zn(s)} \longrightarrow \text{Zn}^{+2} + 2\text{e}^-$
- **Cathode**  $\text{MnO}_2 + \text{NH}_4^+ + \text{e}^- \longrightarrow \text{MnO(OH)} + \text{NH}_3$

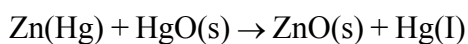
In the cathode reaction, manganese is reduced from the +4 oxidation state to the +3 state. Ammonia is not liberated as a gas but combines with  $\text{Zn}^{2+}$  to form  $\text{Zn}(\text{NH}_3)_4^{2+}$  ion. The cell has a potential of nearly 1.5 V.

### 5.1.2 Mercury cell :

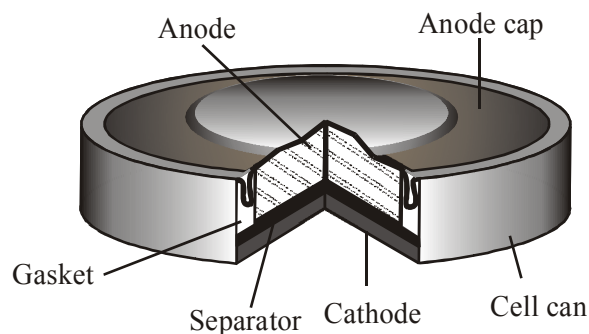
Mercury cell, suitable for low current devices like hearing aids, watches, etc. consists of zinc & mercury amalgam as anode and a paste of  $\text{HgO}$  and carbon as the cathode. The electrolyte is a paste of  $\text{KOH}$  and  $\text{ZnO}$ . The electrode reactions for the cell are given below:



The overall reaction is represented by



The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.



Commonly used mercury cell.  
The reducing agent is zinc and  
the oxidising agent is mercury  
(II) oxide.

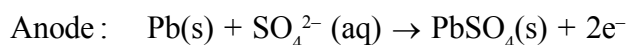
## 5.2 Secondary Batteries

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles.

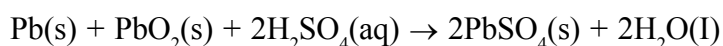
### 5.2.1 Lead storage cell :

The most important secondary cell is the lead storage battery commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide ( $\text{PbO}_2$ ) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

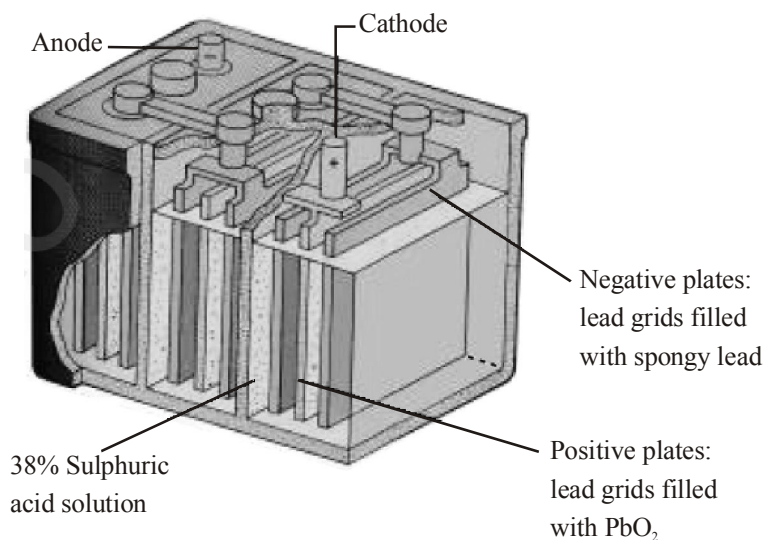
The cell reactions when the battery is in use are given below:



i.e., overall cell reaction consisting of cathode and anode reactions is:



On charging the battery the reaction is reversed and  $\text{PbSO}_4(\text{s})$  on anode and cathode is converted into Pb and  $\text{PbO}_2$ , respectively.

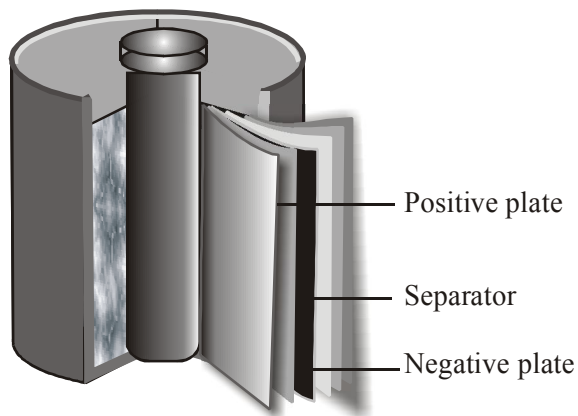


The Lead storage battery



### 5.2.2 Nickel-cadmium cell :

Another important secondary cell is the nickel-cadmium cell which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is:



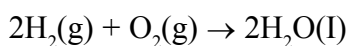
A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide

### 5.3 FUEL CELLS

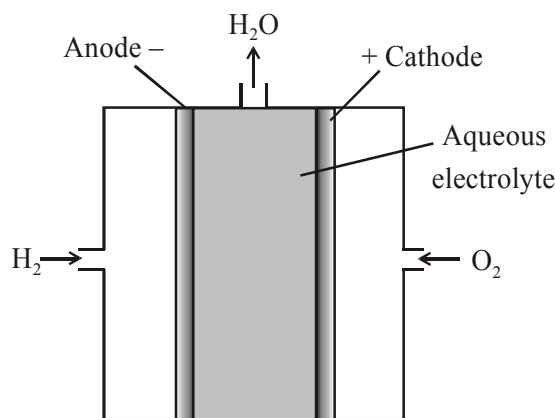
Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment. Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells. One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:



Overall reaction being :



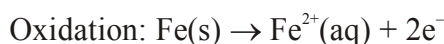
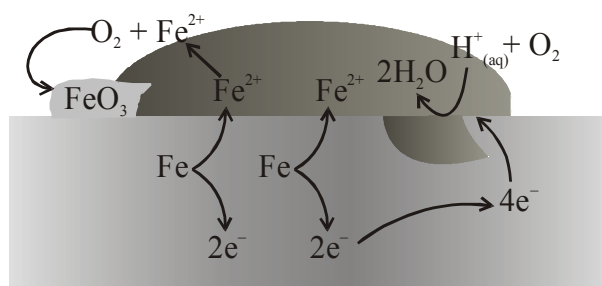
The cell runs continuously as long as the reactions are supplied. Fuel cells produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on an experimental basis. Fuel cells are pollution free and in view of their future importance, a variety of fuel cells have been fabricated and tried.



Fuel cell using H<sub>2</sub> and O<sub>2</sub> produces electricity

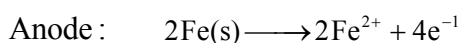
## 6. CORROSION :

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. We lose crores of rupees every year on account of corrosion. In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction



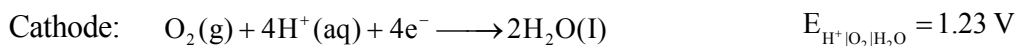
Atmospheric

### Corrosion of iron in atmosphere

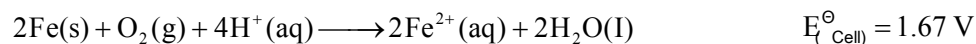


$$E_{(\text{Fe}^{2+}/\text{Fe})}^{\ominus} = -0.44 \text{ V}$$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of  $H^+$  (which is believed to be available from  $H_2CO_3$  formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction



The overall reaction being:

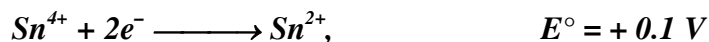
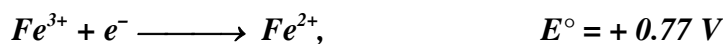
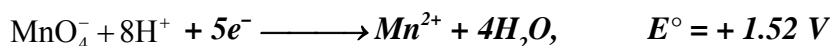


The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ( $Fe_2O_3 \cdot xH_2O$ ) and with further production of hydrogen ions.

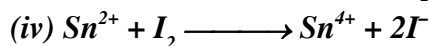
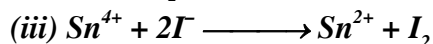
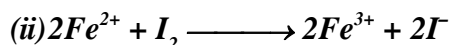
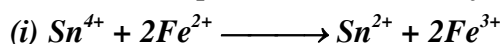
Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol). Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.). Which corrodes itself but saves the object.

### SOLVED EXAMPLES

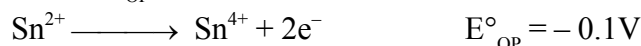
**Ex.1**  $E^\ominus$  of some oxidants are given as :



- (a) Select the strongest reductant and oxidant in these.  
 (b) Select the weakest reductant and oxidant in these.  
 (c) Select the spontaneous reaction from the changes given below.



**Sol.** (a) More the  $E^\ominus_{OP}$ , more is the tendency for oxidation. Therefore, since maximum  $E^\ominus_{OP}$  stands for :



$\therefore$  Strongest reductant :  $Sn^{2+}$

and weakest oxidant :  $Sn^{4+}$

(b) More +ve is  $E^\ominus_{RP}$ , more is the tendency for reduction. Therefore, since maximum  $E^\ominus_{RP}$  stands for :



$\therefore$  Strongest oxidant :  $MnO_4^-$

and weakest reductant :  $Mn^{2+}$

**Note :-** Stronger is oxidant, weaker is its conjugate reductant and vice-versa.

$$(c) \text{ For (i) } E_{\text{Cell}}^{\circ} = E_{\text{OP}_{\text{Fe}^{2+}/\text{Fe}^{3+}}}^{\circ} + E_{\text{RP}_{\text{Sn}^{4+}/\text{Sn}^{2+}}}^{\circ} = -0.77 + 0.1$$

$\text{Fe}^{2+}$  oxidizes and  $\text{Sn}^{4+}$  reduces in change.

$$\therefore E_{\text{Cell}}^{\circ} = E_{\text{OP}_{\text{Fe}^{2+}/\text{Fe}^{3+}}}^{\circ} + E_{\text{RP}_{\text{Sn}^{4+}/\text{Sn}^{2+}}}^{\circ} = -0.77 + 0.1 = -0.67 \text{ V}$$

$E_{\text{Cell}}^{\circ}$  is negative.

$\therefore$  (i) Is non-spontaneous change.

$$\text{For (ii) } E_{\text{Cell}}^{\circ} = E_{\text{OP}_{\text{Fe}^{2+}/\text{Fe}^{3+}}}^{\circ} + E_{\text{RP}_{\text{I}_2/\text{I}^-}}^{\circ} = -0.77 + 0.54 = -0.23 \text{ V}$$

$\therefore$  (ii) reaction is non-spontaneous change.

$$\text{For (iii) } E_{\text{Cell}}^{\circ} = E_{\text{OP}_{\text{I}_2/\text{I}^-}}^{\circ} + E_{\text{RP}_{\text{Sn}^{4+}/\text{Sn}^{2+}}}^{\circ} = -0.54 + 0.1 = -0.44 \text{ V}$$

$\therefore$  (iii) Reaction is non-spontaneous change.

$$\text{For (iv) } E_{\text{Cell}}^{\circ} = E_{\text{OP}_{\text{Sn}^{2+}/\text{Sn}^{4+}}}^{\circ} + E_{\text{RP}_{\text{I}_2/\text{I}^-}}^{\circ} = -0.1 + 0.54 = +0.44 \text{ V}$$

(iv) Reaction is spontaneous change.

**Ex.2** Given the standard electrode potentials ;

$$K^+|K = -2.93 \text{ V}, Ag^+|Ag = 0.80 \text{ V}, Hg^{2+}|Hg = 0.79 \text{ V}, Mg^{2+}|Mg = -2.37 \text{ V}, Cr^{3+}|Cr = -0.74 \text{ V}.$$

Arrange these metals in their increasing order of reducing power.

**Sol.** More is  $E_{\text{RP}}^{\circ}$ , more is the tendency to get reduced or more is the oxidising power or lesser is reducing power.  $Ag < Hg < Cr < Mg < K$

**Ex.3** A cell is prepared by dipping a copper rod in 1 M  $\text{CuSO}_4$  solution and a nickel rod in 1M  $\text{NiSO}_4$ . The standard reduction potentials of copper and nickel electrodes are + 0.34 V and -0.25 V respectively.

(i) Which electrode will work as anode and which as cathode ?

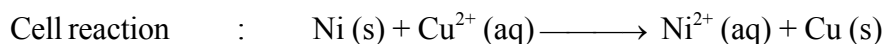
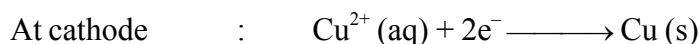
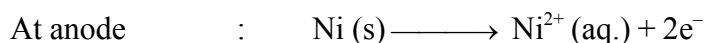
(ii) What will be the cell reaction ?

(iii) How is the cell represented ?

(iv) Calculate the EMF of the cell.

**Sol.** (i) The nickel electrode with smaller  $E^{\circ}$  value (-0.25 V) will work as anode while copper electrode with more  $E^{\circ}$  value (+0.34V) will work as cathode.

(ii) The cell reaction may be written as :

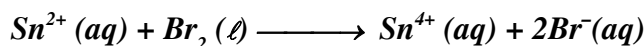


(iii) The cell may be represented as :



(iv) EMF of cell =  $E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = (+0.34) - (-0.25) = 0.59 \text{ V}$

**Ex.4** Predict whether the following reaction can occur under standard conditions or not.



**Given :**  $E^{\circ}_{\text{Sn}^{4+}|\text{Sn}^{2+}} = +0.15$ ;  $E^{\circ}_{\text{Br}_2|\text{Br}^{-}} = 1.06\text{V}$ .

**Sol.**  $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 1.06 - 0.15 = 0.91\text{V}$ .

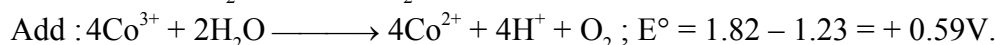
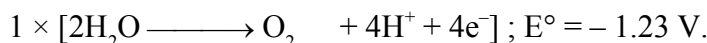
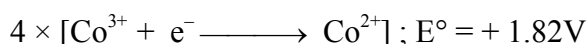
Since,  $E^{\circ}_{\text{cell}}$  comes out to be positive, this means that the reaction can occur.

**Ex.5** Given that,  $\text{Co}^{3+} + e^{-} \longrightarrow \text{Co}^{2+}$   $E^{\circ} = +1.82\text{V}$



**Explain why  $\text{Co}^{3+}$  is not stable in aqueous solutions.**

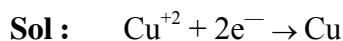
**Sol.** The  $E^{\circ}_{\text{cell}}$  can be calculated as follows :



Since,  $E^{\circ}_{\text{cell}}$  is positive, the cell reaction is spontaneous. This means that  $\text{Co}^{3+}$  ions will take part in the reaction. Therefore,  $\text{Co}^{3+}$  is not stable.

**Ex.6** The 0.1 M copper sulphate solution in which copper electrode is dipped at 25°C. Calculate the electrode reduction potential of copper electrode.

[Given :  $E^{\circ}_{\text{Cu}^{2+}|\text{Cu}} = 0.34\text{V}$ ]



$$E_{\text{red}} = E^{\circ}_{\text{red}} - \frac{0.059}{n} \log Q = E^{\circ}_{\text{Cu}^{2+}|\text{Cu}} - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

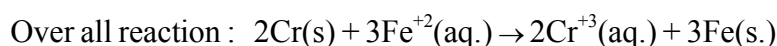
$$\text{So } E = 0.34 - \frac{0.0591}{2} \log 10$$

$$= 0.34 - 0.03 = 0.31 \text{ volts}$$

**Ex.7** Calculate the EMF of the cell :  $\text{Cr}|\text{Cr}^{+3} (0.1\text{M}) || \text{Fe}^{+2} (0.01\text{M})|\text{Fe}$

(Given :  $E^{\circ}_{\text{Cr}^{+3}|\text{Cr}} = -0.75\text{V}$ ,  $E^{\circ}_{\text{Fe}^{+2}|\text{Fe}} = -0.45\text{V}$ )

**Sol.** Half cell reactions are :



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Cr}|\text{Cr}^{+3}} + E^{\circ}_{\text{Fe}^{+2}|\text{Fe}} = 0.75 + (-0.45) = 0.30\text{V}$$

$$E_{\text{cell}} = E^{\circ} - \frac{0.0591}{n} \log Q = 0.30 - \frac{0.0591}{6} \log \frac{[\text{Cr}^{+3}]^2}{[\text{Fe}^{+2}]^3} = 0.30 - \frac{0.0591}{6} \log \frac{[0.1]^2}{[0.01]^3} = 0.26\text{V}$$

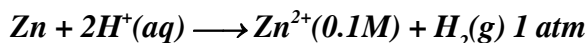
**Ex.8** The measured e.m.f. at 25°C for the cell reaction,  
 $Zn(s) + Cu^{2+}_{(aq)}(1.0M) \longrightarrow Cu(s) + Zn^{2+}_{(aq)}(0.1M)$  is 1.3 volt, Calculate  $E^\circ$  for the cell reaction.

**Sol.** Using Nernst equation (at 298 K),  $E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$

Here,  $E_{cell} = 1.3$  V,  $[Cu^{2+}(aq)] = 1.0$  M,  $[Zn^{2+}(aq)] = 0.1$  M,  $E^\circ_{cell} = ?$

Substituting the values,  $E^\circ_{cell} = 1.27$  V

**Ex.9** The emf of a cell corresponding to the reaction



is 0.28 volt at 25°C. Calculate the pH of the solution at the hydrogen electrode.

$E^\circ_{Zn^{2+}|Zn} = -0.76$  volt and  $E^\circ_{H^+|H_2} = 0$

**Sol.**  $E^\circ_{cell} = 0.76$  volt

Applying Nernst equation,  $E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}$

$$0.28 = 0.76 - \frac{0.0591}{2} \log \frac{(0.1) \times 1}{[H^+]^2}, \text{ pH} = 8.62$$

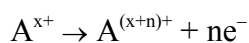
**Ex.10** The half cell oxidation potential of a half-cell  $A^{x+}, A^{(x+n)+} | Pt$  were found to be as follows :

% of reduced form	24.4	48.8
Cell potential  V	0.101	0.115

Determine the value of n. [Take  $\frac{2.303RT}{F} = 0.06$ ,  $\log_{10} 24.4 = 1.387$ ,  $\log_{10} 75.6 = 1.878$ ,  $\log_{10} 48.8$

$= 1.688$ ,  $\log_{10} 51.2 = 1.709$ ]

**Sol.** The half-cell reaction is -



Its Nernst equation is -

$$E = E^\circ - 2.303 \frac{RT}{nF} \log \frac{[A^{(x+n)+}]}{[A^{x+}]} = E^\circ - \left( \frac{0.06V}{n} \right) \log \left( \frac{\text{oxidized form}}{\text{reduced form}} \right)$$

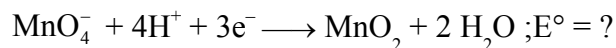
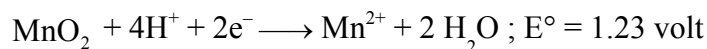
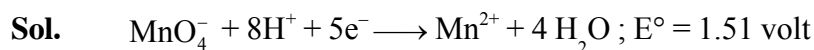
Substituting the given values, we get

$$0.101 \text{ V} = E^\circ - \left( \frac{0.06V}{n} \right) \log \frac{75.6}{24.4} = E^\circ - \left( \frac{0.06V}{n} \right) (0.491) \dots\dots(i)$$

$$0.115 \text{ V} = E^\circ - \left( \frac{0.06V}{n} \right) \log \frac{51.2}{48.8} = E^\circ - \left( \frac{0.06V}{n} \right) (0.021) \dots\dots(ii)$$

eq. (ii) - (i),  $n = 2$

**Ex.11** What is the standard electrode potential for the electrode  $MnO_4^- | MnO_2$  in solution  $E^\circ_{MnO_4^- | MnO_2} =$   
**1.51 volt**,  $E^\circ_{MnO_2 | Mn^{2+}} = 1.23$  volt



$$E^\circ = \frac{5 \times 1.51 - 2 \times 1.23}{3} = \frac{7.55 - 2.45}{3} = \frac{5.09}{3} = 1.70 \text{ volt}$$

**Ex.12** Calculate  $\Delta G^\circ$  for the reaction :  $Cu^{2+} (aq) + Fe (s) \rightleftharpoons Fe^{2+} (aq) + Cu (s)$  .

Given that  $E^\circ_{Cu^{2+} | Cu} = +0.34$  V,  $E^\circ_{Fe^{2+} / Fe} = -0.44$  V

**Sol.** The cell reactions are :

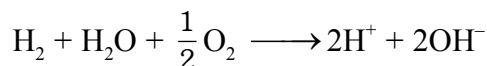


We know that :  $\Delta G^\circ = -nF E^\circ_{cell}$  ;  $n = 2$

$$E^\circ_{cell} = [E^\circ_{(Cu^{2+} / Cu)} - E^\circ_{(Fe^{2+} / Fe)}] = (+0.34 \text{ V}) - (-0.44 \text{ V}) = +0.78 \text{ V and } F = 96500 \text{ C}$$

$$\therefore \Delta G^\circ = -nF E^\circ_{cell} = -(2) \times (96500 \text{ C}) \times (+0.78 \text{ V}) = -150540 \text{ CV} = -150540 \text{ J}$$

**Ex.13** At 298 K the standard free energy of formation of  $H_2O(l)$  is  $-256.5$  kJ/mol &  $OH^-$  is  $80$  kJ/mol. What will be emf at 298 K of the cell  $H_2(g, 1 \text{ bar}) | H^+(1M) || OH^-(1M) | O_2(g, 1 \text{ bar})$



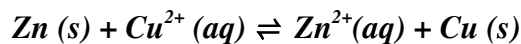
$$\Delta G^\circ = -256.5 + 2 \times 80 = -96.5 \text{ kJ}$$

$$-\Delta G^\circ = nFE^\circ$$

$$+96.5 \times 1000 = 2 \times 96500 \times E^\circ$$

$$E^\circ = 0.5 \text{ Volt}$$

**Ex.14** Calculate the equilibrium constant for the reaction at 298 K.



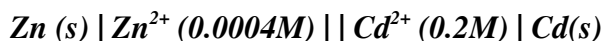
Given,  $E^\circ_{Zn^{2+} | Zn} = -0.76$  V and  $E^\circ_{Cu^{2+} | Cu} = +0.34$  V

**Sol.** We know that,  $\log K_c = \frac{nE^\circ_{cell}}{0.0591}$

$$E^\circ_{cell} = [E^\circ_{Cathode} - E^\circ_{Anode}] = [(+0.34 \text{ V}) - (-0.76 \text{ V})] = 1.10 \text{ V, } n = 2,$$

$$\therefore \log K_c = \frac{2 \times (1.10 \text{ V})}{(0.0591 \text{ V})} = 37.29, K_c = \text{Antilog } 37.29 = 1.95 \times 10^{37}$$

**Ex.15** Calculate the cell e.m.f. and  $\Delta G$  for the cell reaction at 298 K for the cell.



Given,  $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.763 \text{ V}$ ;  $E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} = -0.403 \text{ V}$  at 298 K.  $F = 96500 \text{ C mol}^{-1}$ .

**Sol.** **Step I.** Calculation of cell e.m.f. :

According to Nernst equation,

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cd}^{2+}(\text{aq})]}$$

$$E_{\text{cell}}^{\circ} = E_{(\text{Cd}^{2+}/\text{Cd})}^{\circ} - E_{(\text{Zn}^{2+}/\text{Zn})}^{\circ} = (-0.403) - (-0.763) = 0.36 \text{ V}$$

$$[\text{Zn}^{2+}(\text{aq})] = 0.0004 \text{ M}, [\text{Cd}^{2+}(\text{aq})] = 0.2 \text{ M}, n = 2$$

$$E = (0.36) - \frac{(0.059\text{V})}{2} \log \frac{0.0004}{0.2} = 0.36 - \frac{(0.059\text{V})}{2} \times (-2.69990) = 0.36 \text{ V} + 0.08 = 0.44 \text{ V}$$

**Step II.** Calculation of  $\Delta G$  :

$$\Delta G = -nFE_{\text{cell}}$$

$$E_{\text{cell}} = 0.44 \text{ V}, n = 2 \text{ mol}, F = 96500 \text{ C mol}^{-1}$$

$$\therefore \Delta G = -(2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.44 \text{ V}) \\ = -84920 \text{ CV} = -84920 \text{ J}$$

**Ex.16** The cell  $\text{Pt} \mid \text{H}_2(\text{g}) (1 \text{ atm}) \mid \text{H}^+ ; \text{pH} = x \parallel \text{Normal calomel electrode}$  has EMF of 0.64 volt at 25°C. The standard reduction potential of normal calomel electrode is 0.28 V. What is the pH of solution in anodic compartment. Take  $\frac{2.303RT}{F} = 0.06$  at 298 K.

**Sol.**  $E_{\text{H}^+/\text{H}_2} = -0.06 \log \frac{1}{[\text{H}^+]} = -0.06 \text{pH}$

$$\Rightarrow 0.64 = E_{\text{cathode}} - E_{\text{Anode}} = 0.28 - (-0.06 \text{ pH})$$

$$\Rightarrow \text{pH} = \frac{0.64 - 0.28}{0.06} = \frac{0.36}{0.06} = 6$$

**Ex.17** Consider a Galvanic cell,



by what factor, the electrolyte in anodic half cell should be diluted to increase the emf by 9 milli volt at 298 K.

**Ans.**  $E = E_{\text{cell}}^{\circ} - \frac{0.06}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$

$$E_1 = E_{\text{cell}}^{\circ} - 0.03 \log \frac{(0.1)}{(0.1)}$$

$$E_2 = E_{\text{cell}}^{\circ} - 0.03 \log \frac{(0.1/x)}{(0.1)} \quad \{x \text{ is the factor by which electrolyte is diluted.}\}$$



$$E_2 - E_1 = 9 \times 10^{-3} = 0 - 0.03 \log\left(\frac{1}{x}\right)$$

$$0.009 = 0.03 \log X$$

$$\frac{9 \times 10^{-3}}{3 \times 10^{-2}} = 0.3 = \log X$$

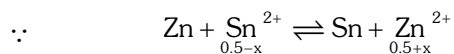
$$X = 2$$

**Ex.18** A disposable galvanic cell  $\text{Zn} | \text{Zn}^{2+} || \text{Sn}^{2+} | \text{Sn}$  is produced using 1.0 mL of 0.5 M  $\text{Zn}(\text{NO}_3)_2$  and 1.0 mL of 0.50 M  $\text{Sn}(\text{NO}_3)_2$ . It is needed to power a pace-maker that draws a constant current of  $10^{-6}$  Amp to run it and requires atleast 0.50 V to function. Calculate the value of  $[\text{Zn}^{2+}]$  when cell reaches 0.5 V at 298 K.

(Given :  $E^\circ (\text{Zn}^{2+} | \text{Zn}) = -0.76\text{V}$ ;  $E^\circ (\text{Sn}^{2+} | \text{Sn}) = -0.14\text{V}$ ).

**Ans.** 1

$$E = 0.5\text{V} = 0.62 - \frac{0.059}{2} \log \frac{0.5+x}{0.5-x}$$



$$\Rightarrow \log \frac{0.5+x}{0.5-x} = \frac{0.12 \times 2}{0.0592} \approx 4$$

$$\Rightarrow \frac{0.5+x}{0.5-x} = 10^4$$

$$\text{or } x \approx 0.5\text{M}$$

$$\therefore [\text{Zn}^{2+}] = 1.0\text{M}$$

**Ex.19** An alloy of Pb-Ag weighing 54 mg was dissolved in desired amount of  $\text{HNO}_3$  & volume was made upto 500ml. An Ag electrode was dipped in solution and then connected to standard hydrogen electrode anode. Then calculate % of Ag in alloy.

$$\text{Given : } E_{\text{cell}} = 0.5\text{V}; E_{\text{Ag}^+ | \text{Ag}}^\circ = 0.8\text{V} \quad \frac{2.303RT}{F} = 0.06$$

**Ans.**  $\text{Ag}^+ + 1\text{e}^- \longrightarrow \text{Ag}$

$$E_{\text{cell}} = 0.5 = 0.8 + \frac{0.06}{1} \log [\text{Ag}^+]$$

$$\log [\text{Ag}^+] = \frac{-0.30}{0.06} = -5$$

$$[\text{Ag}^+] = 10^{-5} \text{ mol/L}$$

$$\text{moles of Ag}^+ \text{ in } 500 \text{ ml} = \frac{10^{-5}}{2}$$

$$\text{Mass of Ag} = \frac{10^{-5}}{2} \times 108$$

$$\% \text{ Ag} = \frac{10^{-5}}{2} \times 108 \times 100 = 1$$

**Ex.20.** A solution contains  $A^+$  and  $B^+$  in such a concentration that both deposit simultaneously. If current of 9.65 amp was passed through 100 ml solution for 55 seconds then find the final concentration of  $A^+$  ions if initial concentration of  $B^+$  is 0.1M.



$$\frac{2.303RT}{F} = 0.06$$

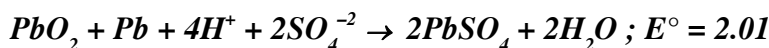
**Sol.**  $-0.5 - \frac{0.06}{1} \log \frac{1}{[A^+]} = -0.56 - \frac{0.06}{1} \log \frac{1}{[B^+]}$

$$0.06 = \frac{0.06}{1} \log \frac{[B^+]}{[A^+]}$$

$$\frac{[B^+]}{[A^+]} = 10$$

$$[A^+]_{\text{initial}} = 0.01M$$

**Ex.21** While the discharging of a lead storage battery following reaction take place.



Calculate the energy (in kJ) obtained from a lead storage battery in which 0.014 mol of lead is consumed. Assume a constant concentration of 10.M  $H_2SO_4$  ( $\log 2 = 0.3$ )

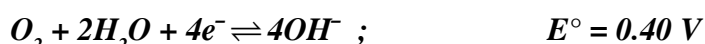
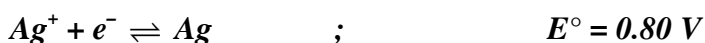
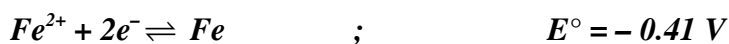
**Ans.**  $E = E^\circ - \frac{0.059}{n} \log \frac{1}{[H^+]^4 [SO_4^{2-}]^2} = 2.01 - \frac{0.059}{2} \log \frac{1}{[20]^4 [10]^2} = 2.22$  V

$$\text{Energy} = qE$$

$$= 2 \times 0.014 \times 96500 \times 2.22$$

$$= 6000 \text{ J} = 6 \text{ kJ}$$

**Ex.22** Consider the following standard reduction potentials :-



What would happen if a block of silver metal is connected to a buried iron pipe via a wire:-

(A) The silver metal would corrode, a current would be produced in the wire, and  $O_2$  would be reduced on the surface of the iron pipe.

(B) The silver metal would corrode, a current would be produced in the wire, and  $Fe^{2+}$  would be reduced on the surface of the iron pipe.

(C) The iron pipe would corrode, a current would be produced in the wire, and  $Ag^+$  would be reduced on the surface of the silver metal.

(D) The iron pipe would corrode, no current would be produced in the wire, and  $O_2$  would be reduced on the surface of the iron pipe.

**Sol.** (D)

## 7. ELECTROLYSIS :

The process of decomposition of an electrolyte by the passage of electricity is called *electrolysis* or electrolytic dissociation. It is carried out in electrolytic cell where electrical energy is converted into chemical energy. For electrolysis to take place two suitable electrodes are immersed in the liquid or solution of an electrolyte containing ions. When an electric potential is applied between the electrodes, the positively charged ions move towards the negative cathode and negatively ions move towards the positive anode, when a cation reaches the cathode, it takes up electron(s) and thus gets its charge neutralised. Thus the gain of electrons (decrease in oxidation number) means reduction takes place at the cathode.

Similarly when an anion it reaches the anode, gives up electron(s) and thus gets discharged. Loss of electrons (Increase in oxidation number) means oxidation takes place at anode.

- The tendency of an electrode to lose electrons is known as the *oxidation potential*.
- The tendency of an electrode to gain electrons is known as the *reduction potential*.
- *Greater oxidation potential means stronger is tendency to get oxidised and act as a reducing agent or reductant.*
- *Greater reduction potential means stronger is tendency to get reduced and act as an oxidising agent (oxidant).*

### (a) Electrolysis of fused sodium chloride :

When fused sodium chloride is electrolysed,  $\text{Na}^+$  ions moves towards the cathode and  $\text{Cl}^-$  ions moves towards the anode. At cathode  $\text{Na}^+$  ions accept electrons to form sodium metal. At anode each  $\text{Cl}^-$  ion loses an electron to form  $\text{Cl}_2$  gas.

- **At anode :**  $\text{Cl}^- \longrightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^- ; E_{\text{OP}}^0 = -1.36\text{V}$
- **At cathode :**  $\text{Na}^+ + \text{e}^- \longrightarrow \text{Na(s)} ; E_{\text{RP}}^0 = -2.71\text{V}$

### (b) Electrolysis of aqueous solution of KBr

The solution of KBr contain  $\text{K}^+$ ,  $\text{Br}^-$  & small amounts of  $\text{H}^+$ ,  $\text{OH}^-$  (due to small dissociation of water)

- **At anode :**  $2\text{Br}^-(\text{aq.}) \longrightarrow \text{Br}_2(\text{g}) + 2\text{e}^-$
- **At cathode :**  $2\text{H}_2\text{O}(\ell) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
- If more than one types of ions are present at a given electrode, then the one ion is the liberated which requires least energy. The energy required to liberate an ion is provided by the applied potential between electrodes. This potential is called *discharge or deposition potential*.

#### Note :

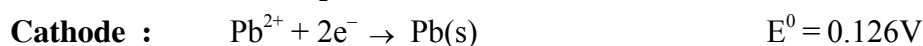
1. In aqueous solution most electropositive metal cations for eg. (s-block &  $\text{Al}^{3+}$ ) will not discharge at cathode instead  $\text{H}_2\text{O}$  is reduced.  $2\text{H}_2\text{O}(\ell) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
2. In aqueous solution cations of moderately electropositive metals (Mn, Co, Fe, Zn etc.) and least electropositive metals (Cu, Hg, Au, Ag, Pt) get discharged at cathode first.

### 3. Active vs Inactive electrodes :

- Sometimes the metal electrodes in the cell are active and the metals themselves are components of the half reactions or influence the reaction of electrode.
- For many redox reactions, however, there are no reactants or products capable of serving as electrodes. Inactive electrodes are used, most commonly rods of graphite or platinum, materials that conduct electrons into or out of the cell but cannot take part in the half-reactions.
- Platinum is used  $\because$  highly conducting, unreactive.  
highly malleable and ductile.

#### ❖ Examples of Electrolysis :

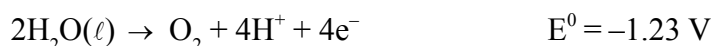
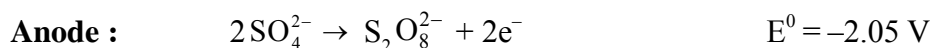
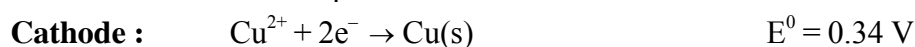
- **Electrolysis of aq.  $\text{PbBr}_2$**  (Using inert (Pt|graphite) electrodes).



$$E_{\text{cell}} = -0.126 - (0.108) \times 10 = -1.206\text{V}$$

$$E_{\text{ext}} > 1.206\text{V}$$

- **Electrolysis of aq.  $\text{CuSO}_4$**  (Using inert (Pt|graphite) electrodes).



$\therefore$  Cu discharged at cathode and  $\text{O}_2$  at anode.

- **Electrolysis of aq.  $\text{NaCl}$**  (Using inert (Pt|graphite) electrodes).



Rate of production of  $\text{Cl}_2$  is more than rate of production of  $\text{O}_2$  gas because of greater activation energy barrier for  $\text{O}_2$  production, therefore  $\text{Cl}_2$  is released at anode and  $\text{H}_2$  at cathode.

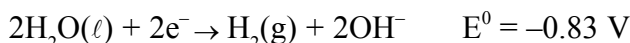
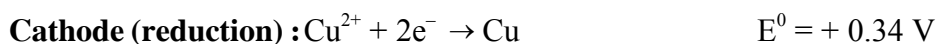
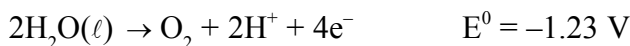
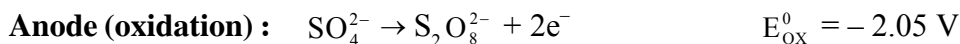
**Note:(i)** As observed from electrode potential values discharge potential for  $\text{O}_2$  is less than for  $\text{Cl}_2$ . According to thermodynamics, oxidation of  $\text{H}_2\text{O}$  to produce  $\text{O}_2$  should take place on anode but experimentally (experiment from chemical kinetics) the rate of oxidation of water is found to be very slow. To increase it's rate, the greater potential difference has to be applied called over voltage or over potential.

Because of this oxidation of  $\text{Cl}^-$  ions also become feasible and this takes place at anode. Electrode potential values do not take into account such effects as : Activation energy of process or non-uniform ionic concentration in solution.

**(ii)** Electrode potentials are thermodynamic intensive properties obtained experimentally under ideal & standard conditions. Sometimes in working conditions additional potentials are required for discharging. This difference is termed as overvoltage or overpotential.

❖ **Electrolysis using attackable (reactive) electrodes :**

• **Electrolysis of aq.  $\text{CuSO}_4$  using Cu electrode.**



∴ Both oxidation and reduction of copper occurs and density of solution remains constant.

• **Electrolytic Refining**

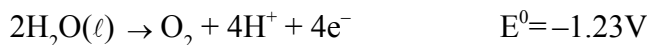
**Electrolysis of  $\text{AgNO}_3(\text{aq})$  using Ag cathode & Ag anode.**

Impure metal  $\rightarrow$  Anode ;

Pure Metal  $\rightarrow$  Cathode ;

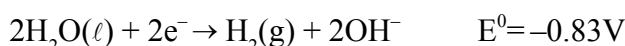
Metal salt solution  $\rightarrow$  Electrolyte

**Anode :**  $\text{NO}_3^- \rightarrow \text{X}$  (No reaction)

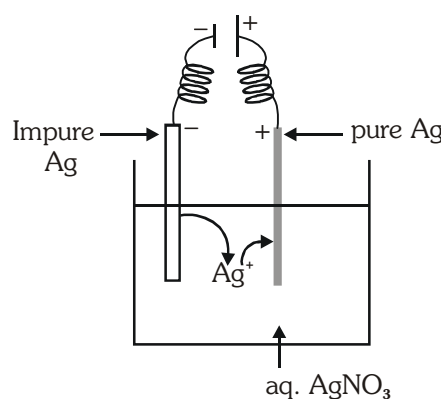


(impure)

**Cathode :**  $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}(\text{s})$  (pure)  $E^0 = 0.8 \text{ V}$



∴ Both oxidation and reduction of Ag occurs and mass transfer of Ag occurs from anode (impure Ag) to cathode (pure Ag). Electrical energy provided by battery is used for mass transfer of Ag from anode to cathode.



**PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES**

S.No.	Electrolyte	Electrode	Product obtained at anode	Product obtained at cathode
(i)	Fused NaCl(molten)	Pt or Graphite	$\text{Cl}_2$	Na
(ii)	Aqueous NaCl(conc.)	Pt or Graphite	$\text{Cl}_2$	$\text{H}_2$
(iii)	dil. NaCl	Pt or Graphite	$\text{O}_2$	$\text{H}_2$
(iv)	Aqueous NaOH	Pt or Graphite	$\text{O}_2$	$\text{H}_2$
(v)	Fused NaOH	Pt or Graphite	$\text{O}_2$	Na
(vi)	Aqueous $\text{CuSO}_4$	Pt or Graphite	$\text{O}_2$	Cu
(vii)	Dilute HCl	Pt or Graphite	$\text{Cl}_2$	$\text{H}_2$
(viii)	Dilute $\text{H}_2\text{SO}_4$	Pt or Graphite	$\text{O}_2$	$\text{H}_2$
(ix)	Aqueous $\text{AgNO}_3$	Pt of Graphite	$\text{O}_2$	Ag
(x)	Aqueous $\text{CH}_3\text{COONa}$	Pt of Graphite	$\text{CH}_3-\text{CH}_3 + \text{CO}_2$	$\text{H}_2$

### 8. FARADAY'S LAWS OF ELECTROLYSIS :

Michael Faraday on basis of experiments deduced two important laws :

- (a) **Faraday's first law of electrolysis :** This law states that "*The amount of a substance deposited or discharged at an electrode is directly proportional to the charge passing through the electrolytic solution*".

If a current of  $I$  amperes is passed for  $t$  seconds, (the quantity of charge  $Q$  in coulombs). If  $W$  gram of substances is deposited by  $Q$  coulombs of electricity, then

$$W \propto Q \propto i \times t$$

$$W = Z \times i \times t = \frac{E}{96500} \times i \times t = \eta \times \frac{E}{F} \times i \times t$$

$$\text{moles of } e^- = n_e = \frac{\eta \times i \times t}{F} = \text{no. of equivalents of species discharged During electrolysis :}$$

Where 1 Faraday (1F) is defined as charge of 1 mole electrons =  $eN_A = 1 F \cong 96500 C$

**Hence faraday (F) is the quantity of charge in coulombs required to deposit one g equivalent of any substance.**

$E$  = Equivalent mass of species discharged

$\eta$  = current efficiency in fraction if current efficiency is not mentioned, by default it is assumed to be 1 (100%).

$Z$  is constant of proportionality and is known as **electrochemical equivalent**. Its value is different for different species, when  $Q = 1$  coulomb,  $W = Z$ , thus electro chemical equivalent may be defined as the weight in grams of an element liberated by the passage of 1 coulomb of electricity.

Electrochemical equivalent of species ( $Z$ ) =  $\frac{E}{96500}$  gm | coulomb.

- (b) **Faraday's second law :** This law states that the amounts of different substances deposited in different solutions connected in series at electrodes by passage of the same quantity of electricity are proportional to their equivalent masses( $E$ ).

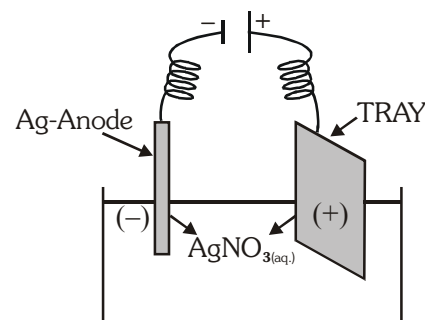
$$W \propto E \quad (E = \text{equivalent mass})$$

If  $W_1$  and  $W_2$  be the amounts of two different substances deposited at electrodes and  $E_1$  and  $E_2$  be the equivalent weights respectively then -

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

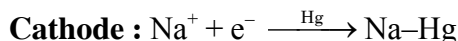
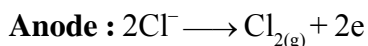
### 9. APPLICATION OF ELECTROLYSIS

- (i) **Electroplating :** Metal used for plating  $\rightarrow$  ANODE  
Object to be plated  $\rightarrow$  CATHODE
- (ii) **Electrorefining :** Impure metal  $\rightarrow$  ANODE (see fig.)  
Pure metal  $\rightarrow$  CATHODE  
Metal salt solution  $\rightarrow$  electrolyte



**(iii) Electro-metallurgy :** (Electrolytic reduction)

Ex. Electrolysis of NaCl (from seawater) Using Hg-cathode.

**EXERCISE # 3**

- Which of the substances Na, Hg, S, Pt and graphite can be used as electrodes in electrolytic cells having aqueous solution ?  
 (A) Hg and Pt  
 (B) Hg, Pt and graphite  
 (C) Na, S  
 (D) Na, Hg, S
- When an electric current is passed through acid diluted water, 112 ml. of hydrogen gas at STP collects at the cathode in 965 second. The current passed, in ampere is :  
 (A) 1.0                      (B) 0.5                      (C) 0.1                      (D) 2.0
- A factory produces 40 kg. of calcium in two hours by electrolysis. How much aluminium can be produced by the same current in two hours- (**At wt. of Ca = 40, Al = 27**)  
 (A) 22 kg.                      (B) 18 kg.                      (C) 9 kg.                      (D) 27 kg.
- Calculate the volume of hydrogen at STP obtained by passing a current of 0.536 ampere through acidified water for 30 minutes.  
 (A) 0.1135 litre                      (B) 0.227 litre                      (C) 0.057 litre                      (D) 0.454 litre
- An electric current is passed through silver voltameter connected to a water voltameter in series. The cathode of the silver voltameter weighed 0.108g more at the end of the electrolysis. The volume of oxygen evolved at STP is:  
 (A) 56.75cm<sup>3</sup>                      (B) 567.5 cm<sup>3</sup>                      (C) 5.675 cm<sup>3</sup>                      (D) 113.5 cm<sup>3</sup>
- When, during electrolysis of a solution of AgNO<sub>3</sub>, 9650 coulombs of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be : **[AIEEE 2003]**  
 (A) 21.6g                      (B) 108g                      (C) 1.08g                      (D) 10.8g
- Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal ( 1 Faraday = 96500 Coulombs). The cathode reaction is **[AIEEE 2005]**  

$$\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$$
 To prepare 5.12 kg of aluminium metal by this method would require,  
 (A)  $5.49 \times 10^4$  C of electric charge  
 (B)  $5.49 \times 10^1$  C of electric charge  
 (C)  $5.49 \times 10^7$  C of electric charge  
 (D)  $1.83 \times 10^7$  C of electric charge

## SOLVED EXAMPLES

**Ex.23** How much charge is present on 1 mole of  $\text{Cu}^{+2}$  ion in faraday. (1 Faraday = 96500 coulomb)

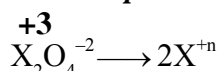
**Ans.** 1 mole  $e^-$  = 1 mol proton = 1F

2 Faraday

**Ex.24** For an element 'X' the process of oxidation is :  $\text{X}_2\text{O}_4^{-2} \longrightarrow$  product

If 965 A current when passed for 100 seconds for 0.1 mol of  $\text{X}_2\text{O}_4^{-2}$ , find oxidation state of X in new compound ?

**Ans.**



$\therefore$  oxidation process  $3 < n$ , N-factor =  $2(n-3)$

$$\text{so } 0.1 \times 2(n-3) = \frac{i \times t}{96500} = \frac{965 \times 100}{96500}$$

$$2(n-3) = 10, n-3 = 5, n = 8$$

**Ex.25** How many litres of chlorine at 1atm & 273K will be deposited by 100 amp. current flowing for 5 hours through molten NaCl?

**Sol :**  $Q = It = 100 \times 5 \times 60 \times 60 = 18 \times 10^5 \text{C}$

$$W = ZQ = \frac{E}{96500} \times 18 \times 10^5 = \frac{18E}{96500} \times 10^5 = 662.2 \text{ g}, \left( E_{\text{Cl}_2} \frac{71}{2} = 35.5 \right)$$

$\therefore$  Volume of 71 g  $\text{Cl}_2$  at 1atm & 273K = 22.4 L

$\therefore$  Volume of 662.2 g  $\text{Cl}_2$  at NTP =  $\frac{22.4}{71} \times 662.2 = 208.9 \text{ L}$

**Ex.26** How much time is required for complete decomposition of two moles of water at anode using 4 amperes current ?

**Sol.**  $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

$$\text{For } \text{H}_2 : 2 \times 2 = \frac{4 \times t}{96500} \Rightarrow t = 96500 \text{ sec,}$$

**Ex.27** How much charge (in F) must flow through solution during electrolysis of aq.  $\text{Na}_2\text{SO}_4$  at  $0^\circ\text{C}$  and 1 atm to produce 33.6 L of product gases at 50% current efficiency ?

**Ans.**  $\text{H}_2\text{O} \xrightarrow{2F} \text{H}_2 + \frac{1}{2}\text{O}_2$

$$V \quad V/2 \quad \therefore \frac{3}{2}V = 33.6 \text{ L} \quad \therefore V = 22.4 \text{ L}$$

$$Q \times \frac{50}{100} = 2F \quad \therefore Q = 4F$$



**Ex.28** Calculate the time required to coat a metal surface of  $80 \text{ cm}^2$  with  $0.005 \text{ mm}$  thick layer of silver (density =  $10.5 \text{ g cm}^{-3}$ ) with the passage of  $3 \text{ A}$  current through silver nitrate solution.

**Sol.**  $\therefore$  Volume of layer of silver =  $0.005 \times 10^{-1} \times 80 = 0.04 \text{ cm}^3$

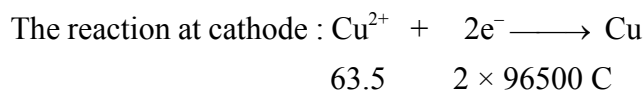
$\therefore$  Mass = Density  $\times$  volume =  $10.5 \times 0.04 = 0.42 \text{ g}$

$$\text{So } w = \frac{E}{96500} \times It \Rightarrow 0.42 = \frac{108}{96500} \times 3 \times t$$

$$t = \frac{0.42 \times 96500}{108 \times 3} = 125.09 \text{ seconds.}$$

**Ex.29** A Solution of copper (II) sulphate is electrolysed between copper electrodes by a current of  $10.0 \text{ amperes}$  passing for one hour. What changes occur at the electrodes and in the solution?

**Sol.** According to Faraday's first law of electrolysis :



The quantity of charge passed =  $I \times t = (10 \text{ amp}) \times (60 \times 60\text{s}) = 36000 \text{ C}$ .

$2 \times 96500 \text{ C}$  of charge deposit copper -  $63.5 \text{ g}$

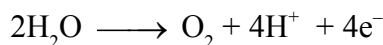
$$36500 \text{ C of charge deposit copper} = \frac{(63.5 \text{ g})}{(2 \times 96500 \text{ C})} \times (36000 \text{ C}) = 11.84 \text{ g}$$

Thus,  $11.84 \text{ g}$  of copper will dissolve from the anode and the same amount from the solution will get deposited on the cathode. The concentration of the solution will remain unchanged.

**Ex.30** An aqueous solution of  $\text{Na}_2\text{SO}_4$  was electrolysed for  $10 \text{ min}$ .  $82 \text{ ml}$  of a gas was produced at anode and collected over water at  $27^\circ\text{C}$  at a total pressure of  $580 \text{ torr}$ . Determine the current that was used in amp. , Given : Vapour pressure of  $\text{H}_2\text{O}$  at  $27^\circ\text{C} = 10 \text{ torr}$ ,  $R = 0.082 \text{ atm L/mol-K}$

**Ans** (1.6A)

At anode reaction will be



$\text{V}_{\text{O}_2}$  collected =  $82 \text{ ml}$

$$\text{By PV} = nRT \quad \frac{(580 - 10)}{760} \times \frac{82}{1000} = (n_{\text{O}_2}) \times 0.0821 \times 300, \quad n_{\text{O}_2} = \frac{1}{400}$$

$$\text{By Faraday law } \frac{W}{E} = \frac{i \times t}{96500}$$

$$\left(\frac{W}{M}\right) \times n = \frac{i \times t}{96500}, \quad \left(\frac{1}{400} \times 4\right) = \frac{i \times 10 \times 60}{96500}, \quad i = 1.6 \text{ A}$$

**Ex.31** The same current if passed through solution of silver nitrate and cupric salt connected in series. If the weight of silver deposited is  $1.08 \text{ g}$ . calculate the weight of copper deposited.

**Sol.** According to faradays second law

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \Rightarrow \frac{1.08}{W_2} = \frac{108}{31.75} \Rightarrow W_2 = 0.3175 \text{ g}$$

## 10 ELECTROLYTIC CONDUCTANCE

### 10.1 Resistance (R) :

Metallic and electrolytic conductors obey ohm's law according to which the resistance of a conductor is the ratio of the applied potential difference (V) to the current following (I).

$$R = \frac{V}{I} \quad \bullet \text{ R is expressed in ohms.}$$

- In the case of solution of electrolytes, the resistance offered by the solution to the flow of current is –

- (a) Directly proportional to the distance between the electrodes

$$R \propto \ell$$

- (b) Inversely proportional to the area of cross section of the electrodes

$$R \propto \frac{1}{A}$$

### 10.2 Conductance or resistivity (G) :

The conductance of a conductor is equal to reciprocal of resistance.

$$G = \frac{1}{R} \quad \bullet \text{ G is expressed in mho or } \Omega^{-1} \text{ or Siemen(S). [1S = 1W}^{-1} \text{ S.I. unit]}$$

### 10.3 Specific resistance or conductivity ( $\rho$ ) :

The resistance (R) of a conductor of uniform cross section is directly proportional to its length( $\ell$ ) and inversely proportional to its area of cross section (A).

$$R \propto \frac{\ell}{A} \quad R = \rho \frac{\ell}{A}$$

where  $\rho$  is a constant and called resistivity or specific resistance.

When  $\ell = 1$ ,  $A = 1$ , then  $\rho = R$  thus the specific resistance may be defined as the resistance of a conductor of unit length and unit area of cross section.

- Unit of  $\rho \rightarrow \text{ohm.cm}$

### 10.4 Specific conductance ( $\kappa$ ) :

It is defined as the reciprocal of specific resistance

$$\kappa = \frac{1}{\rho}$$

$$G = \kappa / G^*, \quad G^* = \frac{l}{a} = \text{cell constant}$$

If  $\ell = 1 \text{ cm}$  &  $A = 1 \text{ cm}^2$  then  $\kappa = G$

Hence conductivity or specific conductance (F) of a solution is defined as the conductance of one centimeter cube of the solution of the electrolyte.

- Cell constant is a fixed quantity for a particular cell and is defined as the distance between two parallel electrodes of a cell divided by the area of cross section of the electrodes.

$$\kappa = G \times \text{cell constant}$$

- Unit of  $\kappa \rightarrow \text{ohm}^{-1} \text{ cm}^{-1}$
- SI unit of  $\kappa \rightarrow \text{S m}^{-1}$
- $1 \text{ S m}^{-1} = 100 \text{ ohm}^{-1} \text{ cm}^{-1}$

**10.5 Molar conductance ( $\lambda_m$  or  $\Lambda_m$ ):** It is defined as the product of specific conductance ( $\kappa$ ) and the volume (V in mL) in which contains one mole of the electrolyte.

$$\Lambda_m = \kappa \times V \quad \text{and} \quad \Lambda_m = \frac{\kappa \times 1000}{M} \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad [\text{SI unit : S m}^2 \text{ mol}^{-1}]$$

- It can also be defined as conductance of 1 mole electrolyte completely dissolved between two plates separated by unit distance.

**10.6 Equivalent conductance ( $\lambda_{eq}$  or  $\Lambda_{eq}$ ):** It is defined as the product of specific conductance ( $\kappa$ ) and the volume (V in mL) in which contains one equivalent of the electrolyte.

$$\Lambda_m = \kappa \times V \quad \text{and} \quad \Lambda_m = \frac{\kappa \times 1000}{M} \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1} \quad [\text{SI unit : S m}^2 \text{ eq}^{-1}]$$

- It can also be defined as conductance of 1 equivalent electrolyte completely dissolved between two plates separated by unit distance.

• **Relation between  $\Lambda_{eq}$  and  $\Lambda_m$ :**

$$\Lambda_m = \frac{\kappa \times 1000}{M} \quad \text{and} \quad \Lambda_{eq} = \frac{\kappa \times 1000}{N}$$

We know that, **Normality = Valency Factor  $\times$  Molarity**

$$\text{or} \quad N = n \times M \Rightarrow \lambda_{eq} = \frac{\lambda_m}{n}$$

#  $n$  = total cationic (or anionic) charge of salt.

$$\text{Ex.} \quad \Lambda_{eq}[\text{Al}_2(\text{SO}_4)_3] = \frac{\Lambda_m[\text{Al}_2(\text{SO}_4)_3]}{6}, \quad L_{eq \text{ NaCl}} = \frac{\Lambda_m \text{ NaCl}}{1}, \quad L_{eq \text{ CaCl}_2} = \frac{\Lambda_m \text{ CaCl}_2}{2}$$

## 11 EFFECT OF DILUTION ON THE CONDUCTIVITY OF ELECTROLYTES

(i) The degree of ionisation of weak electrolytes increases with the increase of dilution of the solution the conductivity is increases due to increasing the number of ions.

(ii) Effect of dilution on specific conductance :

Specific conductance decreases with the increase of dilution of the solution due to the presence of no. of ions in 1 cm<sup>3</sup> solution decreases conductance also decrease on dilution.

(iii) Effect of dilution on equivalent|molar conductivity :

The equivalent|molar conductivity increases with dilution. For strong electrolyte  $\lambda_m$  or  $\lambda_{eq}$  increases very slowly but for weak electrolytes  $\lambda_m$  &  $\lambda_{eq}$  increase sharply on dilution.

- When the whole of the electrolyte has ionised, further addition of the water brings a small change in the value of equivalent|molar conductance. This stage is called **infinite dilution**.

- The ratio of equivalent conductivity at any dilution to equivalent conductivity at infinite dilution is called **conductivity ratio** or degree of dissociation of solute -

$$\alpha = \frac{\lambda_{eq}}{\lambda_m^\infty} = \frac{\lambda_m}{\lambda_m^\infty}$$

[  $\lambda_m^\infty$  = molar conductance at  $\infty$  dilution.]

❖ **Variation of conductivity and molar conductivity with concentration :**

- Conductance and conductivity always decreases with the decrease in concentration both for weak and strong electrolytes.
- It is because the number of ions per unit volume that carry the current in a solution decreases on dilution decreasing  $I$ ,  $C$  and  $K$ .

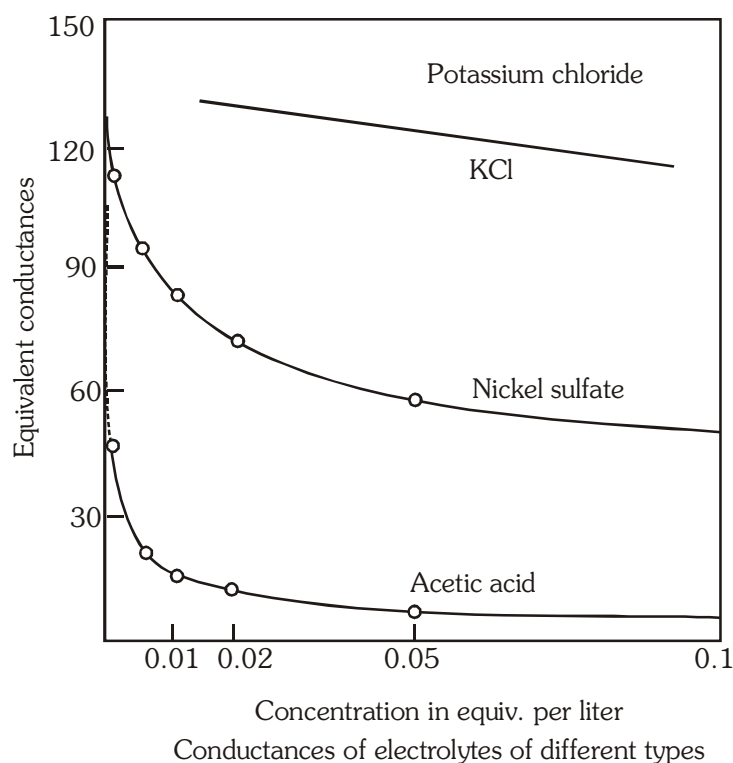
❖ **Strong Electrolytes :**

- For strong electrolytes,  $\Lambda$  increases slowly with dilution and can be represented by the equation  $\Lambda = \Lambda^\circ - A C^{1/2}$ .  $A = \text{constant}$   
On dilution interionic separation increases causing free movement & less hindrance. This increases  $\Lambda_m$  &  $\Lambda_{eq.}$   
For strong electrolytes  $\Lambda^\circ$  or  $\Lambda^\infty$  can be calculated graphically from y-intercept.

It can be seen that if we plot  $\Lambda_m$  against  $c^{1/2}$ , we obtain a straight line with intercept equal to  $\Lambda_m^\circ$  and slope equal to  $-A$ . The value of the constant  $A$  for a given solvent and temperature depends on the type of the electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus,  $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$  are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for  $A$ .

❖ **Weak electrolytes :**

- Weak electrolytes like acetic acid have lower degree of dissociation at higher concentration and hence for such electrolytes, the change in  $\Lambda$  with dilution is due to increase in the number of ions solution containing a given amount of electrolyte.



$\text{KCl} \rightarrow \text{Strong}$

$\text{Ni}_2\text{SO}_4 \rightarrow \text{Moderate}$

$\text{CH}_3\text{COOH} \rightarrow \text{Weak electrolyte}$

- Note :** (A) Weaker the electrolyte more sharp will be increase of  $\Lambda_m$  or  $\Lambda_{eq}$  on dilution.  
 (B) same plot is also observed for  $\Lambda_m$  vs. molarity of respective electrolytes.

## 12. KOHLARAUSCH'S LAW

- "At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions."

$$\text{i.e., for } A_{n^+} B_{n^-} \quad \begin{cases} \Lambda_{eq}^\infty = \Lambda_{eq}^\infty (+) + \Lambda_{eq}^\infty (-) \\ \Lambda_m^\infty = v_+ \Lambda_m^\infty (+) + v_- \Lambda_m^\infty (-) \end{cases}$$

$v_+$  = no. of cation in one formula unit of electrolyte.

$v_-$  = no. of anions in one formula unit of electrolyte.

**Note :**  $\lambda^\infty = \lambda^\circ$

$$\lambda_{eq+}^0 = \frac{\lambda_m^0}{\text{charge on the cation}} \quad \lambda_{eq}^0 \cdot Al^{3+} = \frac{\lambda_m^0 Al^{3+}}{3}$$

$$\lambda_{eq-}^0 = \frac{\lambda_m^0}{\text{charge on the anion}} \quad \lambda_{eq}^0, \text{ electrolyte} = \frac{\lambda_m^0 \text{ electrolyte}}{\text{total +ve charge on cations in electrolyte}} \\ \text{or} \\ \text{total -ve charge on anions in electrolyte}$$

**The Independent Migration of Ions.** A survey of equivalent conductances at infinite dilution of a number of electrolytes having an ion in common will bring to light certain regularities ;

### COMPARISON OF EQUIVALENT CONDUCTANCES AT INFINITE DILUTION

Electrolyte	$\Lambda_0$	Electrolyte	$\Lambda_0$	Difference
KCl	130.0	NaCl	108.9	21.1
KNO <sub>3</sub>	126.3	NaNO <sub>3</sub>	105.2	21.1
K <sub>2</sub> SO <sub>4</sub>	133.0	Na <sub>2</sub> SO <sub>4</sub>	111.9	21.1

Observations of this kind were first made by **Kohlrausch (1879, 1885)** by comparing equivalent conductances at high dilutions; described them to the fact that under these conditions every ion makes a definite contribution towards the equivalent conductance of the electrolyte, irrespective of the nature of the other ion with which it is associated in the solution. The value of the equivalent conductance at infinite dilution may thus be regarded as made up of the sum of two independent factors, one characteristic of each ion; this result is known as Kohlrausch's law of independent migration of ions.

The ion conductance is a definite constant for each ion, in a given solvent, its value depending only on the temperature.

It will be seen later that the ion conductances at infinite dilution are related to the speeds with which the ions move under the influence of an applied potential gradient.

❖ **Applications of Kohlrausch's law :**

- **Calculate  $\Lambda^\circ$  for any electrolyte from the  $\Lambda^\circ$  of individual ions.**

An important use of ion conductances is to determine the equivalent conductance at infinite dilution of certain electrolytes which cannot be, or have not been, evaluated from experimental data. For example, with a weak electrolyte the extrapolation to infinite dilution is very uncertain, and with sparingly soluble salts the number of measurements which can be made at appreciably different concentrations is very limited. The value of  $\Lambda^\circ$  can, however, be obtained by adding the ion conductances. For example, the equivalent conductance of acetic acid at infinite dilution is the sum of the conductances of the hydrogen and acetate ions; the former is derived from a study of strong acids and the latter from measurements on acetates. It follows, therefore, that at 25°.

$$\Lambda^\circ_{(\text{CH}_3\text{CO}_2\text{H})} = \lambda_{\text{H}^+}^0 + \lambda_{\text{CH}_3\text{CO}_2^-}^0 = 349.8 + 40.9 = 390.7 \text{ ohms}^{-1} \text{ cm}^2$$

The same result can be derived in another manner which is often convenient since it avoids the necessity of separating the conductance of an electrolyte into the contributions of its constituent ions. The equivalent conductance of any weak electrolyte MA at infinite dilution it follows, therefore, that

$$\Lambda^\circ(\text{MA}) = \Lambda^\circ(\text{MCl}) + \Lambda^\circ(\text{NaA}) - \Lambda^\circ(\text{NaCl}), \quad [\text{MCl}, \text{NaA}, \text{NaCl} \text{ are strong electrolytes}]$$

where  $\Lambda^\circ(\text{MCl})$ ,  $\Lambda^\circ(\text{NaA})$  and  $\Lambda^\circ(\text{NaCl})$  are the equivalent conductances at infinite dilution of the chloride of the metal M, i.e., MCl, of the sodium salt of the anion A, i.e., NaA, and of sodium chloride, respectively. Any convenient anion may be used instead of the chloride ion, and similarly the sodium ion may be replaced by another metallic cation or by the hydrogen ion. For example, if  $\text{M}^+$  is the hydrogen ion and  $\text{A}^-$  is the acetate ion, it follows that

$$\begin{aligned} \Lambda^\circ(\text{CH}_3\text{COOH}) &= \Lambda^\circ(\text{HCl}) + \Lambda^\circ(\text{CH}_3\text{COONa}) - \Lambda^\circ(\text{NaCl}) \\ &= 426.16 + 91.0 - 126.45 \\ &= 390.71 \text{ ohms}^{-1} \text{ cm}^2 \text{ at } 25. \end{aligned}$$

Similarly :

$$\Lambda_m^\circ[\text{BaSO}_4] = \Lambda_m^\circ[\text{BaCl}_2] + \Lambda_m^\circ[\text{Na}_2\text{SO}_4] - 2\Lambda_m^\circ[\text{NaCl}]$$

- **Degree of dissociation :**

∴ Degree of dissociation

$$\frac{\text{equivalent conductance at a given concentration}}{\text{equivalent conductance at infinite dilution}}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{\Lambda_{\text{eq}}^c}{\Lambda_{\text{eq}}^\circ}$$

- **Dissociation constant of weak electrolyte :**

$$K_c = \frac{C\alpha^2}{1-\alpha} \frac{C\left(\frac{\Lambda_m^c}{\Lambda_m^\circ}\right)^2}{1-\frac{\Lambda_m^c}{\Lambda_m^\circ}}$$

• **Solubility(s) and  $K_{sp}$  of any sparingly soluble salt.**

Sparingly soluble salt = Very small solubility

Solubility = molarity  $\cong S \rightarrow 0$

So, solution can be considered to be of zero conc or infinite dilution.

$$\Lambda_m^s \approx \Lambda_m^s = \kappa = \frac{1000}{s}$$

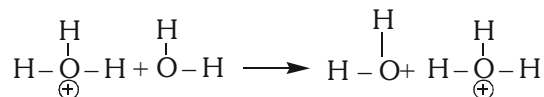
$$s = \frac{\kappa \times 1000}{\Lambda_m^0}$$

### EXERCISE # 4

- Electrolytic conduction differs from metallic conduction from the fact that in the former
  - The resistance increases with increasing temperature
  - The resistance decreases with increasing temperature
  - The resistance remains constant with increasing temperature
  - The resistance is independent of the length of the conductor
- Which of the following solution of KCl has the lowest value of specific conductance :
  - 1 M
  - 0.1 M
  - 0.01 M
  - 0.001 M
- Which of the following solutions of KCl has the lowest value of equivalent conductance ?
  - 1 M
  - 0.1 M
  - .01 M
  - .001 M
- The molar conductance at infinite dilution of  $\text{AgNO}_3$ ,  $\text{AgCl}$  and  $\text{NaCl}$  are 115, 120 and 110 respectively. The molar conductance of  $\text{NaNO}_3$  is :-
  - 110
  - 105
  - 130
  - 150
- The equivalent conductivity of 0.1 N  $\text{CH}_3\text{COOH}$  at 25 °C is 80 and at infinite dilution 400. The degree of dissociation of  $\text{CH}_3\text{COOH}$  is :
  - 1
  - 0.2
  - 0.1
  - 0.5
- The specific conductance of a 0.01 M solution of KCl is  $0.0014 \text{ ohm}^{-1} \text{ cm}^{-1}$  at 25° C. Its equivalent conductance ( $\text{cm}^2 \text{ ohm}^{-1} \text{ equiv}^{-1}$ ) is :-
  - 140
  - 14
  - 1.4
  - 0.14
- The resistance of 0.1 N solution of a acetic acid is 250 ohm. When measured in a cell of cell constant  $1.15 \text{ cm}^{-1}$ . The equivalent conductance (in  $\text{ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ ) of 0.1 N acetic acid is
  - 46
  - 9.2
  - 18.4
  - 0.023
- If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of  $0.4 \text{ cm}^{-1}$  then its molar conductance in  $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  is :
  - 10
  - $10^2$
  - $10^3$
  - $10^4$

❖ **Abnormal ion conductances of  $\text{H}^+$  and  $\text{OH}^-$  :**

It is supposed, as already indicated, that the hydrogen ion in water is  $\text{H}_3\text{O}^+$  with three hydrogen atoms attached to the central oxygen atom. When a potential gradient is applied to an aqueous solution containing hydrogen ions, the latter travel to some extent by the same mechanism as do other ions, but there is in addition another mechanism which permits of a more rapid ionic movement. This second process is believed to involve the transfer of a proton ( $\text{H}^+$ ) from a  $\text{H}_3\text{O}^+$  ion to an adjacent water molecule; thus



The resulting  $\text{H}_3\text{O}^+$  ion can now transfer a proton to another water molecule, and in this way the positive charge will be transferred a considerable distance in a short time. The electrical conductance will thus be much greater than that due solely to the normal mechanism.

### 13. CONDUCTOMETRIC TITRATION :

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added. In order to reduce the influence of errors in the conductometric titration to a minimum, the angle between the two branches of the titration curve should be as small as possible (see Fig. 6.2). If the angle is very obtuse, a small error in the conductance data can cause a large deviation. The following approximate rules will be found

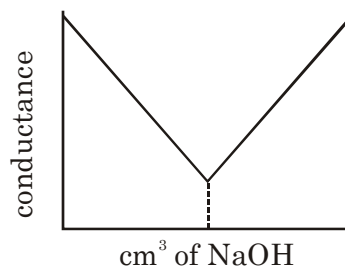
- The smaller the conductivity of the ion which replaces the reacting ion, the more accurate will be the result. Thus it is preferable to titrate a silver salt with lithium chloride rather than with HCl. Generally, cations should be titrated with lithium salts and anions with acetates as these ions have low conductivity
- The larger the conductivity of the anion of the reagent which reacts with the cation to be determined, or vice versa, the more acute is the angle of titration curve.
- The titration of a slightly ionized salt does not give good results, since the conductivity increases continuously from the commencement. Hence, the salt present in the cell should be virtually completely dissociated; for a similar reason; the added reagent should also be as strong electrolyte. The main advantages to the conductometric titration are its applicability to very dilute, and coloured solutions and to systems that involve relative incomplete reactions. For example, which neither a potentiometric, nor indicator method can be used for the neutralization titration of phenol ( $K_a \times 10^{-10}$ ) a conductometric endpoint can be successfully applied.

Cation	$\text{H}_3\text{O}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Na}^+$	$\text{Ag}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$
$\lambda_m^\infty / (\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$	350.0	73.5	73.5	50.1	62.1	118.0	106.1
Anion	$\text{OH}^-$	Br	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{CH}_3\text{COO}^-$	$\text{SO}_4^{2-}$	
$\lambda_m^\infty / (\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$	199.2	78.1	76.5	71.4	40.0	159.6	

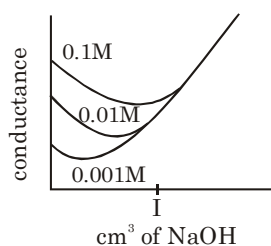
#### Some Typical Conductometric Titration Curves are :

- 13.1** Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as  $\text{H}^+$  ions react with  $\text{OH}^-$  ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large.

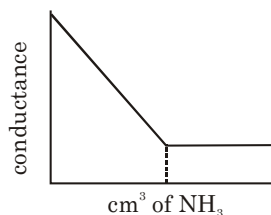




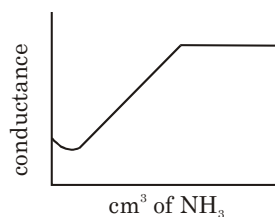
**13.2 Weak Acid with a Strong Base, e.g. acetic acid with NaOH:** Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of  $H^+$  by  $Na^+$  but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated  $CH_3COOH$  to  $CH_3COONa$  which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt  $CH_3COONa$ . Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting  $OH$  ions.



**13.3 Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia:** Initially the conductance is high and then it decreases due to the replacement of  $H^+$ . But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate.

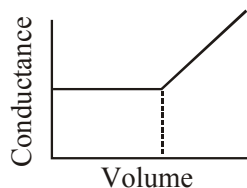


**13.4 Weak Acid with a Weak Base:** The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting



**13.5 Precipitation Titration and Complex Formation Titration:** A reaction may be made the basis of a conductometric precipitation titration provided the reaction product is sparingly soluble or is a stable complex. The solubility of the precipitate (or the dissociation of the complex) should be less than 5%. The addition of ethanol is sometimes recommended to reduce the solubility in the precipitations. An experimental curve is given in Fig. 6.8 (ammonium sulphate in aqueous-ethanol solution with barium acetate).

If the solubility of the precipitate were negligibly small, the conductance at the equivalence point should be given by AB and not the observed AC. The addition of excess of the reagent depresses the solubility of the precipitate and, if the solubility is not too large, the position of the point B can be determined by continuing the straight portion of the two arms of the curve until they intersect



AgNO<sub>3</sub>(aq.) vs NaCl

#### 14. IONIC MOBILITY :

It is the speed of ion under unit potential gradient applied through solution.

$$u = \frac{\text{speed of ion (s)}}{\text{Potential gradient} \left( \frac{dV}{dx} \right)} = \frac{\text{cm}^2}{\text{volt} - \text{sec.}} = \frac{\Lambda}{ZF}$$

$u/10^{-8} \text{ m}^2\text{-s}^{-1}\text{-v}^{-1}$  in H<sub>2</sub>O at 298 K

Li <sup>+</sup>	4.01 4.65	Ca <sup>+2</sup>	6.17	Rb <sup>+</sup>	7.92	CH <sub>3</sub> COO <sup>-</sup>	7.92	CO <sub>3</sub> <sup>-2</sup>	7.91	SO <sub>4</sub> <sup>-2</sup>	8.29	OH <sup>-</sup>	20.64
Na <sup>+</sup>	5.19	Ag <sup>+</sup>	6.24	H <sup>+</sup>	7.92	F <sup>-</sup>	7.92	Cl <sup>-</sup>	7.96	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	7.96		
Cu <sup>+2</sup>	5.47 5.56	NH <sub>4</sub> <sup>+</sup>	7.43	H <sup>+</sup>	36.23	NO <sub>3</sub> <sup>-</sup>	7.40	I <sup>-</sup>	7.91	[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	11.4		

#### SOLVED EXAMPLES

**Ex.32** The resistance of a 1 N solution of salt is 50 Ω. Calculate the equivalent conductance of the solution, if the two platinum electrodes in solution are 2.1 cm apart and each having an area of 4.2 cm<sup>2</sup>.

**Sol :**  $\kappa = \frac{1}{\rho} = \frac{1}{R} \left( \frac{l}{A} \right) = \frac{1}{50} \times \frac{2.1}{4.2} = \frac{1}{100}$  and  $\lambda_{\text{eq.}} = \frac{\kappa \times 1000}{N} = \frac{1}{100} \times \frac{1000}{1} = 10 = \Omega^{-1} \text{cm}^2 \text{-eq}^{-1}$

**Ex.33** Which of the following have maximum molar conductivity.

(i) 0.08 M solution and its specific conductivity is  $2 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ .

(ii) 0.1 M solution and its resistivity is 50 Ω cm.

**Sol.** (i)  $\Lambda_m = \frac{\kappa \times 1000}{M} = 2 \times 10^{-2} \times \frac{1000}{0.08} = 250 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$

(ii)  $\Lambda_m = \frac{\kappa \times 1000}{M}$   $\therefore \kappa = \frac{1}{\rho}$   $\therefore \Lambda_m = \frac{1}{50} \times \frac{1000}{0.1} = 200 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$

So, the molar conductivity of 0.08 M solution will be greater than 0.1 M solution.

**Ex.34** The equivalent conductivity of  $H_2SO_4$  at infinite dilution is  $384 \Omega^{-1} cm^2 eq^{-1}$ . If 49 g  $H_2SO_4$  per litre is present in solution and specific resistance is  $18.4 \Omega\text{-cm}$  then calculate the degree of dissociation.

**Sol :** Equivalent of  $H_2SO_4 = \frac{49}{49} = 1 N$

$$\text{Specific conductance} = \frac{1}{\text{specific resistance}} = \frac{1}{18.4}$$

$$\Rightarrow \lambda_{eq.} = \frac{1000 \times \kappa}{N} = \frac{1000 \times 1}{18.4} = 55$$

$$\text{Degree of dissociation } (\alpha) = \frac{\lambda_{eq.}^C}{\lambda_{eq.}^\infty} = \frac{55}{384} = 0.14 \Rightarrow \alpha \% = 14\%$$

**Ex.35** Explain following ionic conductance data of  $25^\circ C$  for various fatty acid anions.

Anion	Formula	$\lambda_{-}^0$ AT $25^\circ C$ (in $ohm^{-1}cm^2eq^{-1}$ )
Formate	$HCO_2^-$	-52
Acetate	$CH_3CO_2^-$	40.9
Propionate	$CH_3CH_2CO_2^-$	35.8
Butyrate	$CH_3(CH_2)_2CO_2^-$	32.6
Valerianate	$CH_3(CH_2)_3CO_2^-$	~29
Caproate	$CH_3(CH_2)_4CO_2^-$	~28

**Sol.** With increasing chain length bulk increases decreasing ionic mobility and thus equivalent conductance decreases.

$\therefore$  Charge is identical  $\lambda_m$  also decreases.

**Ex.36** The resistance of a  $0.01 N$  solution of an electrolyte was found to  $210 ohm$  at  $298 K$  using a conductivity cell with a cell constant of  $0.88 cm^{-1}$ . Calculate specific conductance and equivalent conductance of solution.

**Sol.** Given, for  $0.01 N$  solution.

$$R = 210 ohm, \frac{\ell}{a} = 0.88 cm^{-1}$$

Specific conductance,

$$\therefore \kappa = \frac{1}{R} \times \frac{\ell}{a} \Rightarrow \kappa = \frac{1}{210} \times 0.88 = 4.19 \times 10^{-3} mho cm^{-1}$$

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \frac{4.19 \times 10^{-3} \times 1000}{0.01} = 419 mho cm^2 eq^{-1}.$$

**Ex.37** The conductivity of pure water in a conductivity cell with electrodes of cross-sectional area  $4 \text{ cm}^2$  placed at a distance  $2 \text{ cm}$  apart is  $8 \times 10^{-7} \text{ S cm}^{-1}$ . Calculate;

(a) The resistance of water.

(b) The current that would flow through the cell under the applied potential difference of 1 volt.

**Sol.** Cell constant  $= \frac{\ell}{a} = \frac{2}{4} = \frac{1}{2} \text{ cm}^{-1}$

(a) Also,  $\kappa = \frac{1}{R} \times \frac{\ell}{a}$

$$R = \frac{1}{\kappa} \times \frac{\ell}{a} = \frac{1}{8 \times 10^{-7}} \times \frac{1}{2} = 6.25 \times 10^5 \text{ ohm}$$

(b) From Ohm's law,  $\frac{V}{i} = R$

$$\therefore i = \frac{1}{6.25 \times 10^5} = 1.6 \times 10^{-6} \text{ ampere}$$

**Ex.38** Molar conductance of 1 M solution of weak acid HA is  $20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Find % dissociation of HA:

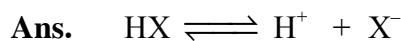
$$\left( \begin{array}{l} \Lambda_m^\circ(\text{H}^+) = 350 \text{ S cm}^2 \text{ mol}^{-1} \\ \Lambda_m^\circ(\text{A}^-) = 50 \text{ S cm}^2 \text{ mol}^{-1} \end{array} \right)$$

**Ans.**  $\Lambda_m^\circ(\text{HA}) = 350 + 50 = 400$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} \times 100 = \frac{20}{400} \times 100 = 5 \%$$

**Ex.39** Conductivity of an aqueous solution of 0.1 M HX (a weak mono-protic acid) is  $5 \times 10^{-4} \text{ Sm}^{-1}$ .

Find  $\text{p}K_a[\text{HX}]$ . Given :  $\Lambda_m^\circ[\text{H}^+] = 0.04 \text{ Sm}^2 \text{ mol}^{-1}$  ;  $\Lambda_m^\circ[\text{X}^-] = 0.01 \text{ Sm}^2 \text{ mol}^{-1}$



$$0.1(1-\alpha) \quad 0.1\alpha \quad 0.1\alpha$$

$$\wedge_m = k \times \frac{1000}{C} \Rightarrow 5 \times 10^{-4} \times \frac{1000}{0.1} = 0.05 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$a = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{0.05}{50} \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} = 10^{-4}$$

$$K_a = C\alpha^2 = 0.1 \times (10^{-4})^2 = 10^{-9}$$

$$\text{p}K_a = 9$$

**Ex.40** Specific conductance of  $10^{-4}$  M n-Butyric acid aqueous solution is  $1.9 \times 10^{-9}$  S  $m^{-1}$ . If molar conductance of n-Butyric acid at infinite dilution is  $380 \times 10^{-4}$  S  $m^2$   $mol^{-1}$ , then  $K_a$  for n-Butyric acid is :

**Sol.**  $\Lambda_m = 1000 \times \frac{1.9 \times 10^{-9}}{10^{-4}} = 1.9 \times 10^{-2}$

$$\alpha = \frac{1.9 \times 10^{-2}}{380 \times 10^{-4}} = 0.5$$

$$K_a = \frac{10^{-4}(0.5)^2}{1-0.5} = 5 \times 10^{-5} \text{ M}$$

**Ex.41** The specific conductance of a saturated AgCl solution is found to be  $2.12 \times 10^{-6}$  S  $cm^{-1}$  and that for water is  $6 \times 10^{-8}$  S  $cm^{-1}$ . The solubility of AgCl is : ( $t_{eq.}^{\ominus} = 103$  S  $equiv^{-1}$   $cm^2$ )

**Sol.**  $S_o = 241.67$  S  $cm^2$   $mol^{-1}$

$$S = \frac{(F_{Ag_{sol.}} - F_{H_2O}) \times 1000}{(\Lambda_{eq.}^{\ominus})_{AgCl}} = 2 \times 10^{-5} \text{ M}$$

**Ex.42** The value of  $\mu^\circ$  for  $NH_4Cl$ ,  $NaOH$  and  $NaCl$  are 129.8, 248.1 and 126.4  $ohm^{-1}$   $cm^2$   $mol^{-1}$  respectively. Calculate  $\mu^\circ$  for  $NH_4OH$  solution.

**Sol.**  $\mu_{NH_4OH}^\infty = \mu_{NH_4Cl}^\infty + \mu_{NaOH}^\infty - \mu_{NaCl}^\infty$   
 $= 129.8 + 248.1 - 126.4$

$$\mu_{NH_4OH}^\infty = 251.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

**Ex.43** Calculate molar conductance for  $NH_4OH$ , given that molar conductances for  $Ba(OH)_2$ ,  $BaCl_2$  and  $NH_4Cl$  are 523.28, 280.0 and 129.8  $ohm^{-1}$   $cm^2$   $mol^{-1}$  respectively.

**Sol.**  $\mu_{Ba(OH)_2}^\infty = \lambda_{Ba^{2+}}^\infty + 2\lambda_{OH^-}^\infty = 523.28$  ..... (i)

$$\mu_{BaCl_2}^\infty = \lambda_{Ba^{2+}}^\infty + 2\lambda_{Cl^-}^\infty = 280.00$$
 ..... (ii)

$$\mu_{NH_4Cl}^\infty = \lambda_{NH_4^+}^\infty + \lambda_{Cl^-}^\infty = 129.80$$
 ..... (iii)

$$\mu_{NH_4OH}^\infty = \lambda_{NH_4^+}^\infty + \lambda_{OH^-}^\infty = ?$$

$$\text{Eq. (iii)} + \frac{\text{Eq. (i)}}{2} - \frac{\text{Eq. (ii)}}{2} \text{ will gives}$$

$$\lambda_{NH_4^+}^\infty + \lambda_{OH^-}^\infty = \lambda_{NH_4OH}^\infty = \frac{502.88}{2} = 251.44 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

**Ex.44** The equivalent conductivities of acetic acid at 298 K at the concentrations of 0.1 M and 0.001 M are 5.20 and 49.2 S cm<sup>2</sup> eq.<sup>-1</sup> respectively. Calculate the degree of dissociation of acetic acid at these concentrations. Given that,  $\lambda^\infty(\text{H}^+)$  and  $\lambda^\infty(\text{CH}_3\text{COO}^-)$  are 349.8 and 40.9 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> respectively.

**Sol.** Degree of dissociation is given by  $\alpha = \frac{\lambda^c}{\lambda^\infty}$

(i) Evaluation of  $\lambda_{\text{CH}_3\text{COOH}}^\infty$  :

$$\begin{aligned}\lambda_{\text{CH}_3\text{COOH}}^\infty &= \lambda_{\text{CH}_3\text{COO}^-}^\infty + \lambda_{\text{H}^+}^\infty \\ &= 40.9 + 349.8 = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq.}^{-1}\end{aligned}$$

(ii) Evaluation of degree of dissociation :

$$\text{At } C = 0.1 \text{ M } \alpha = \frac{\lambda^c}{\lambda^\infty} = \frac{5.20}{390.7} = 0.013$$

i.e. 1.3%

$$\text{At } C = 0.001 \text{ M } \alpha = \frac{\lambda^c}{\lambda^\infty} = \frac{49.2}{390.7} = 0.125$$

i.e. 12.5%

**Ex.45** At infinite dilution the molar conductance of  $\text{Al}^{+3}$  and  $\text{SO}_4^{-2}$  ion are 189 and 160  $\Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$  respectively. Calculate the equivalent and molar conductivity at infinite dilute of  $\text{Al}_2(\text{SO}_4)_3$ .

**Sol.**

$$\begin{aligned}\lambda_{\text{eq.}[\text{Al}_2(\text{SO}_4)_3]}^\infty &= \frac{1}{3}\lambda_{\text{Al}^{+3}}^\infty + \frac{1}{2}\lambda_{\text{SO}_4^{-2}}^\infty \\ &= \frac{1}{3} \times 189 + \frac{1}{2} \times 160 \\ &= 143 \Omega^{-1} \text{ cm}^2 \text{ eq.}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Molar conductivity} &= \lambda_{\text{eq}} \times \text{V. F.} = 143 \times 6 \\ &= 858 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}\end{aligned}$$

**Ex.46** Find  $\Lambda_m^\infty$  (in  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) for strong electrolyte  $\text{AB}_2$  in water at 25° from the following data.

Conc. C(mole/L)	0.25	1
$\Lambda_m(\text{W}^{-1} \text{ cm}^2 / \text{mol})$	160	150

**Sol.**  $160 = \Lambda_m^\infty - b \times \sqrt{0.25}$  ....(A)

$150 = \Lambda_m^\infty - b \times \sqrt{1}$  ....(B)

$b = 20$  and  $\Lambda_m^\infty = 170$

$y = 170 - 20x$

Intercept = 170

$\Lambda_m^\infty = 170 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

**Ex.47** For any sparingly soluble salt  $[M(NH_3)_4Br_2]H_2PO_2$

Given :  $\lambda_{M(NH_3)_4Br_2}^0 = 400 \text{ S-m}^2\text{-mol}^{-1}$ ,

$\lambda_{H_2PO_2}^0 = 100 \text{ S-m}^2\text{-mol}^{-1}$

Specific resistance of saturated  $[M(NH_3)_4Br_2]H_2PO_2$  solution is  $200 \text{ }\Omega\text{-cm}$ .

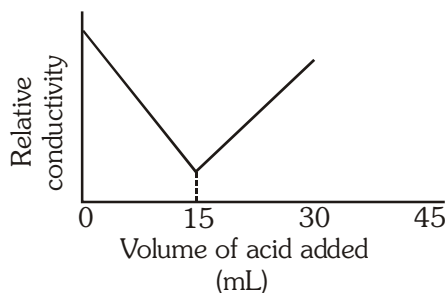
If solubility product constant of the above salt is  $10^{-x}$ . What will be the value of  $x$ .

**Ans.**  $\Lambda_m^\infty = \kappa \times \frac{1000}{m} \times 10^{-6}$

$500 = \frac{1}{200} \times \frac{1000}{5} \times 10^{-6}$

$S = 10^{-8} \text{ mol/L}$ ,  $K_{sp} = S^2 = 10^{-16}$

**Ex.48** 20 mL of KOH solution was titrated with 0.2 M  $H_2SO_4$  solution in a conductivity cell. The data obtained were plotted to give the graph shown below :



the concentration of KOH solution was -

- (A) 0.3 M                      (B) 0.15 M                      (C) 0.12 M                      (D) 0.075 M

**Sol.** (A)

$20 \times M = 0.2 \times 2 \times 15 \Rightarrow M = 0.15$

**ANSWER KEY****EXERCISE # 1**

- |            |             |            |
|------------|-------------|------------|
| 1. Ans.(C) | 2. Ans. (C) | 3. Ans.(B) |
| 4. Ans.(A) | 5. Ans.(C)  | 6. Ans.(C) |

**EXERCISE # 2**

- |            |            |            |
|------------|------------|------------|
| 1. Ans.(B) | 2. Ans.(D) | 3. Ans.(A) |
| 4. Ans.(B) | 5. Ans.(B) | 6. Ans.(C) |

**EXERCISE # 3**

- |            |            |            |
|------------|------------|------------|
| 1. Ans.(B) | 2. Ans.(A) | 3. Ans.(B) |
| 4. Ans.(A) | 5. Ans.(C) | 6. Ans.(D) |
| 7. Ans.(C) |            |            |

**EXERCISE # 4**

- |            |            |            |
|------------|------------|------------|
| 1. Ans.(B) | 2. Ans.(D) | 3. Ans.(A) |
| 4. Ans.(B) | 5. Ans.(B) | 6. Ans.(A) |
| 7. Ans.(A) | 8. Ans.(C) |            |



## SOME PREVIOUS YEAR SOLVED EXAMPLES

1. Find the solubility product of a saturated solution of  $\text{Ag}_2\text{CrO}_4$  in water at 298 K if the emf of the cell  $\text{Ag}|\text{Ag}^+(\text{satd. Ag}_2\text{CrO}_4 \text{ soln.})||\text{Ag}^+(0.1 \text{ M})|\text{Ag}$  is 0.164 V at 298K. [JEE 1998]

1. **Ans.** ( $K_{\text{sp}} = 2.287 \times 10^{-12}$ )

**Sol.**  $\text{Ag}|\text{Ag}^+(\text{sat. sol}^n)||\text{Ag}^+(0.1 \text{ M})|\text{Ag}$   
 $\text{AgClO}_4$ )

$$0.164 = 0 - \frac{.059}{1} \log \frac{[\text{Ag}^+]_A}{0.1}$$

$$\therefore [\text{Ag}^+]_A = (1.66 \times 10^{-4}) \times (.83 \times 10^{-4}) \\ = 2.287 \times 10^{-12}$$

2. Calculate the equilibrium constant for the reaction,  $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$ . The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for  $\text{Fe}^{3+}|\text{Fe}^{2+}$  and  $\text{I}_3^-|\text{I}^-$  couples. [JEE 1998]

2. **Ans.** ( $K_{\text{C}} = 6.26 \times 10^7$ )

**Sol.**  $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$

$$E^\circ = 0.77 + (-.54) = 0.23, \text{Keq} = 10^{\frac{2 \times .23}{.059}}$$

$$\text{Keq} = 6.26 \times 10^7$$

3. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y and 1 M Z at 25°C. If the reduction potential of  $Z > Y > X$ , then [JEE 1999]

(A) Y will oxidise X and not Z

(B) Y will oxidise Z and X

(C) Y will oxidise both X and Z

(D) Y will reduce both X and Z.

3. **Ans.** (A)

4. The following electrochemical cell has been set up



$$E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V and } E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.61 \text{ V}$$

If an ammeter is connected between the two platinum electrodes. predict the direction of flow of current. Will the current increase or decrease with time? [JEE 2000]

4. **Ans.** (decrease with time)

**Sol.**  $E^\circ_{\text{cell}}$  is (+) ve so cell will work and current will flow from cathode to anode. Current will decrease with time

5. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 mintue. It was found that after electrolysis, the absorbance (concentration) of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. [JEE 2000]

5. **Ans.** ( $7.95 \times 10^{-5} \text{M}$ )

$$\text{Sol. } (n_{\text{Cu}^{+2}})_{\text{reduced}} = \frac{2 \times 10^{-3} \times 16 \times 60}{96500 \times 2} = \frac{.96}{96500}$$

$$(n_{\text{Cu}^{+2}})_{\text{originally present}} = \frac{1.92}{96500}$$

$$\therefore M = \frac{1.92}{96500} \times \frac{1000}{250} = 7.958 \times 10^{-5}$$

$$E_{\text{cell}}^{\circ} = -.77 + 1.61 = 0.84$$

6. For the electrochemical cell,  $M | M^{+} || X^{-} | X$ ,  $E^{\circ}(M^{+}|M) = 0.44 \text{ V}$  and  $E^{\circ}(X|X^{-}) = 0.33 \text{ V}$ . From this data, one can deduce that [JEE 2000]

(A)  $M + X \longrightarrow M^{+} + X^{-}$  is the spontaneous reaction

(B)  $M^{+} + X^{-} \longrightarrow M + X$  is the spontaneous reaction

(C)  $E_{\text{cell}} = 0.77 \text{ V}$

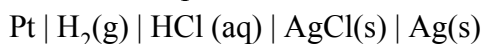
(D)  $E_{\text{cell}} = -0.77 \text{ V}$

6. **Ans.(B)**

$$\text{Sol. } E_{\text{cell}}^{\circ} = E_{\text{MM}^{+}}^{\circ} + E_{\text{M/M}^{+}}^{\circ} + E_{\text{X}^{-}/\text{X}}^{\circ} = -.44 + -.33 = -0.77 \text{ V}$$

so (B)

7. The standard potential of the following cell is  $0.23 \text{ V}$  at  $15^{\circ} \text{C}$  &  $0.21 \text{ V}$  at  $35^{\circ} \text{C}$



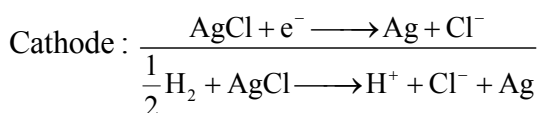
(i) Write the cell reaction.

(ii) Calculate  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  for the cell reaction by assuming that these quantities remain unchanged in the range  $15^{\circ} \text{C}$  to  $35^{\circ} \text{C}$ .

(iii) Calculate the solubility of  $\text{AgCl}$  in water at  $25^{\circ} \text{C}$ . Given standard reduction potential of the  $\text{Ag}^{+}|\text{Ag}$  couple is  $0.80 \text{ V}$  at  $25^{\circ} \text{C}$ . [JEE 2001]

7. **Ans.  $\Delta H^{\circ} = -49987 \text{ J mol}^{-1}$ ,  $\Delta S^{\circ} = -96.5 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $s = 1.47 \times 10^{-5} \text{ M}$**

$$\text{Sol. (i) Anode: } \frac{1}{2} \text{H}_2 \longrightarrow \text{H}^{+} + \text{e}^{-}$$



$$(ii) \quad \frac{\partial E}{\partial T} = \frac{.21 - .23}{308 - 288} = \frac{.02}{10} = -2 \times 10^{-3}$$

$$\Delta G^{\circ} = -nFE^{\circ} \text{ so } (\Delta G^{\circ})_{288\text{K}} = -22195 \text{ J}, (\Delta G^{\circ})_{308\text{K}} = -20265 \text{ J}$$

$$\text{now using } \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \Rightarrow \Delta H^{\circ} = -49987 \text{ J}, \Delta S^{\circ} = -96.5 \text{ J}$$

$$(iii) \quad E_{25^{\circ}\text{C}}^{\circ} = 0.22 \text{ V} \quad E_{\text{cell}}^{\circ} = E_{\text{Cl}^{-}/\text{AgCl}/\text{Ag}}^{\circ} = 0.22$$

$$\text{so } -.8 + 0.22 = \frac{0.59}{1} \log K_{\text{sp}}$$

$$\therefore K_{\text{sp}} = 1.47 \times 10^{-10} \Rightarrow S = 1.21 \times 10^{-5}$$

8. Saturated solution of  $\text{KNO}_3$  is used to make salt bridge because

- (A) velocity of  $\text{K}^+$  is greater than that of  $\text{NO}_3^-$   
 (B) velocity of  $\text{NO}_3^-$  is greater than that of  $\text{K}^+$   
 (C) velocities of both  $\text{K}^+$  and  $\text{NO}_3^-$  are nearly the same  
 (D)  $\text{KNO}_3$  is highly soluble in water

[JEE 2001]

8. **Ans.(C)**

**Sol. Fact**

9. The correct order of equivalent conductance at infinite dilution of  $\text{LiCl}$ ,  $\text{NaCl}$  and  $\text{KCl}$  is

- (A)  $\text{LiCl} > \text{NaCl} > \text{KCl}$  (B)  $\text{KCl} > \text{NaCl} > \text{LiCl}$  [JEE 2001]  
 (C)  $\text{NaCl} > \text{KCl} > \text{LiCl}$  (D)  $\text{LiCl} > \text{KCl} > \text{NaCl}$

9. **Ans.(B)**

**Sol. Fact**

10. The reaction,

[JEE 2001]



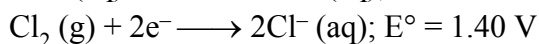
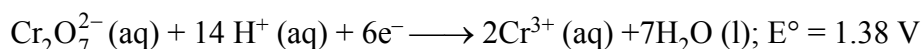
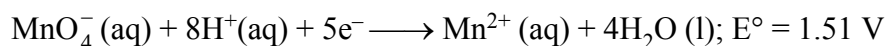
is an example of

- (A) Oxidation reaction (B) Reduction reaction  
 (C) Disproportionation reaction (D) Decomposition reaction

10. **Ans.(C)**

**Sol. Fact**

11. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below: [JEE 2002]



Identify the only incorrect statement regarding quantitative estimation of aqueous  $\text{Fe}(\text{NO}_3)_2$

- (A)  $\text{MnO}_4^-$  can be used in aqueous  $\text{HCl}$   
 (B)  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous  $\text{HCl}$   
 (C)  $\text{MnO}_4^-$  can be used in aqueous  $\text{H}_2\text{SO}_4$   
 (D)  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous  $\text{H}_2\text{SO}_4$

11. **Ans.(A)**

**Sol.**  $\text{MnO}_4^-$  will oxidise  $\text{Cl}^-$  into  $\text{Cl}_2$  so  $\text{MnO}_4^-$  can not be used in aqueous  $\text{HCl}$

12. Two students use same stock solution of  $\text{ZnSO}_4$  and a solution of  $\text{CuSO}_4$ . The e.m.f of one cell is 0.03 V higher than the other. The conc. of  $\text{CuSO}_4$  in the cell with higher e.m.f value is 0.5 M. Find out the conc. of  $\text{CuSO}_4$  in the other cell  $\left(\frac{2.303RT}{F} = 0.06\right)$ . [JEE 2003]

12. Ans.(0.05)

Sol.  $E_1 = E^\circ - \log \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]_1}$

$$E_2 = E^\circ - \log \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]_2}$$

$$E_2 - E_1 = -0.03 \log \frac{[\text{Cu}^{+2}]_1}{[\text{Cu}^{+2}]_2} \Rightarrow 0.03 = -\frac{.059}{2} \log \frac{[\text{Cu}^{+2}]_1}{[\text{Cu}^{+2}]_2}$$

$$\therefore 0.03 = -0.03 \log \frac{[\text{Cu}^{+2}]_1}{[\text{Cu}^{+2}]_2} \Rightarrow [\text{Cu}^{+2}]_2 = .05 \text{ M}$$

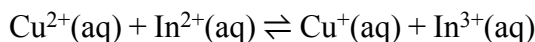
13. In the electrolytic cell, flow of electrons is from:

- (A) Cathode to anode in solution  
 (B) Cathode to anode through external supply  
 (C) Cathode to anode through internal supply  
 (D) Anode to cathode through internal supply.

[JEE 2003]

13. Ans.(C)

14. Find the equilibrium constant at 298 K for the reaction,



Given that  $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15\text{V}$ ,  $E^\circ_{\text{In}^{3+}/\text{In}^{2+}} = -0.42\text{V}$ ,  $E^\circ_{\text{In}^{2+}/\text{In}^+} = -0.40\text{V}$

[JEE 2004]

14. Ans.( $K_C = 10^{10}$ )

Sol.  $E^\circ_{\text{Cell}} = E^\circ_{\text{In}^{2+}/\text{In}^{3+}} + E^\circ_{\text{Cu}^{2+}/\text{Cu}^+}$   
 $= .44 + .15 = .59$

$$E^\circ_{\text{In}^{2+}/\text{In}^{3+}} = \frac{1\alpha - 0.4 + 2\alpha(0.42)}{1} = .44$$

$$K_{\text{eq}} = 10^{\frac{1 \times .59}{.059}} = 10^{10}$$

15.  $\text{Zn} | \text{Zn}^{2+} (a = 0.1\text{M}) || \text{Fe}^{2+} (a = 0.01\text{M}) | \text{Fe}$ . The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is

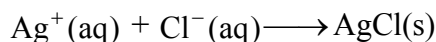
- (A)  $10^{0.32|0.0591}$  (B)  $10^{0.32|0.0295}$  (C)  $10^{0.26|0.0295}$  (D)  $e^{0.32|0.295}$  [JEE 2004]

15. Ans.(B)

Sol.  $0.2905 = E^\circ - \frac{.059}{2} \log \frac{.1}{0.01} \Rightarrow E^\circ = .32$

$$\therefore K_{\text{sp}} = 10^{\frac{2 \times .32}{0.0591}} = 10^{0.0295} \Rightarrow \text{B}$$

16. (a) Calculate  $\Delta G_f^0$  of the following reaction



Given :  $\Delta G_f^0(\text{AgCl}) = -109 \text{ kJ/mole}$ ,  $\Delta G_f^0(\text{Cl}^-) = -129 \text{ kJ/mole}$ ,  $\Delta G_f^0(\text{Ag}^+) = 77 \text{ kJ/mole}$

Represent the above reaction in form of a cell

Calculate  $E^0$  of the cell. Find  $\log_{10} K_{\text{sp}}$  of AgCl

- (b)  $6.539 \times 10^{-2} \text{ g}$  of metallic Zn ( $\text{amu} = 65.39$ ) was added to 100 ml of saturated solution of AgCl.

Calculate  $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$ , given that



Also find how many moles of Ag will be formed?

[JEE 2005]

16. **Ans. (a)  $E^0 = 0.59 \text{ V}$ ,  $\log_{10} K_{\text{sp}} = -10$  (b)  $52.8, 10^{-6} \text{ moles}$**

**Sol.** (a)  $\Delta G^0 = (-109) - [-129 + 77] = -57$

$$E^0 = \frac{-57 \times 1000}{1 \times 96500} = 0.59$$

$$\Delta G^0 = -2.303RT \log K_{\text{sp}} \Rightarrow \log K_{\text{sp}} = \frac{-57 \times 1000}{-2.303 \times 8.314 \times 298}$$

$$\log K_{\text{sp}} = 9.989 \cong 10$$

- (b)  $\text{Zn} + 2\text{Ag}^+ \longrightarrow \text{Zn}^{2+} + 2\text{Ag} \quad E_{\text{cell}}^0 = 1.56$

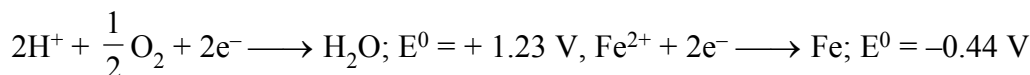
$$\therefore \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = \frac{1.56 \times 2}{.059} = 52.8$$

$$[\text{Ag}^+] = \sqrt{K_{\text{sp}}} = \sqrt{10^{-10}} = 10^{-5}$$

$$\therefore n_{\text{Ag}^+} = 10^{-5} \times .1 = 10^{-6}$$

17. The half cell reactions for rusting of iron are:

[JEE 2005]



$\Delta G^0$  (in kJ) for the reaction is:

(A) -76

(B) -322

(C) -122

(D) -176

17. **Ans. (B)**

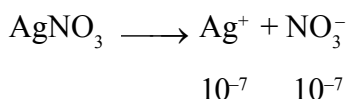
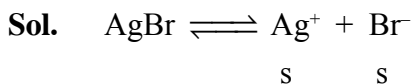
**Sol.**  $\Delta G^0 = -nFE^0$

$$= \frac{-2 \times 96500 \times 1.67}{1000} = -322$$

18. We have taken a saturated solution of  $\text{AgBr}$ .  $K_{\text{sp}}$  of  $\text{AgBr}$  is  $12 \times 10^{-14}$ . If  $10^{-7}$  mole of  $\text{AgNO}_3$  are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of  $10^{-7} \text{ S m}^{-1}$  [JEE 2006]

Given :  $\lambda_{(\text{Ag}^+)}^0 = 6 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$  ;  $\lambda_{(\text{Br}^-)}^0 = 8 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$  ;  $\lambda_{(\text{NO}_3^-)}^0 = 7 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$

18. Ans.(55  $\text{S m}^{-1}$ )



$\therefore (K_{\text{sp}})_{\text{AgBr}} = [\text{Ag}^+][\text{Br}^-] \Rightarrow 12 \times 10^{-14} = (s + 10^{-7}) \cdot (s)$

$s^2 + 10^{-7}s - 12 \times 10^{-14} = 0 \Rightarrow s = 3 \times 10^{-7}$

$\therefore [\text{Ag}^+] = 4 \times 10^{-7} \text{ [Br]} = 3 \times 10^{-7} \text{ [NO}_3^-] = 10^{-7}$

now  $\Lambda_{\text{M}}^{\infty} = \frac{1000k}{\text{M}}$

for  $\text{Ag}^+ \Rightarrow 6 \times 10^{-3} \times 10^4 = \frac{1000k}{4 \times 10^{-7}} \Rightarrow k_{\text{Ag}^+} = 24$

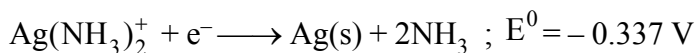
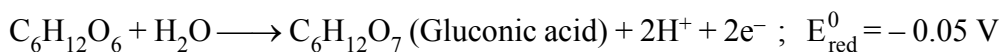
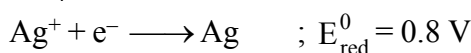
$\text{Br}^- \Rightarrow 8 \times 10^{-3} \times 10^4 = \frac{1000k}{3 \times 10^{-7}} \Rightarrow k_{\text{Br}^-} = 24$

$\text{NO}_3^- \Rightarrow 7 \times 10^{-3} \times 10^4 = \frac{1000k}{10^{-7}} \Rightarrow R_{\text{NO}_3^-} = 7$

Ans. 55

**Question No. 19 to 21 (3 questions)**

Tollen's reagent is used for the detection of aldehyde when a solution of  $\text{AgNO}_3$  is added to glucose with  $\text{NH}_4\text{OH}$  then gluconic acid is formed



[Use  $2.303 \times \frac{RT}{F} = 0.0592$  and  $\frac{F}{RT} = 38.92$  at 298 K]

[JEE 2006]

19.  $2\text{Ag}^+ + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \longrightarrow 2\text{Ag(s)} + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}^+$   
Find  $\ln K$  of this reaction

(A) 66.13

(B) 58.38

(C) 28.30

(D) 46.29

19. Ans.(A)

Sol.  $\log K = \frac{2.303 \times n \times E^0}{.059} = \frac{2.303 \times 2 \times .85}{.059} = 66.13$

20. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?

- (A)  $E_{\text{oxd}}$  will increase by a factor of 0.65 from  $E_{\text{oxd}}^0$   
 (B)  $E_{\text{oxd}}$  will decrease by a factor of 0.65 from  $E_{\text{oxd}}^0$   
 (C)  $E_{\text{red}}$  will increase by a factor of 0.65 from  $E_{\text{red}}^0$   
 (D)  $E_{\text{red}}$  will decrease by a factor of 0.65 from  $E_{\text{red}}^0$

20. **Ans.(A)**

**Sol.** Since  $\text{H}^+$  is involved in oxidation half reaction so  $E_{\text{oxd}}$  will be affected and it will increase

$$E_{\text{oxd}} = E_{\text{oxd}}^0 - \frac{.059}{2} \log \frac{[\text{C}_6\text{H}_{12}\text{O}_7][\text{H}^+]^2}{[\text{C}_2\text{H}_{12}\text{O}_6]}$$

21. Ammonia is always added in this reaction. Which of the following must be incorrect?

- (A)  $\text{NH}_3$  combines with  $\text{Ag}^+$  to form a complex.  
 (B)  $\text{Ag}(\text{NH}_3)_2^+$  is a weaker oxidising reagent than  $\text{Ag}^+$ .  
 (C) In absence of  $\text{NH}_3$  silver salt of gluconic acid is formed.  
 (D)  $\text{NH}_3$  has affected the standard reduction potential of glucose|gluconic acid electrode.

21. **Ans.(D)**

**Sol.**  $E_{\text{Red}}^0$  in a constant quantity

*Paragraph for Question Nos. 22 to 24 (3 questions)*

Chemical reactions involve interaction of atoms and molecules. A large number of atoms|molecules (approximately  $6.023 \times 10^{23}$ ) are present in a few grams of any chemical compound varying with their atomic|molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical| electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass : Na = 23, Hg = 200; 1 Faraday = 96500 coulombs) **[JEE 2007]**

22. The total number of moles of chlorine gas evolved is

- (A) 0.5 (B) 1.0 (C) 2.0 (D) 3.0

22. **Ans.(B)**

**Sol.** At anode  $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2e^-$

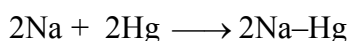


23. If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is

- (A) 200 (B) 225 (C) 400 (D) 446

23. **Ans.(D)**

**Sol.** At cathode  $2\text{Na}^+ + 2e^- \longrightarrow 2\text{Na(s)}$



24. The total charge (coulombs) required for complete electrolysis is  
 (A) 24125 (B) 48250 (C) 96500 (D) 193000

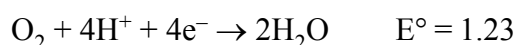
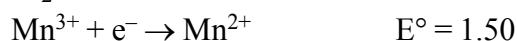
24. **Ans.(D)**

**Sol.** 2 moles on  $e^- = 2F = 193000 \text{ C}$

**Paragraph for Question Nos. 25 & 26 (2 questions)**

Redox reactions play a pivoted role in chemistry and biology. The values of standard redox potential ( $E^\circ$ ) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their  $E^\circ$  (V with respect to normal hydrogen electrode) values.

Using this data obtain the correct explanations to Questions 14-16.



[JEE 2007]

25. Among the following, identify the correct statement.

- (A) Chloride ion is oxidised by  $\text{O}_2$  (B)  $\text{Fe}^{2+}$  is oxidised by iodine  
 (C) Iodine ion is oxidised by chlorine (D)  $\text{Mn}^{2+}$  is oxidised by chlorine

25. **Ans.(C)**

**Sol.** as  $E^\circ$  will be positive

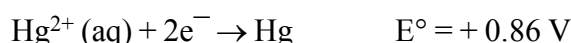
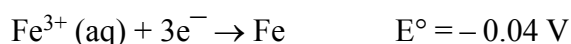
26. While  $\text{Fe}^{3+}$  is stable,  $\text{Mn}^{3+}$  is not stable in acid solution because

- (A)  $\text{O}_2$  oxidises  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$   
 (B)  $\text{O}_2$  oxidises both  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$   
 (C)  $\text{Fe}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$   
 (D)  $\text{Mn}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$

26. **Ans.(D)**

**Sol.** as  $E^\circ$  will be positive

27. For the reaction of  $\text{NO}_3^-$  ion in an aqueous solution,  $E^\circ$  is +0.96 V. Values of  $E^\circ$  for some metal ions are given below





The pair(s) of metal that is(are) oxidised by  $\text{NO}_3^-$  in aqueous solution is(are)

[JEE 2009]

- (A) V and Hg (B) Hg and Fe  
(C) Fe and Au (D) Fe and V

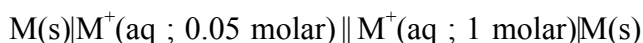
27. Ans.(A,B,D)

Sol. (A,B,D) as  $E^\circ$  will be positive

*Paragraph for Questions 28 to 29*

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is :

[JEE 2010]



For the above electrolytic cell the magnitude of the cell potential  $|E_{\text{cell}}| = 70 \text{ mV}$ .

28. For the above cell :-

- (A)  $E_{\text{cell}} < 0$  ;  $\Delta G > 0$  (B)  $E_{\text{cell}} > 0$  ;  $\Delta G < 0$   
(C)  $E_{\text{cell}} < 0$  ;  $\Delta G^0 > 0$  (D)  $E_{\text{cell}} > 0$  ;  $\Delta G^0 < 0$

28. Ans.(B)

Sol.  $E_1 = -\frac{.059}{1} \log \frac{.05}{1} = (+)\text{ve} \Rightarrow \text{so}$

29. If the 0.05 molar solution of  $\text{M}^+$  is replaced by a 0.0025 molar  $\text{M}^+$  solution, then the magnitude of the cell potential would be :-

- (A) 35 mV (B) 70 mV (C) 140 mV (D) 700 mV

29. Ans.(C)

Sol.  $E_2 = -\frac{.059}{1} \log \frac{0.0025}{1}$

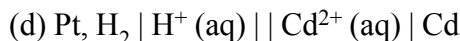
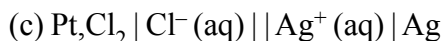
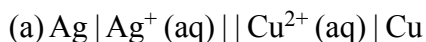
$$= 2 \times E_1 = 140 \text{ mV} \Rightarrow \text{so}$$

## EXERCISE # (S-I)

Note : If not given in question Use :  $\frac{2.303RT}{F} = 0.059$

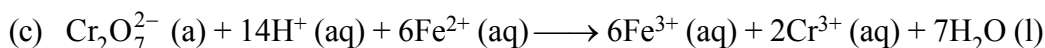
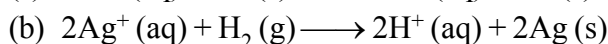
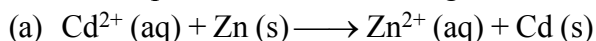
**Electrode potential cell emf.**

1. Write cell reaction of the following cells :



EC0001

2. Write cell representation for following cells.



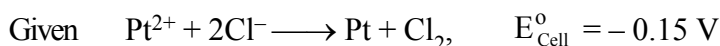
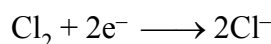
EC0002

3. For the cell reaction  $2\text{Ce}^{4+} + \text{Co} \longrightarrow 2\text{Ce}^{3+} + \text{Co}^{2+}$

$E_{\text{cell}}^{\circ}$  is 1.89 V. If  $E_{\text{Co}^{2+}|\text{Co}}^{\circ}$  is  $-0.28$  V, what is the value of  $E_{\text{Ce}^{4+}|\text{Ce}^{3+}}^{\circ}$  ?

EC0003

4. Determine the standard reduction potential for the half reaction :



EC0193

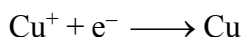
5. If  $E_{\text{Fe}^{2+}|\text{Fe}}^{\circ} = -0.44$  V,  $E_{\text{Fe}^{3+}|\text{Fe}^{2+}}^{\circ} = 0.77$  V. Calculate  $E_{\text{Fe}^{3+}|\text{Fe}}^{\circ}$ .

EC0005

6. If for the half cell reactions



Calculate  $E^{\circ}$  of the half cell reaction



also predict whether  $\text{Cu}^+$  undergoes disproportionation or not.

EC0004

7. The reduction potential of hydrogen electrode when placed in a buffer solution is found to be  $-0.413$  V. The pH of the buffer is -

EC0014

8. Calculate the EMF of a Daniel cell when the concentration of  $\text{ZnSO}_4$  and  $\text{CuSO}_4$  are  $0.001$  M and  $0.1$  M respectively. The standard potential of the cell is  $1.1$  V.

EC0006

9. Calculate  $E^{\circ}$  and  $E$  for the cell  $\text{Sn} | \text{Sn}^{2+} (1\text{M}) || \text{Pb}^{2+} (10^{-3}\text{M}) | \text{Pb}$ ,  $E^{\circ} (\text{Sn}^{2+} | \text{Sn}) = -0.14$  V,  $E^{\circ} (\text{Pb}^{2+} | \text{Pb}) = -0.13$  V. Is cell representation is correct?

EC0007

10. At what concentration of  $\text{Cu}^{2+}$  in a solution of  $\text{CuSO}_4$  will the electrode potential be zero at  $25^{\circ}\text{C}$ ?

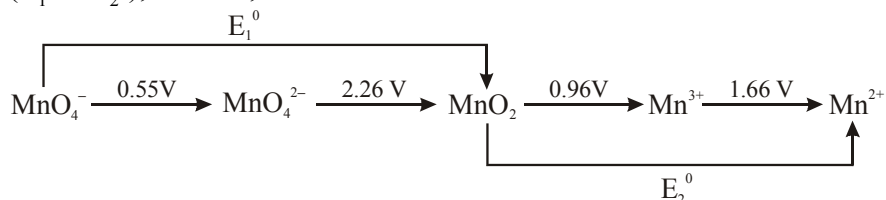
Given :  $E^{\circ} (\text{Cu} | \text{Cu}^{2+}) = -0.34$  V.  $[10^{-11.525} = 2.99 \times 10^{-12}]$

EC0008

11. Is 1.0 M  $H^+$  solution under  $H_2SO_4$  at 1.0 atm capable of oxidising silver metal in the presence of 1.0 M  $Ag^+$  ion?  $E^\circ_{Ag^+|Ag} = 0.80 V$ ,  $E^\circ_{H^+|H_2(Pt)} = 0.0 V$  **EC0194**
12. For a cell  $Mg(s) | Mg^{2+}(aq) || Ag^+(aq) | Ag$ ,  
 (i) Calculate the equilibrium constant at  $25^\circ C$ .  
 (ii) Also find the maximum work per mole Mg that can be obtained by operating the cell in standard condition.  
 $E^\circ_{(Mg^{2+}|Mg)} = -2.3565V$ ,  $E^\circ_{(Ag^+|Ag)} = 0.8 V$ . **EC0195**
13. The  $pK_{sp}$  of AgI is 16.07. If the  $E^\circ$  value for  $Ag^+ | Ag$  is 0.7991 V. Find the  $E^\circ$  for the half cell reaction  $AgI(s) + e^- \longrightarrow Ag + I^-$ .  $[16.07 \times 0.059 = 0.94813]$  **EC0009**
14. A zinc electrode is placed in a 0.1M solution at  $25^\circ C$ . Assuming that the salt ( $ZnX$ ) is 20% dissociated at this dilutions calculate the electrode reduction potential.  $E^\circ(Zn^{2+} | Zn) = -0.76V$ . **EC0010**

**EQUILIBRIUM CONSTANT**

15. Calculate the equilibrium constant for the reaction :  $[10^{12.88} = 7.585 \times 10^{12}]$   
 $Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$ , [Given :  $E^\circ_{Ce^{4+}|Ce^{3+}} = 1.44 V$ ;  $E^\circ_{Fe^{3+}|Fe^{2+}} = 0.68 V$ ] **EC0011**
16. Calculate the equilibrium constant for the reaction  $Fe + CuSO_4 \rightleftharpoons FeSO_4 + Cu$  at  $25^\circ C$ .  
 Given  $E^\circ(Fe|Fe^{2+}) = 0.44V$ ,  $E^\circ(Cu|Cu^{2+}) = -0.337V$ .  $[10^{26.3389} = 2.18 \times 10^{26}]$  **EC0196**
17. At  $25^\circ C$  the value of K for the equilibrium  $Fe^{3+} + Ag \rightleftharpoons Fe^{2+} + Ag^+$  is 0.531 mol/litre. The standard electrode potential for  $Ag^+ + e^- \rightleftharpoons Ag$  is 0.799V. What is the standard potential for  $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ ?  $[\log(0.531) = -0.27]$  **EC0197**
18. The standard reduction potential at  $25^\circ C$  for the reduction of water  $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$  is  $-0.8277$  volt. Calculate the equilibrium constant for the reaction  $2H_2O \rightleftharpoons H_3O^+ + OH^-$  at  $25^\circ C$ .  $[193 \times 0.8277 = 159.75]$   $[2.303 RT = 5705.35 J/mol]$  **EC0198**
19. For the reaction,  $4Al(s) + 3O_2(g) + 6H_2O + 4 OH^- \rightleftharpoons 4 [Al(OH)_4^-]$ ;  $E^\circ_{cell} = 2.73 V$ .  
 If  $\Delta G^\circ_f(OH^-) = -157 kJ mol^{-1}$  and  $\Delta G^\circ_f(H_2O) = -237.2 kJ mol^{-1}$ , determine  $\Delta G^\circ_f [Al(OH)_4^-]$ .  
 $[96.5 \times 2.73 = 263.445]$  **EC0199**
20. For the cell reaction :  $Hg_2Cl_2(s) + 2Ag(s) \rightarrow 2Hg(l) + 2AgCl(s)$   
 temperature coefficient of cell emf is found to be  $0.02 VK^{-1}$ . Find  $\Delta_r S^\circ$  for cell reaction in  $kJ mole^{-1}$  **EC0012**
21. From the standard potential in acidic medium as shown in the following Latimer diagram, the value of  $(E_1^\circ + E_2^\circ)$ , in volts, is -



**EC0013**

## CONCENTRATION CELLS :

22. Calculate the EMF of the following cell  

$$\text{Zn} | \text{Zn}^{2+} (0.01\text{M}) || \text{Zn}^{2+} (0.1\text{M}) | \text{Zn}$$
 at 298 K. **EC0015**
23. Calculate pH using the following cell :  

$$\text{Pt} (\text{H}_2) | \text{H}^+ (x\text{M}) || \text{H}^+ (1\text{M}) | \text{Pt} (\text{H}_2)$$
 if  $E_{\text{cell}} = 0.2364\text{V}$ .  
 1 atm 1 atm **EC0016**
24. Equinormal Solutions of two weak acids, HA ( $\text{pK}_a = 3$ ) and HB ( $\text{pK}_a = 5$ ) are each placed in contact with equal pressure of hydrogen electrode at 25°C. When a cell is constructed by interconnecting them through a salt bridge, find the emf of the cell. **EC0200**
25. In two vessels each containing 500ml water, 0.5m mol of aniline ( $K_b = 10^{-9}$ ) and 50mmol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately. **EC0201**

## ELECTROLYTIC CELL :

26. Calculate the no. of electrons lost or gained during electrolysis of  
 (a) 3.55 gm of  $\text{Cl}^-$  ions (b) 1 gm  $\text{Cu}^{2+}$  ions (c) 2.7 gm of  $\text{Al}^{3+}$  ions **EC0017**
27. How many faradays of electricity are involved in each of the case  
 (a) 0.25 mole  $\text{Al}^{3+}$  is converted to Al.  
 (b) 27.6 gm of  $\text{SO}_3$  is converted to  $\text{SO}_3^{2-}$   
 (c) The  $\text{Cu}^{2+}$  in 1100 ml of 0.5 M  $\text{Cu}^{2+}$  is converted to Cu. **EC0018**
28. 0.5 mole of electron is passed through two electrolytic cells in series. One contains silver ions, and the other zinc ions. Assume that only cathode reaction in each cell is the reduction of the ion to the metal. How many gm of each metals will be deposited. [At weight Zn = 65, Ag = 108] **EC0019**
29. If 0.224 litre of  $\text{H}_2$  gas is formed at the cathode, how much  $\text{O}_2$  gas is formed at the anode under identical conditions? **EC0022**
30. Chromium metal can be plated out from an acidic solution containing  $\text{CrO}_3$  according to following equation :  

$$\text{CrO}_3(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{Cr}(\text{s}) + 3\text{H}_2\text{O}$$
 Calculate :  
 (i) How many grams of chromium will be plated out by 24125 coulombs and  
 (ii) How long will it take to plate out 1.5 gm of chromium by using 12.5 ampere current **EC0202**
31. The electrosynthesis of  $\text{MnO}_2$  is carried out from a solution of  $\text{MnSO}_4$  in  $\text{H}_2\text{SO}_4$  (aq). If a current of 25.5 ampere is used with a current efficiency of 85%, how long would it take to produce 1 kg of  $\text{MnO}_2$ ?  

$$\left[ \frac{965}{87 \times 25.5 \times 85} = 5.12 \times 10^{-3} \right]$$
 **EC0020**
32. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 percent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed? **EC0203**

33. A constant current of 30 A is passed through an aqueous solution of NaCl for a time of 1.0 hr. How many grams of NaOH are produced? What is volume of  $\text{Cl}_2$  gas at 1 atm, 273K produced (in litre)? **EC0021**
34. Assume 96500 C as one unit of electricity. If cost of electricity of producing x gm Al is Rs x, what is the cost of electricity of producing x gm Mg? **EC0023**
35. A metal is known to form fluoride  $\text{MF}_2$ . When 10A of electricity is passed through a molten salt for 330 sec., 1.95g of metal is deposited. Find the atomic weight of M. What will be the quantity of electricity required to deposit the same mass of Cu from  $\text{CuSO}_4$ ?  

$$\left[ \frac{1.95 \times 965}{63.5} = 29.63, \frac{1.95 \times 965}{33} = 57 \right]$$
 **EC0024**
36. After electrolysis of NaCl solution with inert electrodes for a certain period of time. 600 mL of the solution was left. Which was found to be 1N in NaOH. During the same time, 31.75 g of Cu was deposited in the copper voltameter in series with the NaCl electrolytic cell. Calculate the percentage yield of NaOH obtained. **EC0204**
37. A solution of  $\text{Ni}(\text{NO}_3)_2$  is electrolysed between platinum electrodes using a current of 5 ampere for 20 mintue. What mass of Ni is deposited at the cathode? **EC0025**
38. A current of 3.7A is passed for 6hrs. between Ni electrodes in 0.5L of 2M solution of  $\text{Ni}(\text{NO}_3)_2$ . What will be the molarity of  $\text{Ni}(\text{NO}_3)_2$  solution at the end of electrolysis? **EC0026**

### CONDUCTANCE

39. A solution containing 2.08 g of anhydrous barium chloride is 500 CC of water has a specific conductivity  $0.005 \text{ ohm}^{-1} \text{ cm}^{-1}$ . What are molar and equivalent conductivities of this solution. **EC0031**

### Application of Kohlrausch's law

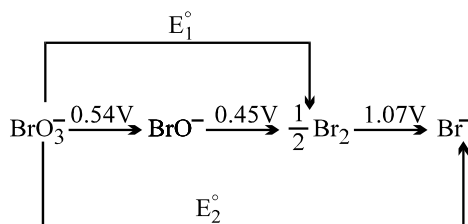
40. The resistance of a conductivity cell filled with 0.01N solution of NaCl is 200 ohm at  $18^\circ\text{C}$ . Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is  $0.88 \text{ cm}^{-1}$ . **EC0027**
41. The molar conductivity of 0.1 M  $\text{CH}_3\text{COOH}$  solution is  $4 \text{ S cm}^2 \text{ mole}^{-1}$ . What is the specific conductivity and resistivity of the solution? **EC0028**
42. The conductivity of pure water in a conductivity cell with electrodes of cross sectional area  $4 \text{ cm}^2$  and 2 cm apart is  $8 \times 10^{-7} \text{ S cm}^{-1}$ .  
 (i) What is resistance of conductivity cell?  
 (ii) What current would flow through the cell under an applied potential difference of 1 volt? **EC0029**
43. For 0.01N KCl, the resistivity 800 ohm cm. Calculate the conductivity and equivalent conductance. **EC0030**
44. Specific conductance of a saturated solution of AgBr is  $8.075 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $25^\circ\text{C}$ . Specific conductance of pure water at  $25^\circ\text{C}$  is  $0.75 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-2}$ .  $\Lambda_m^\infty$  for KBr, AgNO<sub>3</sub> and KNO<sub>3</sub> are 140, 130, 110 ( $\text{S cm}^2 \text{ mol}^{-1}$ ) respectively. Calculate the solubility of AgBr in gm/litre. **EC0032**

45. Equivalent conductance of 0.01 N  $\text{Na}_2\text{SO}_4$  solution is  $120 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ . The equivalent conductance at infinite dilution is  $150 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ . What is the degree of dissociation in 0.01 N  $\text{Na}_2\text{SO}_4$  solution?  
**EC0205**
46. Saturated solution of AgCl at  $25^\circ\text{C}$  has specific conductance of  $1.12 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The  $\lambda_\infty(\text{Ag}^+)$  and  $\lambda_\infty(\text{Cl}^-)$  are 54 and  $58 \text{ ohm}^{-1} \text{ cm}^2 \text{ | eq}^{-1}$  respectively. Calculate the solubility product of AgCl at  $25^\circ\text{C}$ .  
**EC0206**
47. The value of  $\Lambda_m^\infty$  for HCl, NaCl and  $\text{CH}_3\text{CO}_2\text{Na}$  are 425, 125 and  $100 \text{ S cm}^2 \text{ mol}^{-1}$  respectively. Calculate the value of  $\Lambda_m^\infty$  for acetic acid. If the equivalent conductivity of the given acetic acid is 48 at  $25^\circ\text{C}$ , calculate its degree of dissociation.  
**EC0034**
48. For the strong electrolytes NaOH, NaCl and  $\text{BaCl}_2$  the molar ionic conductivities at infinite dilution are  $240 \times 10^{-4}$ ,  $125 \times 10^{-4}$  and  $280.0 \times 10^{-4} \text{ mho cm}^2 \text{ mol}^{-1}$  respectively. Calculate the molar conductivity of  $\text{Ba}(\text{OH})_2$  at infinite dilution.  
**EC0035**
49. Hydrofluoric acid is weak acid. At  $25^\circ\text{C}$ , the molar conductivity of 0.002M HF is  $200 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ . If its  $\Lambda_m^\infty = 400 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ , calculate its degree of dissociation and equilibrium constant at the given concentration.  
**EC0033**
50. At  $25^\circ\text{C}$ ,  $\lambda_\infty(\text{H}^+) = 3.5 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$  and  $\lambda_\infty(\text{OH}^-) = 2 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$ . Given: Sp. conductance =  $5.5 \times 10^{-6} \text{ S m}^{-1}$  for  $\text{H}_2\text{O}$ , determine pH and  $K_w$ .  
**EC0207**

## EXERCISE # S-II

1. Calculate the emf of the cell : [ $\log(1.8) = 0.26$ ]  
 $\text{Pt, H}_2(1.0 \text{ atm}) | \text{CH}_3\text{COOH}(0.1 \text{ M}) || \text{NH}_3(\text{aq}, 0.01 \text{ M}) | \text{H}_2(1.0 \text{ atm}),$   
 $\text{Pt } K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}, K_b(\text{NH}_3) = 1.8 \times 10^{-5}.$   
**EC0036**
2. The Edison storage cell is represented as  $\text{Fe(s)} | \text{FeO(s)} | \text{KOH(aq)} | \text{Ni}_2\text{O}_3(\text{s}) | \text{NiO(s)}$  The half-cell reaction are  
 $\text{Ni}_2\text{O}_3(\text{s}) + \text{H}_2\text{O(l)} + 2\text{e}^- \rightleftharpoons 2\text{NiO(s)} + 2\text{OH}^-$ ,  $E^0 = +0.40 \text{ V}$   
 $\text{FeO(s)} + \text{H}_2\text{O(l)} + 2\text{e}^- \rightleftharpoons \text{Fe(s)} + 2\text{OH}^-$ ,  $E^0 = -0.87 \text{ V}$   
 (i) What is the cell reaction?  
 (ii) What is the cell e.m.f.? How does it depend on the concentration of KOH?  
 (iii) What is the maximum amount of electrical energy that can be obtained from one mole of  $\text{Ni}_2\text{O}_3$ ?  
**EC0037**
3. The standard reduction potential for  $\text{Cu}^{2+} | \text{Cu}$  is 0.34 V. Calculate the reduction potential at  $\text{pH} = 14$  for the above couple.  $K_{\text{sp}}$  of  $\text{Cu(OH)}_2$  is  $1 \times 10^{-19}$ .  
**EC0038**
4. The emf of the cell  $\text{Ag} | \text{AgI} | \text{KI}(0.05 \text{ M}) || \text{AgNO}_3(0.05 \text{ M}) | \text{Ag}$  is 0.788V. Calculate the solubility product of AgI. [ $10^{-0.788/0.059} = 4.4 \times 10^{-14}$ ]  
**EC0039**
5. Consider the cell  $\text{Ag} | \text{AgBr(s)} | \text{Br}^- || \text{Cl}^- | \text{AgCl(s)} | \text{Ag}$  at  $25^\circ \text{C}$ . The solubility product constants of AgBr & AgCl are respectively  $5 \times 10^{-13}$  &  $1 \times 10^{-10}$ . For what ratio of the concentrations of  $\text{Br}^-$  &  $\text{Cl}^-$  ions would the emf of the cell be zero?  
**EC0208**
6. For the galvanic cell :  $\text{Ag} | \text{AgCl(s)} | \text{KCl}(0.2 \text{ M}) || \text{KBr}(0.001 \text{ M}) | \text{AgBr(s)} | \text{Ag}$ , Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at  $25^\circ \text{C}$ . [ $\log(4.24) = 0.627$ ]  
 $[\text{K}_{\text{sp}}(\text{AgCl}) = 2.8 \times 10^{-10}; \text{K}_{\text{sp}}(\text{AgBr}) = 3.3 \times 10^{-13}]$   
**EC0209**
7. Given,  $E^0 = -0.268 \text{ V}$  for the  $\text{Cl}^- | \text{PbCl}_2 | \text{Pb}$  couple and  $-0.126 \text{ V}$  for the  $\text{Pb}^{2+} | \text{Pb}$  couple, determine  $K_{\text{sp}}$  for  $\text{PbCl}_2$  at  $25^\circ \text{C}$ ? [ $10^{-0.284/0.059} = 1.54 \times 10^{-5}$ ]  
**EC0210**
8. Calculate the equilibrium constant for the reaction:  
 $3\text{Sn(s)} + 2\text{Cr}_2\text{O}_7^{2-} + 28\text{H}^+ \longrightarrow 3\text{Sn}^{4+} + 4\text{Cr}^{3+} + 14\text{H}_2\text{O}$   
 $E^0$  for  $\text{Sn} | \text{Sn}^{2+} = 0.136 \text{ V}$     $E^0$  for  $\text{Sn}^{2+} | \text{Sn}^{4+} = -0.154 \text{ V}$   
 $E^0$  for  $\text{Cr}_2\text{O}_7^{2-} | \text{Cr}^{3+} = 1.33 \text{ V}$   
 $\left[ \frac{15.852}{0.059} \approx 268 \right]$   
**EC0211**
9. One of the methods of preparation of per disulphuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ , involve electrolytic oxidation of  $\text{H}_2\text{SO}_4$  at anode ( $2\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{H}^+ + 2\text{e}^-$ ) with oxygen and hydrogen as by-products. In such an electrolysis, 2.27 L of  $\text{H}_2$  and 0.5675 L of  $\text{O}_2$  were generated at STP. What is the weight of  $\text{H}_2\text{S}_2\text{O}_8$  formed?  
**EC0040**
10. A current of 3 amp was passed for 2 hour through a solution of  $\text{CuSO}_4$ , 3 g of  $\text{Cu}^{2+}$  ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.  
**EC0041**

11. Dal lake has water  $8.2 \times 10^{12}$  litre approximately. A power reactor produces electricity at the rate of  $1.5 \times 10^6$  coulomb per second at an appropriate voltage. How many years would it take to electrolyse the lake?  
**EC0212**
12. The equivalent conductance of 0.10 N solution of  $\text{MgCl}_2$  is  $97.1 \text{ mho cm}^2 \text{ eq}^{-1}$  at  $25^\circ\text{C}$ . a cell with electrode that are  $1.5 \text{ cm}^2$  in surface area and  $0.5 \text{ cm}$  apart is filled with  $0.1 \text{ N MgCl}_2$  solution. How much current will flow when potential difference between the electrodes is 5 volt.  
**EC0042**
13. When a solution of specific conductance  $1.342 \text{ ohm}^{-1} \text{ metre}^{-1}$  was placed in a conductivity cell with parallel electrodes, the resistance was found to be  $170.5 \text{ ohm}$ . Area of electrodes is  $1.86 \times 10^{-4} \text{ m}^2$ . Calculate separation of electrodes.  
**EC0043**
14. The specific conductance at  $25^\circ\text{C}$  of a saturated solution of  $\text{SrSO}_4$  is  $1.482 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$  while that of water used is  $1.5 \times 10^{-6} \text{ mho cm}^{-1}$ . Determine at  $25^\circ\text{C}$  the solubility in gm per litre of  $\text{SrSO}_4$  in water. Molar ionic conductance of  $\text{Sr}^{2+}$  and  $\text{SO}_4^{2-}$  ions at infinite dilution are  $59.46$  and  $79.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  respectively. [ **Sr = 87.6, S = 32, O = 16** ]  
 $\left[ \frac{1.467}{139.26} = 1.05 \times 10^{-2} \right]$   
**EC0213**
15. The EMF of the cell  $\text{M} | \text{M}^{n+} (0.02\text{M}) || \text{H}^+ (1\text{M}) | \text{H}_2(\text{g}) (1 \text{ atm}), \text{Pt}$  at  $25^\circ\text{C}$  is  $0.81\text{V}$ . Calculate the valency of the metal if the standard oxidation of the metal is  $0.76\text{V}$ .  
**EC0214**
16. From the standard potentials shown in the following diagram, calculate the potentials  $E_1^\circ$  and  $E_2^\circ$ .



17. Calculate the EMF of the cell,  
 $\text{Zn} - \text{Hg}(c_1\text{M}) | \text{Zn}^{2+}(\text{aq}) | \text{Hg} - \text{Zn}(c_2\text{M})$   
at  $25^\circ\text{C}$ , if the concentrations of the zinc amalgam are:  $c_1 = 10\text{g}$  per  $100\text{g}$  of mercury and  $c_2 = 1\text{g}$  per  $100\text{g}$  of mercury.  
**EC0215**
18. How long a current of  $2\text{A}$  has to be passed through a solution of  $\text{AgNO}_3$  to coat a metal surface of  $80\text{cm}^2$  with  $5\mu\text{m}$  thick layer? Density of silver =  $10.8\text{g/cm}^3$ .  
**EC0044**
19.  $10\text{g}$  solution of  $\text{CuSO}_4$  is electrolyzed using  $0.01\text{F}$  of electricity. Calculate:  
(a) The weight of resulting solution  
(b) Equivalents of acid or alkali in the solution.  
**EC0045**
20. Cadmium amalgam is prepared by electrolysis of a solution of  $\text{CdCl}_2$  using a mercury cathode. How long should a current of  $5\text{A}$  be passed in order to prepare  $12\%$   $\text{Cd} - \text{Hg}$  amalgam on a cathode of  $2\text{ gm Hg}$  ( $\text{Cd} = 112.4$ )  
**EC0216**

**EC0217**



## EXERCISE # O-I

NOTE : If not given in question use :  $\frac{2.303RT}{F} = 0.059$

## GALVANIC CELL

- A standard hydrogen electrode has zero electrode potential because  
 (A) hydrogen is easier to oxidise (B) electrode potential is assumed to be zero  
 (C) hydrogen atom has only one electron (D) hydrogen is the lightest element. **EC0047**
- The thermodynamic efficiency of cell is given by-  
 (A)  $\frac{\Delta H}{\Delta G}$  (B)  $\frac{nFE_{\text{cell}}}{\Delta G}$  (C)  $-\frac{nFE_{\text{cell}}}{\Delta H}$  (D) Zero **EC0050**
- From the following  $E^\circ$  values of half cells,  
 (i)  $A + e \rightarrow A^-$ ;  $E^\circ = -0.24 \text{ V}$  (ii)  $B^- + e \rightarrow B^{2-}$ ;  $E^\circ = +1.25 \text{ V}$   
 (iii)  $C^- + 2e \rightarrow C^{3-}$ ;  $E^\circ = -1.25 \text{ V}$  (iv)  $D + 2e \rightarrow D^{2-}$ ;  $E^\circ = +0.68 \text{ V}$   
 What combination of two half cells would result in a cell with the largest potential ?  
 (A) (ii) and (iii) (B) (ii) and (iv) (C) (i) and (iii) (D) (i) and (iv) **EC0055**
- Which of the following will increase the voltage of the cell with following cell reaction  
 $\text{Sn}_{(s)} + 2\text{Ag}^+_{(aq)} \rightarrow \text{Sn}^{2+}_{(aq)} + 2\text{Ag}_{(s)}$   
 (A) Decrease in the concentration of  $\text{Ag}^+$  ions (B) Increase in the concentration of  $\text{Sn}^{2+}$  ions  
 (C) Increase in the concentration of  $\text{Ag}^+$  ions (D) (A) & (B) both **EC0059**
- The standard electrode potentials for the reactions  
 $\text{Ag}^+ (a) + e^- \longrightarrow \text{Ag}(s)$      $\text{Sn}^{2+} (a) + 2e^- \longrightarrow \text{Sn}(s)$   
 at  $25^\circ\text{C}$  are 0.80 volt and  $-0.14$  volt, respectively. The standard emf of the cell.  
 $\text{Sn}_{(s)}|\text{Sn}^{2+}_{(aq)}(1\text{M})||\text{Ag}^+_{(aq)}(1\text{M})|\text{Ag}_{(s)}$  is :  
 (A) 0.66 volt (B) 0.80 volt (C) 1.08 volt (D) 0.94 volt **EC0049**
- $E^\circ(\text{Ni}^{2+}|\text{Ni}) = -0.25$  volt,  $E^\circ(\text{Au}^{3+}|\text{Au}) = 1.50$  volt. The standard emf of the voltaic cell.  
 $\text{Ni}_{(s)}|\text{Ni}^{2+}_{(aq)}(1.0\text{M})||\text{Au}^{3+}_{(aq)}(1.0\text{M})|\text{Au}_{(s)}$  is :  
 (A) 1.25 volt (B)  $-1.75$  volt (C) 1.75 volt (D) 4.0 volt **EC0053**
- $E^\circ$  for  $\text{F}_2 + 2e^- = 2\text{F}^-$  is 2.8 V,  $E^\circ$  for  $\frac{1}{2}\text{F}_2 + e^- = \text{F}^-$  is ?  
 (A) 2.8 V (B) 1.4 V (C)  $-2.8$  V (D)  $-1.4$  V **EC0054**
- If  $\Delta G^\circ$  of the cell reaction,  
 $\text{AgCl}(s) + \frac{1}{2}\text{H}_2(g) \rightarrow \text{Ag}(s) + \text{H}^+ + \text{Cl}^-$  is  $-21.52$  KJ then  
 $\Delta G^\circ$  of  $2\text{AgCl}(s) + \text{H}_2(g) \rightarrow 2\text{Ag}(s) + 2\text{H}^+ + 2\text{Cl}^-$  is :  
 (A)  $-21.52$  KJ (B)  $-10.76$  KJ (C)  $-43.04$  KJ (D) 43.04 KJ **EC0056**

9. The standard emf for the cell reaction,  
 $\text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)} \longrightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}_{(s)}$  is 1.10 volt at 25 °C. The emf for the cell reaction when 0.1 M  $\text{Cu}^{2+}$  and 0.1 M  $\text{Zn}^{2+}$  solution are used at 25°C is :  
 (A) 1.10 volt (B) 0.110 volt (C) -1.10 volt (D) -0.110 volt **EC0064**
10. Given :  $E^0_{\text{Cr}^{3+}/\text{Cr}} = -0.72 \text{ V}$ ,  $E^0_{\text{Fe}^{2+}/\text{Fe}} = -0.42 \text{ V}$ . The potential for the cell  
 $\text{Cr}_{(s)} | \text{Cr}^{3+}_{(aq)} (0.1 \text{ M}) || \text{Fe}^{2+}_{(aq)} (0.01 \text{ M}) | \text{Fe}_{(s)}$  is  
 (A) 0.26 V (B) 0.339 V (C) -0.339 V (D) -0.26 V **EC0218**
11. What is the potential of the cell containing two hydrogen electrodes as represented below  
 $\text{Pt} | \text{H}_2(\text{g}) | \text{H}^+_{(aq)} (10^{-8} \text{ M}) || \text{H}^+_{(aq)} (0.001 \text{ M}) | \text{H}_2(\text{g}) | \text{Pt}$   
 (A) -0.295 V (B) -0.0591 V (C) 0.295 V (D) 0.0591 V **EC0065**
12. Consider the cell,  $\text{Cu} | \text{Cu}^{2+} || \text{Ag}^+ | \text{Ag}$ . If the concentration of  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  ions becomes ten times the emf of the cell :-  
 (A) Becomes 10 times (B) Remains same  
 (C) Increase by 0.0295 V (D) Decrease by 0.0295 V **EC0066**
13. The standard emf of a galvanic cell involving cell reaction with  $n = 4$  is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be,  
 (A)  $1.0 \times 10^{20}$  (B)  $2.0 \times 10^{11}$  (C)  $4.0 \times 10^{12}$  (D)  $1.0 \times 10^2$  **EC0068**
14. The cell  $\text{Zn} | \text{Zn}^{2+}_{(aq)} (1\text{M}) || \text{Cu}^{2+}_{(aq)} (1\text{M}) | \text{Cu}$  ( $E^0_{\text{cell}} = 1.10 \text{ V}$ ) was allowed to be completely discharged at 298 K. The relative concentration of  $\text{Zn}^{2+}$  to  $\text{Cu}^{2+}$ ,  $\left\{ \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right\}$  is :  
 (A)  $9.65 \times 10^4$  (B) Antilog (24.08) (C) 37.3 (D)  $10^{37.3}$  **EC0219**
15. Given the data at 25°C,  
 $\text{Ag}_{(s)} + \text{I}^-_{(aq)} \rightarrow \text{AgI}_{(s)} + \text{e}^-$ ,  $E^0 = 0.152 \text{ V}$   
 $\text{Ag}_{(s)} \rightarrow \text{Ag}^+_{(aq)} + \text{e}^-$ ,  $E^0 = -0.800 \text{ V}$   
 What is the value of  $\log K_{\text{sp}}$  for AgI ? (Where  $K_{\text{sp}}$  = solubility product)  
 $\left( 2.303 \frac{RT}{F} = 0.059 \text{ V} \right)$   
 (A) -8.12 (B) +8.612 (C) -37.83 (D) -16.13 **EC0220**
16. In a cell that utilises the reaction,  
 $\text{Zn}_{(s)} + 2\text{H}^+_{(A)} \longrightarrow \text{Zn}^{2+}_{(aq)} + \text{H}_2(\text{g})$  addition of  $\text{H}_2\text{SO}_4$  to cathode compartment, will :  
 (A) increase the  $E_{\text{cell}}$  and shift equilibrium to the right  
 (B) lower the  $E_{\text{cell}}$  and shift equilibrium to the right  
 (C) lower the  $E_{\text{cell}}$  and shift equilibrium to the left  
 (D) increase the  $E_{\text{cell}}$  and shift equilibrium to the left **EC0221**

17. By how much times will potential of half cell  $\text{Cu}^{+2}|\text{Cu}$  change if, the solution is diluted to 100 times at 298 K :-
- (A) Increases by 59 mV (B) Decrease by 59 mV  
(C) Increases by 29.5 mV (D) Decreases by 29.5 mV

EC0071

**ELECTROLYTIC CELL**

18. When an electric current is passed through a cell containing an electrolyte, positive ions move towards the cathode and negative ions towards the anode. What will happen if the cathode is pulled out of the solution?
- (A) The positive ions will start moving towards the anode and negative ions will stop moving.  
(B) The negative ions will continue to move towards the anode and the positive ions will stop moving  
(C) Both positive and negative ions will move towards the anode.  
(D) None of these movements will take place.

EC0072

19. The products formed when an aqueous solution of NaBr is electrolyzed in a cell having inert electrodes are :
- (A) Na and  $\text{Br}_2$  (B) Na and  $\text{O}_2$   
(C)  $\text{H}_2$ ,  $\text{Br}_2$  and NaOH (D)  $\text{H}_2$  and  $\text{O}_2$

EC0074

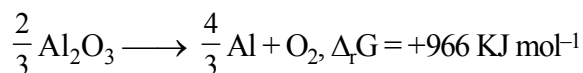
20. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively.
- (A)  $\text{H}_2$ ,  $\text{O}_2$  (B)  $\text{O}_2$ ,  $\text{H}_2$  (C)  $\text{O}_2$ , Na (D) none

EC0076

21. When an aqueous solution of lithium chloride is electrolysed using graphite electrodes
- (A)  $\text{Cl}_2$  is liberated at the anode.  
(B) Li is deposited at the cathode  
(C) as the current flows, pH of the solution remains constant  
(D) as the current flows, pH of the solution decreases.

EC0077

22. The Gibbs energy for the decomposition of  $\text{Al}_2\text{O}_3$  at  $500^\circ\text{C}$  is as follows



The potential difference needed for electrolytic reduction of  $\text{Al}_2\text{O}_3$  at  $500^\circ\text{C}$  is at least :-

- (A) 5.0 V (B) 4.5 V (C) 3.0 V (D) 2.5 V

EC0222

23. Electrolysis of a  $\text{CuSO}_4$  produces :-

- (A) An increase in pH (B) A decrease in pH  
(C) Either decrease or increase (D) None

EC0075

24. The amount of an ion discharged during electrolysis is not directly proportional to :

- (A) resistance  
(B) time  
(C) current strength  
(D) electrochemical equivalent of the element

EC0078

25. Number of electrons involved in the electrodeposition of 63.5 g of Cu from a solution of  $\text{CuSO}_4$  is :  
 $(N_A = 6 \times 10^{23})$   
 (A)  $6 \times 10^{23}$  (B)  $3 \times 10^{23}$  (C)  $12 \times 10^{23}$  (D)  $6 \times 10^{22}$  **EC0079**
26. When one coulomb of electricity is passed through an electrolytic solution the mass deposited on the electrode is equal to :  
 (A) equivalent weight (B) molecular weight  
 (C) electrochemical equivalent (D) one gram **EC0080**
27. Electro chemical equivalent of a substance is 0.0006; its equivalent weight. is :  
 (A) 57.9 (B) 28.95  
 (C) 115.8 (D) cannot be calculated **EC0081**
28. The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate  $[\text{Ni}(\text{NO}_3)_2]$  and chromium nitrate  $[\text{Cr}(\text{NO}_3)_3]$  respectively. If 0.3 g of nickel was deposited in the first cell, the amount of chromium deposited is : (at. wt. of Ni = 59, at. wt. of Cr = 52)  
 (A) 0.1 g (B) 0.17 g (C) 0.3 g (D) 0.6 g **EC0087**
29. W g of copper deposited in a copper voltameter when an electric current of 2 ampere is passed for 2 hours. If one ampere of electric current is passed for 4 hours in the same voltameter, copper deposited will be :  
 (A) W (B)  $W/2$  (C)  $W/4$  (D)  $2W$  **EC0082**
30. When the same electric current is passed through the solution of different electrolytes in series the amounts of elements deposited on the electrodes are in the ratio of their:  
 (A) atomic number (B) atomic masses (C) specific gravities (D) equivalent masses **EC0083**
31. The amount of electricity that can deposit 108 g. of silver from silver nitrate solution is:  
 (A) 1 ampere (B) 1 coulomb  
 (C) 1 Faraday (D) 2 ampere **EC0084**
32. The ratio of weights of hydrogen and magnesium deposited by the same amount of electricity from aqueous  $\text{H}_2\text{SO}_4$  and fused  $\text{MgSO}_4$  are :  
 (A) 1 : 8 (B) 1 : 12 (C) 1 : 16 (D) None of these **EC0085**
33. A current of 9.65 amp. flowing for 10 minute deposits 3.0 g of a metal. The equivalent wt. of the metal is :  
 (A) 10 (B) 30 (C) 50 (D) 96.5 **EC0086**
34. 1 mole of Al is deposited by X coulomb of electricity passing through aluminium nitrate solution. The number of moles of silver deposited by X coulomb of electricity from silver nitrate solution is  
 (A) 3 (B) 4 (C) 2 (D) 1 **EC0092**
35. The electric charge for electro deposition of 1 equivalent of a substance is :  
 (A) one ampere per second (B) 4 faraday  
 (C) one ampere for one hour (D) charge on one mole of electrons **EC0088**

36. 3.17 g., of a substance was deposited by the flow of 0.1 mole of electrons. The equivalent weight of the substance is :  
 (A) 3.17 (B) 0.317 (C) 317 (D) 31.7 **EC0089**
37. A current of 9.65 amp. passing for 16 min. 40 sec. through a molten tin salt deposits 5.95 g. of tin. The oxidation state of the tin in the salt is : (at. wt of Sn = 119)  
 (A) +4 (B) +3 (C) +2 (D) +1 **EC0090**
38. The time required for a current of 3 amp. to decompose electrolytically 18 g of H<sub>2</sub>O is:  
 (A) 18 hour (B) 36 hour (C) 9 hour (D) 18 seconds **EC0091**
39. An ion is reduced to the element when it absorbs  $6 \times 10^{20}$  electrons. The number of gm equivalents of the ion is :  
 (A) 0.10 (B) 0.01 (C) 0.001 (D) 0.0001 **EC0093**
40. How many coulombs of electric charge are required for the oxidation of 1 mole of H<sub>2</sub>O to O<sub>2</sub> ?  
 (A)  $9.65 \times 10^4$  C (B)  $4.825 \times 10^5$  C  
 (C)  $1.93 \times 10^5$  C (D)  $1.93 \times 10^4$  C **EC0095**
41. The time required to coat a meter surface of 80 cm<sup>2</sup> with  $5 \times 10^{-3}$  cm thick layer of silver (density 1.08 g cm<sup>-3</sup>) with the passage of 9.65A current through a silver nitrate solution is :  
 (A) 10 sec. (B) 40 sec. (C) 30 sec. (D) 20 sec. **EC0099**
42. One gm metal M<sup>+2</sup> was discharged by the passage of  $1.2 \times 10^{22}$  electrons. What is the atomic weight of metal?  
 (A) 25 (B) 50 (C) 100 (D) 75 **EC0100**
43. One mole of electron passes through each of the solution of AgNO<sub>3</sub>, CuSO<sub>4</sub> and AlCl<sub>3</sub> when Ag, Cu and Al are deposited at cathode. The molar ratio of Ag, Cu and Al deposited are  
 (A) 1 : 1 : 1 (B) 6 : 3 : 2 (C) 6 : 3 : 1 (D) 1 : 3 : 6 **EC0101**
44. During electrolysis of an aqueous solution of sodium sulphate, 2.4 L of oxygen at STP was liberated at anode. The volume of hydrogen at STP, liberated at cathode would be  
 (A) 1.2 L (B) 2.4 L (C) 2.6 L (D) 4.8 L **EC0102**
45. The charge required for the oxidation of one mole Mn<sub>3</sub>O<sub>4</sub> into MnO<sub>4</sub><sup>2-</sup> in presence of alkaline medium is  
 (A)  $5 \times 96500$  C (B) 96500 C (C)  $10 \times 96500$  C (D)  $2 \times 96500$  C **EC0103**

**CONDUCTANCE**

46. Equivalent conductances of Ba<sup>+2</sup> and Cl<sup>-</sup> ions are 127 & 76 ohm<sup>-1</sup> cm<sup>2</sup> eq<sup>-1</sup> respectively. Equivalent conductance of BaCl<sub>2</sub> at infinite dilution is -  
 (A) 379 (B) 139.5 (C) 203 (D) 330 **EC0114**

47. If  $x$  is specific resistance of the electrolyte solution and  $y$  is the molarity of the solution, then  $\Lambda_m$  is given by  
 (A)  $\frac{1000x}{y}$  (B)  $1000 \frac{y}{x}$  (C)  $\frac{1000}{xy}$  (D)  $\frac{xy}{1000}$

EC0115

48. The conductivity of a saturated solution of  $\text{BaSO}_4$  is  $3.06 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  and its molar conductance is  $1.53 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . The  $K_{sp}$  of  $\text{BaSO}_4$  will be :  
 (A)  $2 \times 10^{-4}$  (B)  $4 \times 10^{-4}$  (C)  $4 \times 10^{-3}$  (D)  $4 \times 10^{-6}$

EC0113

49. The limiting molar conductivities  $\Lambda^0$  for  $\text{NaCl}$ ,  $\text{KBr}$  and  $\text{KCl}$  are 126, 152 and  $150 \text{ S cm}^2 \text{ mol}^{-1}$  respectively.

The  $\Lambda_m^0$  for  $\text{NaBr}$  is :

- (A)  $278 \text{ S cm}^2 \text{ mol}^{-1}$  (B)  $176 \text{ S cm}^2 \text{ mol}^{-1}$   
 (C)  $128 \text{ S cm}^2 \text{ mol}^{-1}$  (D)  $302 \text{ S cm}^2 \text{ mol}^{-1}$

EC0223

50. **Electrolyte**  $\Lambda^\infty (\text{S cm}^2 \text{ mol}^{-1})$

KCl	149.9
$\text{KNO}_3$	145.0
HCl	426.2
NaOAc	91.0
NaCl	126.5

Calculate  $\Lambda_{\text{HOAc}}^\infty$  using appropriate molar conductances of the electrolytes listed above at infinite dilution in  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$

- (A) 390.7 (B) 217.5 (C) 517.2 (D) 552.7

EC0224

51. The highest electrical conductivity of the following aqueous solution is of

- (A) 0.1 M fluoroacetic acid (B) 0.1 M difluoroacetic acid  
 (C) 0.1 M acetic acid (D) 0.1 M chloroacetic acid

EC0225

52. The molar conductivities,  $\Lambda_{\text{NaOAc}}^0$  and  $\Lambda_{\text{HCl}}^0$  at infinite dilution in water at  $25^\circ\text{C}$  are 91.0 and  $426.2 \text{ S cm}^2 \text{ mol}^{-1}$  respectively. To calculate  $\Lambda_{\text{HOAc}}^0$  the additional value required is :

- (A) KCl (B) NaOH (C) NaCl (D)  $\text{H}_2\text{O}$

EC0226

53. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1M is  $100\Omega$ . The conductivity of this solution is  $1.29 \text{ S m}^{-1}$ . Resistance of the same cell when filled with 0.02M of the same solution is  $520\Omega$ . The molar conductivity of 0.02M solution of the electrolyte will be.

- (A)  $124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$  (B)  $1240 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$   
 (C)  $1.24 \times 10^4 \text{ S m}^2 \text{ mol}^{-1}$  (D)  $12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$

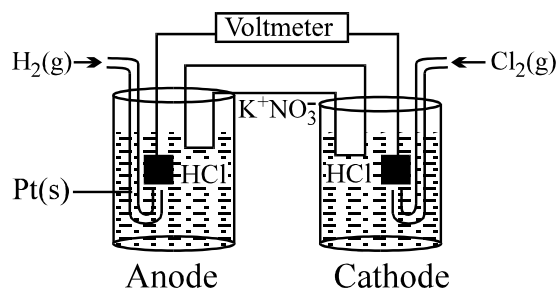
EC0227

## EXERCISE # O-II

## Single correct :

1. Consider the reaction,  $\text{Cl}_{2(g)} + 2\text{Br}^-_{(aq)} \longrightarrow 2\text{Cl}^-_{(aq)} + \text{Br}_{2(g)}$   
The emf of the cell when  $[\text{Cl}^-] = [\text{Br}^-] = 0.01\text{M}$  and  $\text{Cl}_2$  gas at 1 atm pressure while  $\text{Br}_2(g)$  at 0.01 atm will be ( $E^\circ$  for the above reaction is = 0.29 volt) :  
(A) 0.54 volt (B) 0.35 volt (C) 0.24 volt (D) -0.29 volt **EC0116**
2. How much will the reduction potential of a hydrogen electrode change when its solution initially at pH = 0 is neutralised to pH = 7 ?  
(A) increase by 0.059V (B) decrease by 0.059V  
(C) increase by 0.413V (D) decrease by 0.413V **EC0117**
3. If the pressure of  $\text{H}_2$  gas is increased from 1 atm to 100 atm keeping  $\text{H}^+$  concentration constant at 1 M, the change in reduction potential of hydrogen half cell at  $25^\circ\text{C}$  will be  
(A) 0.059 V (B) 0.59 V (C) 0.0295 V (D) 0.118 V **EC0228**
4. A silver wire dipped in 0.1 M HCl solution saturated with AgCl develops oxidation potential of -0.209 V. If  $E^\circ_{\text{Ag}/\text{Ag}^+} = -0.799\text{V}$ , the  $K_{\text{sp}}$  of AgCl in pure water will be  
(A)  $3 \times 10^{-11}$  (B)  $10^{-11}$  (C)  $4 \times 10^{-11}$  (D)  $3 \times 10^{-11}$  **EC0229**
5. Salts of A (atomic weight = 7), B (atomic weight = 27) and C (atomic weight = 48) were electrolysed under identical conditions using the same quantity of electricity. It was found that when 2.1 g of A was deposited, the weights of B and C deposited were 2.7 and 7.2 g. The valencies of A, B and C respectively are  
(A) 3, 1 and 2 (B) 1, 3 and 2 (C) 3, 1 and 3 (D) 2, 3 and 2 **EC0230**
6. During electro refining of Cu by electrolysis of an aqueous solution of  $\text{CuSO}_4$  using copper electrodes, if 2.5 g of Cu is deposited at cathode, then at anode  
(A) decrease of more than 2.5 g of mass takes place (B) 450 ml of  $\text{O}_2$  at STP is liberated  
(C) 2.5 g of copper is deposited (D) a decrease of 2.5 g of mass takes place **EC0118**
7. The conductivity of a saturated solution of  $\text{Ag}_3\text{PO}_4$  is  $9 \times 10^{-6}\text{S m}^{-1}$  and its equivalent conductivity is  $1.50 \times 10^{-4}\text{S m}^2\text{ equivalent}^{-1}$ . The  $K_{\text{sp}}$  of  $\text{Ag}_3\text{PO}_4$  is  
(A)  $4.32 \times 10^{-18}$  (B)  $1.8 \times 10^{-9}$  (C)  $8.64 \times 10^{-13}$  (D) None of these **EC0119**
8. Equal volumes of 0.015 M  $\text{CH}_3\text{COOH}$  & 0.015 M NaOH are mixed together. What would be molar conductivity of mixture if conductivity of  $\text{CH}_3\text{COONa}$  is  $6.3 \times 10^{-4}\text{S cm}^{-1}$   
(A)  $8.4\text{S cm}^2\text{ mol}^{-1}$  (B)  $84\text{S cm}^2\text{ mol}^{-1}$  (C)  $4.2\text{S cm}^2\text{ mol}^{-1}$  (D)  $42\text{S cm}^2\text{ mol}^{-1}$  **EC0120**
9. For the fuel cell reaction  $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l)$ ;  $\Delta_f H_{298}^\circ(\text{H}_2\text{O}, l) = -285.5\text{kJ/mol}$   
What is  $\Delta S_{298}^\circ$  for the given fuel cell reaction?  
Given:  $\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \longrightarrow 2\text{H}_2\text{O}(l)$  ;  $E^\circ = 1.23\text{V}$   
(A) -0.322 J/K (B) -0.635 kJ/K (C) 3.51 kJ/K (D) -0.322 kJ/K **EC0231**

10. Consider the following Galvanic cell.



By what value the cell voltage change when concentration of ions in anodic and cathodic compartments both increased by factor of 10 at 298 K

- (A) +0.0590 (B) -0.0590 (C) -0.1180 (D) 0

EC0121

11. The standard reduction potentials at 25°C for the following half reactions are :



Which is the strongest reducing agent ?

- (A) Zn (B) Cr (C)  $\text{H}_2(\text{g})$  (D)  $\text{Fe}^{2+}(\text{aq})$

EC0122

12. Using the standard electrode potential values given below, decide which of the statements, I, II, III and IV are correct. Choose the right answer from (A), (B), (C) and (D).



I. Copper can displace iron from  $\text{FeSO}_4$  solution.

II. Iron can displace copper from  $\text{CuSO}_4$  solution.

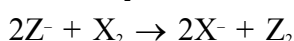
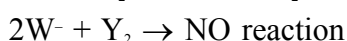
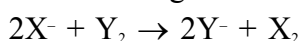
III. Silver can displace copper from  $\text{CuSO}_4$  solution.

IV. Iron can displace silver from  $\text{AgNO}_3$  solution.

- (A) I and II (B) II and III (C) II and IV (D) I and IV

EC0232

13. The following facts are available :-



Which of the following statements is correct :-

(A)  $E^{\circ}_{\text{W}^-/\text{W}_2} > E^{\circ}_{\text{Y}^-/\text{Y}_2} > E^{\circ}_{\text{X}^-/\text{X}_2} > E^{\circ}_{\text{Z}^-/\text{Z}_2}$

(B)  $E^{\circ}_{\text{W}^-/\text{W}_2} < E^{\circ}_{\text{Y}^-/\text{Y}_2} < E^{\circ}_{\text{X}^-/\text{X}_2} < E^{\circ}_{\text{Z}^-/\text{Z}_2}$

(C)  $E^{\circ}_{\text{W}^-/\text{W}_2} < E^{\circ}_{\text{Y}^-/\text{Y}_2} > E^{\circ}_{\text{X}^-/\text{X}_2} > E^{\circ}_{\text{Z}^-/\text{Z}_2}$

(D)  $E^{\circ}_{\text{W}^-/\text{W}_2} > E^{\circ}_{\text{Y}^-/\text{Y}_2} < E^{\circ}_{\text{X}^-/\text{X}_2} < E^{\circ}_{\text{Z}^-/\text{Z}_2}$

EC0233

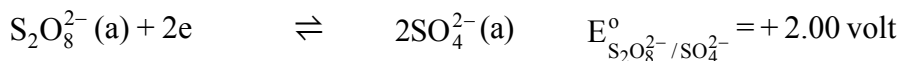
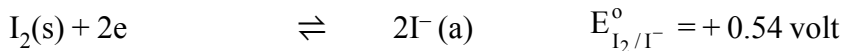
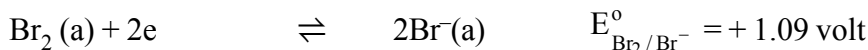
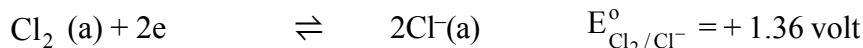


14. The cost of electricity required to deposit 1 g of Mg is Rs. 5.00. How much would it cost to deposit 9 g of Al (At wt. Al = 27, Mg = 24)  
 (A) Rs. 10                      (B) Rs. 27                      (C) Rs. 40                      (D) Rs. 60 **EC0234**
15. 4.5g of aluminium (at. mass 27 amu) is deposited at cathode from  $\text{Al}^{3+}$  solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from  $\text{H}^+$  ions in solution by the same quantity of electric charge will be –  
 (A) 45.4L                      (B) 11.35L                      (C) 22.7L                      (D) 5.675 L **EC0123**
16. The density of A is  $10 \text{ g cm}^{-3}$ . The quantity of electricity needed to plate an area  $10 \text{ cm} \times 10 \text{ cm}$  to a thickness of  $10^{-2} \text{ cm}$  using  $\text{ASO}_4$  solution would be (Atomic mass of A = 193)  
 (A) 5000 C                      (B) 10000 C                      (C) 40000 C                      (D) 20000 C **EC0124**
17. The resistance of 0.5 M solution of an electrolyte in a cell was found to be  $50 \Omega$ . If the electrodes in the cell are 2.2 cm apart and have an area of  $4.4 \text{ cm}^2$  then the molar conductivity (in  $\text{S m}^2 \text{ mol}^{-1}$ ) of the solution is  
 (A) 0.2                      (B) 0.02                      (C) 0.002                      (D) None of these **EC0125**
18. Equivalent conductance of 0.1 M HA (weak acid) solution is  $10 \text{ Scm}^2 \text{ equivalent}^{-1}$  and that at infinite dilution is  $200 \text{ Scm}^2 \text{ equivalent}^{-1}$  Hence pH of HA solution is  
 (A) 1.3                      (B) 1.7                      (C) 2.3                      (D) 3.7 **EC0126**
19. The dissociation constant of n-butyric acid is  $1.6 \times 10^{-5}$  and the molar conductivity at infinite dilution is  $380 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$ . The specific conductance of the 0.01 M acid solution is  
 (A)  $1.52 \times 10^{-5} \text{ Sm}^{-1}$                       (B)  $1.52 \times 10^{-2} \text{ Sm}^{-1}$   
 (C)  $1.52 \times 10^{-3} \text{ Sm}^{-1}$                       (D) None **EC0127**

**Multiple correct :**

20. During discharging of lead storage battery, which of the following is/are true ?  
 (A)  $\text{H}_2\text{SO}_4$  is produced                      (B)  $\text{H}_2\text{O}$  is consumed  
 (C)  $\text{PbSO}_4$  is formed at both electrodes                      (D) Density of electrolytic solution decreases **EC0128**
21. Which of the following arrangement will produce oxygen at anode during electrolysis ?  
 (A) Dilute  $\text{H}_2\text{SO}_4$  solution with Cu electrodes.  
 (B) Dilute  $\text{H}_2\text{SO}_4$  solution with inert electrodes.  
 (C) Fused NaOH with inert electrodes.  
 (D) Dilute NaCl solution with inert electrodes. **EC0235**
22. If 270.0 g of water is electrolysed during an experiment performed by miss Abhilasha with 75% current efficiency then  
 (A) 168 L of  $\text{O}_2$  (g) will be evolved at anode at 1 atm & 273 K  
 (B) Total 504 L gases will be produced at 1 atm & 273 K.  
 (C) 336 L of  $\text{H}_2$  (g) will be evolved at anode at 1 atm & 273 K  
 (D) 45 F electricity will be consumed **EC0129**

23. Pick out the correct statements among the following from inspection of standard reduction potentials (Assume standard state conditions).



- (A)  $\text{Cl}_2$  can oxidise  $\text{SO}_4^{2-}$  from solution  
 (B)  $\text{Cl}_2$  can oxidise  $\text{Br}^-$  and  $\text{I}^-$  from aqueous solution  
 (C)  $\text{S}_2\text{O}_8^{2-}$  can oxidise  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  from aqueous solution  
 (D)  $\text{S}_2\text{O}_8^{2-}$  is added slowly,  $\text{Br}^-$  can be reduce in presence of  $\text{Cl}^-$

EC0236

24. The EMF of the following cell is 0.22 volt.  
 $\text{Ag}(\text{s}) | \text{AgCl}(\text{s}) | \text{KCl} (1\text{M}) | \text{H}^+(1\text{M}) | \text{H}_2(\text{g}) (1\text{atm}) ; \text{Pt}(\text{s})$ .  
 Which of the following will decrease the EMF of cell.

- (A) increasing pressure of  $\text{H}_2(\text{g})$  from 1 atm to 2 atm  
 (B) increasing  $\text{Cl}^-$  concentration in Anodic compartment  
 (C) increasing  $\text{H}^+$  concentration in cathodic compartment  
 (D) decreasing  $\text{KCl}$  concentration in Anodic compartment.

EC0130

#### Assertion & Reasoning type questions :

25. Statement -1 : The voltage of mercury cell remains constant for long period of time.  
 Statement -2 : It is because net cell reaction does not involve active species.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

EC0237

26. Statement -1 : The SRP of three metallic ions  $\text{A}^+$ ,  $\text{B}^{2+}$ ,  $\text{C}^{3+}$  are  $-0.3$ ,  $-0.5$ ,  $0.8$  volt respectively, so oxidising power of ions is  $\text{C}^{3+} > \text{A}^+ > \text{B}^{2+}$ .  
 Statement -2 : Higher the SRP, higher the oxidising power.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

EC0131

27. Statement -1 : We can add the electrode potential in order to get electrode potential of net reaction.  
 Statement -2 : Electrode potential is an intensive property.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

EC0132

Table type :

1 TABLE (3Q)

Column-I	Column-II	Column-III
(P) $\text{Zn(s)}   \text{ZnSO}_4(0.1\text{M})$ $    \text{Zn(NO}_3)_2(0.01\text{M})   \text{Zn(s)}$	(A) Has metal -insoluble salt - anion electrode.	(I) $E_{\text{cell}} < 0$
(Q) $\text{Pt, Cl}_2(0.1\text{bar})   \text{KCl}(1\text{M})$ $    \text{NaCl}(1\text{M})   \text{Cl}_2(1\text{bar}), \text{Pt}$	(B) Electrolytic concentration cell	(II) $E_{\text{cell}}^0 = 0$
(R) $\text{Ag(s)}   \text{AgCl(s)}   \text{KCl}$ $(0.1\text{M})     \text{Ag}^+(0.1\text{M})   \text{Ag(s)}$ $K_{\text{sp}}[\text{AgCl}] = 10^{-10}$ .	(C) Electrode concentration cell	(III) $E_{\text{cell}} > 0$
(S) $\text{Pt, H}_2(1\text{bar})   \text{H}_2\text{SO}_4$ $(0.05\text{M})     \text{HNO}_3(0.1\text{M})  $ $\text{H}_2(1\text{bar}), \text{Pt}$	(D) Has gas-ion electrode	(IV) $E_{\text{cell}} = 0$

(1) Use :  $\frac{2.303RT}{F} = 0.06$

(2) Assume constant P,T condition of operation.

28. Which option is incorrectly matched ?

(A) P - B - II

(B) Q - C - II

(C) R - A - I

(D) S - D - IV

**EC0133**

29. For galvanic cell in option 'Q' on increasing concentration of KCl, cell potential will -

(A) Increase

(B) decrease

(C) remains constant

(D) cannot predict

**EC0134**30. On increasing  $\text{Ag}^+$  concentration in anodic compartment in option (R) cell potential will

(A) Remain same

(B) increase

(C) decrease

(D) can't predict

**EC0135****Match the column**

31.

**Column I****Column II****(Electrolysis product using inert electrode)**

(A) Dilute solution of HCl

(P)  $\text{O}_2$  evolved at anode

(B) Dilute solution of NaCl

(Q)  $\text{H}_2$  evolved at cathode

(C) Concentrated solution of NaCl

(R)  $\text{Cl}_2$  evolved at anode(D)  $\text{AgNO}_3$  solution

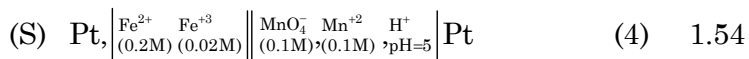
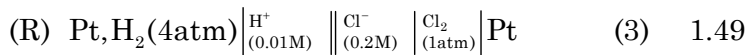
(S) Ag deposition at cathode

**EC0136**

## 32. Column-I

## Column-II

Cell notation :

 $E_{\text{cell}}$ 

Given :

$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34\text{V}$$

$$K_{\text{sp}}(\text{AgBr}) = 10^{-13}$$

$$E_{\text{Mn}^{2+}/\text{Mn}}^0 = -1.18\text{V}$$

$$\frac{2.303RT}{F} = 0.06$$

$$E_{\text{Ag}^+/\text{Ag}}^0 = 0.8\text{V}$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.77\text{V}$$

$$E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 = 1.52\text{V}$$

$$E_{\text{Cl}_2/\text{Cl}^-}^0 = 1.36\text{V}$$

Code:

	P	Q	R	S
(A)	4	3	4	4
(B)	2	3	1	4
(C)	3	2	4	1
(D)	4	3	2	1

EC0238

## EXERCISE # J-MAINS

1. Resistance of 0.2 M solution of an electrolyte is 50  $\Omega$ . The specific conductance of the solution is 1.3 S m<sup>-1</sup>. If resistance of the 0.4M solution of the same electrolyte is 260  $\Omega$ , its molar conductivity is :- [AIEEE 2011]

- (1) 6250 S m<sup>2</sup> mol<sup>-1</sup> (2) 6.25  $\times 10^{-4}$  S m<sup>2</sup> mol<sup>-1</sup>  
 (3) 625  $\times 10^{-4}$  S m<sup>2</sup> mol<sup>-1</sup> (4) 62.5 S m<sup>2</sup> mol<sup>-1</sup>

EC0137

2. The reduction potential of hydrogen half-cell will be negative if :- [AIEEE 2011]

- (1) p(H<sub>2</sub>) = 2 atm [H<sup>+</sup>] = 1.0 M (2) p(H<sub>2</sub>) = 2 atm and [H<sup>+</sup>] = 2.0 M  
 (3) p(H<sub>2</sub>) = 1 atm and [H<sup>+</sup>] = 2.0 M (4) p(H<sub>2</sub>) = 1 atm and [H<sup>+</sup>] = 1.0 M

EC0138

3. The standard reduction potentials for Zn<sup>2+</sup> | Zn, Ni<sup>2+</sup> | Ni and Fe<sup>2+</sup> | Fe are - 0.76, - 0.23 and - 0.44 V respectively. The reaction X + Y<sup>2+</sup>  $\rightarrow$  X<sup>2+</sup> + Y will be spontaneous when [AIEEE 2012]

- (1) X = Zn, Y = Ni (2) X = Ni, Y = Fe (3) X = Ni, Y = Zn (4) X = Fe, Y = Zn

EC0139

4. Given : [JEE-MAINS 2013]

$$E_{\text{Cr}^{3+}/\text{Cr}}^0 = -0.74 \text{ V} ; E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 = 1.51 \text{ V}$$

$$E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^0 = 1.33 \text{ V} ; E_{\text{Cl}^-/\text{Cl}_2}^0 = 1.36 \text{ V}$$

Based on the data given above, strongest oxidising agent will be :

- (1) Cl<sup>-</sup> (2) Cr<sup>3+</sup> (3) Mn<sup>2+</sup> (4) MnO<sub>4</sub><sup>-</sup>

EC0140

5. The equivalent conductance of NaCl at concentration C and at infinite dilution are  $\lambda_C$  and  $\lambda_\infty$ , respectively. The correct relationship between  $\lambda_C$  and  $\lambda_\infty$  is given as : [JEE-MAINS 2014]

(where the constant B is positive)

- (1)  $\lambda_C = \lambda_\infty - (2)\sqrt{C}$  (2)  $\lambda_C = \lambda_\infty + (2)\sqrt{C}$   
 (3)  $\lambda_C = \lambda_\infty + (2)C$  (4)  $\lambda_C = \lambda_\infty - (2)C$

EC0141

6. Resistance of 0.2 M solution of an electrolyte is 50  $\Omega$ . The specific conductance of the solution is 1.4 S m<sup>-1</sup>. The resistance of 0.5 M solution of the same electrolyte is 280  $\Omega$ . The molar conductivity of 0.5 M solution of the electrolyte in S m<sup>2</sup> mol<sup>-1</sup> is : [JEE-MAINS 2014]

- (1) 5  $\times 10^3$  (2) 5  $\times 10^2$  (3) 5  $\times 10^{-4}$  (4) 5  $\times 10^{-3}$

EC0142

7. At 298 K, the standard reduction potentials are 1.51 V for MnO<sub>4</sub><sup>-</sup>|Mn<sup>2+</sup>, 1.36 V for Cl<sub>2</sub>|Cl<sup>-</sup>, 1.07 V for Br<sub>2</sub>|Br<sup>-</sup>, and 0.54 V for I<sub>2</sub>|I<sup>-</sup>. At pH=3, permanganate is expected to oxidize  $\left(\frac{RT}{F} = 0.059 \text{ V}\right)$  :- [JEE-MAINS (ONLINE) 2015]

- (1) Cl<sup>-</sup> and Br<sup>-</sup> (2) Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> (3) Br<sup>-</sup> and I<sup>-</sup> (4) I<sup>-</sup> only

EC0143

8. A variable, opposite external potential ( $E_{\text{ext}}$ ) is applied to the cell  
 $\text{Zn}|\text{Zn}^{2+} (1 \text{ M})||\text{Cu}^{2+} (1 \text{ M})|\text{Cu}$ , of potential 1.1 V. When  $E_{\text{ext}} < 1.1 \text{ V}$  and  $E_{\text{ext}} > 1.1 \text{ V}$ , respectively electrons flow from : **[JEE-MAINS (ONLINE) 2015]**  
 (1) anode to cathode in both cases (2) anode to cathode and cathode to anode  
 (3) cathode to anode in both cases (4) cathode to anode and anode to cathode **EC0144**
9. Two Faraday of electricity is passed through a solution of  $\text{CuSO}_4$ . The mass of copper deposited at the cathode is : **[JEE-MAINS 2015]**  
 (at. mass of Cu = 63.5 amu)  
 (1) 2g (2) 127 g (3) 0 g (4) 63.5 g **EC0145**
10. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1M  $\text{ZnSO}_4$   
 (1) The copper metal will dissolve and zinc metal will be deposited  
 (2) No reaction will occur **[JEE-MAINS (ONLINE) 2016]**  
 (3) The copper metal will dissolve with evolution of oxygen gas  
 (4) The copper metal will dissolve with evolution of hydrogen gas **EC0146**
11. Oxidation of succinate ion produces ethylene and carbon dioxide gases. On passing 0.2 Faraday electricity through on aqueous solution of potassium succinate, the total volume of gases (at both cathode and anode) at STP (1 atm and 273 K) is : **[JEE-MAINS (ONLINE) 2016]**  
 (1) 8.96 L (2) 2.24 L (3) 4.48 L (4) 6.72 L **EC0147**
12. Given **[JEE-MAINS - 2017]**  
 $E_{\text{Cl}_2/\text{Cl}^-}^\circ = 1.36 \text{ V}, E_{\text{Cr}^{3+}/\text{Cr}}^\circ = -0.74 \text{ V} ; E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^\circ = 1.33 \text{ V}, E_{\text{MnO}_4^-/\text{Mn}^{2+}}^\circ = 1.51 \text{ V} .$   
 Among the following, the strongest reducing agent is  
 (1) Cr (2)  $\text{Mn}^{2+}$  (3)  $\text{Cr}^{3+}$  (4)  $\text{Cl}^-$  **EC0148**
13. What is the standard reduction potential ( $E^\circ$ ) for  $\text{Fe}^{3+} \rightarrow \text{Fe}$  ? **[JEE-MAINS (ONLINE) 2017]**  
 Given that :  
 $\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe} ; E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.47 \text{ V}$   
 $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} ; E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = +0.77 \text{ V}$   
 (1) +0.30 V (2) +0.057 V (3) -0.057 V (4) -0.30 V **EC0149**
14. To find the standard potential of  $\text{M}^{3+}|\text{M}$  electrode, the following cell is constituted:  $\text{Pt}|\text{M}|\text{M}^{3+} (0.001 \text{ mol L}^{-1})|\text{Ag}^+(0.01 \text{ mol L}^{-1})|\text{Ag}$  **[JEE-MAINS (ONLINE) 2017]**  
 The emf of the cell is found to be 0.421 volt at 298 K. The standard potential of half reaction  $\text{M}^{3+} + 3e^- \rightarrow \text{M}$  at 298 K will be : **(Given  $E_{\text{Ag}^+/\text{Ag}}^\circ$  at 298 K = 0.80 Volt)**  
 (1) +0.30 V (2) +0.057 V (3) -0.057 V (4) -0.30 V **EC0150**

15. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane ? [JEE-MAINS (OFFLINE) 2017]  
(Atomic weight of B = 10.8 u)

(1) 0.8 hours                      (2) 3.2 hours                      (3) 1.6 hours                      (4) 6.4 hours

EC0151

16. When an electric current is passed through acidified water, 112 mL of hydrogen gas at N.T.P. was collected at the cathode in 965 seconds. The current passed, in ampere, is :

[JEE-MAINS (ONLINE) 2018]

(1) 2.0                      (2) 1.0                      (3) 0.1                      (4) 0.5

EC0152

17. When 9.65 ampere current was passed for 1.0 hour into nitrobenzene in acidic medium, the amount of p-aminophenol produced is :-

[JEE-MAINS (ONLINE) 2018]

(1) 10.9 g                      (2) 98.1 g                      (3) 109.0 g                      (4) 9.81 g

EC0153

18. For the cell  $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{M}^{x+}(\text{aq}) | \text{M(s)}$ , different half cells and their standard electrode potentials are given below :

[JEE-MAINS (ONLINE) 2019]

$\text{M}^{x+}(\text{aq})/\text{M(s)}$	$\text{Au}^{3+}(\text{aq})/\text{Au(s)}$	$\text{Ag}^{+}(\text{aq})/\text{Ag(s)}$	$\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$	$\text{Fe}^{2+}(\text{aq})/\text{Fe(s)}$
$E_{\text{M}^{x+}/\text{M}^{(s)}}^{\circ}$	1.40	0.80	0.77	-0.44

If  $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$ , which cathode will give a maximum value of  $E_{\text{cell}}^{\circ}$  per electron transferred ?

(1)  $\text{Fe}^{3+} / \text{Fe}^{2+}$                       (2)  $\text{Ag}^{+} / \text{Ag}$                       (3)  $\text{Au}^{3+} / \text{Au}$                       (4)  $\text{Fe}^{2+} / \text{Fe}$

EC0154

19. If the standard electrode potential for a cell is 2 V at 300 K, the equilibrium constant (K) for the reaction



at 300 K is approximately. ( $R = 8 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $F = 96000 \text{ C mol}^{-1}$ )

(1)  $e^{160}$                       (2)  $e^{320}$                       (3)  $e^{-160}$                       (4)  $e^{-80}$

EC0155

20. Given the equilibrium constant :

[JEE-MAINS (ONLINE) 2019]

$K_c$  of the reaction :

$\text{Cu(s)} + 2\text{Ag}^{+}(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}$  is  $10 \times 10^{15}$ , calculate the  $E_{\text{cell}}^{\circ}$  of this reaction at 298 K.

$$\left[ 2.303 \frac{RT}{F} \text{ at } 298 \text{ K} = 0.059 \text{ V} \right]$$

(1) 0.04736 V                      (2) 0.4736 V                      (3) 0.4736 mV                      (4) 0.04736 mV

EC0156

21. The standard electrode potential  $E^\ominus$  and its temperature coefficient  $\left(\frac{dE^\ominus}{dT}\right)$  for a cell are 2V and  $-5 \times 10^{-4} \text{ VK}^{-1}$  at 300 K respectively. The cell reaction is **[JEE-MAINS (ONLINE) 2019]**  
 $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$   
 The standard reaction enthalpy ( $\Delta_r H^\ominus$ ) at 300 K in  $\text{kJ mol}^{-1}$  is,  
**[Use :  $R = 8\text{JK}^{-1} \text{ mol}^{-1}$  and  $F = 96,000 \text{ Cmol}^{-1}$ ]**  
 (1)  $-412.8$  (2)  $-384.0$  (3)  $206.4$  (4)  $192.0$  **EC0157**
22.  $\wedge_m^\ominus$  for NaCl, HCl and NaA are  $126.4$ ,  $425.9$  and  $100.5 \text{ S cm}^2 \text{ mol}^{-1}$ , respectively. If the conductivity of  $0.001 \text{ M HA}$  is  $5 \times 10^{-5} \text{ S cm}^{-1}$ , degree of dissociation of HA is : **[JEE-MAINS (ONLINE) 2019]**  
 (1)  $0.75$  (2)  $0.125$  (3)  $0.25$  (4)  $0.50$  **EC0158**
23. Consider the following reduction processes : **[JEE-MAINS (ONLINE) 2019]**  
 $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn(s)}; E^\ominus = -0.76 \text{ V}$   $\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca(s)}; E^\ominus = -2.87 \text{ V}$   
 $\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg(s)}; E^\ominus = -2.36 \text{ V}$   $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni(s)}; E^\ominus = -0.25 \text{ V}$   
 The reducing power of the metals increases in the order : **[JEE-MAINS (ONLINE) 2019]**  
 (1)  $\text{Ca} < \text{Zn} < \text{Mg} < \text{Ni}$  (2)  $\text{Ni} < \text{Zn} < \text{Mg} < \text{Ca}$   
 (3)  $\text{Zn} < \text{Mg} < \text{Ni} < \text{Ca}$  (4)  $\text{Ca} < \text{Mg} < \text{Zn} < \text{Ni}$  **EC0159**
24. In the cell : **[JEE-MAINS (ONLINE) 2019]**  
 $\text{Pt(s)} | \text{H}_2(\text{g}, 1 \text{ bar}) | \text{HCl}(\text{aq}) | \text{AgCl(s)} | \text{Ag(s)} | \text{Pt(s)}$   
 the cell potential is  $0.92 \text{ V}$  when a  $10^{-6} \text{ molal HCl}$  solution is used. The standard electrode potential of (AgCl/Ag,Cl<sup>-</sup>) electrode is :  
 $\left\{ \text{given, } \frac{2.303RT}{F} = 0.06 \text{ V at } 298 \text{ K} \right\}$   
 (1)  $0.20 \text{ V}$  (2)  $0.76 \text{ V}$  (3)  $0.40 \text{ V}$  (4)  $0.94 \text{ V}$  **EC0160**
25. The anodic half-cell of lead-acid battery is recharged using electricity of  $0.05 \text{ Faraday}$ . The amount of  $\text{PbSO}_4$  electrolyzed in g during the process in : **(Molar mass of  $\text{PbSO}_4 = 303 \text{ g mol}^{-1}$ )**  
 (1)  $22.8$  (2)  $15.2$  **[JEE-MAINS (ONLINE) 2019]**  
 (3)  $7.6$  (4)  $11.4$  **EC0161**
26. Given that the standard potentials ( $E^\ominus$ ) of  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Cu}^+/\text{Cu}$  are  $0.34 \text{ V}$  and  $0.522 \text{ V}$  respectively, the  $E^\ominus$  of  $\text{Cu}^{2+}/\text{Cu}^+$  is : **[JEE-MAINS (ONLINE) 2020]**  
 (1)  $+0.158 \text{ V}$  (2)  $0.182 \text{ V}$  (3)  $-0.182 \text{ V}$  (4)  $-0.158 \text{ V}$  **EC0162**



27. The equation that is incorrect is -

[JEE-MAINS (ONLINE) 2020]

$$(1) (\Lambda_m^0)_{\text{NaBr}} - (\Lambda_m^0)_{\text{NaI}} = (\Lambda_m^0)_{\text{KBr}} - (\Lambda_m^0)_{\text{NaBr}}$$

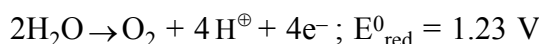
$$(2) (\Lambda_m^0)_{\text{H}_2\text{O}} = (\Lambda_m^0)_{\text{HCl}} + (\Lambda_m^0)_{\text{NaOH}} - (\Lambda_m^0)_{\text{NaCl}}$$

$$(3) (\Lambda_m^0)_{\text{KCl}} - (\Lambda_m^0)_{\text{NaCl}} = (\Lambda_m^0)_{\text{KBr}} - (\Lambda_m^0)_{\text{NaBr}}$$

$$(4) (\Lambda_m^0)_{\text{NaBr}} - (\Lambda_m^0)_{\text{NaCl}} = (\Lambda_m^0)_{\text{KBr}} - (\Lambda_m^0)_{\text{KCl}}$$

EC0163

28. What would be the electrode potential for the given half cell reaction at pH = 5 ? \_\_\_\_\_



(R = 8.314 J mol<sup>-1</sup> K<sup>-1</sup> ; Temp = 298 K; oxygen under std. atm. pressure of 1 bar)

EC0164

29. For an electrochemical cell

[JEE-MAINS (ONLINE) 2020]



the ratio  $\frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]}$  when this cell attains equilibrium is \_\_\_\_\_.

$$\text{(Given } E_{\text{Sn}^{2+}|\text{Sn}}^0 = -0.14\text{V, } E_{\text{Pb}^{2+}|\text{Pb}}^0 = -0.13\text{V, } \frac{2.303RT}{F} = 0.06)$$

EC0165

30. 108 g of silver (molar mass 108 g mol<sup>-1</sup>) is deposited at cathode from AgNO<sub>3</sub>(aq) solution by a certain quantity of electricity. The volume (in L) of oxygen gas produced at 273 K and 1 bar pressure from water by the same quantity of electricity is \_\_\_\_\_.

[JEE-MAINS (ONLINE) 2020]

EC0166

31. Amongst the following, the form of water with the lowest ionic conductance at 298 K is:

(1) distilled water

(2) water from a well

(3) saline water used for intravenous injection

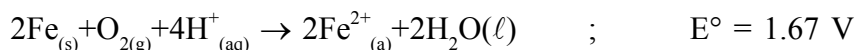
(4) sea water

[JEE-MAINS (ONLINE) 2020]

EC0167

## EXERCISE # J-ADVANCED

1. Consider the following cell reaction : [JEE 2011]

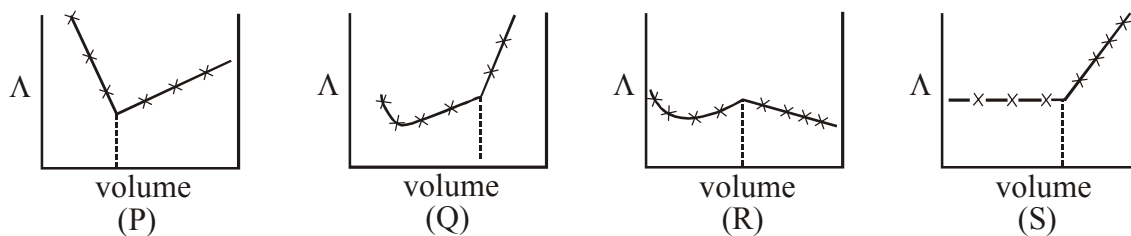


At  $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$ ,  $P(\text{O}_2) = 0.1 \text{ atm}$  and  $\text{pH} = 3$ , the cell potential at  $25^\circ\text{C}$  is -

- (A) 1.47 V                      (B) 1.77 V                      (C) 1.87 V                      (D) 1.57 V

EC0178

2.  $\text{AgNO}_3(a)$  was added to an aqueous  $\text{KCl}$  solution gradually and the conductivity of the solution was measured. the plot of conductance ( $\Lambda$ ) versus the volume of  $\text{AgNO}_3$  is - [JEE 2011]



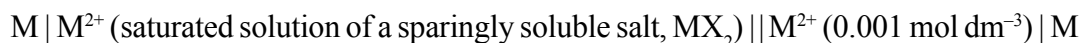
- (A) (P)                      (B) (Q)                      (C) (R)                      (D) (S)

EC0179

*Paragraph for Question 3 and 4*

The electrochemical cell shown below is a concentration cell.

[JEE 2012]



The emf of the cell depends on the difference in concentrations of  $\text{M}^{2+}$  ions at the two electrodes. The emf of the cell at  $298 \text{ K}$  is  $0.059 \text{ V}$ .

3. The value of  $\Delta G$  ( $\text{kJ mol}^{-1}$ ) for the given cell is (take  $I_f = 96500 \text{ C mol}^{-1}$ )
- (A)  $-5.7$                       (B)  $5.7$                       (C)  $11.4$                       (D)  $-11.4$

EC0180

4. The solubility product ( $K_{sp}$ ;  $\text{mol}^3 \text{ dm}^{-9}$ ) of  $\text{MX}_2$  at  $298 \text{ K}$  based on the information available for the given concentration cell is (take  $2.303 \times R \times 298 | F = 0.059 \text{ V}$ )

- (A)  $1 \times 10^{-15}$                       (B)  $4 \times 10^{-15}$                       (C)  $1 \times 10^{-12}$                       (D)  $1 \times 10^{-12}$

EC0181

5. The standard reduction potential data at  $25^\circ\text{C}$  is given below

[JEE-Adv. 2013]

$$E^\circ (\text{Fe}^{3+}, \text{Fe}^{2+}) = +0.77 \text{ V} ;$$

$$E^\circ (\text{Fe}^{2+}, \text{Fe}) = -0.44 \text{ V} ;$$

$$E^\circ (\text{Cu}^{2+}, \text{Cu}) = +0.34 \text{ V} ;$$

$$E^\circ (\text{Cu}^+, \text{Cu}) = +0.52 \text{ V} ;$$

$$E^\circ (\text{O}_2(g) + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}) = +1.23 \text{ V} ;$$

$$E^\circ [(\text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-)] = +0.40 \text{ V} ;$$

$$E^\circ (\text{Cr}^{3+}, \text{Cr}) = -0.74 \text{ V} ;$$

$$E^\circ (\text{Cr}^{2+}, \text{Cr}) = -0.91 \text{ V} ;$$

Match  $E^\circ$  of the redox pair in List-I with the values given in List-II and select the correct answer using the code given below the lists :

List-I		List-II	
(P)	$E^\circ(\text{Fe}^{3+}, \text{Fe})$	(1)	-0.18 V
(Q)	$E^\circ(4\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + 4\text{OH}^-)$	(2)	-0.4 V
(R)	$E^\circ(\text{Cu}^{2+} + \text{Cu} \rightarrow 2\text{Cu}^+)$	(3)	-0.04 V
(S)	$E^\circ(\text{Cr}^{3+}, \text{Cr}^{2+})$	(4)	-0.83 V

Codes :

	P	Q	R	S		P	Q	R	S
(A)	4	1	2	3	(B)	2	3	4	1
(C)	1	2	3	4	(D)	3	4	1	2

EC0182

6. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List-I. The variation in conductivity of these reactions is given in List-II. Match List-I with List-II and select the correct answer using the code given below the lists : [JEE-Adv. 2013]

List-I		List-II	
(P)	$(\text{C}_2\text{H}_5)_3\text{N} + \text{CH}_3\text{COOH}$ X            Y	(1)	Conductivity decreases and then increases
(Q)	$\text{KI}(0.1\text{M}) + \text{AgNO}_3(0.01\text{M})$ X            Y	(2)	Conductivity decreases and then does not change much
(R)	$\text{CH}_3\text{COOH} + \text{KOH}$ X            Y	(3)	Conductivity increases and then does not change much
(S)	$\text{NaOH} + \text{HI}$ X            Y	(4)	Conductivity does not change much and then increases

Codes :

	P	Q	R	S		P	Q	R	S
(A)	3	4	2	1	(B)	4	3	2	1
(C)	2	3	4	1	(D)	1	4	3	2

EC0183

7. In a galvanic cell, the salt bridge - [JEE-Adv. 2014]  
 (A) Does not participate chemically in the cell reaction  
 (B) Stops the diffusion of ions from one electrode to another  
 (C) Is necessary for the occurrence of the cell reaction  
 (D) Ensures mixing of the two electrolytic solutions  
**EC0184**
8. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.1 M). If  $\lambda_{X^-}^0 \approx \lambda_{Y^-}^0$ , the difference in their  $pK_a$  values,  $pK_a(\text{HX}) - pK_a(\text{HY})$ , is (consider degree of ionization of both acids to be  $\ll 1$ ). [JEE-Adv. 2015]  
**EC0185**
9. All the energy released from the reaction  $X \rightarrow Y$ ,  $\Delta_r G^\circ = -193 \text{ kJ mol}^{-1}$  is used for the oxidizing  $M^+$  and  $M^+ \rightarrow M^{3+} + 2e^-$ ,  $E^\circ = -0.25 \text{ V}$ . [JEE-Adv. 2015]  
 Under standard conditions, the number of moles of  $M^+$  oxidized when one mole of X is converted to Y is - [ $F = 96500 \text{ C mol}^{-1}$ ]  
**EC0186**
10. For the following electrochemical cell at 298K, [JEE-Adv. 2016]  
 $\text{Pt(s)} \mid \text{H}_2(\text{g}, 1\text{bar}) \mid \text{H}^+(\text{aq}, 1\text{M}) \parallel \text{M}^{4+}(\text{aq}), \text{M}^{2+}(\text{aq}) \mid \text{Pt(s)}$   
 $E_{\text{cell}} = 0.092 \text{ V}$  when  $\frac{[\text{M}^{2+}(\text{aq})]}{[\text{M}^{4+}(\text{aq})]} = 10^x$   
 Given :  $E_{\text{M}^{4+}/\text{M}^{2+}}^\circ = 0.151 \text{ V}$  ;  $2.303 \frac{RT}{F} = 0.059 \text{ V}$   
 The value of x is -  
 (A) -2 (B) -1 (C) 1 (D) 2  
**EC0187**
11. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of  $1 \text{ cm}^2$ . The conductance of this solution was found to be  $5 \times 10^{-7} \text{ S}$ . The pH of the solution is 4. The value of limiting molar conductivity ( $\Lambda_m^0$ ) of this weak monobasic acid in aqueous solution is  $Z \times 10^2 \text{ S cm}^{-1} \text{ mol}^{-1}$ . The value of Z is.  
**EC0188**

12. For the following cell :

[JEE-Adv. 2017]



when the concentration of  $\text{Zn}^{2+}$  is 10 times the concentration of  $\text{Cu}^{2+}$ , the expression for  $\Delta G$  (in  $\text{J mol}^{-1}$ ) is

[F is Faraday constant, R is gas constant, T is temperature,  $E^\circ(\text{cell}) = 1.1\text{V}$ ]

- (A)  $2.303 RT + 1.1F$  (B)  $2.303 RT - 2.2F$  (C)  $1.1 F$  (D)  $-2.2 F$

EC0189

13. Consider an electrochemical cell:  $\text{A(s)} \mid \text{A}^{n+} \text{ (aq, 2M)} \parallel \text{B}^{2n+} \text{ (aq, 1M)} \mid \text{B(s)}$ . The value of  $\Delta H^\circ$  for the cell reaction is twice that of  $\Delta G^\circ$  at 300 K. If the emf of the cell is zero, the  $\Delta S^\circ$

(in  $\text{JK}^{-1} \text{ mol}^{-1}$ ) of the cell reaction per mole of B formed at 300 K is \_\_\_\_\_. [JEE-Adv. 2018]

(Given :  $\ln(2) = 0.7$ , R (universal gas constant) =  $8.3 \text{ J K}^{-1} \text{ mol}^{-1}$ . H, S and G are enthalpy, entropy and Gibbs energy, respectively.)

EC0190

14. For the electrochemical cell,



the standard emf of the cell is 2.70 V at 300 K. When the concentration of  $\text{Mg}^{2+}$  is changed to x M, the cell potential changes to 2.67 V at 300 K. The value of x is \_\_\_\_\_. [JEE-Adv. 2018]

(Given,  $\frac{F}{R} = 11500 \text{ KV}^{-1}$ , where F is the Faraday constant and R is the gas constant,  $\ln(10) = 2.30$ )

EC0191

## ANSWER KEY

## EXERCISE # S-I

- Ans. (a)  $2\text{Ag} + \text{Cu}^{2+} \longrightarrow 2\text{Ag}^+ + \text{Cu}$ ,  
 (b)  $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$   
 (c)  $2\text{Cl}^- + 2\text{Ag}^+ \longrightarrow 2\text{Ag} + \text{Cl}_2$ , (d)  $\text{H}_2 + \text{Cd}^{2+} \longrightarrow \text{Cd} + 2\text{H}^+$
- Ans. (a)  $\text{Zn} | \text{Zn}^{2+} || \text{Cd}^{2+} | \text{Cd}$ , (b)  $\text{Pt}, \text{H}_2 | \text{H}^+ || \text{Ag}^+ | \text{Ag}$ ,  
 (c)  $\text{Pt} | \text{Fe}^{2+}, \text{Fe}^{3+} || \text{Cr}_2\text{O}_7^{2-}, \text{H}^+ | \text{Cr}^{3+} | \text{Pt}$
- Ans. 1.61 V
- Ans. -0.0367 V
- Ans. (7)
- Ans. 1.35 V
- Ans. 0.53 V, disproportionation
- Ans.  $E = 1.159\text{V}$
- Ans.  $E^0_{\text{cell}} = +0.01\text{V}$ ,  $E_{\text{cell}} = -0.0785\text{V}$ , correct representation is  $\text{Pb} | \text{Pb}^{2+} (10^{-3}\text{M}) || \text{Sn}^{2+} (1\text{M}) | \text{Sn}$
- Ans.  $[\text{Cu}^{2+}] = 2.97 \times 10^{-12}\text{M}$  for  $E = 0$
- Ans. (i)  $K_c = 10^{107}$  (ii) 609.20 kJ
- Ans.  $E = -0.81\text{V}$
- Ans.  $K_c = 7.6 \times 10^{12}$
- Ans.  $K_c = 2.18 \times 10^{26}$
- $E^0 = 0.7826\text{V}$
- Ans.  $K_w \approx 10^{-14}$
- 1303.14 kJ/mol
- Ans. 3.86
- Ans. (3)
- Ans. 0.0295 V
- Ans. pH = 4
- Ans.  $E = 0.059$
- Ans.  $E = 0.41\text{ Volt}$
- Ans. (a)  $6.02 \times 10^{22}$  electrons lost,  
 (c) (b)  $1.80 \times 10^{23}$  electrons gained
- (b)  $1.89 \times 10^{22}$  electrons gained,
- Ans. (a) 0.75 F, (b) 0.69 F, (c) 1.1 F
- Ans. (i) 54 gm, (ii) 16.35 gm
- Ans. 0.112 litre
- Ans. (i) 2.17 gm ; (ii) 1336.15 sec
- Ans.  $1.023 \times 10^5$  sec
- Ans. 115800C, 347.40 kJ
- Ans. 44.77 gm, 12.54 litre
- Ans. Rs. 0.75 x
- Ans.  $A = 114$ ,  $Q = 5926\text{C}$
- Ans. 60 %
- Ans. 1.83g
- Ans. 2M
- Ans. (i) 250 mho  $\text{cm}^2 \text{mol}^{-1}$ ,  
 (ii) 125 mho  $\text{cm}^2 \text{equivalent}^{-1}$
- Ans. 440 S  $\text{cm}^2 \text{equivalent}^{-1}$
- Ans. 0.00040 S  $\text{cm}^{-1}$  ; 2500 ohm cm
- Ans. (i)  $6.25 \times 10^5$  ohm,  
 (ii)  $1.6 \times 10^{-6}$  amp
- Ans. 0.0125 mho  $\text{g equiv}^{-1} \text{m}^2$ ,  $1.25 \times 10^{-3}$  mho  $\text{cm}^{-1}$
- Ans. 0.8
- Ans.  $10^{-10}$  mole<sup>2</sup> |litre<sup>2</sup>
- Ans.  $8.60 \times 10^{-4}$  gm|litre
- Ans.  $510 \times 10^{-4}$  mho  $\text{cm}^2 \text{mol}^{-1}$
- Ans. (i) 400 S  $\text{cm}^2 \text{mol}^{-1}$  (ii) 12 %
- Ans. (i) 7 (ii)  $1 \times 10^{-14}$
- Ans.  $\alpha = 0.5$ ,  $k = 10^{-3}$

## EXERCISE # S-II

- |   |  |
|---|--|
| 1. Ans. $-0.46$ V                                   | 2. Ans. (ii). $1.27$ V, (iii) $245.1$ kJ |
| 3. Ans. $E^0 = -0.22$ V                             | 4. Ans. $K_{sp} = 1.10 \times 10^{-16}$  |
| 5. Ans. $[\text{Br}^-] : [\text{Cl}^-] = 1 : 200$   | 6. Ans. $-0.037$ V                       |
| 7. Ans. $1.54 \times 10^{-5}$                       | 8. Ans. $K = 10^{268}$                   |
| 9. Ans. $9.70$ gm                                   | 10. Ans. $42.20$ %                       |
| 11. Ans. $1.86 \times 10^6$ year                    | 12. Ans. $0.145$                         |
| 13. Ans. $0.04$ metre                               | 14. Ans. $0.19$ gm litre                 |
| 15. Ans. $n = 2$                                    | 16. Ans. $0.52$ V, $0.61$ V              |
| 17. Ans. $0.0295$ V                                 | 18. Ans. $t = 193$ sec                   |
| 19. Ans. Final weight = $9.60$ g, $0.01$ Eq of acid | 20. Ans. $t = 93.65$ sec.                |

## EXERCISE # O-I

- |             |             |             |             |
|-------------|-------------|-------------|-------------|
| 1. Ans.(B)  | 2. Ans.(C)  | 3. Ans.(A)  | 4. Ans.(C)  |
| 5. Ans.(D)  | 6. Ans.(C)  | 7. Ans.(A)  | 8. Ans.(C)  |
| 9. Ans.(A)  | 10. Ans.(A) | 11. Ans.(C) | 12. Ans.(C) |
| 13. Ans.(A) | 14. Ans.(D) | 15. Ans.(D) | 16. Ans.(A) |
| 17. Ans.(B) | 18. Ans.(D) | 19. Ans.(C) | 20. Ans.(A) |
| 21. Ans.(A) | 22. Ans.(D) | 23. Ans.(B) | 24. Ans.(A) |
| 25. Ans.(C) | 26. Ans.(C) | 27. Ans.(A) | 28. Ans.(B) |
| 29. Ans.(A) | 30. Ans.(D) | 31. Ans.(C) | 32. Ans.(B) |
| 33. Ans.(C) | 34. Ans.(A) | 35. Ans.(D) | 36. Ans.(D) |
| 37. Ans.(C) | 38. Ans.(A) | 39. Ans.(C) | 40. Ans.(C) |
| 41. Ans.(B) | 42. Ans.(C) | 43. Ans.(B) | 44. Ans.(D) |
| 45. Ans.(C) | 46. Ans.(C) | 47. Ans.(C) | 48. Ans.(D) |
| 49. Ans.(C) | 50. Ans.(A) | 51. Ans.(B) | 52. Ans.(C) |
| 53. Ans.(A) |             |             |             |

## EXERCISE # O-II

- |                |              |  |              |
|----------------|--------------|--|--------------|
| 1. Ans. B      | 2. Ans. D    | 3. Ans. A                                    | 4. Ans. B    |
| 5. Ans. B      | 6. Ans. A    | 7. Ans. A                                    | 8. Ans. B    |
| 9. Ans. D      | 10. Ans. C   | 11. Ans. A                                   | 12. Ans. C   |
| 13. Ans. B     | 14. Ans. D   | 15. Ans. D                                   | 16. Ans. B   |
| 17. Ans. C     | 18. Ans. C   | 19. Ans. B                                   | 20. Ans. C,D |
| 21. Ans. B,C,D | 22. Ans. A,B | 23. Ans. B,C                                 | 24. Ans. A,D |
| 25. Ans. A     | 26. Ans. A   | 27. Ans. D                                   | 28. Ans. C   |
| 29. Ans. A     | 30. Ans. C   | 31. Ans. (A) P, Q (B) P, Q (C) Q, R, (D) P,S |              |
| 32. Ans.(C)    |              |  |              |

**EXERCISE # J-MAINS**

- 
- |                        |                        |              |                          |
|------------------------|------------------------|--------------|--------------------------|
| 1. Ans.(2)             | 2. Ans.(1)             | 3. Ans.(1)   | 4. Ans.(4)               |
| 5. Ans. (1)            | 6. Ans.(3)             | 7. Ans. (3)  | 8. Ans. (2)              |
| 9. Ans.(4)             | 10. Ans.(2)            | 11. Ans. (1) | 12. Ans. (1)             |
| 13. Ans.(3)            | 14. Ans.(1)            | 15. Ans.(2)  | 16. Ans.(2)              |
| 17. Ans.(4)            | 18. Ans.(2)            | 19. Ans.(1)  | 20. Ans.(2)              |
| 21. Ans.(1)            | 22. Ans.(2)            | 23. Ans.(2)  | 24. Ans.(1)              |
| 25. Ans.(3)            | 26. Ans.(1)            | 27. Ans.(1)  | 28. Ans.(−0.93 to −0.94) |
| 29. Ans.(2.13 to 2.17) | 30. Ans.(5.66 to 5.68) | 31. Ans.(1)  |                          |

**EXERCISE # J-ADVANCED**

- 
- |                  |              |              |             |
|------------------|--------------|--------------|-------------|
| 1. Ans.(D)       | 2. Ans.(D)   | 3. Ans.(D)   | 4. Ans.(B)  |
| 5. Ans.(D)       | 6. Ans.(A)   | 7. Ans.(A,B) | 8. Ans. (3) |
| 9. Ans. (4)      | 10. Ans.(D)  | 11. Ans.(6)  | 12. Ans.(B) |
| 13. Ans.(−11.62) | 14. Ans.(10) |              |             |



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PHYSICAL

**CHEMISTRY**



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## 01

## IDEAL GAS

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## IDEAL GAS

### 1. INTRODUCTION

Matter, as we know, broadly exist in three states - solid, liquid and gas.

There are always two opposite tendencies between particles of matter which determine the state of matter :

- Intermolecular forces.
- The molecular motion / random motion (energy of particles)

Intermolecular forces are the forces of attraction and repulsion between atoms or molecules. Attractive intermolecular forces are known as *vander Waals forces*. These are dispersion forces, dipole-dipole forces & dipole induced forces. When two molecules are brought very close, they will exert repulsive forces. Magnitude of the repulsion rises very rapidly as the distance separating the molecules decreases. This is the reason that liquid & solids are hard to compress. In these states, molecules are already in close contact, therefore they resist further compression (in that case repulsive interaction will increase) Thermal energy is the energy of a body arising from motion of its atoms or molecules. It is directly proportional to the temperature of the substance. It is the measure of average kinetic energy of the particles of the matter and is thus responsible for movement of particles. This movement of particles is called *thermal motion*. Intermolecular forces tend to keep the molecules together but thermal energy of the molecules tends to keep them apart. Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules.

### 2. GENERAL CHARACTERISTICS OF SOLID, LIQUID & GAS

Each physical state of matter possesses characteristics properties of its own. For example,

#### ❖ Solids :

All solids show the following characteristics :

- (i) Solids are rigid and incompressible.
- (ii) Solids have fixed shape and definite volume.
- (iii) Solids have their melting and boiling points above room temperature.
- (iv) Density of solid is high.

#### ❖ Liquids :

All liquids show the following characteristics :

- (i) Liquids are almost incompressible but less incompressible than solids.
- (ii) Liquids have fixed volume but no fixed shape.
- (iii) Liquids have their melting points below room temperature and boiling points above room temperature, under normal conditions.
- (iv) Density of liquids is lower than that of solids but much higher than that of gases.

#### ❖ Gases :

All gases show the following characteristics :

- (i) Gases are highly compressible, i.e. gases can be compressed easily by applying pressure.

- (ii) Gases have no fixed volume and shape. Gases fill the container of any size and shape completely.
- (iii) Gases can diffuse into each other rapidly.
- (iv) Gases have their melting and boiling points both below room temperature.
- (v) Gases generally have low density.

### 3. MEASURABLE PROPERTIES OF GASES

The characteristics of gases are described fully in terms of four parameters or measurable properties :

- (I) Amount of the gas (i.e., mass or number of moles).
- (II) Volume (V) of the gas.
- (III) Temperature (T)
- (IV) Pressure (P)

#### I. Amount of the gas :

- (i) The mass of a gas can be determined by weighing the container in which the gas is enclosed and again weighing the container after removing the gas. The difference between the two masses gives the mass of the gas.

$$\text{Mass of gas (m)} = \text{Mass of filled container} - \text{mass of empty container}$$

- (ii) The mass of the gas is related to the number of moles of the gas as

$$\text{Moles of gas (n)} = \text{Mass in grams} / \text{Molar mass} = m/M$$

- (iii) Mass is expressed in gram or kg.

#### II. Gas volume :

- (i) Since gases occupy the entire space available to them, the measurement of volume of a gas only requires a measurement of the container confining the gas.
- (ii) Volume is expressed in litres (L), millilitres (mL) or cubic centimeters (cm<sup>3</sup>) or cubic meters (m<sup>3</sup>).
- (iii) 1 L = 1000 mL ; 1 L = 1 dm<sup>3</sup> = 10<sup>-3</sup> m<sup>3</sup>  
1 m<sup>3</sup> = 10<sup>3</sup> dm<sup>3</sup> = 10<sup>6</sup> cm<sup>3</sup> = 10<sup>6</sup> mL = 10<sup>3</sup> L  
1 mL or 1 cc = 1 cm<sup>3</sup>

#### III. Temperature :

- (i) Gases expand on increasing the temperature.
- (ii) Temperature is measured in degree centigrade (°C) or Celsius degree with the help of thermometers. Temperature is also measured in degree Fahrenheit (°F).
- (iii) S.I. unit of temperature is kelvin (K) or absolute degree  
K = °C + 273
- (iv) Relation between °F and °C is  
°C/5 = (°F - 32) / 9

#### IV. Pressure :

Force exerted by the gas per unit area of the walls of the container in all directions. Thus,

$$\text{Pressure (P)} = \text{Force(F)} / \text{Area(A)}$$

#### ❖ Atmospheric pressure :

The pressure exerted by atmosphere on earth's surface at sea level is called atmospheric pressure. Generally its unit is atm.

$$\text{Pressure(P)} = \text{Force(F)} / \text{Area(A)}$$

$$\begin{aligned}
 &= \text{Mass}(m) \times \text{Acceleration}(g) / \text{Area}(a) \\
 &= \text{Volume} \times \text{density} \times \text{Acceleration}(g) / \text{Area}(a) \\
 &= \text{Area}(a) \times \text{height}(h) \times \text{density}(\rho) \times \text{Acceleration}(g) / \text{Area}(a)
 \end{aligned}$$

$$\text{Pressure}(P) = h\rho g$$

where  $h$  = Height of mercury column in the barometer.

$\rho$  = Density of mercury.

$g$  = Acceleration due to gravity.

Pressure does not depend on the cross section of tube, but only on the vertical height of the Hg. If area is doubled, volume also gets doubled and mass will also get doubled. Now it will rest on twice area but pressure exerted remains same.

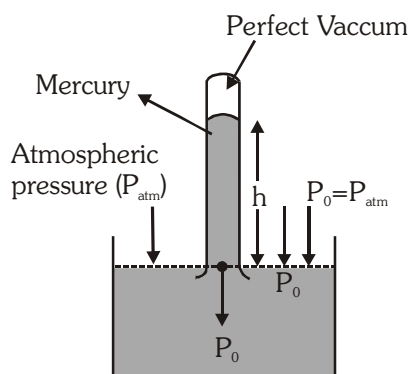
$$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N/m}^2 = 1.013 \times 10^5 \text{ Pa}$$

$$1 \text{ atm} = 76 \text{ cm of Hg} = 760 \text{ mm of Hg} = 760 \text{ torr}$$

### □ PRESSURE MEASURING DEVICES

Generally, the instruments used for the calculation of pressure of a gas are **barometer** and **manometer**.

- (i) **Barometer** : A barometer is an instrument that is used for the measurement of atmospheric pressure. The construction of the barometer is as follows -



A thin narrow calibrated capillary tube is filled up to the brim, with a liquid such as mercury, and is inverted into a trough filled with the same fluid. Now depending on the external atmospheric pressure, the level of the mercury inside the tube will adjust itself, the reading of which can be monitored. When the mercury column inside the capillary comes to rest, then the net forces on the column should be balanced.

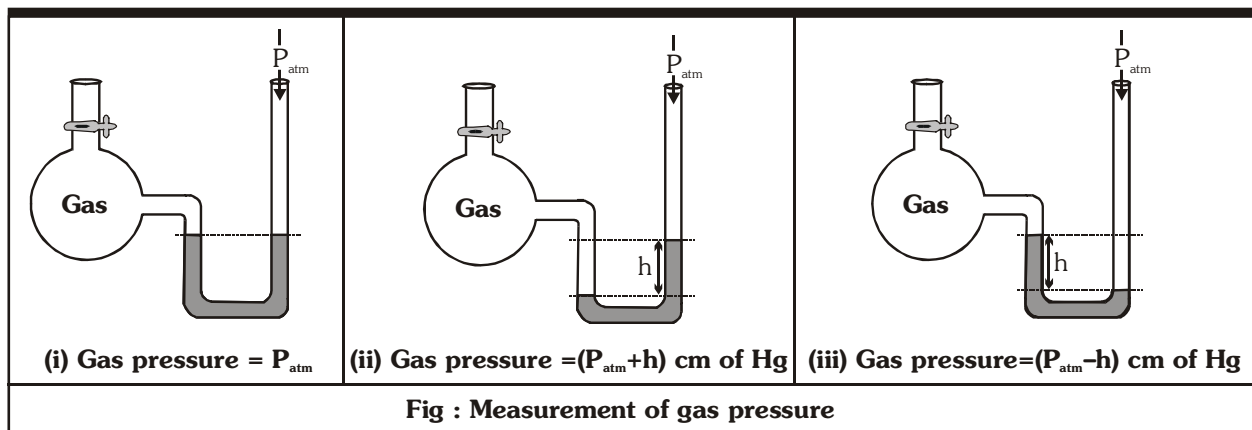
$$\Rightarrow P_0 \times A = \rho A \times gh$$

$$\Rightarrow \boxed{P_0 = \rho gh} \quad ; \text{ where } \rho \text{ is the density of the fluid.}$$

- (ii) **Manometer** :

(a) **Open end manometer** :

It consists of a U-shaped tube partially filled with mercury. One limb of the tube is shorter than the other. The shorter limb is connected to the vessel containing the gas whereas the longer limb is open as shown in fig. The mercury in the longer tube is subjected to the atmospheric pressure while mercury in the shorter tube is subjected to the pressure of the gas.



Where  $P_{\text{atm}} = 76$  cm of Hg and  $h =$  Height in cm of Hg

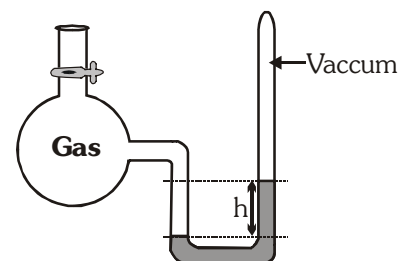
There are three possibilities as described below :

- (i) If the level of Hg in the two limbs is same, then gas pressure = atmospheric pressure ( $P_{\text{atm}}$ ).
- (ii) If the level of Hg in the longer limbs is higher, gas pressure
- $$= P_{\text{atm}} + (\text{difference between the two levels})$$
- $$= P_{\text{atm}} + h.$$
- (iii) If the level of Hg in the shorter limb is higher, then gas pressure
- $$= P_{\text{atm}} - (\text{difference between the two levels})$$
- $$= P_{\text{atm}} - h.$$

**(b) Closed end manometer :**

This is generally used to measure low gas pressure.

It also consists of U-tube with one limb shorter than the other and partially filled with mercury as shown in fig. The space above mercury on the closed end is completely evacuated. The shorter limb is connected to the vessel containing gas. The gas exerts pressure on the mercury in the shorter limb and forces its level down.



**Closed end manometer**

**Gas pressure = [Difference in the Hg level in two limbs]**

**Ex.1 Why mercury is used in the barometer tube?**

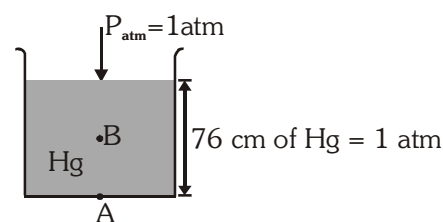
**Sol.** Mercury, a liquid with very high density, is normally used in the barometer because it does not stick to the surface of the glass tube. Mercury is also non-volatile at room temperature. Therefore, there are hardly any vapours of mercury above the liquid column and their pressure, if any, can be neglected. Due to high density of mercury, height of mercury column will be small and can be easily measured.

**Ex.2** An open tank is filled with Hg upto a height of 76cm.

Find the pressure at the

- (a) Bottom (A) of the tank  
 (b) Middle (B) of the tank.

(If atmospheric pressure is 1 atm)





Sol. (a) At bottom,

$$P_A = P_{atm} + P_{Hg}$$

$$= 1 + 1 = 2 \text{ atm}$$

(b) At middle,

$$P_B = P_{atm} + P_{Hg}$$

$$= 1 + \frac{1}{2} = 1.5 \text{ atm}$$

Ex.3 Find the height of water upto which water must be filled to create the same pressure at the bottom, as in above problem.

Given that  $d_w = 1 \text{ gm/cm}^3$ ,  $d_{Hg} = 13.6 \text{ gm/cm}^3$ ,  $h_{Hg} = 76 \text{ cm}$

Sol.  $P_{water} = P_{Hg}$

$$h_w d_w g = h_{Hg} d_{Hg} g$$

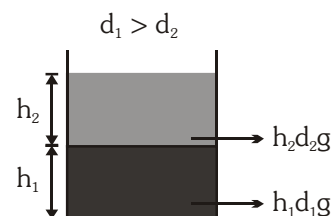
$$h_w d_w = h_{Hg} d_{Hg}$$

$$h_w \times 1 \text{ g/cm}^3 = 76 \text{ cm} \times 13.6 \text{ g/cm}^3$$

$$h_w = 1033.6 \text{ cm}$$

Ex.4 What will be the pressure if two immiscible fluid is filled according to given diagram.

- (a) Find the pressure at the bottom of tank.
- (b) Find the pressure at the middle point of bottom layer.

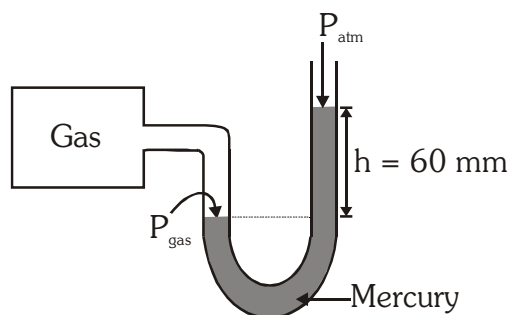


Sol. (a)  $P_{atm} + h_2 d_2 g + h_1 d_1 g$ ;

(b)  $P_{atm} + h_2 d_2 g + \frac{h_1}{2} d_1 g$

Ex.5 Find the pressure of the gas inside a container if the open manometer attached to the container shows a difference of 60 mm.

Sol. Case-I :  $P_{atm} < P_{gas}$

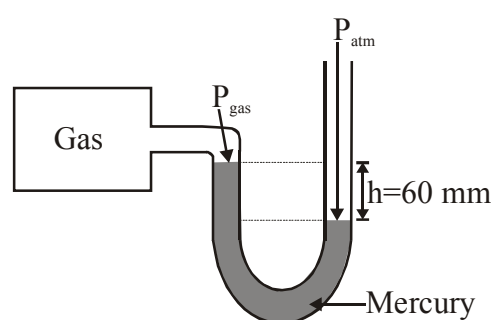


$$P_{gas} = P_{atm} + 60 \text{ mm}$$

$$= 760 \text{ mm} + 60 \text{ mm}$$

$$= 820 \text{ mm of Hg}$$

Case-II :  $P_{atm} > P_{gas}$



$$P_{atm} = P_{gas} + 60 \text{ mm}$$

$$760 \text{ mm} = P_{gas} + 60$$

$$P_{gas} = 700 \text{ mm}$$

#### 4. GAS LAWS

The behaviour of the gases is governed by same general laws, which were discovered as a result of their experimental studies. These laws are relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and mass are very important because relationships between these variables describe state of the gas.

The first reliable measurement on properties of gases was made by Anglo-Irish scientist Robert Boyle in 1662. The law which he formulated is known as **Boyle's Law**. Later on attempts to fly in air with the help of hot air balloons motivated Jaccques Charles and Joseph Lewis Gay Lussac to discover additional gas laws. Contribution from *Avogadro* and others provided lot of information about gaseous state.

##### 4.1 Boyle's Law :

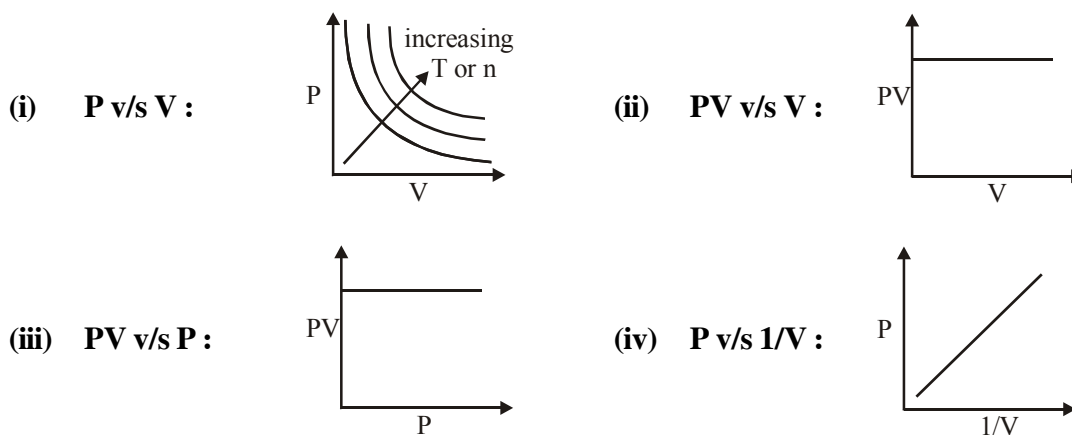
For a fixed amount of gas at constant temperature, the volume occupied by the gas is inversely proportional to the pressure applied on the gas or pressure of the gas.

$$\Rightarrow V \propto \frac{1}{P}$$

$$\Rightarrow \text{Hence, } PV = \text{const. (K)}$$

$$\Rightarrow \boxed{P_1V_1 = P_2V_2}$$

##### ❖ Graphical representation of Boyle's law :



##### 4.2. Charle's Law :

For a fixed amount of gas at constant pressure, volume occupied by the gas is directly proportional to temperature of the gas on absolute scale of temperature.

$$\Rightarrow V \propto T$$

$$\Rightarrow V = KT$$

$$\boxed{\frac{V}{T} = \text{constant (K)}}$$

T = Temperature on absolute scale, kelvin scale or ideal gas scale.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V = V_0 + bt$$

$$V = b'T$$

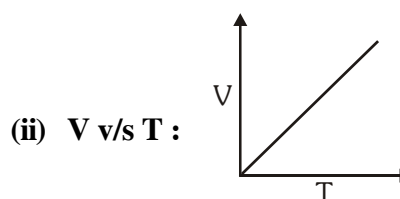
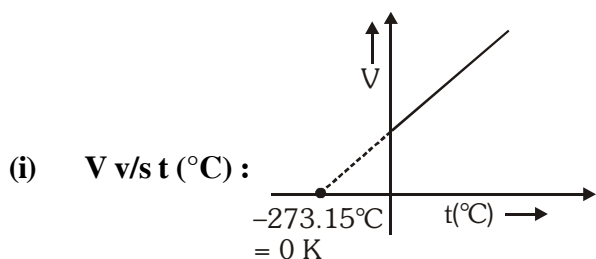
t = temperature on centigrade scale.

T = absolute temperature (K)

$V_0$  = volume of gas at  $0^\circ\text{C}$ .

b, b' = constants

❖ **Graphical representation of Charle's Law :**



❖ **Important Points :**

- Since volume is proportional to absolute temperature, the volume of a gas should be theoretically zero at absolute zero temperature.
- In fact, no substance exists as gas at a temperature near absolute zero, though the straight line plots can be interpolated to zero volume. Absolute zero can never be attained practically though it can be approached only.
- By considering  $-273.15^\circ\text{C}$  as the lowest approachable limit, Kelvin developed temperature scale which is known as absolute scale.

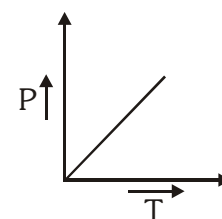
**4.3. Gay-lussac's law :**

For a fixed amount of gas at constant volume, pressure of the gas is directly proportional to temperature of the gas on absolute scale of temperature.

$$\Rightarrow P \propto T$$

$$\frac{P}{T} = \text{constant (K)}$$

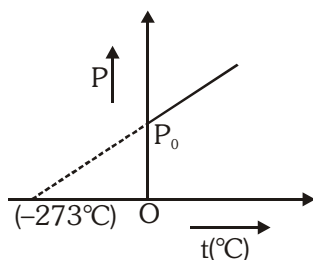
$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ Temperature on absolute scale, kelvin scale or ideal gas scale.}$$



**Note:** Originally, the law was developed on the centigrade scale, where it was found that pressure is a

linear function of temperature  $\Rightarrow P = P_0 + bt$ ,

where 'b' is a constant and ' $P_0$ ' is pressure at zero degree centigrade.



But for kelvin scale :  $P = b''T$  where T is in K.

#### 4.4. Avogadro's law :

Equal volumes of all the gases under similar conditions of temperature and pressure contains equal number of molecules or moles of molecules (not atoms).

$$V \propto N \quad (\text{Temperature and pressure constant})$$

$$V \propto n \quad (\text{Temperature and pressure constant})$$

Where, N = number of molecules, n = number of moles of molecules

$$\boxed{\frac{V_1}{N_1} = \frac{V_2}{N_2} \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}}$$

Since volume of a gas is directly proportional to the number of moles; one mole of each gas at standard temperature and pressure (STP) will have same volume.

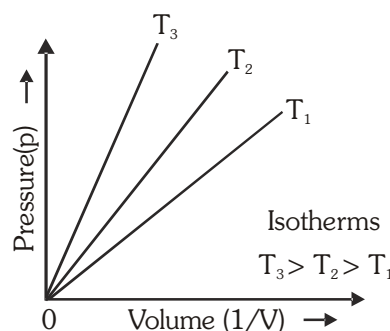
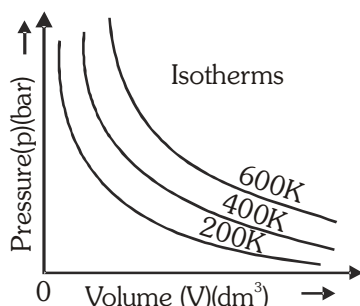
Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (i.e., exactly  $10^5$  pascal) pressure. At STP, molar volume of an ideal gas or a combination of ideal gases is  $22.71098 \text{ L mol}^{-1}$ .

#### Molar volume in litres per mole of some gases at 273.15 K and 1 bar (STP).

Argon	22.37
Carbon dioxide	22.54
Dinitrogen	22.69
Dioxygen	22.69
Dihydrogen	22.72
Ideal gas	22.71

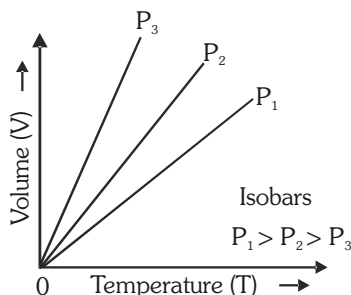
**Ex.6** What is a pressure-volume isotherm ?

**Sol.** Graph between P & V at constant temperature is called *PV-isotherm*.



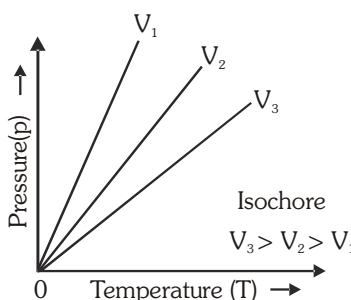
**Ex.7** What is Isobar ?

**Sol.** Graph plotted at constant pressure is called isobar. Graph between V & T at constant pressure is called VT-isobar.



**Ex.8** What is Isochore ?

**Sol.** Graph plotted at constant volume is called isochore. Graph between P & T at constant volume is called PT-isochore.



## 5. IDEAL GAS EQUATION

A single equation which is combination of Boyle's, Charle's & Avogadro's Law is known as **Ideal gas equation**. Or we can say a single equation which describe the simultaneous effects of the change in temperature & pressure on volume of the given amount of the gas is called the **Ideal gas equation**.

$$PV = nRT$$

According to Boyle's law,  $V \propto \frac{1}{P}$  (at constant T and n)

According to Charle's law,  $V \propto T$  (at constant P and n)

According to Avogadro's law,  $V \propto n$  (at constant T and P)

According to the three laws,  $V \propto \frac{nT}{P}$  or  $PV \propto nT$

or  $PV = nRT$  [Equation of state or combined gas law]

Where R is a constant called **Universal gas constant**, which does not depend on variables (P, V, n, T) and nature of gas.

- Molar volume is the volume of 1 mole of gas.

$$\text{Molar volume } (V_m) = \frac{\text{Volume}}{\text{mole}}$$

$$PV_m = RT$$

Volume of 1 mole of an ideal gas under STP conditions (273.15 K and 1 bar pressure) is  $22.7 \text{ L mol}^{-1}$ .

• **Dimension of R :**

$$R = \frac{PV}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{Mole} \times \text{Temperature}} = \frac{(\text{Force} / \text{Area}) \times (\text{Area} \times \text{Length})}{\text{Mole} \times \text{Temperature (K)}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Mole} \times \text{Temperature (K)}} = \frac{\text{Work or energy}}{\text{Mole} \times \text{Temperature (K)}}$$

• **Physical significance of R :**

The dimensions of R are energy per mole per kelvin and hence it represents the amount of work (or energy) that can be obtained from one mole of a gas when its temperature is raised by 1 K isobarically.

• **Units of R :**

(i) In lit-atm  $R = \frac{1 \text{ atm} \times 22.4 \text{ lit.}}{1 \text{ mol} \times 273 \text{ K}} = \mathbf{0.0821 \text{ lit-atm mol}^{-1} \text{K}^{-1}}$

(ii) In C.G.S system  $R = \frac{1 \times 76 \times 13.6 \times 980 \text{ dyne cm}^{-2} \times 22400 \text{ cm}^3}{1 \text{ mol} \times 273 \text{ K}}$   
 $= \mathbf{8.314 \times 10^7 \text{ erg mole}^{-1} \text{K}^{-1}}$ .

(iii) In M.K.S.system  $R = \mathbf{8.314 \text{ Joule mole}^{-1} \text{K}^{-1}}$ .  $[10^7 \text{ erg} = 1 \text{ joule}]$   
 (SI units)

(iv) In calories,  $R = \frac{8.314 \times 10^7 \text{ erg mole}^{-1} \text{K}^{-1}}{4.184 \times 10^7 \text{ erg}}$   
 $= 1.987 \approx \mathbf{2 \text{ calorie mol}^{-1} \text{K}^{-1}}$ .

**Ex.9** A sample of gas occupies  $100 \text{ dm}^3$  at 1 bar pressure and at  $T^\circ \text{C}$ . If the volume of the gas is reduced to  $5 \text{ dm}^3$  at the same temperature, what additional pressure must be applied ?

**Sol.** From the given data :

$$P_1 = 1 \text{ bar} \quad P_2 = ?$$

$$V_1 = 100 \text{ dm}^3 \quad V_2 = 5 \text{ dm}^3$$

Since the temperature is constant, Boyle's law can be applied

$$P_1 V_1 = P_2 V_2 = P_2 = \frac{P_1 V_1}{V_2}$$

$$P_2 = \frac{(1 \text{ bar}) \times (100 \text{ dm}^3)}{(5 \text{ dm}^3)} = 20 \text{ bar}$$

$\therefore$  Additional pressure applied =  $20 - 1 = \mathbf{19 \text{ bar}}$

**Ex.10** A certain amount of a gas at  $27^\circ \text{C}$  and 1 bar pressure occupies a volume of  $25 \text{ m}^3$ . If the pressure is kept constant and the temperature is raised to  $77^\circ \text{C}$ , what will be the volume of the gas ?

**Sol.** From the available data :

$$V_1 = 25 \text{ m}^3 \quad T_1 = 27 + 273 = 300 \text{ K}$$

$$V_2 = ? \quad T_2 = 77 + 273 = 350 \text{ K}$$

Since the pressure of the gas is constant, Charles law is applicable

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

$$\text{or } V_2 = \frac{V_1 \times T_2}{T_1}$$

$$V_2 = \frac{(25 \text{ m}^3) \times (350 \text{ K})}{(300 \text{ K})} = 29.17 \text{ m}^3$$

**Ex.11** The density of a gas is found to be  $1.56 \text{ g dm}^{-3}$  at  $0.98 \text{ bar}$  pressure and  $65^\circ\text{C}$ . Calculate the molar mass of the gas.

**Use  $R = 0.083 \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$**

**Sol.** We know that :

$$M = \frac{dRT}{P} = \frac{(1.56 \text{ g dm}^{-3}) \times (0.083 \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}) \times 338 \text{ K}}{(0.98 \text{ bar})} = 44.66 \text{ g mol}^{-1}$$

**Ex.12** A glass bulb of  $2 \text{ L}$  capacity is filled by helium gas at  $10 \text{ atm}$  pressure. Due to a leakage the gas leaks out. What is the volume of gas leaked if the final pressure in container is  $1 \text{ atm}$ .

**Sol.**  $P_1 \times 2 \text{ L} = P_2 \times V$

$$\Rightarrow 10 \times 2 = 1 \times V$$

$$\Rightarrow 20 = V$$

$$V = V' + 2 \text{ L}$$

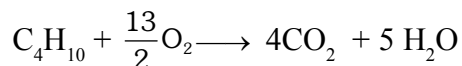
$$20 = V' + 2 \text{ L}$$

$$V' = 18 \text{ L}$$

$\Rightarrow$  total volume of gas leaked

**Ex.13** LPG is a mixture of n-butane & iso-butane. What is the volume of oxygen needed to burn  $1 \text{ kg}$  of LPG at  $1 \text{ atm}$ ,  $273 \text{ K}$  ?

**Sol.** During the burning of LPG following reaction takes place -



Now, for complete combustion of  $1 \text{ mole}$  of LPG  $\longrightarrow \frac{13}{2}$  moles of  $\text{O}_2$  are required.

$\therefore$  for  $\frac{1000}{58}$  moles of LPG  $\longrightarrow \frac{13}{2} \times \frac{1000}{58}$  moles of  $\text{O}_2$  are required.

Thus, the volume of oxygen needed to burn  $1 \text{ kg}$  of LPG at  $1 \text{ atm}$  &  $273 \text{ K}$  would be

$$\text{Vol. of O}_2 = \text{Moles of O}_2 \times 22.4 \text{ L} = \frac{13}{2} \times \frac{1000}{58} \times 22.4 = 2510 \text{ L}$$

**Ex.14** The best vacuum so far attained in laboratory is  $10^{-10}$  mm of Hg. What is the number of molecules of gas remain per  $\text{cm}^3$  at  $20^\circ\text{C}$  in this vacuum ?

**Sol.** Given conditions -

$$P = 10^{-10} \text{ mmHg} = \frac{10^{-10}}{760} \text{ atm} ; V = 1 \text{ cm}^3 = \frac{1}{1000} \text{ L} ; T = 20^\circ\text{C} = 293 \text{ K}$$

No. of molecules,  $N = ?$

Now, applying

$$PV = nRT$$

$$\therefore \text{number of molecules per cm}^3, N = \frac{N_A \times P \times V}{RT}$$

$$\Rightarrow N = \frac{6.023 \times 10^{23} \times (10^{-10}/760) \times (1/1000)}{(0.0821)(293)}$$

$$N = 3.29 \times 10^6 \text{ molecules}$$

## 6. DALTON'S LAW OF PARTIAL PRESSURES

### 6.1 Partial pressure :

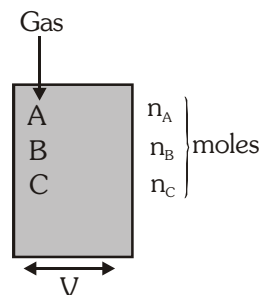
In a mixture of non-reacting gases, partial pressure of any component gas is defined as the pressure exerted by the individual gas if whole of the volume of mixture had been occupied by this component only.

Partial pressure of component gases are -

$$P_A = \frac{n_A RT}{V} = \text{partial pressure of A}$$

$$P_B = \frac{n_B RT}{V} = \text{partial pressure of B}$$

$$P_C = \frac{n_C RT}{V} = \text{partial pressure of C}$$



### 6.2 Dalton's Law :

Dalton's law of partial pressure states "at a given temperature, the total pressure exerted by two or more non-reacting gases occupying a definite volume is equal to the sum of the partial pressures of the component gases."

$$P_{\text{Total}} = p_1 + p_2 + p_3 + \dots \text{ (At constant V and T)}$$

$$= \left( \frac{n_1}{V} + \frac{n_2}{V} + \frac{n_3}{V} + \dots \right) RT = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V} = \frac{nRT}{V}$$

Where  $n = n_1 + n_2 + n_3 + \dots = \text{Total moles}$ ,  $V = \text{Total volume}$

$$P_{\text{Total}} = \sum p_i = \frac{RT}{V} \sum n_i$$



- Dalton's law of partial pressure is applicable only to non-reacting gases.

If the two non-reacting gases A and B having  $n_A$  and  $n_B$  number of moles respectively are filled in a vessel of volume  $V$  at temperature  $T$ , then

$$\frac{p_A}{P} = \frac{n_A RT/V}{(n_A + n_B)RT/V} = \frac{n_A}{n_A + n_B} = x_A \text{ (mole fraction of A)}$$

$$p_A = x_A \times P, \quad \text{Similarly } p_B = x_B \times P$$

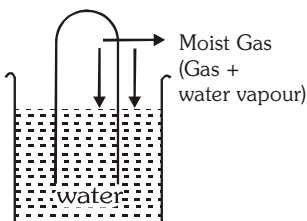
**Partial pressure of a component = Mole fraction  $\times$  total pressure.**

- 6.3 It has been observed that gases are generally collected over water and therefore are moist.

$$P_{\text{dry gas}} = P_{\text{moist gas}} - P_{\text{water vapour}}$$

**or Pressure of dry gas = Pressure of moist gas – aqueous tension**

The pressure exerted by water vapour is constant when it is in equilibrium with liquid water at a particular temperature. It is called vapour pressure of water or **aqueous tension**, which varies with the temperature and becomes 760 mm at 100°C.



- 6.4 Relative Humidity (RH) =  $\frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water (aq.tension)}}$

## 7. AMAGAT'S LAW OF PARTIAL VOLUME

### 7.1 Partial Volume :

Partial volume of any component is defined as the volume occupied by that particular component when it is kept at same total pressure and temperature as of the mixture.

### 7.2 Amagat's law :

According to this law at constant temperature and pressure, the total volume of mixture of non-reacting gases is equal to the sum of partial volumes of each component present in mixture.

$$V_T = V_1 + V_2 + V_3 + \dots$$

Let us consider three non-reacting gases A, B and C are present in a container which have no. of moles  $n_A$ ,  $n_B$  and  $n_C$  respectively. For each gas partial volume is

$$V_A = n_A \left( \frac{RT}{P} \right) = \text{partial volume of A}$$

$$V_B = n_B \left( \frac{RT}{P} \right) = \text{partial volume of B}$$

$$V_C = n_C \left( \frac{RT}{P} \right) = \text{partial volume of C}$$

- **Total volume :**

$$V_T = V_A + V_B + V_C = (n_A + n_B + n_C) \left( \frac{RT}{P} \right) = n_T \left( \frac{RT}{P} \right)$$

$$\frac{V_A}{V_T} = \frac{n_A}{n_T} = x_A \quad \text{(Mole fraction of gas A)}$$

$$\frac{V_B}{V_T} = \frac{n_B}{n_T} = x_B \quad (\text{Mole fraction of gas B})$$

$$\frac{V_C}{V_T} = \frac{n_C}{n_T} = x_C \quad (\text{Mole fraction of gas C})$$

$\therefore$  **Partial volume of a gas = Mole fraction  $\times$  Total volume**

**Ex.15** (a) Find the total pressure and partial pressure of each component if a container of volume 8.21 lit. contains 2 moles of A and 3 mole of B at 300K.

(b) What will be the final pressure and partial pressure of each component if 5 moles of C is also added to the container at same temperature.

**Sol.** (a)  $P_A = \frac{n_A RT}{V} = \frac{2 \times 0.821 \times 300}{8.21} = 6 \text{ atm}$

$$P_B = \frac{n_B RT}{V} = \frac{3 \times 0.821 \times 300}{8.21} = 9 \text{ atm}$$

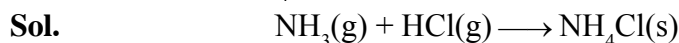
$$\text{Total pressure } P_T = P_A + P_B = 6 + 9 = 15 \text{ atm}$$

(b)  $P_C = \frac{n_C RT}{V} = \frac{5 \times 0.821 \times 300}{8.21} = 15 \text{ atm}$

**Note:** If we add or remove a non reacting gas partial pressure of other gases remains unchanged.

$$P_T = P_A + P_B + P_C = 6 + 9 + 15 = 30 \text{ atm}$$

**Ex.16** 2 moles of  $\text{NH}_3(\text{g})$  and 1 mole of  $\text{HCl}(\text{g})$  are taken in a container of capacity 8.21 lit at 300K to produce  $\text{NH}_4\text{Cl}(\text{s})$ . Find the total pressure after the reaction.



initial        2        1

after rxn     1        0

In this reaction HCl is L.R. so it will be completely consumed. We don't consider pressure due to solid.

$$\therefore P_T = \frac{nRT}{V} = \frac{1 \times 0.821 \times 300}{8.21} = 3 \text{ atm}$$

**Ex.17** A closed container containing  $\text{O}_2$  and some liquid water was found to exert 740 mm pressure at  $27^\circ\text{C}$ .

(a) Then calculate the pressure exerted by  $\text{O}_2$  if aqueous tension at  $27^\circ\text{C}$  is 20 mm.

(b) What will be the final pressure if volume is reduced to half.

(consider volume of liquid water negligible)

(c) What will be the final pressure if volume is doubled.

**Sol.** (a)  $P_T = P_{\text{dry gas}} + P_{\text{aq. tension}}$

$$740 = P_{\text{O}_2} + 20$$

$$P_{\text{O}_2} = 740 - 20 = 720 \text{ mm}$$

(b)  $(P_{O_2} V_{O_2})_{\text{initial}} = (P_{O_2} V_{O_2})_{\text{final}}$  (Boyle's law)

$$720 \times V = P_{O_2} \times \frac{V}{2}$$

$$P_{O_2} = 1440 \text{ mm}$$

$$P_T = P_T = P_{O_2} + P_{aq.}$$

$$= 1440 + 20 = 1460 \text{ mm}$$

(c)  $(P_{O_2} V_{O_2})_{\text{initial}} = (P_{O_2} V_{O_2})_{\text{final}}$

$$720 \times V = P_{O_2} \times 2V$$

$$P_{O_2} = 360 \text{ mm}$$

$$P_T = P_{O_2} + P_{aq.}$$

$$= 360 + 20 = \mathbf{380 \text{ mm}}$$

## 8. PROBLEM RELATED WITH DIFFERENT TYPE OF CONTAINERS

### I. Closed Container :

In this case gas can neither go outside nor it can come inside. So number of moles of gas is always constant.

Closed container can be of following types -

(a) **Closed rigid container** : In this case number of moles constant, volume constant.

At this condition :

Initial		Final
$\frac{P_1}{T_1}$	=	$\frac{P_2}{T_2}$

Example : Gas cylinder

(b) **Closed non rigid container : (fitted with freely movable piston)**

In this kind of container inside pressure is always equal to outside pressure, i.e., atmospheric pressure so that  $n = \text{constant}$ ,  $p = \text{constant}$

**Ex:** Balloon, Water bubble

Initial		Final
$\frac{V_1}{T_1}$	=	$\frac{V_2}{T_2}$

**Ex.18** A balloon is inflated to  $\frac{7}{8}$  of its maximum volume at  $27^\circ\text{C}$  then calculate the minimum temperature above which it will burst.

**Sol.**

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{7V}{8 \times 300} = \frac{V}{T}$$

$$T = 342.8 \text{ K}$$

**Ex.19** A gas cylinder containing cooking gas can withstand a pressure of 18 atm. The pressure gauge of cylinder indicates 12 atm at 27°C. Due to sudden fire in building the temperature start rising at what temperature will the cylinder explode.

**Sol.**  $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\frac{12}{300} = \frac{18}{T}$$

$$T = 450 \text{ K}$$

## II. Tyre tube type container :

In this case temperature is always constant. Initially on adding gas volume of tube will increase and pressure of tube will remain constant until it will gain maximum volume.

$$\therefore V \propto n$$

Initial      Final

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

after attaining maximum volume on adding gas pressure reach to a maximum possible pressure.

Hence at this condition volume constant or temperature constant.

$$V = \text{constant} \quad T = \text{constant}$$

$$P \propto n$$

$$\frac{P_1}{n_1} = \frac{P_2}{n_2}$$

**Ex.20** A tyre tube of maximum volume 8.21 lit. can withstand a pressure of 10 atm. Initially the tube is empty.

(i) Calculate the number of moles required to inflate completely the tube upto a pressure of 1 atm & 300 K temperature.

(ii) Calculate the minimum number of moles required to burst the tyre tube at 300 K.

**Sol.** (i)  $PV = nRT$

$$1 \times 8.21 = n_1 \times 0.0821 \times 300$$

$$n_1 = \frac{1}{3}$$

(ii)  $PV = nRT$

$$10 \times 8.21 = n_2 \times 0.0821 \times 300$$

$$n_2 = \frac{10}{3}$$

**III. Open rigid container :** When air is heated in an open vessel, pressure is always atmospheric pressure i.e., constant and volume is also constant.

At this condition

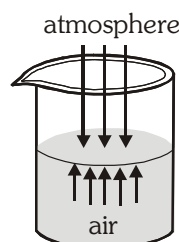
Initial      Final

$$n_1 T_1 = n_2 T_2$$

$n_1$  = initial number of moles

$n_2$  = final number of moles

$$n_{\text{initial}} = n_{\text{final}} + n_{\text{removed}}$$



**Ex.21** An open flask contains air at 27°C. Calculate the temperature at which it should be heated so that

- (a) 1/3<sup>rd</sup> of air measured in the container at 27°C escape out.
- (b) 1/3<sup>rd</sup> of air measured in the container at final temperature escape out.

**Sol.**

(a)  $n_{\text{initial}} - n_{\text{final}} = n_{\text{expelled}}$

$$\frac{PV}{R \times 300} - \frac{PV}{R \times T} = \frac{1}{3} \times \frac{PV}{R \times 300} = \frac{1}{300} - \frac{1}{T} = \frac{1}{900}$$

$$\frac{1}{T} = \frac{1}{300} - \frac{1}{900} = \frac{3-1}{900} = \frac{2}{900} \Rightarrow T = 450 \text{ K} = 177^\circ\text{C}$$

(b)  $n_{\text{initial}} - n_{\text{final}} = n_{\text{expelled}}$

$$\frac{PV}{R \times 300} - \frac{PV}{R \times T} = \frac{1}{3} \times \frac{PV}{R \times T}$$

$$\frac{1}{300} - \frac{1}{T} = \frac{1}{3 \times T}$$

$$\Rightarrow T = 400 \text{ K} = 127^\circ\text{C}$$

**Ex.22** A bulb of unknown volume containing air is heated from 27°C to 227°C at constant pressure. The expelled air is measured at different temperature of determine volume of container. What will be volume of container if -

- (a) 200 ml of air measured at 227°C was expelled.
- (b) 200 ml of air measured at 27°C was expelled.
- (c) 200 ml of air measured at 127°C was expelled.

**Sol.**

(a)  $n_{\text{initial}} - n_{\text{final}} = n_{\text{expelled}}$

$$\frac{PV}{R \times 300} - \frac{PV}{R \times 500} = \frac{P \times 200}{R \times 500}$$

$$\frac{V}{3} - \frac{V}{5} = \frac{200}{5}$$

$$\frac{5V - 3V}{15} = \frac{200}{5}$$

$$\Rightarrow 2V = \frac{200 \times 15}{5} \Rightarrow V = 300 \text{ ml}$$

(b)  $\frac{PV}{R \times 300} - \frac{PV}{R \times 500} = \frac{P \times 200}{R \times 300} = \frac{2V}{15} = \frac{200}{3} \Rightarrow V = \frac{100 \times 15}{2 \times 3} = 500 \text{ ml}$

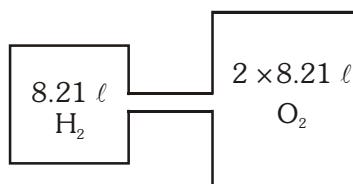
(c)  $\frac{PV}{R \times 300} - \frac{PV}{R \times 500} = \frac{P \times 200}{R \times 400}$

$$\frac{2V}{15} = \frac{200}{4} \Rightarrow V = \frac{200 \times 15}{2 \times 4} = 375 \text{ ml}$$

**IV. Connected Container :**

If containers are connected for substantial time then gases move from one container to another container till partial pressure of each component of mixtures becomes equal in all connected containers (irrespective whether containers have same or different temperature and volumes)

**Ex.23** A container of 8.21 lit. capacity is filled with 1 mole of  $H_2$  at 300 K and it is connected to another container of capacity  $2 \times 8.21$  lit. containing 4 moles of  $O_2$  at 300 K, then find the final pressure & partial pressure of each gas.



**Sol.**  $P_f V_f = n_f RT$   
 $P_f (3 \times 8.21) = 5 \times 0.0821 \times 300$   
 $P_f = 5 \text{ atm}$   
 $P_{H_2} = x_{H_2} P_f = \frac{1}{1+4} \times 5 = 1 \text{ atm}$   
 $P_{O_2} = x_{O_2} P_f = \frac{4}{1+4} \times 5 = 4 \text{ atm}$

**Ex.24** A 10 litre container consist of 1 mole of gas at 300 K. It is connected to another container having volume 40 litre and is initially at 300 K. The nozzle connecting two containers is opened for a long time and once the movement of gas stopped, the larger container was heated to a temperature of 600 K. Calculate

- (a) Moles and pressure of gas in both the containers before heating.  
 (b) Moles and pressure in two containers after heating.  
 (Assume that initially the larger container is completely evacuated.)

**Sol.** (a) Before heating :

$$P_I = P_{II}$$

$$\frac{(1-x)R \times 300}{10} = \frac{x \times R \times 300}{40}$$

$$x = 0.8 \text{ moles}$$

$$n_I = 1 - x = 0.2 \text{ mole}$$

$$n_{II} = x = 0.8 \text{ mole}$$

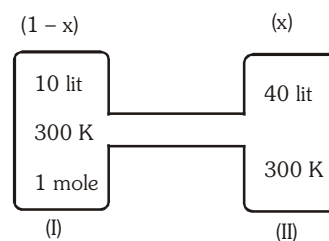
$$\text{Pressure} = \frac{x \times R \times T}{V} = \frac{0.8 \times R \times 300}{40} = 0.492 \text{ atm}$$

(b) After heating :

$$\frac{(1-x_1)R \times 300}{10} = \frac{x_1 \times R \times 600}{40}$$

$$x_1 = 0.67 \text{ moles, Given } T_1 = 600 \text{ K}$$

$$\text{Pressure} = \frac{x_1 \times R \times T_1}{V} = \frac{0.67 \times 0.0821 \times 600}{40} = 0.821 \text{ atm}$$

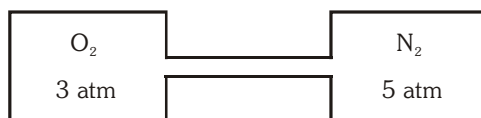


## 9. GRAHAM'S LAW OF DIFFUSION & EFFUSION

### 9.1 Diffusion :

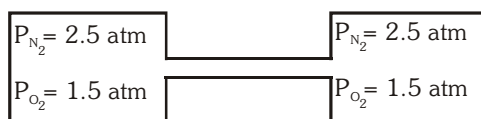
The *diffusion* is the process of gradual mixing of molecules of one gas with molecules of another gas due to their molecular motion (kinetic energy). The diffusion always proceeds from a region of high concentration to a region of lower concentration (or high partial pressure to low partial pressure). For example, when a bottle of perfume is opened at one end of the room, the person sitting at the other end of the room can smell the perfume because of the diffusion process of perfume molecules.

Note : Initially



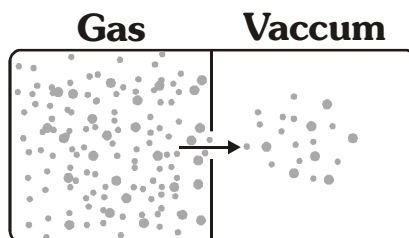
When stop cock is removed flow will be from both sides, N<sub>2</sub> will try to equalise its partial pressure in both the vessels, and so will O<sub>2</sub>.

Finally



### 9.2 Effusion :

The effusion is the process of forcing a gas through a pin hole or small orifice from one compartment to another empty (vacuum) compartment.



### 9.3 Graham's Law :

Under similar condition of pressure (partial pressure) and temperature, the rate of diffusion of different gases is inversely proportional to square root of their density.

$$\Rightarrow \text{rate of diffusion, } r \propto \frac{1}{\sqrt{d}}$$

$$\Rightarrow \frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \frac{\sqrt{V \cdot D_2}}{\sqrt{V \cdot D_1}}$$

where, d = density of gas

V.D = vapour density

M = molar mass of gas

- Under conditions of same temperature but different pressure, we have -

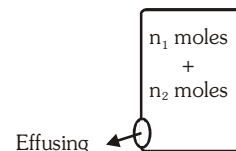
$$r \propto \frac{P}{\sqrt{M}}$$

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

If both gases are present in the same container at same temperature.

$$P \propto n$$

$$\Rightarrow \frac{r_1}{r_2} = \frac{n_1}{n_2} \sqrt{\frac{M_2}{M_1}}$$



**Rate of diffusion/effusion can be expressed as -**

$$r = \frac{\text{volume diffused}}{\text{time taken}} \text{ or } \frac{\text{moles diffused}}{\text{time taken}} \text{ or } \frac{\text{pressure dropped}}{\text{time taken}}$$

or 
$$\frac{\text{distance travelled in horizontal tube of uniform cross-section}}{\text{time taken}}$$

**Ex.25** 32 ml of He effuses through a fine orifice in 1 minute. Then what volume of  $\text{CH}_4$  will diffuse in 1 minute under the similar condition.

**Sol.**  $\therefore r \propto \frac{1}{\sqrt{M}}$

$$r = \frac{\text{volume diffused}}{\text{time}}$$

$\therefore$  time is same so

$$\frac{V_{\text{CH}_4}}{V_{\text{He}}} = \sqrt{\frac{M_{\text{He}}}{M_{\text{CH}_4}}}$$

$$\frac{V_{\text{CH}_4}}{32} = \sqrt{\frac{4}{16}}$$

$$V_{\text{CH}_4} = \frac{1}{2} \times 32 = 16 \text{ mL}$$

**Ex.26** 20 dm<sup>3</sup> of Ne diffuse through a porous partition in 60 seconds. What volume of  $\text{SO}_3$  will diffuse under similar conditions in 30 sec. (Atomic wt. of Ne = 20, S = 32)

**Sol.**  $\frac{r_{\text{Ne}}}{r_{\text{SO}_3}} = \sqrt{\frac{M_{\text{SO}_3}}{M_{\text{Ne}}}} \Rightarrow \frac{V_{\text{Ne}}/t_{\text{Ne}}}{V_{\text{SO}_3}/t_{\text{SO}_3}} = \sqrt{\frac{M_{\text{SO}_3}}{M_{\text{Ne}}}}$

$$\Rightarrow V_{\text{SO}_3} = \frac{V_{\text{Ne}} \times t_{\text{SO}_3}}{t_{\text{Ne}}} \times \sqrt{\frac{M_{\text{Ne}}}{M_{\text{SO}_3}}} = \frac{20 \times 30}{60} \times \sqrt{\frac{20}{80}} = \frac{10}{2} = 5 \text{ dm}^3$$

**Ex.27** A gaseous mixture of  $\text{O}_2$  and X containing 20% (mole %) of X, diffused through a small hole in 234 seconds while pure  $\text{O}_2$  takes 224 seconds to diffuse through the same hole. Molecular weight of X is :

**Sol.**  $\frac{t_{\text{mix}}}{t_{\text{O}_2}} = \sqrt{\frac{M_{\text{mix}}}{M_{\text{O}_2}}}$

$$\frac{234}{224} = \sqrt{\frac{M_{\text{mix}}}{32}}$$

$$\therefore M_{\text{mix}} = 34.921.$$

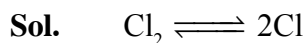
As the mixture contains 20% (mole %) of X, the molar ratio of  $\text{O}_2$  and X may be represented as 0.8n : 0.2n, n being the total no. of moles.



$$\therefore M_{\text{mix}} = \frac{32 \times 0.8n + M_x \times 0.2n}{n} = 34.921$$

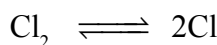
$$\therefore M_x (\text{mol. wt. of X}) = 46.6$$

**Ex.28** At 1200°C, mixture of Cl<sub>2</sub> and Cl atoms (both in gaseous state) effuses 1.16 times as fast as krypton effuses under identical conditions. Calculate the fraction of chlorine molecules dissociated into atoms. M (Kr) = 83.8 g mol<sup>-1</sup>.



$$\frac{r(\text{Cl}_2 \text{ and Cl mix})}{r(\text{Kr})} = 1.16 \sqrt{\frac{M(\text{Kr})}{M_{\text{av}}(\text{Cl}_2 + \text{Cl})}} = \sqrt{\frac{83.8}{M_{\text{av}}}}$$

$$\therefore M_{\text{av}} = \frac{83.8}{(1.16)^2} = 62.28 \text{ g mol}^{-1}$$



Initial mole                    1            0

After dissociation            (1 - x)    2x

(x = degree of dissociation)

Total moles after dissociation = 1 - x + 2x = (1 + x)

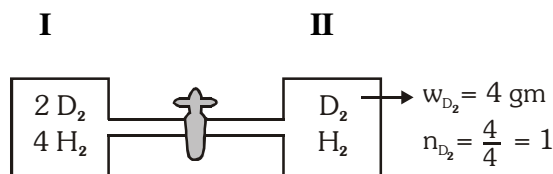
$$\therefore \frac{(1-x)M(\text{Cl}_2) + 2xM(\text{Cl})}{(1+x)} = 62.28 \Rightarrow \frac{(1-x) \times 71 + 2x \times 35.5}{1+x} = 62.28$$

$$x = 0.14$$

$$\therefore \% \text{ dissociation} = 14\%$$

**Ex.29** A mixture containing 2 moles of D<sub>2</sub> and 4 moles of H<sub>2</sub> is taken inside a container which is connected to another empty container through a nozzle. The nozzle is opened for certain time and then closed. The second bulb was found to contain 4 gm D<sub>2</sub>. Then find % by moles of the lighter gases in second container.

**Sol.**



lighter gas = H<sub>2</sub>

$$\frac{r_{\text{H}_2}}{r_{\text{D}_2}} = \frac{n_{\text{H}_2}}{n_{\text{D}_2}} \sqrt{\frac{M_{\text{D}_2}}{M_{\text{H}_2}}} = \frac{n_{\text{H}_2} / t}{n_{\text{D}_2} / t}$$

$$(\% \text{ mole of H}_2)_{\text{II}} = \left( \frac{n_{\text{H}_2}}{n_{\text{H}_2} + n_{\text{D}_2}} \right) \times 100$$

$$\therefore \frac{n_{\text{H}_2}}{n_{\text{D}_2}} \sqrt{\frac{M_{\text{D}_2}}{M_{\text{H}_2}}} = \frac{n'_{\text{H}_2}}{n'_{\text{D}_2}} \Rightarrow \frac{4}{2} \sqrt{\frac{4}{2}} = \frac{n'_{\text{H}_2}}{1}$$

$$\Rightarrow n_{\text{H}_2} = 2\sqrt{2} \Rightarrow n'_{\text{D}_2} = 1$$

$$(\% \text{ mole of H}_2)_{\text{II}} = \frac{(2\sqrt{2})}{(2\sqrt{2} + 1)} \times 100 = \frac{2 \times 1.44}{[(2 \times 1.44) + 1]} \times 100 = \frac{(2.8)}{(2.8 + 1)} \times 100 = \frac{(2.8)}{(2.8 + 1)} \times 100$$

$$= 73.87\%$$

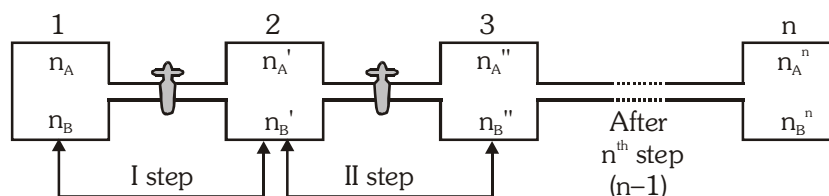
**Ex.30** Why a heavier gas from a gas mixture effuses at slower rates ?

**Sol.** In a gas mixture, the average kinetic energy of each gas  $\left(\frac{1}{2}mv^2\right)$  is the same  $\left(\frac{3}{2}RT\right)$ . Hence, heavier gas has smaller speed.

#### 9.4 APPLICATION OF GRAHAM'S LAW OF DIFFUSION IN ENRICHMENT OF ISOTOPES

##### ❖ Enrichment factor or Isotopic separation factor :

When two gases present in a container are allowed to diffuse in another container then gas having lower molecular mass will diffuse more and if this process is continued for large number of steps then we can obtain a mixture which is rich in a gas having lower molecular mass. Hence ultimately in the ultimate (last) container amount of lighter gas is larger as compared to heavier gas.



where,  $M_A > M_B$  [similar condition of T and V] &  $n_B^n \gg \gg \gg n_A^n$

Enrichment factor (f) is defined as the ratio of final ratio of moles in the mixture [after  $n^{\text{th}}$  step] with initial mole ratio of the mixture.

$$f = \frac{\left(\frac{n_A^n}{n_B^n}\right)}{\left(\frac{n_A}{n_B}\right)} = \left(\sqrt{\frac{M_B}{M_A}}\right)^n = \frac{\text{final molar ratio}}{\text{initial molar ratio}}$$

## 10. KINETIC THEORY OF GASES

This is a theoretical model for ideal gas which can correlate the experimental facts (like Boyle's law, Charle's law & Avogadro's law etc.). It was presented by **Bernoulli in 1738** and developed in 1860 by **Clausius, Maxwell, Kroning and Boltzmann**. Postulates of kinetic theory of gases are :

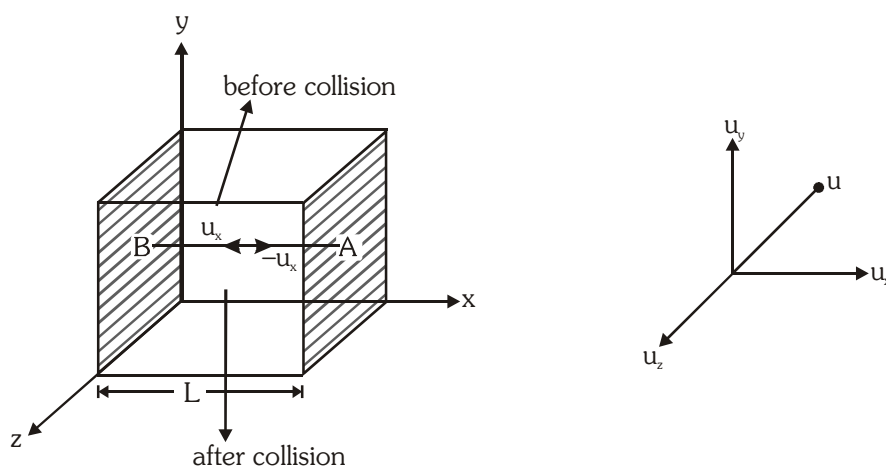
- (i) All the gases consist of very small molecules or atoms whose volume is negligible compared to volume of container.
- (ii) There are no attractive or repulsive forces between the molecules.
- (iii) The gaseous molecules are under a continuous state of motion which is unaffected by gravity (the random straight line motion is known as brownian motion)
- (iv) Due to the continuous motion, collision between gaseous molecules and with the wall of container occurs. The collision with the wall of container are responsible for pressure exerted by the gas on the wall of container.

- (v) The molecule moves with different speed, however the speed of each molecule keep on changing as the collision occur.
- (vi) Collision among gas particles molecules is perfectly elastic, i.e., there is no loss in kinetic energy and moment during such collision.
- (vii) The average kinetic energy of gas particles will depends on absolute temperature only.

**10.1 Kinetic gas equation :**

Let us consider a cube of side  $L$ , that has  $N$  molecules each of mass  $m$  moving with velocity  $u$  in all direction and thus colliding with one each other and against sides of the container. Velocity  $u$  can be resolved into three components  $u_x$ ,  $u_y$  and  $u_z$  along there axis such that

$$u^2 = u_x^2 + u_y^2 + u_z^2$$



For a simplest case we consider motion of a molecule along x-axis only in which it moves towards face B with velocity  $u_x$ . After collision against face B it moves towards face A with velocity  $(-u_x)$  collision being elastic (which results in change in direction but not speed)

- $\therefore$  Momentum before collision on face B =  $mu_x$
- Momentum after collision on face B =  $-mu_x$
- Change in momentum due to one collision on face B =  $mu_x - (-mu_x) = 2mu_x$
- To strike face B again distance travelled =  $2L$

Time taken to strike face B again =  $\frac{2L}{u_x}$  seconds

$\therefore$  Number of collisions per second on face B along x-axis =  $\frac{u_x}{2L}$

$\therefore$  Rate of change in momentum due to  $\frac{u_x}{2L}$  collisions per second on face B along x-axis.

$$= 2mu_x \cdot \frac{u_x}{2L} = \frac{mu_x^2}{L}$$

Similarly for y-axis change in momentum per second =  $\frac{mu_y^2}{L}$  and for z-axis =  $\frac{mu_z^2}{L}$

Net force by  $N$  molecules on a wall ,  $F_x = \frac{mu_{x_1}^2}{L} + \frac{mu_{x_2}^2}{L} \dots\dots + \frac{mu_{x_N}^2}{L} = \frac{M}{L} \cdot \Sigma u_x^2$

Now pressure =  $\frac{\text{Force}}{\text{Area of six faces}} = \frac{\frac{m}{L} \cdot \Sigma u_x^2}{L^2} = \frac{m \cdot \Sigma u_x^2}{L^3} = \frac{m \cdot \Sigma u^2}{V}$  [ $L^3 = \text{volume } V$ ]

$$\therefore PV = m \cdot \Sigma u_x^2$$

As  $\Sigma u_x^2 = \Sigma u_y^2 = \Sigma u_z^2$  and  $\Sigma u_x^2 + \Sigma u_y^2 + \Sigma u_z^2 = \Sigma u^2$

$$\therefore PV = m \cdot \Sigma u_x^2 = \frac{1}{3} m \cdot \Sigma u^2$$

$$PV = \frac{1}{3} m \left( \frac{u_1^2 + u_1^2 + \dots + u_N^2}{N} \right) \cdot N$$

$$\therefore PV = \frac{1}{3} m N u_{\text{rms}}^2$$

*This equation is called kinetic gas equation.*

## 10.2 Kinetic energy of gas molecules :

Total translational K.E. of molecules

$$= \frac{1}{2} m u_1^2 + \frac{1}{2} m u_2^2 + \dots + \frac{1}{2} m u_N^2 = \frac{1}{2} m \cdot \Sigma u^2 = \frac{1}{2} m N \cdot u_{\text{rms}}^2 = \frac{3}{2} PV = \frac{3}{2} nRT$$

$$\therefore \text{Average translational K.E. per mole} = \frac{3}{2} RT$$

$$\text{and (K.E.)}_{\text{per molecule}} = \frac{3}{2} \left( \frac{R}{N_A} \right) T = \frac{3}{2} kT$$

$$\text{Where } k = \text{Boltzman constant} = \frac{R}{N_A} = \frac{8.314 \text{ J/molK}}{6.02 \times 10^{23}} = 1.3806 \times 10^{-23} \text{ J K}^{-1}$$

- (K.E.)<sub>per molecule</sub> and (K.E.)<sub>per mol</sub> is only depend on absolute temperature. It is does not depend on the nature of gas. This conclusion is known as "*Maxwell's Generalisation*".

**Ex.31** Calculate the kinetic energy of 8 gram methane (CH<sub>4</sub>) at 27°C temperature.

**Sol.**  $n = \frac{8}{16} = \frac{1}{2}$ ,  $T = (27^\circ + 273) = 300 \text{ K}$ ,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$(\text{K.E.})_{\text{n mol}} = n \times \frac{3}{2} RT = \frac{1}{2} \times \frac{3}{2} \times 8.314 \times 300 = 1870.65 \text{ J}$$

**Ex.32** Calculate the pressure exerted by  $10^{23}$  gas molecules, each of mass  $10^{-25}$  kg, in a container of volume  $1 \times 10^{-3} \text{ m}^3$  and having root mean square velocity of  $10^3 \text{ ms}^{-1}$ . Also calculate total kinetic energy and Temperature of the gas.

**Sol.** By kinetic theory

$$P = \frac{1}{3} \frac{m N u^2}{V} = \frac{1 \times 10^{-25} \times 10^{23} \times (10^3)^2}{3 \times 10^{-3}} = 3.33 \times 10^6 \text{ N m}^{-2}$$

$$\text{Total KE} = \left( \frac{1}{2} m u_{\text{rms}}^2 \right) \times N = \frac{1}{2} \times 10^{-25} \times (10^3)^2 \times 10^{23} = \frac{1}{2} \times 10^4 = 0.5 \times 10^4 \text{ J}$$

$$\text{Also total KE} = \frac{3}{2} nRT, \text{ where } n (\text{mole}) = \frac{10^{23}}{N_A} = \frac{10^{23}}{6.023 \times 10^{23}}$$

$$0.5 \times 10^4 = \frac{3}{2} \times \frac{10^{23}}{6.023 \times 10^{23}} \times 8.314 \times T$$

$$\therefore T = \frac{0.5 \times 10^4 \times 2 \times 6.023}{3 \times 8.314} = 2415 \text{ K}$$

**10.3 Root Mean Square Velocity ( $u_{\text{rms}}$ ) by kinetic gas equation :**

$$PV = \frac{1}{3} mN u_{\text{rms}}^2$$

$$\therefore u_{\text{rms}} = \sqrt{\frac{3PV}{mN}} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3RT}{M}}$$

**10.4 Different kind of speed of molecules :**

$$(i) \text{ Average or mean speed, } u_{\text{av}} = \frac{u_1 + u_2 + \dots + u_N}{N} = \sqrt{\frac{8RT}{\pi M}}$$

$$(ii) \text{ Root mean square speed, } u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \dots + u_N^2}{N}} = \sqrt{\frac{3RT}{M}}$$

$$(iii) \text{ Most probable speed, } u_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

It is the speed at which maximum fraction of molecules are travelling

**❖ Ratio of speeds :**

$$U_{\text{rms}} : U_{\text{avg}} : U_{\text{mps}} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{2RT}{M}}$$

$$= \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = 1.22 : 1.13 : 1.00 = 1.00 : 0.92 : 0.816$$

**11. MAXWELL'S DISTRIBUTION OF SPEEDS**

It has already been pointed out that a gas is a collection of tiny particles separated from one another by large empty spaces and moving rapidly at random in all directions. In the course of their motion, they collide with one another and also with the walls of the container. Due to frequent collisions, the speeds and directions of motion of the molecules keep on changing. Thus, all the molecules in a sample of gas do not have same speed. Although it is not possible to find out the speeds of individual molecule, yet from probability considerations it has become possible to work out the distribution of molecules in different speed intervals. This distribution is referred to as the Maxwell-Boltzmann distribution in honour of the scientists who developed it. It may be noted that the distribution of speeds remains constant at a particular temperature although individual speeds of molecules may change.

$$dN = 4\pi N \left[ \frac{M}{2\pi RT} \right]^{\frac{3}{2}} e^{-\frac{Mu^2}{2RT}} u^2 du = 4\pi N \left[ \frac{m}{2\pi kT} \right]^{\frac{3}{2}} e^{-\frac{mu^2}{2kT}} \cdot u^2 \cdot du$$

Here,  $dN$  = Number of molecules having speeds between  $u$  and  $u + du$ .

$N$  = Total number of molecules.

$M$  = Molar mass of gas (kg/mol)

$u$  = Root mean square velocity

$du$  = Velocity interval

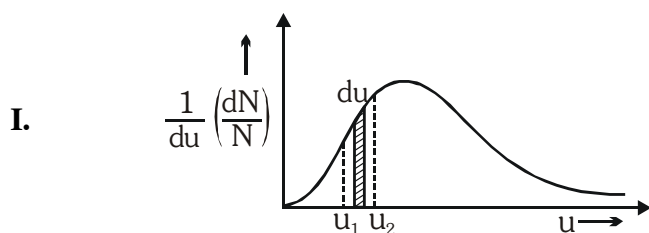
$$\frac{dN}{N} = 4\pi \left[ \frac{M}{2\pi RT} \right]^{\frac{3}{2}} e^{-\frac{Mu^2}{2RT}} u^2 du$$

Here,  $dN/N$  = fraction of molecules having speeds between  $u$  and  $u + du$ .

and  $\frac{1}{N} \left( \frac{dN}{du} \right)$  = fraction of molecules having speed between  $u$  to  $u + du$  per unit interval of speed.  
= Maxwell distribution function.

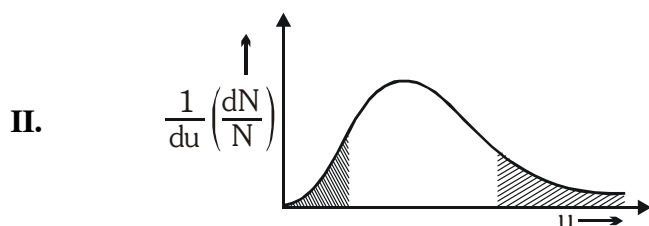
According to this expression, the fraction  $\frac{dN}{N}$  of molecules depends only on temperature having speeds between  $u$  and  $u + du$  for a gas of molar mass  $M$ . Thus for a given temperature, this fraction has a constant value.

### 11.1 Properties of Maxwell's graph :

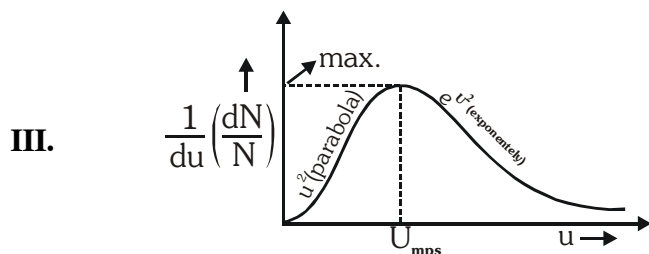


$$\text{Area between } u_1 \text{ and } u_2 = \int_{u_1}^{u_2} \frac{1}{N} \left( \frac{dN}{du} \right) du = \int_{u_1}^{u_2} \left( \frac{dN}{N} \right)$$

Hence, total fraction of particles with speed between  $u_1$  and  $u_2$   
= Area under the curve represents fraction of molecules.

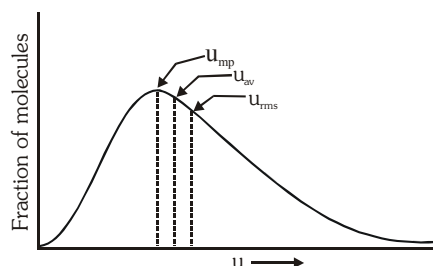


It can be seen from the above figure, that the fraction of molecules having either very low speeds or very high speeds are small in numbers.

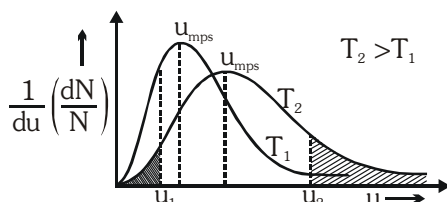


The curve at any temperature is parabolic near the origin, since the factor  $u^2$  is dominant in this region, the exponential function being approximately equal to unity. At high values of  $u$ , however, the exponential factor dominates the behaviour of the function, causing it to decrease rapidly in value. As a consequence of the contrasting behaviour of two factors, the product function passes through a maximum at a speed known as the most probable speed ( $u_{mps}$ ). Thus, the most probable speed is the speed possessed by the maximum fraction of the molecules.

IV Graph between fraction of molecules vs molecular speeds :



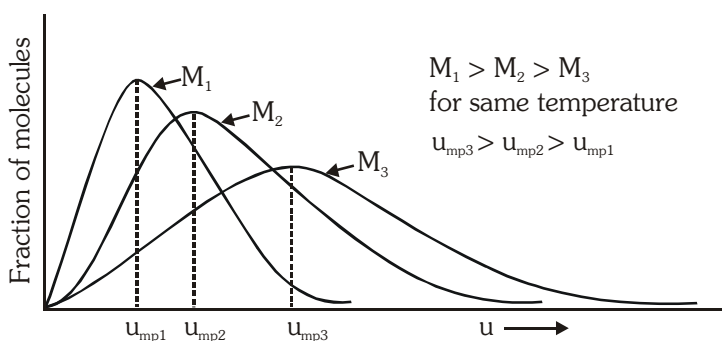
V.



Total area under the curve will be constant and will be unity at all temperatures. The above figure illustrates the distribution of speeds at two temperatures  $T_1$  and  $T_2$ . Since the total no. of molecules is same at both temperatures, increase in the K.E. of the molecules results decrease in fraction of molecules having lower speed range and increase in fraction of molecules having higher speed range on increasing the temperature.

On increasing temperature the value of  $u_{mps}$  (most probable speed) will increase. Also the curve at the higher temperature  $T_2$  has its  $u_{mps}$  shifted to a higher value compared with that for  $T_1$ , whereas corresponding fraction of molecules has decreased. But at the same time, the curve near  $u_{mps}$  has become broader at the higher temperature indicating the more molecules possess speeds near to most probable speed.

VI.

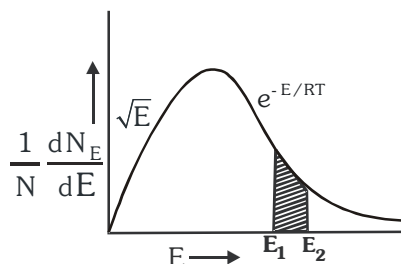


At a given temperature  $u_{mps}$  will be more for lighter gas ( $M_3$ ) but fraction of molecules moving with  $u_{mps}$  will be more for heavier gas ( $M_1$ ).

**Note :** Effect of M and T are opposite.

11.2 Maxwell Distribution of kinetic energy :

**By Maxwell equation :** 
$$dN = 4\pi N \left( \frac{M}{2\pi RT} \right)^{3/2} \cdot e^{-\frac{Mu^2}{2RT}} u^2 \cdot du = 2\pi \left( \frac{1}{\pi RT} \right)^{3/2} \sqrt{E} \cdot e^{-E/RT} \cdot dE$$



The shaded area of this graph indicate the fraction of particles having energy between  $E_1$  and  $E_2$

**Ex.33** Four particles have speed 2, 3, 4 and 5 cm/s respectively. Find their avg. & rms speed :

**Sol.** 
$$U_{\text{avg.}} = \frac{U_1 + U_2 + U_3 + \dots + U_N}{N}$$

$$U_{\text{avg.}} = \frac{2 + 3 + 4 + 5}{4} = 3.5 \text{ cm/s}$$

$$U_{\text{r.m.s.}} = \sqrt{\frac{U_1^2 + U_2^2 + U_3^2 + \dots}{N}}$$

$$u_{\text{rms}} = \sqrt{\frac{2^2 + 3^2 + 4^2 + 5^2}{4}} = \frac{\sqrt{54}}{2} \text{ cm/s}$$

**Ex.34** At what temperature do the average speed of  $\text{CH}_4$  molecule equal the average speed of  $\text{O}_2$  molecule at 300 K ?

**Sol.**  $(U_{\text{avg}})_{\text{CH}_4} = (U_{\text{avg}})_{\text{O}_2}$

$$\sqrt{\frac{8RT}{\pi \times 16}} = \sqrt{\frac{8 \times R \times 300}{\pi \times 32}}$$

$$T = 150 \text{ K}$$

**Ex.35** At  $27^\circ\text{C}$  find the ratio of root mean square speeds of ozone to oxygen :-

**Sol.** 
$$\frac{U_{\text{rms}}(\text{O}_3)}{U_{\text{rms}}(\text{O}_2)} = \sqrt{\frac{3RT}{M.W_{\text{O}_3}}} = \sqrt{\frac{M.W_{\text{O}_2}}{M.W_{\text{O}_3}}} = \sqrt{\frac{32}{48}} = \sqrt{\frac{2}{3}}$$

**Ex.36** The temperature at which  $U_{\text{rms}}$  of He becomes equal to  $U_{\text{mp}}$  of  $\text{CH}_4$  at 500 K.

**Sol.**  $(U_{\text{rms}})_{\text{He}} = (U_{\text{mp}})_{\text{CH}_4}$

$$\sqrt{\frac{3RT_{\text{He}}}{M_{\text{He}}}} = \sqrt{\frac{2RT_{\text{CH}_4}}{M_{\text{CH}_4}}}$$

$$\frac{3T}{4} = \frac{2 \times 500}{16}$$

$$T = \frac{250}{3} \text{ K}$$



**Ex.37** Calculate the root mean square speed of H<sub>2</sub> molecules under following condition.

- (a) 2 mole of H<sub>2</sub> at 27°C.
- (b) 3 mole of H<sub>2</sub> in a 5 lit container at 10<sup>5</sup> Pa.
- (c) 4 mole of H<sub>2</sub> at the density of 1 gm/ml at 10<sup>5</sup> Pa.

**Sol.** (a)  $U_{r.m.s.} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \text{ J/molK} \times 300\text{K}}{2 \times 10^{-3} \text{ kg}}} = 1934.24 \text{ m/sec.}$

(b)  $U_{r.m.s.} = \sqrt{\frac{3PV}{nM}} = \sqrt{\frac{3 \times 10^5 \text{ Pa} \times 5 \times 10^{-3} \text{ m}^3}{3 \text{ mol} \times 2 \times 10^{-3} \text{ kg}}} = 500 \text{ m/sec.}$

(c)  $U_{r.m.s.} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 10^5 \text{ Pa}}{10^3 \text{ kg/m}^3}} = 17.32 \text{ m/sec.}$

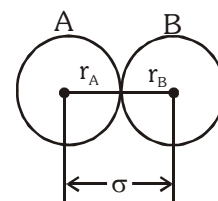
**12. COLLISION PARAMETERS :**

**Assumption :**

All the particles (molecules or atoms) have rigid , similar shape and size and are spherical in nature that will not change after collision.

**12.1 Collision diameter :** It is the closest distance between the centres of two molecules taking part in collision.

Collision diameter ( $\sigma$ ) =  $r_A + r_B$



**12.2 Collision Frequency :**

It is the total number of molecular collisions taking place per second per unit volume of the gas. The no. of collisions made by a single molecule with other molecules per unit time (**collision number**) are given by

$$Z_1 = \sqrt{2} \pi \sigma^2 U_{avg} N^*$$

The total number of bimolecular collision per unit time per unit volume is given as  $Z_{11}$  (**collision frequency**)

$$Z_{11} = \frac{1}{2} (Z_1 N^*) = \frac{1}{2} \times N^* \times \sqrt{2} \pi \sigma^2 U_{avg} N^*$$

$$Z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 U_{avg} N^{*2}$$

(f) If the collisions involve two unlike molecules, the no. of bimolecular collision is given as  $Z_{12}$ .

$$Z_{12} = \pi \sigma_{12}^2 \left( \frac{8kT}{\pi \mu} \right)^{\frac{1}{2}} N_1^* N_2^*$$

Where  $N_1^*$  and  $N_2^*$  are the no. of molecules per unit volume of the two types of gases,  $\sigma_{12}$

is the average diameter of two molecules, that is  $\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}$  &  $\mu$  is the reduced mass,

that is  $\mu = \frac{m_1 m_2}{(m_1 + m_2)}$ ,  $m_1$  &  $m_2$  are the mass of single molecule respectively 1 and 2.

**12.3 Mean free path :**

The mean free path is the average distance travelled by a molecule between two successive collisions. We can express it as follows :

$$\lambda = \frac{\text{distance travelled per unit time}}{\text{No. of collisions made by single molecule per unit time}}$$

$$= \frac{U_{\text{avg}}}{Z_1} = \frac{U_{\text{avg}}}{\sqrt{2}\pi\sigma^2 U_{\text{avg}} N^*} = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

**12.4 Wall collision :** It represents the total number of molecules colliding at the wall per unit area per unit time.

$$Z_w = \frac{1}{4} \cdot N^* \cdot u_{\text{av}} = \frac{P \cdot N_A}{\sqrt{2}\pi MRT}$$

**12.5 Rate of effusion :**

If the cross-section area of orifice in the vessel is 'A', then the number of molecules effusing out per unit time is

$$r_{\text{eff.}} = Z_w \cdot A = \frac{P \cdot N_A \cdot A}{\sqrt{2}\pi MRT}$$

**Ex.38.** Calculate  $\lambda$ ,  $Z_1$  and  $Z_{11}$  for oxygen at 298 K and  $10^{-3}$  mm Hg. Given  $\sigma = 3.61 \times 10^{-8}$  cm.

**Sol.**  $N^* = \frac{P}{kT} = \frac{10^{-3} \times 101325}{760 \times 1.38 \times 10^{-23} \times 298} = 0.324 \times 10^{20}$

$$U_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{3.14 \times \frac{8.314 \times 298}{32 \times 10^{-3}}} = 444.138 \text{ m/sec}$$

$$Z_1 = \sqrt{2} \pi \sigma^2 U_{\text{avg}} N^* = \sqrt{2} \times 3.14 \times 3.61 \times 10^{-10} \text{ m} \times 444.138 \text{ m} \times 0.324 \times 10^{20}$$

$$= 8.326 \times 10^3 \text{ sec}^{-1}$$

$$Z_{11} = \frac{1}{2} Z_1 N^* = \frac{1}{2} \times 8.326 \times 10^3 \text{ sec}^{-1} \times 0.324 \times 10^{20} = 13.488 \times 10^{22} \text{ m}^{-3} \text{ sec}^{-1};$$

$$\lambda = \frac{U_{\text{avg.}}}{Z_1} = \frac{444.138 \text{ m/sec}}{8.326 \times 10^3 \text{ sec}^{-1}} = 5.334 \times 10^{-2} \text{ m}$$

**Ex.39** Two flask A and B have equal volume. A is maintained at 300 K and B at 600 K while A contains  $\text{H}_2$  gas, B has an equal mass of  $\text{CH}_4$  gas. Assuming ideal behaviour for both the gases, find the following.

- Flask containing greater number of moles
- Flask in which pressure is greater
- Flask in which  $U_{\text{avg}}$  of the molecules are greater
- Flask with greater mean free path of molecules (Collision diameters of  $\text{H}_2$  &  $\text{CH}_4$  may be taken same)
- Flask with greater molar kinetic energy.
- Flask in which the total kinetic energy is greater
- Flask in which  $Z_1$  and  $Z_{11}$  are greater

**Sol.**

A	B
$\text{H}_2$	$\text{CH}_4$
300K	600K

(a)  $N_{H_2} = \frac{m}{2} N_A$  ;  $N_{CH_4} = \frac{m}{16} N_A$   
 $\therefore$  molecules of  $H_2$  in flask A > molecules of  $CH_4$  in flask B

(b)  $P_A V = n_A RT_A$  ;  $P_B V = n_B RT_B$   
 $\Rightarrow \frac{P_A}{P_B} = \frac{n_A T_A}{n_B T_B} = \frac{m/2}{m/16} \times \frac{300}{600} = 4$

$\therefore$  pressure of  $H_2$  in flask A > pressure of  $CH_4$  in flask B

(c)  $(U_{avg})_A = \sqrt{\frac{8 RT_A}{\pi M_A}}$  ;  $(U_{avg})_B = \sqrt{\frac{8 RT_B}{\pi M_B}}$

$$\frac{(U_{avg})_A}{(U_{avg})_B} = \sqrt{\frac{T_A}{T_B} \times \frac{M_B}{M_A}} = \sqrt{\frac{300}{600} \times \frac{16}{2}} = 2$$

$\therefore U_{avg}$  of  $H_2$  in flask A >  $U_{avg}$  of  $CH_4$  in flask B

(d)  $\lambda = \frac{1}{\sqrt{2\pi\sigma^2 N^*}} = \frac{1}{\sqrt{2\pi\sigma^2 \times P}} \times kT$  [where  $N^* = P/kT$ ]

$$\frac{\lambda_A}{\lambda_B} = \frac{T_A}{T_B} \times \frac{P_B}{P_A} = \frac{300}{600} \times \frac{1}{4} = \frac{1}{8}$$

$\therefore \lambda_B > \lambda_A$

(e) molar K.E. =  $\frac{3}{2} RT$

$\therefore T_B > T_A$

$\therefore$  KE of  $CH_4$  in flask B > KE of  $H_2$  in flask A

(f)  $(KE)_{total} = \frac{3}{2} RT \times n$

$$\frac{(KE)_{T,A}}{(KE)_{T,B}} = \frac{(300 \times \frac{m}{2})}{(600 \times \frac{m}{16})} = \frac{1}{2} \times 8 = 4$$

$\therefore (KE)_{T,A} > (KE)_{T,B}$

(g) (i)  $Z_1 = \sqrt{2\pi\sigma^2} U_{avg} N^*$

$$\frac{(Z_1)_A}{(Z_1)_B} = \frac{(U_{avg})_A}{(U_{avg})_B} \times \frac{N_A^*}{N_B^*} = 2 \times \frac{N_A}{N_B} = 2 \times 8 = 16$$

$\therefore (Z_1)_A > (Z_1)_B$  ;  $(Z_1)_A > (Z_1)_B$

(ii)  $Z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 U_{avg} N^{*2}$

$$\frac{(Z_{11})_A}{(Z_{11})_B} = \frac{(U_{avg})_A}{(U_{avg})_B} \times \frac{(N_A^*)^2}{(N_B^*)^2} = 2 \times \frac{N_A}{N_B} = 2 \times 8^2 = 128$$

$\therefore (Z_{11})_A > (Z_{11})_B$

### MISCELLANEOUS PREVIOUS YEARS QUESTION

1. Calculate the total pressure in a 10 litre cylinder which contains 0.4 g He, 1.6 g oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressure of He gas in the cylinder. Assume ideal behaviour for gases. [JEE 1997]

**Ans. 0.492 atmp ; 0.246 atmp**

**Sol.** Given,  $V = 10$  litre,  $T = 27 + 273 = 300\text{K}$

$$\text{Mole of He} = \frac{0.4}{4} = 0.1 ; \text{mole of O}_2 = \frac{1.6}{32} = 0.05 ;$$

$$\text{Mole of N}_2 = \frac{1.4}{28} = 0.05$$

$$\therefore \text{Total moles} = 0.1 + 0.05 + 0.05 = 0.20$$

$$P_M = \frac{nRT}{V} = \frac{0.2 \times 0.082 \times 300}{10} = 0.492 \text{atm}$$

$$\therefore P'_{\text{He}} = P_M \times \text{Mole fraction of He} = 0.492 \times \frac{0.05}{0.2} = 0.246 \text{ atm}$$

$$P'_{\text{O}_2} = P_M \times \text{Mole fraction of O}_2 = 0.492 \times \frac{0.05}{0.2} = 0.123 \text{ atm}$$

$$P'_{\text{N}_2} = P_M \times \text{Mole fraction of N}_2 = 0.492 \times \frac{0.05}{0.2} = 0.123 \text{ atm}$$

2. According to Graham's law, at a given temperature the ratio of the rates of diffusion  $\frac{r_A}{r_B}$  of gases A and B is given by : [JEE 1998]

$$(A) \frac{P_A}{P_B} \left( \frac{M_A}{M_B} \right)^{1/2} \quad (B) \left( \frac{M_A}{M_B} \right) \left( \frac{P_A}{P_B} \right)^{1/2} \quad (C) \frac{P_A}{P_B} \left( \frac{M_B}{M_A} \right)^{1/2} \quad (D) \frac{M_A}{M_B} \left( \frac{P_B}{P_A} \right)^{1/2}$$

**Ans. (C)**

3. An evacuated glass vessel weighs 50.0 g when empty, 148.0 gm when filled with a liquid of density 0.98 g/mL and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas. [JEE 1998]

**Ans. 123**

**Sol.** Weight of liquid = 148 – 50 = 98 g

$$\text{Volume of liquid} = \frac{98}{0.98} = 100 \text{mL} = \text{volume of vessel}$$

Thus, vessel of 100 ml contains ideal gas at 760 mm of Hg at 300K.

$$\text{Weight of gas} = 50.5 - 50 = 0.5 \text{ g}$$

Using  $PV = nRT$

$$\frac{760}{760} \times \frac{100}{1000} \times \frac{0.5}{m} = 0.0821 \times 300$$

$$\therefore \text{Molecular weight of gas (m)} = 123$$

4. The pressure exerted by 12 g of an ideal gas at temperature  $t^\circ\text{C}$  in a vessel of volume  $V$  is one atmp. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10%. Calculate the temperature 't' and volume 'V'. [Molecular weight of gas = 120] [JEE 1999]

Ans.  $-173^\circ\text{C}$ ,  $0.82\text{ L}$

Sol.  $P_1 = 1 = 1\text{ atm}$ ,  $T_1 = t + 273$

$$P_2 = 1 + \frac{10}{100} = 1.1\text{ atm}, T_2 = t + 283$$

$$\frac{1 \times V}{1.1 \times V} = \frac{\frac{12}{M} \times R(t + 273)}{\frac{12}{M} \times R(t + 283)}$$

$$t = -173^\circ\text{C} = 100\text{K}$$

$$1 \times V = \frac{12}{120} \times 0.082 \times 100$$

$$V = 0.82\text{ lite}$$

5. One mole of  $\text{N}_2$  gas at 0.8 atmp takes 38 sec to diffuse through a pin hole, whereas one mole of an unknown compound of Xenon with F at 1.6 atmp takes 57 sec to diffuse through the same hole. Calculate the molecular formula of the compound. (At. wt.  $\text{Xe} = 138$ ,  $\text{F} = 19$ ) [JEE 1999]

Ans.  $\text{XeF}_6$

Sol.  $\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$

$$\frac{n_1}{t_1} \times \frac{t_2}{n_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

$$\frac{1}{38} \times \frac{57}{1} = \frac{0.8}{1.6} \sqrt{\frac{M}{28}}$$

$$M = 252$$

$$138 + 19 \times n = 252 \Rightarrow n = 6 \Rightarrow \text{XeF}_6$$

6. The r. m. s. velocity of hydrogen is  $\sqrt{7}$  times the r. m. s. velocity of nitrogen. If  $T$  is the temperature of the gas: [JEE 2000]

(A)  $T(\text{H}_2) = T(\text{N}_2)$

(B)  $T(\text{H}_2) > T(\text{N}_2)$

(C)  $T(\text{H}_2) < T(\text{N}_2)$

(D)  $T(\text{H}_2) = \sqrt{7} T(\text{N}_2)$

Ans. (C)

Sol.  $(u_{\text{rms}})_{\text{H}_2} = \sqrt{7} \times (u_{\text{rms}})_{\text{N}_2}$

$$\sqrt{\frac{3RT_1}{2}} = \sqrt{7} \times \sqrt{\frac{3RT_2}{28}}$$

$$\frac{3RT_1}{2} = \frac{7 \times 3RT_2}{28}$$

$$2T_1 = T_2 \Rightarrow T_{\text{N}_2} > T_{\text{H}_2}$$

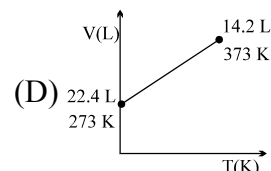
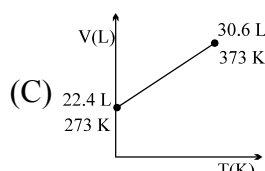
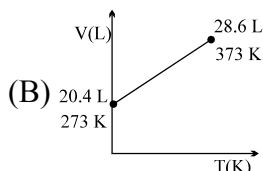
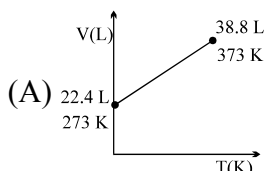
7. The root mean square velocity of an ideal gas at constant pressure varies with density as  
 (A)  $d^2$  (B)  $d$  (C)  $d^{1/2}$  (D)  $1/d^{1/2}$  [JEE 2001]

Ans. (D)

Sol.  $u_{\text{rms}} = \sqrt{\frac{3P}{d}}$

$$u_{\text{rms}} \propto \frac{1}{d^{1/2}}$$

8. Which one of the following V, T plots represents the behaviour of one mole of an ideal gas at one atmp? [JEE 2002]



Ans. (C)

Sol.  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$\frac{22.4}{273} = \frac{30.6}{373}$$

9. The average velocity of gas molecules is 400 m/sec. Calculate its (rms) velocity at the same temperature. [JEE 2003]

Ans. 434.17 m/sec

Sol.  $u_{\text{rms}} = \sqrt{\frac{3\pi}{8}} \times u_{\text{avg}}$

$$= \sqrt{\frac{3 \times 3.14}{8}} \times 400 = 434 \text{ m/s}$$

10. The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be  
 (A) 4 (B) 2 (C) 1 (D) 0.5 [JEE 2005]

Ans. (B)

Sol.  $\frac{r_{\text{He}}}{r_{\text{CH}_4}} = \sqrt{\frac{16}{4}} = 2$

11. At 400 K, the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of the gas Y is [JEE 2009]

Ans. (4)

Sol.  $(u_{\text{rms}})_x = (u_{\text{mp}})_y$

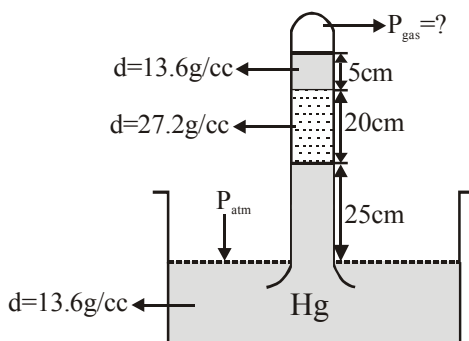
$$\frac{\sqrt{3RT_x}}{M_x} = \frac{\sqrt{2RT_x}}{M_y}$$

$$\frac{3 \times 400}{40} = \frac{2 \times 60}{M_y}$$

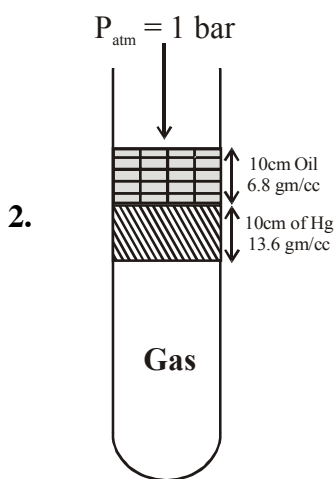
$$M_y = \frac{2 \times 60 \times 40}{3 \times 400} = 4$$

EXERCISE # S-I

1. In the following arrangement find the pressure of gas (in cm of Hg).  
(Assume that atmospheric pressure  $P_{atm} = 75$  cm of Hg)



IG0001

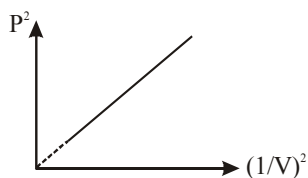


Find pressure of gas in cm of Hg enclosed in tube.

IG0002

BOYLE'S LAW

3. Consider the following graph



Graph is plotted for 1 mol of gas at 400K, find slope of curve.

[Take :  $R = 0.08 \frac{\text{L} - \text{atm}}{\text{mol} - \text{K}}$ ]

IG0003

4. Two glass bulbs A and B are connected by a very small tube having a stop cock. Bulb A has a volume of 100 ml and contained the gas, while bulb B was empty on opening the stop cock, the pressure fell down to 40% at constant temperature. Find out the volume of bulb B in mL.

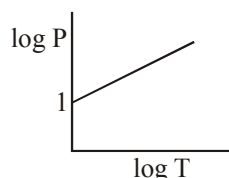
IG0004

5. A glass bulb of 2 L capacity is filled by helium gas at 10 atm pressure. Due to a leakage the gas leaks out. What is the volume of gas leaked if the final pressure in container is 1 atm.

IG0005

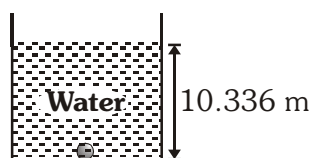
## CHARLES LAW

6. Calculate the volume which 4 litre of gas at  $0^{\circ}\text{C}$  will occupied at  $100^{\circ}\text{C}$  and the same pressure.
7. In constant volume container of 0.821 litre,  $\log P$  vs  $\log T$  is plotted as shown in graph. Calculate number of moles of ideal gas present in container :



IG0007

8. A certain amount of a gas at  $27^{\circ}\text{C}$  and 1 bar pressure occupies a volume of  $25\text{ m}^3$ . If the pressure is kept constant and the temperature is raised to  $77^{\circ}\text{C}$ , what will be the volume of the gas ?
9. (a) Radius of a bubble at the bottom of the tank shown below was found to be 1 cm, then find the radius of the bubble at the surface of water considering the temperature at the surface & bottom being same.



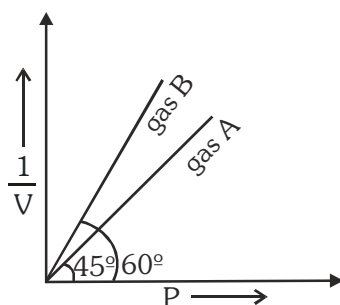
- (b) If absolute temperature at the surface is 4 times that at the bottom, then find radius of bubble at the surface.

IG0009

10. (a) Plot the curve between  $PT$  vs  $T$  at const  $V$  & constant no. of moles.  
 (b) Find the number of moles of gas taken when the volume of the vessel is 82.1 ml and  $\frac{d}{dT} [PT]$  at  $300\text{ K} = 300$  for the given curve.

IG0010

11. At constant temperature of  $273\text{ K}$ ,  $\left(\frac{1}{V}\right)$  v/s  $P$  are plotted for two ideal gases A and B as shown. ( $V$  in litre &  $P$  in atm)



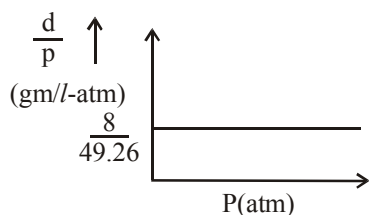
Find out the number of moles of gas A and B.

IG0011



IDEAL GAS EQUATION

12. For an ideal gas, the following graph is obtained at constant temperature of 300 K. The molar mass of gas (in gm/mol) is -



IG0012

13. The density of phosphorus vapours at 327°C and 1 atm is 2.52 gm/lit. If molecular formula of phosphorus is P<sub>x</sub>, then calculate 'X'. (Atomic weight of : P = 31)

IG0013

14. Density of ideal gas at 2.46 atm and 300 K is 0.8 gm/l. Hence gm-molar mass of gas is [R = 0.082L-atm/mol-K]

IG0014

15. In a hospital respiratory unit the pressure gauge reads 4500 mm Hg for 10 L tank containing compressed O<sub>2</sub>, how many litres of O<sub>2</sub> can be delivered from tank at atmospheric pressure of 750 mm Hg. (Take temperature to be constant at TK)

IG0015

16. While resting, the average human male use 0.2 dm<sup>3</sup> of O<sub>2</sub> per hour at 1 atm & 300 K for each kg of body mass. Assume that all this O<sub>2</sub> is used to produce energy by oxidising glucose in the body . What is the mass of glucose required per hour by a resting male having mass 60 kg . What volume, at 1 atm & 300 K of CO<sub>2</sub>

would be produced (R = 0.08  $\frac{\text{L-atm}}{\text{mol-K}}$ )

IG0016

17. A human adult breathes in approximately 0.50 dm<sup>3</sup> of air at 1.00 bar with each breath. If an air tank holds 100 dm<sup>3</sup> of air at 200 bar, how many breathes the tank will supply ?

IG0017

18. A gas at a pressure of 5.0 bar is heated from 0°C to 546°C and simultaneously compressed to one third of its original volume. What will be the final pressure ?

IG0018

19. 3.6 g of an ideal gas was injected into a bulb of internal volume of 8 L at pressure P atm and temp T K. The bulb was then placed in a thermostat maintained at (T + 15)K, 0.6 g of the gas was let off to keep the original pressure. Find P and T if mol weight of gas is 44.

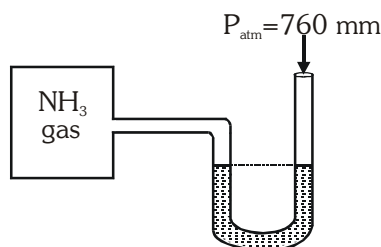
IG0019

DALTON'S LAW OF PARTIAL PRESSURE

20. The partial pressures of N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> in a vessel are 38 cm of Hg, 190 torr and 0.5 atm, respectively . The total pressure of the mixture at the same temperature is.

IG0020

21. Equal masses of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is. IG0021
22. A mixture of hydrogen and oxygen at one bar pressure contains 20% , by weight of hydrogen. The partial pressure of hydrogen will be. IG0022
23. A closed vessel contains equal number of nitrogen and oxygen molecules at pressure of P mm. If nitrogen is removed from the system, then the pressure will be. IG0023
24. If 2 lit. of gas A at 1.5 atm and 3 lit. of gas B at 2 atm are mixed in a 5 lit. container then find the final pressure, considering all are at same temperature. IG0024
25. One mole of  $N_2$  and 3 moles of  $H_2$  are taken in a container of capacity 8.21 lit. at 300 K to produce  $NH_3$ . Find the partial pressures of  $N_2$  and  $H_2$  if partial pressure of  $NH_3$  after sufficient time was found to be 3 atm. IG0025
26. A manometer attached to a flask contains  $NH_3$  gas have no difference in mercury level initially as shown in diagram. After the sparking into the flask, it have difference of 19 cm in mercury level in two columns. Calculate % dissociation of ammonia.



27. A gaseous mixture at 760 mm in a cylinder has 65%  $N_2$ , 15%  $O_2$  and 20%  $CO_2$  by volume. Calculate the partial pressure of each gas. IG0026

IG0027

### CONTAINER PROBLEMS

28. A toy balloon originally held 1.0 gm of He gas and had a radius 10 cm. During the night, 0.875 gm of the gas effused from the balloon. Assuming ideal gas behaviour, under these constant P and T conditions, what was the radius of the balloon the next morning. IG0028
29. The density of a mixture of  $O_2$  and  $N_2$  gases at 1 atm and 273K is 0.0013 gm/ml. If partial pressure of  $O_2$  in the mixture is A then calculate value of 25A. IG0029
30. A containers contains air above liquid water. Total pressure was 800 torr. What will be the final pressure if volume is doubled. (Aqueous tension = 40 torr) IG0030

31. One litre flask contains air, water vapour and a small amount of liquid water at a pressure of 200 mmHg. If this is connected to another one litre evacuated flask, what will be the final pressure of the gas mixture at equilibrium? Assume that temperature to be 50°C. Aqueous tension at 50°C = 93 mmHg.

IG0031

**DIFFUSION / EFFUSION**

32. If helium and methane are allowed to diffuse out of the container under the similar conditions of temperature and pressure, then the ratio of rate of diffusion of helium to methane is.

IG0032

33. At a particular fixed temperature the gas  $A_n$  is 52% dissociated according to the following reaction  
 $A_n(g) \rightleftharpoons nA(g)$

The equilibrium mixture effuses 1.25 times slower than pure oxygen gas under identical condition. If atomic wt. of A is 32, then find "n" ?

IG0033

34.  $H_2$  and  $O_2$  are kept in mass ratio 1 : 8 respectively at 6 atm. If small orifice is made then relative rate of effusion of  $H_2$  with respect to  $O_2$  initially is.

IG0034

35. A mixture of  $H_2$  and  $O_2$  in 2 : 1 mole ratio is allowed to diffuse through a orifice. Calculate the composition of gases coming out initially.

IG0035

36. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Determine the molecular formula of the compound.

IG0036

37. A mixture of  $N_2$  and  $H_2$  has initially mass ratio of 196 : 1 then find after how many steps we can obtain a mixture containing 1 : 14 mole ratio of  $N_2$  and  $H_2$ .

IG0037

38. Find the ratio of moles of  $SO_2$  to  $CH_4$  after fifth diffusion steps if their initially mole ratio is 8 : 1.

IG0038

**KTG**

39. Calculate the root mean square speed of  $H_2$  molecules under following conditions.

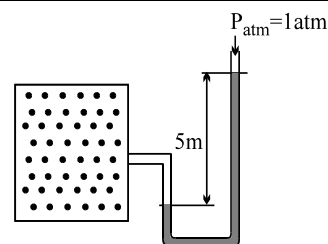
- (a) 2 mole of  $H_2$  at 27°C  
(b) 3 mole of  $H_2$  in a 5 litre container at  $10^5$  Pa  
(c) 4 mole of  $H_2$  at the density of 1 gm / ml at  $10^5$  Pa

IG0039

40. Root mean square speed of an unknown gas at  $727^{\circ}\text{C}$  is  $10^5$  cm/second. Calculate molar mass of unknown gas (in gram/mole) [Take  $R = \frac{25}{3}$  J/mole-K].  
**IG0040**
41. How many times is the rms speed of molecules in 8 gm  $\text{O}_2$  gas at 1200 K and 10 bar, relative to rms speed of molecules in 16 gm  $\text{O}_2$  gas at 300K and 20 bar ?  
**IG0041**
42. Average translational kinetic energy of an ideal gas molecule at  $27^{\circ}\text{C}$  is  $3.88 \times 10^{-x}$  eV. Hence x is ( $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ )  
**IG0042**
43. When the temperature of an ideal gas is increased from  $27^{\circ}\text{C}$  to  $927^{\circ}\text{C}$  the kinetic energy will be increased by x times. Find the value of x ?  
**IG0043**
44. Two flask A and B have equal volume at 100 K and 200 K and have pressure 4 atm and 1 atm respectively. The flask A contains  $\text{H}_2$  gas and B contains  $\text{CH}_4$  gas. The collision diameter of  $\text{CH}_4$  is twice that of  $\text{H}_2$ . Calculate ratio of mean free path of  $\text{CH}_4$  to  $\text{H}_2$ .  
**IG0044**
45. If the mean free path is 10 cm at one bar pressure then its value at 5 bar pressure, if temperature is kept constant.  
**IG0045**

EXERCISE # S-II

1. Calculate the number of moles of gas present in the container of volume 10 lit at 300 K. If the manometer containing glycerin shows 5m difference in level as shown in diagram.



Given:  $d_{\text{glycerin}} = 2.72 \text{ gm/ml}$ ,  $d_{\text{mercury}} = 13.6 \text{ gm/ml}$ .

IG0046

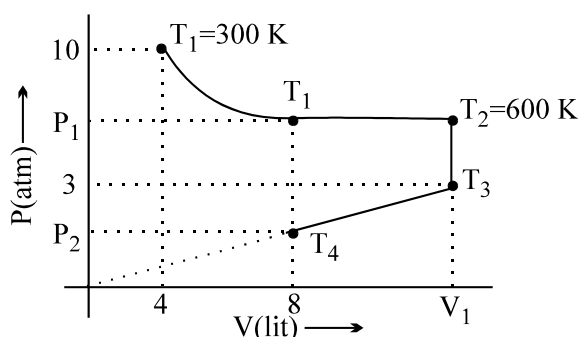
2. The degree of dissociation is 0.4 at 400K and 1 atm for the gaseous reaction  $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ . Assume ideal behaviour of all the gases, calculate the density (in gm/litre) of mixture at 400K and

1 atm [At. wt. of Iodine = 127 ; Use  $R = 0.08 \text{ atm-litre/K-mole}$ ]

Fill your answer as sum of digits (excluding decimal places) till you get the single digit answer.

IG0047

3. Fixed mass of a gas is subjected to the changes as shown in diagram, calculate  $T_3$ ,  $T_4$ ,  $P_1$ ,  $P_2$  and  $V_1$  as shown in diagram. Considering gas obeys  $PV = nRT$  equation.



IG0048

4. A balloon containing 1 mole air at 1 atm initially is filled further with air till pressure increases to 3 atm. The initial diameter of the balloon is 1 m and the pressure at each state is proportion to diameter of the balloon. Calculate :

- (a) No. of moles of air added to change the pressure from 1 atm to 3 atm.  
 (b) balloon will burst if either pressure increases to 7 atm or volume increases to  $36\pi \text{ m}^3$ . Calculate the number of moles of air that must be added after initial condition to burst the balloon.

IG0049

5. One mole of  $\text{NH}_4\text{Cl} (\text{s})$  is kept in an open container & then covered with a lid. The container is now heated to 600 K where all  $\text{NH}_4\text{Cl} (\text{s})$  dissociates into  $\text{NH}_3$  &  $\text{HCl} (\text{g})$ . If volume of the container is 24.63 litres, calculate what will be the final pressure of gases inside the container. Also find whether the lid would stay or bounce off if it can with stand a pressure difference of 5.5 atm. Assume that outside air is at 300 K and 1 atm pressure.

IG0050

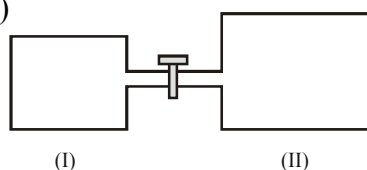
6. One mole of an ideal gas is subjected to a process in which  $P = \frac{1}{8.21} V$  where P is in atm & V in litre. If the process is operating from 1 atm to finally 10 atm (no higher pressure achieved during the process) then what would be the maximum temperature obtained & at what instant will it occur in the process.

IG0051

7. A compound exists in the gaseous state both as a monomer (A) and dimer (A<sub>2</sub>). The molecular weight of the monomer is 48. In an experiment, 96 g of the compound was confined in a vessel of volume 33.6 litres and heated to 273° C. Calculate the pressure developed, if the compound exists as a dimer to the extent of 50 per cent by weight, under these conditions. (R = 0.082)

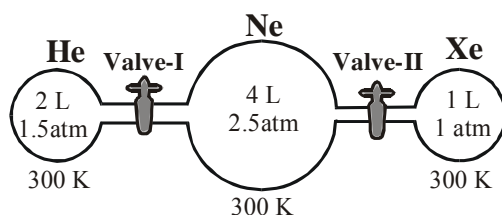
IG0052

8. Two container (I) & (II) with volume 2 litre & 3lt are separated through a stopcock as shown in the diagram. Container (I) contains three gases A, B, & C with mole ratio 1 : 2 : 3 and total pressure 30 atm. If stopcock is opened then calculate the pressure of gas C in container (II). (Assume temperature remains constant)



IG0053

9. For the following diagram calculate final pressure (in atm) when both valves are opened. Given that temperature (T) is same for each container.



IG0054

10. At 30°C dry air [75% N<sub>2</sub> + 25% O<sub>2</sub>] is placed over H<sub>2</sub>O (l) at 800 torr combined pressure of all 3 gases. If pressure is gradually increased isothermally to 1560 torr, then calculate partial pressure of O<sub>2</sub> at high pressure in torr. [V.P.<sub>H<sub>2</sub>O</sub> = 40 torr at 30° C].

Fill your answer as sum of digits (excluding decimal places) till you get the single digit answer.

IG0055

11. 16 gm of O<sub>2</sub> was filled in a container of capacity 8.21 lit. at 300 K. Calculate
- Pressure exerted by O<sub>2</sub>
  - Partial pressure of O<sub>2</sub> and O<sub>3</sub> if 50 % of oxygen is converted into ozone at same temperature.
  - Total pressure exerted by gases if 50% of oxygen is converted into ozone (O<sub>3</sub>) at temperature 50 K.

IG0056

12. A container of capacity 20 L contains  $N_2(g)$ , water vapour and negligible but sufficient amount of liquid water to maintain equilibrium, at 300K and 1 atm. The liquid water is now decomposed completely into  $H_2(g)$  and  $O_2(g)$ , by any means, without changing the temperature. If the final pressure becomes 1.86 atm, the mass of liquid water present initially ( in gm) was (Aqueous tension at 300 K = 0.04 atm,  $R = 0.08 \text{ L-atm/K-mole}$ )

IG0057

13. Find the number of diffusion steps required to separate the isotopic mixture initially containing some amount of  $H_2$  gas and 1 mol of  $D_2$  gas in a container of 3 lit capacity maintained at 24.6 atm & 27 °C to the final mass ratio  $\left(\frac{w_{D_2}}{w_{H_2}}\right)$  equal to  $\frac{1}{4}$ .

IG0058

14. The average speed of molecules in a sample of ozone gas is  $1.84 \times 10^4 \text{ cm s}^{-1}$ . The average translational kinetic energy per molecules is xJ. The value of  $\frac{x}{2} \times 10^{22}$  is

(Given :  $N_A = 6 \times 10^{23}$  ;  $\sqrt{\frac{8}{3\pi}} = 0.92$ )

IG0059

15.  $H_2$  gas is kept inside a container A and container B each having volume 2 litre under different conditions which are described below. Determining the missing values with proper unit.

[ $R = 8 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $N_A = 6 \times 10^{23}$  ,  $N = \text{No. of molecules}$ ]

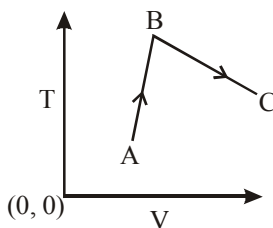
Parameter	Container A	Container B
P	(i)-----	1 atm
T	300K	600 K
N	$6 \times 10^{20}$	(ii)-----
Total Average KE	(iii)-----	(iv)-----
Ratio $U_{\text{mps}}$	(v)-----	
Ratio $Z_{11}$	(vi)-----	

IG0060

## EXERCISE # O-I

## Single Correct :

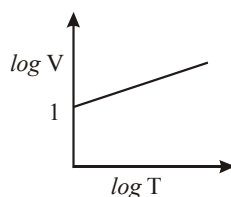
1. In the given isobaric process shown by graph between T & V.



- (A) Moles decreases throughout  
(B) Moles first increases then decreases  
(C) Moles first decreases then increases  
(D) Moles cannot be predicted from given data

IG0061

2. At constant pressure of 0.821 atm ;  $\log V$  vs  $\log T$  is plotted as shown in -  
Then number of moles present in experiment -



- (A) 1 (B) 10 (C) 100 (D) 0.1

IG0062

3. A gas at a pressure of 5.0 atm is heated from  $0^\circ\text{C}$  to  $546^\circ\text{C}$  and simultaneously compressed to one-third of its original volume. Hence final pressure is  
(A) 10 atm (B) 30 atm (C) 45 atm (D) 5 atm

IG0063

4. A flask containing air (open to the atmosphere) is heated from 300 K to 500 K. Then % of air escaped to the atmosphere is -  
(A) 20.0 (B) 40 (C) 60 (D) 80

IG0064

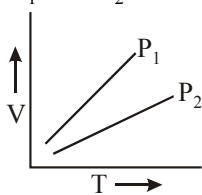
5. 10 g of a gas at 1 atm, 273 K occupies 5 litres. The temp. at which the volume becomes double for the same mass of gas at the same pressure is ?  
(A) 273K (B)  $-273^\circ\text{C}$  (C)  $273^\circ\text{C}$  (D)  $546^\circ\text{C}$

IG0065

6. A gas is found to have a formula  $[\text{CO}]_x$ . If its vapour density is 70 the value of x is  
(A) 2.5 (B) 3.0 (C) 5.0 (D) 6.0

IG0066

7. V versus T curves at constant pressure  $P_1$  and  $P_2$  for an ideal gas are shown in Fig. Which is correct



- (A)  $P_1 > P_2$  (B)  $P_1 < P_2$  (C)  $P_1 = P_2$  (D) All

IG0067



8. A container when is empty weighs 50 gm. After certain liquid of density  $25 \text{ gm/dm}^3$  is filled its mass becomes equal to 100 gm. The volume of the container will be :  
 (A)  $0.25 \text{ dm}^3$  (B)  $0.5 \text{ dm}^3$  (C)  $1 \text{ dm}^3$  (D)  $2 \text{ dm}^3$

IG0068

9. A vessel contains mono atomic 'He' at 1 bar and 300 K, determine its number density -  
 (A)  $2.4 \times 10^{25} \text{ m}^{-3}$  (B)  $6.8 \times 10^{23} \text{ m}^{-3}$  (C)  $4.8 \times 10^{26} \text{ m}^{-3}$  (D)  $9.2 \times 10^{27} \text{ m}^{-3}$

IG0069

10. A rigid container containing 10 gm gas at some pressure and temperature. The gas has been allowed to escape from the container due to which pressure of the gas becomes half of its initial pressure and temperature become  $(2/3)^{\text{rd}}$  of its initial. The mass of gas (in gms) escaped is  
 (A) 7.5 (B) 1.5 (C) 2.5 (D) 3.5

IG0070

11. The density of gas A is twice that of B at the same temperature the molecular weight of gas B is thrice that of A. The ratio of pressure of gas A and gas B will be  
 (A) 1 : 6 (B) 7 : 8 (C) 6 : 1 (D) 1 : 4

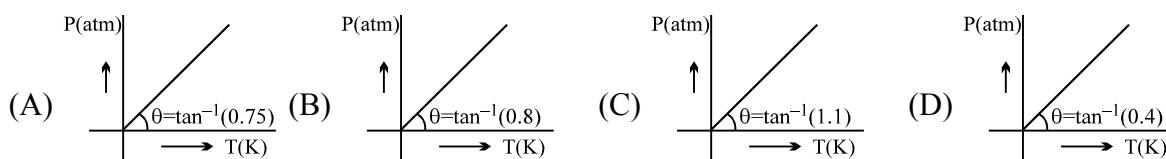
IG0071

12. In a rigid container  $\text{NH}_3$  is kept at certain temperature, if on doubling the temperature it is completely dissociated into  $\text{N}_2$  and  $\text{H}_2$ . Find final pressure to initial pressure ratio :  
 (A) 4 (B) 2 (C)  $\frac{1}{2}$  (D)  $\frac{1}{4}$

IG0072

13. Gas A (1 mol) dissociates in a closed rigid container of volume 0.16 lit. as per following reaction.  
 $2\text{A (g)} \longrightarrow 3\text{B (g)} + 2\text{C (g)}$

If degree of dissociation of A is 0.4 and remains constant in entire range of temperature, then the correct P vs T graph is [Given  $R = 0.08 \text{ lit-atm/mol/K}$ ]



IG0073

14. A gaseous reaction,  
 $3\text{A} \longrightarrow 2\text{B}$   
 is carried out in a 0.0821 litre closed container initially containing 1 mole of gas A. After sufficient time a curve of P (atm) vs T (K) is plotted and the angle with x-axis was found to be  $42.95^\circ$ . The degree of association of gas A is [Given :  $\tan 42.95 = 0.8$ ]  
 (A) 0.4 (B) 0.6 (C) 0.5 (D) 0.8

IG0074

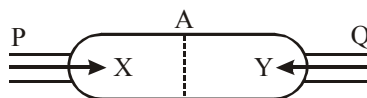
15. 4.0 g of argon has pressure P and temperature T K in a vessel. On keeping the vessel at  $50^\circ$  higher temperature, 0.8 g of argon was given out to maintain the pressure P. The original temperature was :  
 (A) 73 K (B) 100 K (C) 200 K (D) 510 K

IG0075

16. The total pressure exerted by a number nonreacting gases is equal to the sum of partial pressure of the gases under the same conditions is known as :  
 (A) Boyle's law (B) Charle's law (C) Avogadro's law (D) Dalton's law  
**IG0076**
17. Dalton's law cannot be applied for which gaseous mixture at normal temperatures:  
 (A) O<sub>2</sub> and N<sub>2</sub> (B) NH<sub>3</sub> and HCl (C) He and N<sub>2</sub> (D) CO<sub>2</sub> and O<sub>2</sub>  
**IG0077**
18. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is -  
**[AIEEE-2008]**  
 (A) 2/3 (B)  $\frac{1}{3} \times \frac{273}{298}$  (C)  $\frac{1}{3}$  (D)  $\frac{1}{2}$   
**IG0078**
19. A closed vessel contains helium and ozone at a pressure of P atm. The ratio of He and oxygen atoms is 1 : 1. If helium is removed from the vessel, the pressure of the system will reduce to :  
 (A) 0.5 P atm (B) 0.75 P atm (C) 0.25 P atm (D) 0.33 P atm  
**IG0079**
20. At constant temperature 200 cm<sup>3</sup> of N<sub>2</sub> at 720 mm and 400 cm<sup>3</sup> of O<sub>2</sub> at 750 mm pressure are put together in a one litre flask. The final pressure of mixture is  
 (A) 111 mm (B) 222 mm (C) 333 mm (D) 444 mm  
**IG0080**
21. If saturated vapours are compressed slowly (temperature remaining constant) to half the initial volume, the vapour pressure will :  
 (A) Become four times (B) become doubled  
 (C) Remain unchanged (D) Become half  
**IG0081**
22. A box of 1L capacity is divided into two equal compartments by a thin partiion which are filled with 2g H<sub>2</sub> and 16g CH<sub>4</sub> respectively. The pressure in each compartment is recorded as P atm. The total pressure when partition is removed will be :  
 (A) P (B) 2P (C) P/2 (D) P/4  
**IG0082**
23. A vessel has N<sub>2</sub> gas and water vapours at a total pressure of 1 atm. The vapour pressure of water is 0.3 atm. The contents of this vessel are transferred to another vessel having one third of the capacity of original volume, completely at the same temperature the total pressure of this system in the new vessel is -  
 (A) 3.0 atm (B) 1 atm (C) 3.33 atm (D) 2.4 atm  
**IG0083**
24. Which gas effuses fastest under identical conditions -  
 (A) N<sub>2</sub> (B) O<sub>2</sub> (C) Cl<sub>2</sub> (D) CH<sub>4</sub>  
**IG0084**
25. The rate of diffusion of methane at a given temperature is twice that of a gas X. The molecular weight of X is :  
 (A) 64 (B) 32 (C) 4.0 (D) 8.0  
**IG0085**

26. The rate of diffusion of two gases A and B is in the ratio of 1 : 4 and that of B and C in the ratio of 1 : 3 the rate of diffusion of C with respect to A is -  
 (A)  $\frac{1}{12}$  (B) 12 (C) 6 (D) 4
- IG0086**
27. A gas X diffuses three times faster than another gas Y the ratio of their densities i.e.,  $D_x : D_y$  is  
 (A) 1/3 (B) 1/9 (C) 1/6 (D) 1/12
- IG0087**
28. Rate of diffusion of a gas is :  
 (A) directly proportional to its density  
 (B) directly proportional to its molecular weight  
 (C) directly proportional to the square of its molecular weight  
 (D) inversely proportional to the square root of its molecular weight
- IG0088**
29. Since the atomic weights of carbon nitrogen and oxygen are 12, 14 and 16 respectively, among the following pairs of gases, the pair that will diffuse at the same rate is :  
 (A)  $\text{CO}_2$  and  $\text{N}_2\text{O}$  (B)  $\text{CO}_2$  and  $\text{N}_2\text{O}_3$   
 (C)  $\text{CO}_2$  and CO (D)  $\text{CO}_2$  and NO
- IG0089**
30. If the four tubes of a car are filled to the same pressure with  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$  and He separately then which one will be filled first :  
 (A)  $\text{N}_2$  (B)  $\text{O}_2$  (C)  $\text{H}_2$  (D) He
- IG0090**
31. The increasing order of effusion among the gases,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{NH}_3$  and  $\text{CO}_2$  is –  
 (A)  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{O}_2$  (B)  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{O}_2$ ,  $\text{CO}_2$   
 (C)  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{NH}_3$ ,  $\text{CO}_2$  (D)  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2$
- IG0091**
32. The rate of diffusion of hydrogen is about–  
 (A)  $\frac{1}{2}$  that of Helium (B) 1.4 times that of Helium  
 (C) twice that of H (D) Four times that of Helium
- IG0092**
33. Under identical conditions of pressure and temperature. 4 L of gaseous mixture ( $\text{H}_2$  and  $\text{CH}_4$ ) effuses through a hole in 5min whereas 4 L of a gas X of molecular mass 36 takes to 10 min to effuse through the same hole. The mole ratio of  $\text{H}_2 : \text{CH}_4$ , in the mixture is -  
 (A) 1 : 2 (B) 2 : 1 (C) 2 : 3 (D) 1 : 1
- IG0093**

34. 3 mole of gas "X" and 2 moles of gas "Y" enters from end "P" and "Q" of the cylinder respectively. The cylinder has the area of cross-section A, shown as under -



The length of the cylinder is 150 cm. The gas "X" intermixes with gas "Y" at the point A. If the molecular weight of the gases X and Y is 20 and 80 respectively, then what will be the distance of point A from Q?

- (A) 75cm (B) 50cm (C) 37.5 cm (D) 90 cm

IG0094

35. Under identical experiment conditions which of the following pairs of gases will be most easy to separate by using effusion process -

- (A)  $H_2$  and  $T_2$  (B)  $SO_2$  and  $SO_3$  (C)  $NH_3$  and  $CH_4$  (D)  $U^{235}O_2$  and  $U^{238}O_2$

IG0095

36. Certain volume of He gas takes 10 sec for its diffusion, how much time will be taken by  $CH_4$  gas to disffuse it's same volume under identical conditions -

- (A) 5 sec (B) 10 sec (C) 20 sec (D) 40 sec

IG0096

37. A football bladder contains equimolar proportions of  $H_2$  and  $O_2$ . The composition by mass of the mixture effusing out of punctured football is in the ratio ( $H_2 : O_2$ )

- (A) 1 : 4 (B)  $2\sqrt{2} : 1$  (C) 1 :  $2\sqrt{2}$  (D) 4 : 1

IG0097

38. Consider the following pairs of gases A and B.

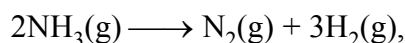
	A	B
(a)	CO	$N_2$
(b)	$O_2$	$O_3$
(c)	$^{235}UF_6$	$^{238}UF_6$

Relative rates of effusion of gases A to B under similar condition is in the order:

- (A)  $a < b < c$  (B)  $a < c < b$  (C)  $a > b > c$  (D)  $a > c > b$

IG0098

39. For the reaction



what is the % of  $NH_3$  converted if the mixture diffuses twice as fast as that of  $SO_2$  under similar conditions.

- (A) 3.125 % (B) 31.25 % (C) 6.25 % (D) 62.5 %

IG0099

40. A 4 : 1 molar mixture of He &  $CH_4$  kept in a vessel at 20 bar pressure. Due to a hole in the vessel, gas mixture leaks out. What is the composition of mixture effusing out initially -

- (A) 8 : 1 (B) 4 : 1 (C) 1 : 4 (D) 4 : 3

IG0100

41. Calculate the ratio of rate of effusion of  $O_2$  and  $H_2$  from a container containing 16gm  $O_2$  and 2gm  $H_2$   
 (A) 1 : 8 (B) 8 : 1 (C) 1 : 4 (D) 4 : 1 **IG0101**
42. The number of effusion steps required to convert a mixture of  $H_2$  and  $O_2$  from 240 : 1600 (by mass) to 3072 : 20 (by mass) is  
 (A) 2 (B) 4 (C) 5 (D) 6 **IG0102**
43. The density of the gaseous mixture in a vessel ( $CH_4$  and He) at 2 atmosphere pressure and 300 K is 0.9756 g/lit. If a small pin-hole is made on the wall of the vessel, through which gases effuse, then which of the followings is the correct composition (by volume) of the gases  $CH_4$  and He effusing out initially ?  
 (A) 1 : 1 (B) 2 : 1 (C) 3 : 1 (D) 1 : 4 **IG0103**
44. At STP, the order of root mean square speed of molecules  $H_2$ ,  $N_2$ ,  $O_2$  and HBr is :  
 (A)  $H_2 > N_2 > O_2 > HBr$  (B)  $HBr > O_2 > N_2 > H_2$   
 (C)  $HBr > H_2 > O_2 > N_2$  (D)  $N_2 > O_2 > H_2 > HBr$  **IG0104**
45. Four particles have speed 2, 3, 4 and 5 cm/s respectively. Their rms speed is :  
 (A) 3.5 cm/s (B)  $\left(\frac{27}{2}\right)$  cm/s (C)  $\sqrt{54}$  cm/s (D)  $\left(\frac{\sqrt{54}}{2}\right)$  cm/s **IG0105**
46. A flask has 10 molecules out of which four molecules are moving at  $7ms^{-1}$  & the remaining are moving at same speed of  $X ms^{-1}$ . If Urms of the gas is  $5 ms^{-1}$ . The value of 'X' will be  
 (A) 5 (B) 3 (C) 9 (D) 16 **IG0106**
47. If the average velocity of  $N_2$  molecules is 0.3 m/sec. at  $27^\circ C$ , then the velocity of 0.6 m/sec will take place at :  
 (A) 273 K (B) 927 K (C) 1000 K (D) 1200 K **IG0107**
48. Which of the following expression does not give root mean square velocity –  
 (A)  $\left(\frac{3RT}{M_w}\right)^{\frac{1}{2}}$  (B)  $\left(\frac{3P}{DM_w}\right)^{\frac{1}{2}}$  (C)  $\left(\frac{3P}{D}\right)^{\frac{1}{2}}$  (D)  $\left(\frac{3PV}{nM_w}\right)^{\frac{1}{2}}$  **IG0108**
49. Which one of the following gases would have the highest R.M.S. velocity at  $25^\circ C$  ?  
 (A) Oxygen (B) Carbon dioxide (C) Sulphur dioxide (D) Carbon monoxide **IG0109**
50. At what temperature would the rms speed of a gas molecule have twice its value at  $100^\circ C$  ?  
 (A) 4192 K (B) 1492 K (C) 9142 K (D) 2491 K **IG0110**

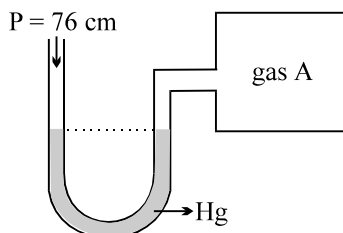
51. Two flasks X and Y have capacity 1L and 2L respectively and each of them contains 1 mole of a gas. The temperature of the flask are so adjusted that average speed of molecules in X is twice as those in Y. The pressure in flask X would be  
(A) same as that in Y (B) half of that in Y (C) twice of that in Y (D) 8 times of that in Y  
**IG0111**
52. Temperature at which most probable speed of  $O_2$  becomes equal to root mean square speed of  $N_2$  is  
[Given :  $N_2$  at  $427^\circ C$ ]  
(A) 732 K (B) 1200 K (C) 927 K (D) 800 K  
**IG0112**
53. The density ratio of  $O_2$  and  $H_2$  is 16 : 1. The ratio of their  $U_{rms}$  is :-  
(A) 4 : 1 (B) 16 : 1 (C) 1 : 4 (D) 1 : 16  
**IG0113**
54. Which of the gas have highest fraction of molecules at  $27^\circ C$  in most probable speed region -  
(A)  $H_2$  (B)  $N_2$  (C)  $O_2$  (D)  $CO_2$   
**IG0114**
55. The av. K.E./mole of an ideal monoatomic gas at  $27^\circ C$  is  
(A) 900 cal (B) 1800 cal (C) 300 cal (D) None  
**IG0115**
56. The average kinetic energy of an ideal gas per molecule in SI units at  $25^\circ C$  will be :  
(A)  $6.17 \times 10^{-21}$  kJ (B)  $6.17 \times 10^{-21}$  J (C)  $6.17 \times 10^{-20}$  J (D)  $7.16 \times 10^{-20}$  J  
**IG0116**
57. At what temperature will be total kinetic energy (KE) of 0.30 mole of He be the same as the total KE of 0.40 mole of Ar at 400 K :  
(A) 400 K (B) 373 K (C) 533 K (D) 300 K  
**IG0117**
58. Average K.E. of  $CO_2$  at  $27^\circ C$  is E. The average kinetic energy of  $N_2$  at the same temperature will be  
(A) E (B) 22E (C) E/22 (D)  $E/\sqrt{2}$   
**IG0118**
59. If a gas expands at constant temperature then :  
(A) No. of gaseous molecule decreases  
(B) kinetic energy of molecule decreases  
(C) K.E. remain same  
(D) K.E. increases  
**IG0119**
60. Total translational kinetic energy possessed by 8 gm methane at  $273^\circ C$   
(R = 2 Cal/mol-K)  
(A) 819 calorie (B) 409.5 calorie (C) 1638 calorie (D) None of these  
**IG0120**

61. Ideal gas equation in terms of K.E. per unit volume  $E$ , is-
- (A)  $P = \frac{3}{2}RT$       (B)  $P = \frac{2}{3}E$       (C)  $P = \frac{2}{3}RT$       (D)  $P = \frac{3}{2}RT$
- IG0121**
62. According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels -
- (A) In a straight line path      (B) with an accelerated velocity  
(C) In a circular path      (D) In a wavy path
- [AIEEE-2003]**  
**IG0122**
63. What volume of hydrogen gas, at 273K and 1 atm pressure will be consumed in obtaining 21.6g of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by hydrogen ?
- [AIEEE-2003]**
- (A) 44.8 L      (B) 22.4 L      (C) 89.6 L      (D) 67.2 L
- IG0123**
64. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by factor of which of the following ?
- [AIEEE-2004]**
- (A) 1/2      (B)  $\sqrt{(313/293)}$       (C) 313/293      (D) 2
- IG0124**
65. Three gases A, B and C are at same temperature. If their r.m.s. speed are in the ratio  $1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$  then their molar masses will be in the ratio :
- (A) 1 : 2 : 3      (B) 3 : 2 : 1      (C)  $1 : \sqrt{2} : \sqrt{3}$       (D)  $\sqrt{3} : \sqrt{2} : 1$
- IG0125**
66. The following gases are present under similar condition of T, P & V. The longest mean free path stands for
- (A)  $H_2$       (B)  $N_2$       (C)  $O_2$       (D)  $Cl_2$
- IG0126**
67. At constant volume,  $Z_{11}$  is directly proportional to -
- (A)  $\sqrt{P}$       (B) P      (C)  $T^2$       (D) T
- IG0127**

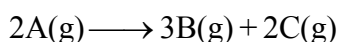
## EXERCISE # O-II

One or more may be correct :

1. An open ended mercury manometer is used to measure the pressure exerted by a trapped gas as shown in the figure. Initially manometer shows no difference in mercury level in both columns as shown in diagram.



After sparking 'A' dissociates according to following reaction

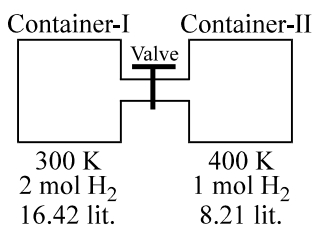


If pressure of Gas "A" decreases to 0.8 atm. Then (Assume temperature to be constant and is 300 K)

- (A) total pressure increased by 1.3 atm  
 (B) total pressure increased by 0.3 atm  
 (C) total pressure increased by 22.3 cm of Hg  
 (D) difference in mercury level is 228 mm.

IG0128

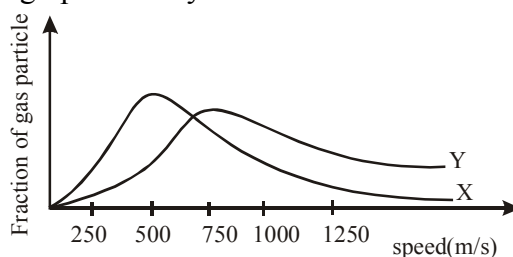
2. Select the correct option(s) :



- (A) Pressure in container-I is 3 atm before opening the valve.  
 (B) Pressure after opening the valve is 3.57 atm.  
 (C) Moles in each compartment are same after opening the valve.  
 (D) Pressure in each compartment are same after opening the valve.

IG0129

3. The graph below shows the distribution of molecular speed of two ideal gases X and Y at 200K. on the basis of the below graph identify the correct statements -



- (A) If gas X is methane, then gas Y can be CO<sub>2</sub>  
 (B) Fraction of molecules of X must be greater than Y in a particular range of speed at 200K  
 (C) Under identical conditions rate of effusion of Y is greater than that of X  
 (D) The molar kinetic energy of gas X at 200K is equal to the molar kinetic energy of Y at 200K

IG0130



4. Identify the correct statements when a fixed amount of ideal gas is heated in a container fitted with a movable piston always operating at constant pressure.
- (A) Average distance travelled between successive collisions will decrease.
- (B) Collisions frequency increases since speed of the molecules increases with increase in temperature.
- (C) Average relative speed of approach remains unaffected.
- (D) Average angle of approach remains unaffected.

IG0131

5. Choose the correct statement(s) among the following
- (A) Average molecular speed of gases increases with decrease in fraction of molecules moving slowly
- (B) Rate of effusion of gases increases with increase in collision frequency at constant volume.
- (C) Rate of effusion is inversely proportional to molecular weight of gas
- (D) Mean free path does not change with change in temperature at constant pressure.

IG0132

6. Which of the following quantities is the same for all ideal gases at the same temperature :
- (A) The kinetic energy of 1 mol
- (B) The kinetic energy of 1 g
- (C) The number of molecules in 1 mol
- (D) The number of molecules in 1 g

IG0133

7. Choose the correct statement(s) among the following -
- (A) The mean free path ( $\lambda$ ) of gaseous molecules is directly proportional to temperature of gas at constant volume
- (B) The mean free path ( $\lambda$ ) of gaseous molecules is inversely proportional to pressure of gas at constant volume
- (C) The mean free path ( $\lambda$ ) of gaseous molecules is directly proportional to volume of gas at constant T
- (D) The mean free path ( $\lambda$ ) of gaseous molecules is directly proportional to volume of gas at constant P

IG0134

8. Which statement is/are correct for postulates of kinetic theory of gases -
- (A) Gases are composed of molecules whose size is negligible compared with the average distance between them
- (B) Molecules move randomly in straight lines in all directions and at various speeds.
- (C) When molecules collide with one another the collisions are elastic. In an elastic collision the loss of kinetic energy takes place
- (D) The average kinetic energy of a molecule is proportional to the absolute temperature.

IG0135

### Paragraph for Question 9 to 11

The constant motion and high velocities of gas particles lead to some important practical consequences. One such consequence is that as minimum rapidly when they come in contact. The mixing of different gases by random molecular motion and with frequent collisions is called diffusion. A similar process in which gas molecules escape through a tiny hole into a vacuum is called effusion.

9. Helium gas at 1 atm and  $\text{SO}_2$  at 2 atm pressure, temperature being the same, are released separately at the same moment into 1 m long evacuated tubes of equal diameters. If helium reaches the other end of the tube in  $t$  sec, what distance  $\text{SO}_2$  would traverse in the same time interval in the other tube ?  
 (A) 25 cm                      (B) 50 cm                      (C) 60 cm                      (D) 75 cm

IG0136

10. 4 g of  $\text{H}_2$  effused through a pinhole in 10 sec at constant temperature and pressure. The amount of oxygen effused in the same time interval and at the same conditions of temperature and pressure would be :  
 (A) 4 g                      (B) 8 g                      (C) 16 g                      (D) 32 g

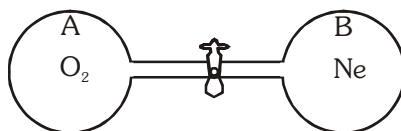
IG0137

11. For 10 min. each at  $27^\circ\text{C}$ , from two identical bulbs helium and an unknown gas X at equal pressures are leaked into a common vessel of 3 L capacity. The resulting pressure is 4.1 atm and the mixture contains 0.4 mol of helium. The molar mass of gas X is :  
 (A) 16                      (B) 32                      (C) 64                      (D) None of these

IG0138

### Paragraph for Question 12 to 13

Initially, flask A contained oxygen gas at  $27^\circ\text{C}$  and 950 mm of Hg, and flask B contained neon gas at  $27^\circ\text{C}$  and 900 mm. Finally, the two flasks were joined by means of a narrow tube of negligible volume equipped with a stopcock and gases were allowed to mix up freely. The final pressure in the combined system was found to be 910 mm of Hg.



12. What is the correct relationship between volumes of the two flasks ?  
 (A)  $V_B = 3V_A$                       (B)  $V_B = 4V_A$                       (C)  $V_B = 5V_A$                       (D)  $V_B = 4.5V_A$

IG0139

13. How many moles of gas are present in flask A in the final condition, if volume of flask B is 304 litre ? ( $R = 0.08 \text{ atm L mol}^{-1} \text{ K}^{-1}$ )  
 (A) 7.58                      (B) 3.79                      (C) 15.16                      (D) None of these

IG0139

TABLE TYPE QUESTION :

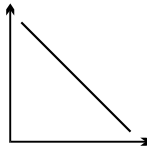
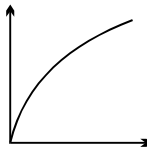
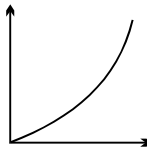
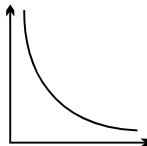
Column-I (Gases at different conditions)	Column-II (Value of speed (m/s))	Column-III
(A) CH <sub>4</sub> at 27°C	(P) U <sub>rms</sub> = 342.5	(I) Molar K.E. = 3750 Joule
(B) SO <sub>2</sub> at 27°C	(Q) U <sub>mp</sub> = 1100	(II) Molar K.E. = 5000 Joule
(C) 4 gm He at 1 atm and 24.6 litre	(R) U <sub>rms</sub> = 685	(III) Average K.E. per gram = 937.5 Joule
(D) 32 gm O <sub>2</sub> at 127°C	(S) U <sub>rms</sub> = 550	(IV) Average K.E. per gram = 234 Joule.

(Given :  $R = \frac{25}{3} \frac{J}{mol \times K}$ ,  $\sqrt{30} = 5.48$ ,  $\sqrt{\frac{2}{3}} = 0.8$ ,  $\sqrt{5} = 2.2$ )

14. Which of the following is correct  
 (A) A ; R ; 4                      (B) A ; R ; 2                      (C) A ; Q ; 4                      (D) B ; R ; 1 IG0140
15. Which of the following is correct  
 (A) B ; Q ; 1                      (B) B ; Q ; 2                      (C) B ; P ; 1                      (D) C ; S ; 3 IG0140
16. Which of the following is correct  
 (A) C ; Q ; 3                      (B) D ; R ; 2                      (C) D ; S ; 1                      (D) D ; S ; 4 IG0140

Match the column:

17. Match the entries in column I with entries in Column II and then pick out correct options.

Column I	Column II
(A) $\frac{1}{V^2}$ vs P for ideal gas at constant T and n.	(P) 
(B) V vs $\frac{1}{T}$ for ideal gas at constant P and n	(Q) 
(C) log P vs log V for ideal gas at constant T and n.	(R) 
(D) V vs $\frac{1}{P^2}$ for ideal gas at constant T and n.	(S) 

IG0141

## EXERCISE # JEE-MAINS

1. The molecular velocity of any gas is :- [AIEEE-2011]  
 (1) inversely proportional to the square root of temperature  
 (2) inversely proportional to absolute temperature  
 (3) directly proportional to square of temperature  
 (4) directly proportional to square root of temperature  
IG0142
2.  $\alpha$ ,  $v$  and  $u$  represent most probable velocity, average velocity and root mean square velocity respectively of a gas at a particular temperature. The correct order among the following is -[JEE(Main)-2012]  
 (1)  $\alpha > u > v$                       (2)  $v > u > \alpha$                       (3)  $u > v > \alpha$                       (4)  $u > \alpha > v$   
IG0143
3. An open vessel at 300 K is heated till  $\frac{2}{5}$ th of the air in it is expelled. Assuming that the volume of the vessel remains constant, the temperature to which the vessel is heated is :-  
[JEE(Main-online)-2012]  
 (1) 750 K                      (2) 400 K                      (3) 500 K                      (4) 1500K  
IG0144
4. For 1 mol of an ideal gas at constant temperature T, the plot of  $(\log P)$  against  $(\log V)$  is a (P : Pressure, V : Volume) :- [JEE(Main-online)-2012]  
 (1) Straight line parallel to x-axis                      (2) Curve starting at origin  
 (3) Straight line with a negative slope                      (4) Straight line passing through origin  
IG0145
5. The relationship among most probable velocity, average velocity and root mean square velocity is respectively :- [JEE(Main-online)-2012]  
 (1)  $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$                       (2)  $\sqrt{2} : \sqrt{3} : \sqrt{8/\pi}$                       (3)  $\sqrt{3} : \sqrt{8/\pi} : \sqrt{2}$                       (4)  $\sqrt{8/\pi} : \sqrt{3} : \sqrt{2}$   
IG0146
6. Which one of the following is the wrong assumption of kinetic theory of gases ? [JEE(Main-online)-2013]  
 (1) All the molecules move in straight line between collision and with same velocity.  
 (2) Molecules are separated by great distances compared to their sizes.  
 (3) Pressure is the result of elastic collision of molecules with the container's wall.  
 (4) Momentum and energy always remain conserved.  
IG0147
7. By how many folds the temperature of a gas would increase when the root mean square velocity of the gas molecules in a container of fixed volume is increased from  $5 \times 10^4$  cm/s to  $10 \times 10^4$  cm/s ? [JEE(Main-online)-2013]  
 (1) Four                      (2) three                      (3) Two                      (4) Six  
IG0148

8. For gaseous state, if most probable speed is denoted by  $C^*$ , average speed by  $\bar{C}$  and mean square speed by  $C$ , then for a large number of molecules the ratios of these speeds are :-

[JEE(Main-offline)-2013]

- (1)  $C^* : \bar{C} : C = 1.225 : 1.128 : 1$                       (2)  $C^* : \bar{C} : C = 1.128 : 1.225 : 1$   
 (3)  $C^* : \bar{C} : C = 1 : 1.128 : 1.225$                       (4)  $C^* : \bar{C} : C = 1 : 1.225 : 1.128$

IG0149

9. A gaseous compound of nitrogen and hydrogen contains 12.5%(by mass) of hydrogen. The density of the compound relative to hydrogen is 16. The molecular formula of the compound is :

[JEE(Main-online)-2014]

- (1)  $NH_2$                       (2)  $NH_3$                       (3)  $N_3H$                       (4)  $N_2H_4$

IG0150

10. The initial volume of a gas cylinder is 750.0 mL. If the pressure of gas inside the cylinder changes from 840.0 mm Hg to 360.0 mm Hg, the final volume the gas will be [JEE(Main-online)-2014]

- (1) 1.750 L                      (2) 7.50 L                      (3) 3.60 L                      (4) 4.032 L

IG0151

11. The temperature at which oxygen molecules have the same root mean square speed as helium atoms have at 300 K is : (Atomic masses : He = 4 u, O = 16 u) [JEE(Main-online)-2014]

- (1) 1200 K                      (2) 600 K                      (3) 300 K                      (4) 2400 K

IG0152

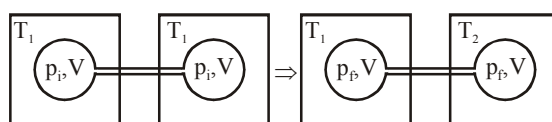
12. Which of the following is not an assumption of the kinetic theory of gases ?

- (1) Gas particles have negligible volume. [JEE-Mains (online)-2015]  
 (2) A gas consists of many identical particles which are in continual motion.  
 (3) At high pressure, gas particles are difficult to compress.  
 (4) Collisions of gas particles are perfectly elastic.

IG0153

13. Two closed bulbs of equal volume(V) containing an ideal gas initially at pressure  $p_i$  and temperature  $T_1$  are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to  $T_2$ . The final pressure  $p_f$  is :-

[JEE-Mains-2016]



- (1)  $2p_i \left( \frac{T_1 T_2}{T_1 + T_2} \right)$                       (2)  $p_i \left( \frac{T_1 T_2}{T_1 + T_2} \right)$                       (3)  $2p_i \left( \frac{T_1}{T_1 + T_2} \right)$                       (4)  $2p_i \left( \frac{T_2}{T_1 + T_2} \right)$

IG0154

14. At 300 K, the density of a certain gaseous molecule at 2 bar is double to that of dinitrogen ( $N_2$ ) at 4 bar. The molar mass of gaseous molecule is:- [JEE-Mains-2017(ONLINE)]

(1) 28 g mol<sup>-1</sup>      (2) 56 g mol<sup>-1</sup>      (3) 224 g mol<sup>-1</sup>      (4) 112 g mol<sup>-1</sup>

IG0155

15. Assuming ideal gas behaviour, the ratio of density of ammonia to that of hydrogen chloride at same temperature and pressure is : (Atomic wt. of Cl = 35.5 u) [JEE-Mains-2018(ONLINE)]

(1) 0.64      (2) 1.64      (3) 1.46      (4) 0.46

IG0156

16. Points I, II and III in the following plot respectively correspond to .

( $V_{mp}$  : most probable velocity)

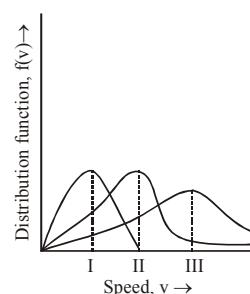
[JEE-Mains-2019(ONLINE)]

(1)  $V_{mp}$  of  $N_2$  (300K);  $V_{mp}$  of  $H_2$ (300K);  $V_{mp}$  of  $O_2$ (400K)

(2)  $V_{mp}$  of  $H_2$  (300K);  $V_{mp}$  of  $N_2$ (300K);  $V_{mp}$  of  $O_2$ (400K)

(3)  $V_{mp}$  of  $O_2$  (400K);  $V_{mp}$  of  $N_2$ (300K);  $V_{mp}$  of  $H_2$ (300K)

(4)  $V_{mp}$  of  $N_2$  (300K);  $V_{mp}$  of  $O_2$ (400K);  $V_{mp}$  of  $H_2$ (300K)



IG0157

17. 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume 10 m<sup>3</sup> at 1000 K. Given R is the gas constant in JK<sup>-1</sup> mol<sup>-1</sup>, x is : [JEE-Mains-2019(ONLINE)]

(1)  $\frac{2R}{4+12}$

(2)  $\frac{2R}{4-R}$

(3)  $\frac{4-R}{2R}$

(4)  $\frac{4+R}{2R}$

IG0158

18. An open vessel at 27°C is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is : [JEE-Mains-2019(ONLINE)]

(1) 750°C

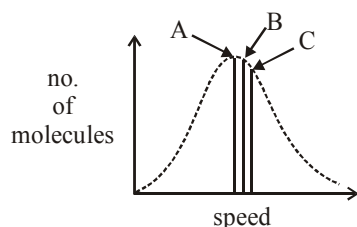
(2) 500°C

(3) 750 K

(4) 500 K

IG0159

19. Identify the correct labels of A, B and C in the following graph from the options given below:



[JEE(Main-online)-2020]

Root mean square speed ( $V_{rms}$ ) ; most probable speed ( $V_{mp}$ ) ; Average speed ( $V_{av}$ )

(1) A –  $V_{rms}$  ; B –  $V_{mp}$  ; C –  $V_{av}$

(2) A –  $V_{av}$  ; B –  $V_{rms}$  ; C –  $V_{mp}$

(3) A –  $V_{mp}$  ; B –  $V_{rms}$  ; C –  $V_{av}$

(4) A –  $V_{mp}$  ; B –  $V_{av}$  ; C –  $V_{rms}$

IG0160

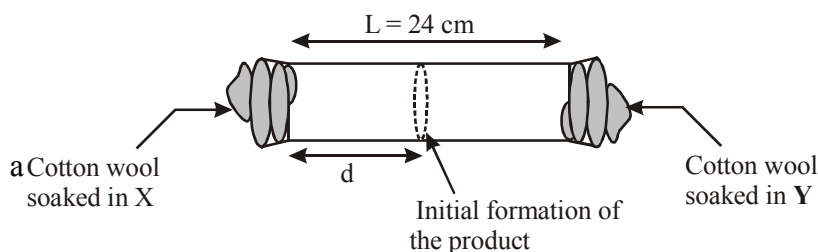
## EXERCISE # JEE-ADVANCED

1. To an evacuated vessel with movable piston under external pressure of 1 atm., 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm. at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to [JEE 2011]

IG0161

## Paragraph for Question 2 &amp; 3

X and Y are two volatile liquids with molar weights of  $10\text{g mol}^{-1}$  and  $40\text{g mol}^{-1}$  respectively. Two cotton plugs, one soaked in X and the other soaked in Y, are simultaneously placed at the ends of a tube of length  $L = 24\text{ cm}$ , as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300K. Vapours of X and Y react to form a product which is first observed at a distance  $d\text{ cm}$  from the plug soaked in X. Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours. [JEE 2014]



2. The value of  $d$  in cm (shown in the figure), as estimated from Graham's law, is -

(A) 8      (B) 12      (C) 16      (D) 20

IG0162

3. The experimental value of  $d$  is found to be smaller than the estimate obtained using Graham's law. This is due to -

(A) Larger mean free path for X as compared to that of Y  
 (B) Larger mean free path for Y as compared to that of X  
 (C) Increased collision frequency of Y with the inert gas as compared to that of X with the inert gas  
 (D) Increased collision frequency of X with the inert gas as compared to that of Y with the inert gas

IG0163

4. A closed tank has two compartments A and B, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Figure 1). If the old partition is replaced by a new partition which can slide and conduct heat but does NOT allow the gas to leak across (Figure 2), the volume (in  $\text{m}^3$ ) of the compartment A after the system attains equilibrium is \_\_\_\_.

[JEE 2018]

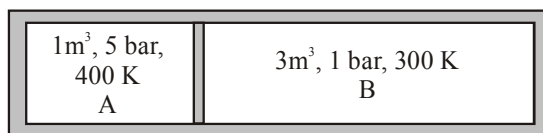


Figure 1

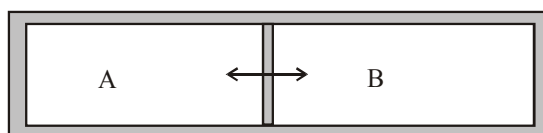


Figure 2

IG0164

5. Which of the following statement(s) is (are) correct regarding the root mean square speed ( $U_{\text{rms}}$ ) and average translational kinetic energy ( $\epsilon_{\text{av}}$ ) of a molecule in a gas at equilibrium ?

- (1)  $U_{\text{rms}}$  is doubled when its temperature is increased four times
- (2)  $\epsilon_{\text{av}}$  at a given temperature does not depend on its molecular mass
- (3)  $U_{\text{rms}}$  is inversely proportional to the square root of its molecular mass
- (4)  $\epsilon_{\text{av}}$  is doubled when its temperature is increased four times

[JEE 2019]

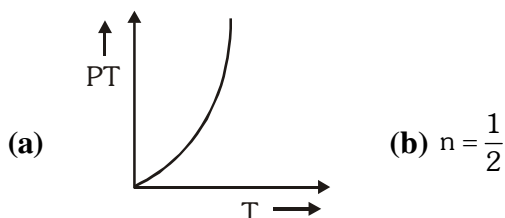
IG0165



ANSWER-KEY

EXERCISE # S-I

1. Ans.(5)                      2. Ans. (90)                      3. Ans.(1024)                      4. Ans. (150)  
 5. Ans.(18)                      6. Ans.(5.46)                      7. Ans. (100)                      8. Ans. 29.17 m<sup>3</sup>  
 9. Ans. (a) 2<sup>1/3</sup>cm ; (b) 2 cm  
 10. Ans.



11. Ans.  $n_A = \frac{1}{22.4}$  ,  $n_B = \frac{1}{22.4\sqrt{3}}$   
 12. Ans.(4)                      13. Ans.(4)                      14. Ans (8)                      15. Ans. (50)  
 16. 15 gm ; 12 dm<sup>3</sup>                      17. Ans.39,800 breaths.                      18. Ans.45 bar  
 19. Ans. T = 75 K , P = 0.062 atm  
 20. Ans.(1.25 atm)                      21. Ans.(15:16)                      22. Ans.(0.8 bar)                      23. Ans.(0.5 P mm)  
 24. 1.8 atm                      25.  $P_{H_2} = 1.5$  atm ,  $P_{N_2} = 4.5$  atm                      26. 25 %  
 27.  $p_{N_2} = 494$  mm ,  $p_{O_2} = 114$  mm ,  $p_{CO_2} = 152$  mm  
 28. 5 cm.                      29. Ans. (7)                      30. Ans. (420)                      31. P = 146.5 mm  
 32. Ans. (2 : 1)                      33. Ans. (4)                      34. Ans. (8)                      35. 8/1  
 36. XeF<sub>6</sub>.                      37. n = 4                      38. 1/4  
 39. Ans.(a) 1934.24 m/sec. (b) 500 m/sec. (c) 17.32 m/sec.  
 40. Ans. (25)                      41. Ans.(2)                      42. Ans. (2)                      43. Ans. (4)  
 44. Ans.(2)                      45. Ans.(2)

EXERCISE # S2

1. Ans. 0.94 mole                      2. Ans.(4)  
 3. Ans. (i) P<sub>1</sub> = 5 atm; (ii) T<sub>3</sub> = 360 K; (iii) V<sub>1</sub> = 16 lit.; (iv) P<sub>2</sub> = 1.5 atm ; (v) T<sub>4</sub> = 90 K  
 4. Ans. P ∝ d; P = kd & k =  $\frac{1 \text{ atm}}{1 \text{ meter}}$  ; (a) 80; (b) 1295 moles  
 5. Ans. 6 atm, No                      6. Ans. 10,000 K  
 7. Ans. 2 atmp                      8. Ans. (6)  
 9. Ans. (2)                      10. Ans. (380)  
 11. (i) 1.5 atm ; (ii) O<sub>2</sub> = 0.75 atm, O<sub>3</sub> = 0.5 atm ; (iii) 0.208 atm  
 12. Ans. (8.4)                      13. Ans. (4)                      14. Ans. (8)  
 15. Ans. (i) 0.012 atm; (ii) 2.5 × 10<sup>22</sup>; (iii) 3.6 J; (iv) 300 J; (v)  $\frac{1}{\sqrt{2}}$  ; (vi) 0.4 × 10<sup>-3</sup> : 1

## EXERCISE # O-I

- |             |             |             |             |
|-------------|-------------|-------------|-------------|
| 1. Ans.(C)  | 2. Ans.(C)  | 3. Ans.(C)  | 4. Ans.(B)  |
| 5. Ans.(C)  | 6. Ans.(C)  | 7. Ans.(B)  | 8. Ans.(D)  |
| 9. Ans.(A)  | 10. Ans.(C) | 11. Ans.(C) | 12. Ans.(A) |
| 13. Ans.(B) | 14. Ans.(B) | 15. Ans.(C) | 16. Ans.(D) |
| 17. Ans.(B) | 18. Ans.(C) | 19. Ans.(C) | 20. Ans.(D) |
| 21. Ans.(C) | 22. Ans.(A) | 23. Ans.(D) | 24. Ans.(D) |
| 25. Ans.(A) | 26. Ans.(B) | 27. Ans.(B) | 28. Ans.(D) |
| 29. Ans.(A) | 30. Ans.(C) | 31. Ans.(D) | 32. Ans.(B) |
| 33. Ans.(D) | 34. Ans.(C) | 35. Ans.(A) | 36. Ans.(C) |
| 37. Ans.(A) | 38. Ans.(B) | 39. Ans.(C) | 40. Ans.(A) |
| 41. Ans.(A) | 42. Ans.(C) | 43. Ans.(A) | 44. Ans.(A) |
| 45. Ans.(D) | 46. Ans.(B) | 47. Ans.(D) | 48. Ans.(B) |
| 49. Ans.(D) | 50. Ans.(B) | 51. Ans.(D) | 52. Ans.(B) |
| 53. Ans.(C) | 54. Ans.(D) | 55. Ans.(A) | 56. Ans.(B) |
| 57. Ans.(C) | 58. Ans.(A) | 59. Ans.(C) | 60. Ans.(A) |
| 61. Ans.(B) | 62. Ans.(A) | 63. Ans.(D) | 64. Ans.(C) |
| 65. Ans.(A) | 66. Ans.(A) | 67. Ans.(A) |             |

## EXERCISE # O-II

- |              |                                       |               |                |
|--------------|---------------------------------------|---------------|----------------|
| 1. Ans.(B,D) | 2. Ans.(A,D)                          | 3. Ans. (C,D) | 4. Ans.(D)     |
| 5. Ans.(A,B) | 6. Ans.(A,C)                          | 7. Ans.(C,D)  | 8. Ans.(A,B,D) |
| 9. Ans.(B)   | 10. Ans.(C)                           | 11. Ans.(C)   | 12. Ans.(B)    |
| 13. Ans.(B)  | 14. Ans.(A)                           | 15. Ans.(C)   |                |
| 16. Ans.(A)  | 17. Ans.(A)→R ; (B)→S ; (C)→P ; (D)→Q |               |                |

## EXERCISE # JEE-MAINS

- |             |             |             |             |
|-------------|-------------|-------------|-------------|
| 1. Ans.(4)  | 2. Ans.(3)  | 3. Ans.(3)  | 4. Ans.(3)  |
| 5. Ans.(1)  | 6. Ans.(1)  | 7. Ans.(1)  | 8. Ans.(3)  |
| 9. Ans.(4)  | 10. Ans.(1) | 11. Ans.(4) | 12. Ans.(3) |
| 13. Ans.(4) | 14. Ans.(4) | 15. Ans.(4) | 16. Ans.(4) |
| 17. Ans.(3) | 18. Ans.(4) | 19. Ans.(4) |             |

## EXERCISE # JEE-ADVANCED

- |                |            |            |               |
|----------------|------------|------------|---------------|
| 1. Ans.(7)     | 2. Ans.(C) | 3. Ans.(D) | 4. Ans.(2,22) |
| 5. Ans.(1,2,3) |            |            |               |



# Chapter Contents

## 02

## REAL GAS

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## REAL GAS

### 1. Introduction :

An ideal gas is a hypothetical gas whose pressure, volume and temperature behaviour is completely described by the ideal gas equation. Actually no gas is ideal or perfect in nature. All gases are real gases.

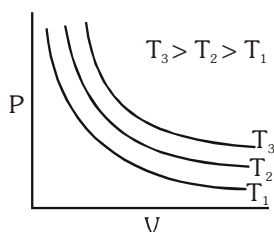
Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure. Real gases deviates from ideal behaviour because of mainly two assumptions of "Kinetic theory of gases".

- (i) The volume of gas particle is negligible compared to volume of container (while the real gas particle may have some significant volume).
- (ii) There is no interaction between gaseous particles (while attraction forces exist between real gas particles).

### 1.1 Comparision between Real and Ideal gas :

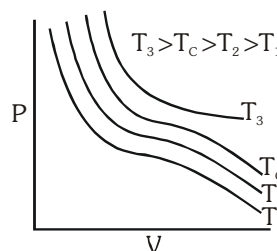
#### IDEAL GAS

- (i)  $PV = nRT$
- (ii) No liquifaction is possible.



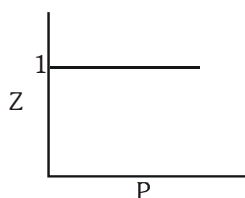
#### REAL GAS

- (i)  $PV \neq nRT$   
 $\Rightarrow$  If  $PV > nRT$  (Gas is less compressible than ideal gas).  
 If  $PV < nRT$  (Gas is more compressible than ideal gas).
- (ii) Liquifaction is possible below a certain temperature.

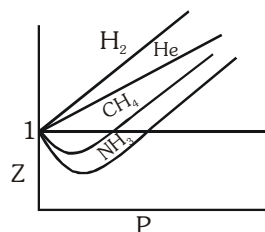


$\Rightarrow$  Follow critical phenomena and can not liquefy above  $T_c$ .

#### (iii)



#### (iii)



- (iv) No interaction force is present between gas particles.
- (v) Volume of gas particles is negligible w.r.t. volume of container.
- (iv) Interaction force exist between gas particles which vary depending upon conditions.
- (v) Volume of gas particles has significant value and can not be neglected normally w.r.t. volume of container.

## 1.2 VANDER WAAL EQUATION OF REAL GASES

The ideal gas equation does not consider the effect of attractive forces and molecular volume.

Van der Waal corrected the ideal gas equation by taking the effect of

- (a) Molecular volume
- (b) Molecular attraction

### (A) Volume correction :

In the ideal gas equation,  $P_i V_i = nRT$ ,  $V_i$  represents the ideal volume where the molecules can move freely. In real gases, a part of the total volume is occupied by the gas molecules. Hence the free volume  $V_i$  is the total volume  $V$  minus the volume occupied by the gas molecules.

Real volume of gas = Actual volume of container – volume occupied by molecules in motion.

$$V_i = V - nb \text{ for } n \text{ mole of gas}$$

Where  $b$  is termed the 'excluded volume' or 'co-volume' per mole.

It is constant and characteristic for each gas.

$$b = 4 \times \text{volumes of one molecules} \times N_A$$

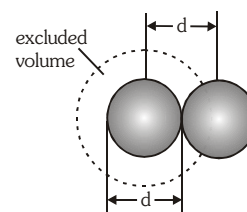
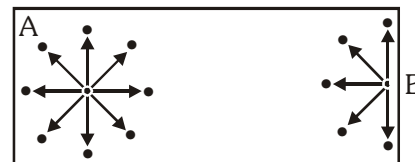


Illustration of excluded volume

### (B) Pressure correction :

In order to take account the effect of intermolecular forces of attraction, let us consider a molecule A in the midst of the vessel.

This molecule is surrounded by other molecules in a symmetrical manner and is being attracted uniformly on all sides by the neighbouring molecules with the result that this molecule on the whole experiences no net force of attraction.



Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only in one side of the vessel, i.e. towards its centre, with the result of that, this molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule, and hence its momentum. Thus, the molecule does not contribute as much force as it would have, had there been no force of attraction. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas.

Van der Waals noted that the total force of attraction on any molecule about to hit a wall is proportional to the concentration of neighbouring molecules,  $n/V$ . However, the number of molecules about to hit the wall per unit wall area is also proportional to the concentration  $n/V$ . Therefore, the force per unit wall area, or pressure, is reduced from that assumed in the ideal gas wall by a factor proportional to  $n^2/V^2$ . Letting  $a$  be the proportionality constant, we can write

$$P(\text{actual}) = P(\text{ideal}) - \frac{an^2}{V^2} \quad \text{or} \quad P(\text{ideal}) = P(\text{actual}) + \frac{an^2}{V^2}$$

'a' is a constant which depends upon the nature of the gas,

Combining the two corrections,

for 1 mole of gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

and for  $n$  mole of gas  $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

**The constants 'a' and 'b' :**

Van der Waals constant for attraction 'a' and volume 'b' are characteristic constants for a given gas.

- (i) The 'a' values for a given gas are measure of intermolecular forces of attraction. More are the intermolecular forces of attraction, more will be the value of a.
- (ii) The gas having higher value of 'a' can be liquefied easily and therefore  $H_2$  and He are not liquefied easily.
- (iii) Unit of 'a' is  $\text{atm lit}^2 \text{mole}^{-2}$  or  $\text{dyne cm}^4 \text{mole}^{-2}$  or  $\text{Nm}^4 \text{mol}^{-2}$
- (iv) Unit of 'b' is  $\text{lit mole}^{-1}$  or  $\text{cm}^3 \text{mole}^{-1}$  or  $\text{m}^3 \text{mol}^{-1}$

□ **The van der Waals constants for some common gases**

Gas	a (atmL <sup>2</sup> mol <sup>-2</sup> )	b (L mol <sup>-1</sup> )
Ammonia	4.17	0.0371
Argon	1.35	0.0322
Carbon dioxide	3.59	0.0427
Carbon monoxide	1.49	0.0399
Chlorine	6.49	0.0562
Ethane	5.49	0.0638
Ethanol	2.56	0.087
Ethylene	4.47	0.0571
Helium	0.034	0.0237
Hydrogen	0.024	0.0266
Hydrogen chloride	3.67	0.0408
Hydrogen bromide	4.45	0.0433
Methane	2.25	0.0428
Neon	0.21	0.0171
Nitric oxide	1.34	0.0279
Nitrogen	1.39	0.0319
Oxygen	1.36	0.0318
Sulphur dioxide	3.71	0.0564
Water	5.44	0.0305

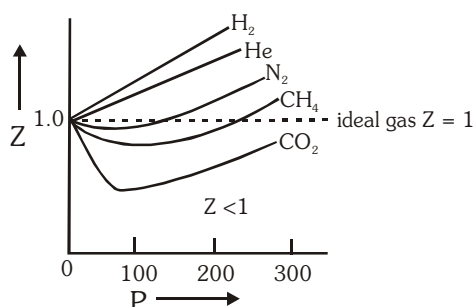
**1.3 COMPRESSIBILITY FACTOR (Z) :**

The extent to which a real gas departs from the ideal behaviour may be expressed in terms of compressibility factor (Z),

$$Z = \frac{(PV)_{\text{real}}}{(PV)_{\text{ideal}}} = \frac{V_m}{V_{m(\text{ideal})}} = \frac{PV_m}{RT} \quad [V_m = \text{molar volume}]$$

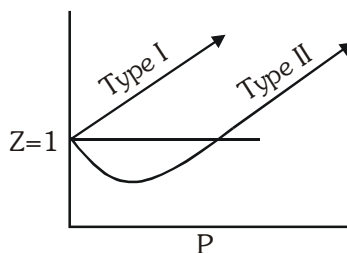
### 1.4 Plots of compressibility factor vs pressure :

- (i) For an ideal gas  $Z = 1$  and is independent of temperature and pressure.
- (ii) Exceptional behaviour of  $H_2$  and He :  
For these gases  $Z > 1$  at  $0^\circ\text{C}$ .
- (iii) Effect of pressure :  
At very low  $P$ ,  $PV_m \approx RT$  i.e.  $Z \approx 1$   
At low  $P$ ,  $PV_m < RT$  i.e.  $Z < 1 \Rightarrow$  attractive forces dominant  
At high  $P$ ,  $PV_m > RT$  i.e.  $Z > 1 \Rightarrow$  repulsive forces dominant
- (iv) For the gases which are easily liquefied (e.g.  $\text{CO}_2$ )  $Z$  dips sharply below the ideal line in the low pressure region.
- (v) Effect of temperature : An increase in temperature shows a decrease in deviation from ideal behaviours,  $Z$  approaches unity with increase in temperature.



### 1.5 Verification of compressibility factor using Van Der Waal's equation :

Variation of  $Z$  with  $P$  for real gas at any temperature is given by following graph.



Van der waal equation :

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

#### (i) At low pressure and constant temperature

At low pressure  $V_m$  will be high hence  $b$  can be neglected in comparison to  $V_m$ . But  $\frac{a}{V_m^2}$  can't be neglected as pressure is low. Thus equation would be

$$\left(P + \frac{a}{V_m^2}\right)V_m = RT$$

$$PV_m + \frac{a}{V_m} = RT$$



$$\frac{PV_m}{RT} + \frac{a}{V_m RT} = 1$$

$$Z = 1 - \frac{a}{V_m RT} \Rightarrow Z < 1$$

Substituting  $V_m = \frac{RT}{P}$  in above equation ;  $Z = 1 - \frac{aP}{R^2 T^2}$

At low pressure, real gas is easily compressible as compared to an ideal gas.

**(ii) At high pressure and constant temperature**

At high pressure the  $V_m$  will be low. So  $b$  can't be neglected in comparison to  $V_m$  but  $\frac{a}{V_m^2}$  can be neglected as compared to much higher values of  $P$ .

Then van der Waals' equation will be

$$P(V_m - b) = RT$$

$$PV_m - Pb = RT$$

$$\frac{PV_m}{RT} = \frac{Pb}{RT} + 1$$

$$Z = \frac{Pb}{RT} + 1 \Rightarrow (Z > 1)$$

At high pressure, gas is more difficult to compress as compared to an ideal gas.

**(iii) At low pressure and very high temperature.**

$V_m$  will be very large, hence 'b' can be neglected and  $\frac{a}{V_m^2}$  can also be neglected as  $V_m$  is very large.

$$PV_m = RT \text{ (ideal gas condition)}$$

**(iv)** For  $H_2$  or  $He$   $a \simeq 0$  because molecules are smaller in size or vander Waal's forces will be very weak.

$$P(V_m - b) = RT$$

So  $Z = 1 + \frac{Pb}{RT}$

This explains type I plot.

**Ex.1.** Calculate the pressure exerted by 5 mole of  $CO_2$  in one litre vessel at  $47^\circ C$  using van der waal's equation. Also report the pressure of gas if it behaves ideal in nature.

Given that  $a = 3.592 \text{ atm lt}^2 \text{ mol}^{-2}$ ,  $b = 0.0427 \text{ L/mol}$ . Also, if the volume occupied by  $CO_2$  molecules is negligible, then calculate the pressure exerted by one mole of  $CO_2$  gas at  $273 \text{ K}$ .

**Sol.** Vander waal's equation

$$\left[ p + \frac{n^2 a}{V^2} \right] [V - nb] = nRT$$

$$n_{\text{CO}_2} = 5, V = 1 \text{ litre}, T = 320 \text{ K}, a = 3.592, b = 0.0427$$

$$\therefore \left[ P + 25 \times \frac{3.592}{1} \right] [1 - 5 \times 0.0427] = 5 \times 0.0821 \times 320$$

$$\therefore P = 77.218 \text{ atm}$$

For ideal behaviour of gas,  $PV = nRT$

$$\therefore P \times 1 = 5 \times 0.0821 \times 320$$

$$\therefore P = 131.36 \text{ atm}$$

For one mole  $\left[ P + \frac{a}{V^2} \right] [V - b] = RT$

$$\therefore P = \frac{RT}{V} - \frac{a}{V^2}$$

$$\therefore P = \frac{0.0821 \times 273}{22.4} - \frac{3.592}{(22.4)^2}$$

$$\therefore P = 0.9922 \text{ atm}$$

The volume occupied by 1 mole at 273 K is 22.4 litre if  $b$  is negligible.

- Ex.2** One mole of  $\text{CCl}_4$  vapours at  $77^\circ\text{C}$  occupies a volume of 35.0 L. If vander waal's constants are  $a = 20.39 \text{ L}^2 \text{ atm mol}^{-2}$  and  $b = 0.1383 \text{ L mol}^{-1}$ , calculate compressibility factor  $Z$  under,  
 (a) low pressure region. (b) high pressure region.

**Sol.** (a) Under low pressure region,  $V$  is high

$$\therefore (V - b) \approx V$$

$$\left( P + \frac{a}{V^2} \right) V = RT$$

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT} + \frac{a}{RTV} = 1$$

$$Z = \frac{PV}{RT} = \left( 1 - \frac{a}{RTV} \right) = 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.98$$

(b) Under high pressure region,  $P$  is high,

$$\left( P + \frac{a}{V^2} \right) \approx P$$

$$\therefore P(V - b) = RT$$

$$PV - Pb = RT$$

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\therefore Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT} \quad \left( \because \frac{PV}{RT} = 1, \text{ or } \frac{P}{RT} = \frac{1}{V} \right)$$

$$Z = 1 + \frac{b}{V} = 1 + \frac{0.1383}{35} = 1 + 0.004 = 1.004$$

- Ex.3** One way of writing the equation of state for real gases is  $PV = RT \left[ 1 + \frac{B}{V} + \dots \right]$  where  $B$  is a constant. Derive an approximate expression for  $B$  in terms of van der Waal's constants  $a$  and  $b$ .

Sol. According to van der Waal's equation

$$\left[ P + \frac{a}{V^2} \right] [V - b] = RT \text{ or } P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

Multiply by V, then

$$PV = \frac{RTV}{(V-b)} - \frac{a}{V} \quad \text{or} \quad PV = RT \left[ \frac{V}{V-b} - \frac{a}{VRT} \right]$$

$$\text{or } PV = RT \left[ \left( 1 - \frac{b}{V} \right)^{-1} - \frac{a}{VRT} \right]$$

$$\therefore \left[ 1 - \frac{b}{V} \right]^{-1} = 1 + \frac{b}{V} + \left( \frac{b}{V} \right)^2 + \dots$$

$$\therefore PV = RT \left[ 1 + \frac{b}{V} + \dots - \frac{a}{VRT} \right]$$

$$PV = RT \left[ 1 + \left( b - \frac{a}{RT} \right) \cdot \frac{1}{V} + \dots \right]$$

$$\therefore B = b - \frac{a}{RT}$$

## 2. BOYLE TEMPERATURE :

(i) It is temperature at which a real gas behave ideally in a wide range of pressure.

(ii) (a) Temperature < Boyle temperature

$Z < 1$ , low pressure range

$Z > 1$ , high pressure range

(b) Temperature = Boyle temperature

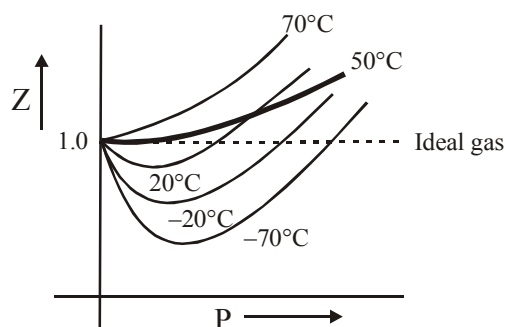
$Z = 1$ , low pressure range

$Z > 1$ , high pressure range

(c) At temperature > Boyle temperature

$Z > 1$ , at all pressure

(d)  $T \rightarrow \infty, Z \rightarrow 1$



On increasing the temperature, the thermal energy increases and simultaneously the attractive forces decreases. Hence a temperature comes at which the thermal energy become too high that it balances the effect of attraction and gas molecules becomes independent.

If at Boyle temperature, pressure is increased, molecules come more closer. Due to repulsive force,  $Z$  becomes greater than 1.

### 2.1 CALCULATION OF $T_B$ :

$$(i) \quad PV_m = RT = \left( 1 + \frac{B}{V_m} + \underbrace{\frac{C}{V_m^2}}_{\text{negligible}} + \dots \right) \text{ at low pressure.}$$

At  $T = T_B$ , the second initial coefficient should be 0

$$B = 0$$

$$\text{or} \quad b - \frac{a}{RT_B} = 0$$

$$\therefore \quad \boxed{T_B = \frac{a}{Rb}}$$

(ii) Calculus method :

At Boyle temperature,  $\left( \frac{\partial Z}{\partial P} \right)_T = 0$  at low pressure.

**Ex.4** Derive the expression for compressibility factor of a vanderwaal gas at Boyle temperature.

$$\text{Solution : } Z = \frac{V_m}{V_m - b} - \frac{a}{V_m - RT}$$

At Boyle temperature,

$$Z = \frac{V_m}{V_m - b} - \frac{a}{V_m R \times \frac{a}{Rb}}$$

$$Z = \frac{V_m}{V_m - b} - \frac{b}{V_m}$$

$$Z = \frac{V_m^2 - V_m b + b^2}{V_m (V_m - b)}$$

$$Z = 1 + \frac{b^2}{V_m (V_m - b)}$$

**Ex.5** Calculate the volume occupied by 2 moles of a vanderwall gas at 5 atm 800 K.

Given :  $a = 4.0 \text{ atm } \ell^2 \text{ mol}^{-2}$ ,  $b = 0.0625 \text{ } \ell \text{ mol}^{-1}$ ,  $R = 0.08 \text{ } \ell \text{-atm/K-mol}$

$$\text{Solution : } T_B = \frac{a}{Rb} = 800\text{K}$$

Gas behave ideally at given condition.

$$PV = nRT$$

$$5 \times V = 2 \times 0.08 \times 800$$

$$V = 25.6 \text{ litre}$$

### 3. LIQUEFACTION OF GASES AND CRITICAL POINTS

The phenomenon of converting a gas into liquid is known as liquefaction. The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that they exist in liquid state. A gas can be liquefied by :

- Increasing pressure :** An increase in pressure results decrease in intermolecular distance.
- Decreasing temperature :** A decrease in temperature results decrease in kinetic energy of molecules.

**Note :** Due to absence of intermolecular forces, ideal gases can never be liquified.

#### 3.1 Andrews Isotherms :

The essential conditions for liquefaction of gases were discovered by Andrews (1869) as a result of his study of P–V–T relationship for CO<sub>2</sub>. The types of isotherms are shown in figure.

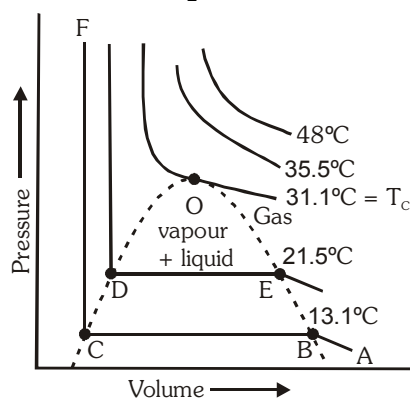


Fig : Isotherms for carbon dioxide

#### Observations from figure :

- At low temperatures :** For the curve ABCF, as the pressure increases, volume of the curve decreases (curve A to B). At point B, at constant pressure, liquefaction commences and the volume decreases rapidly (because gas is converted to liquid with higher density). At point C, liquefaction is complete. The line CF represents the variation of V with P of the liquid state. The steepness of the line CF indicates that the liquid cannot be easily compressed. Thus AB, represent gaseous state, BC represent liquid and vapour in equilibrium and CF represent liquid state.

The pressure corresponding to the line BC is vapour pressure of the liquid at that temperature.

- At lower temperatures :** Similar type of curve as in case (A) is obtained but the width of the horizontal portion is reduced. The pressure corresponding to this portion is higher than at lower temperatures.
- At high temperatures :** (say 48°C), the isotherms are like those of ideal gas. Gas does not liquify, even at very high pressure.
- At temperature (31.1°C) :** The horizontal portion is reduced to a point.

The isotherm at  $T_C$  is called **critical isotherm**.

At point O,  $\frac{dP}{dV} = 0$ .

The point O is called the **point of inflection**.

### 3.2 Critical parameters or critical constants :

**Critical temperature ( $T_C$ )** : The temperature above which a system can never be liquefied by the application of pressure alone i.e. the temperature above which a liquid cannot exist is called the critical temperature  $T_C$ .

**Critical pressure ( $P_C$ )** : The minimum pressure required to liquefy the system at the temperature  $T_C$  is called the critical pressure  $P_C$ .

**Critical volume ( $V_C$ )** : The volume occupied by one mole of the system at critical temperature,  $T_C$  and critical pressure,  $P_C$  is called the critical volume ( $V_C$ ) of the gas.

### 3.3 Determination of value of $P_C$ , $V_C$ and $T_C$ :

The Vander waal's equation is

$$\left(P + \frac{a}{V_m^2}\right) (V_m - b) = RT$$

$$\text{or } V_m^3 - \left(b + \frac{RT}{P}\right)V_m^2 + \frac{a}{P}V_m - \frac{ab}{P} = 0 \quad \dots (1)$$

This equation has three roots in  $V_m$  for given values of  $a$ ,  $b$ ,  $P$  and  $T$ . It is found that either all the three roots are real or one is real and the other two are imaginary.

At temperature lower than  $T_C$ , the isotherm exhibits a maximum and a minimum for certain values of pressures, the equation gives three roots of volume e.g.,  $V_1$ ,  $V_2$  and  $V_3$  at pressure  $P_1$ . On increasing the temperature, the three roots become closer to each other and ultimately at critical temperature, they become identical. Thus, the cubic equation  $V_m$  can be written as

$$(V_m - V') (V_m - V'') (V_m - V''') = 0$$

At the critical point  $V' = V'' = V''' = V_C$

$\therefore$  the equation becomes,

$$(V_m - V_C)^3 = 0$$

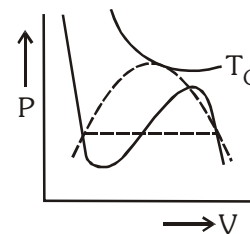
$$\text{or } V_m^3 - V_C^3 - 3V_C V_m^2 + 3V_C^2 V_m = 0 \quad \dots(2)$$

By comparing the coefficients in eq.(1) and eq(2)

$$3V_C = b + \frac{RT_C}{P_C}, \quad 3V_C^2 = \frac{a}{P_C}, \quad V_C^3 = \frac{ab}{P_C}$$

$$\text{By solving, } V_C = 3b, \quad P_C = \frac{a}{27b^2} \quad \text{and} \quad T_C = \frac{8a}{27Rb}$$

- The value of critical compressibility factor in terms of vander wall's constants is



given by

$$Z = \frac{P_c V_c}{RT_c} = \frac{\frac{a}{27b^2} \times 3b}{R \times \frac{8b}{27Rb}} = \frac{3}{8} = 0.375$$

If we compare the value of  $\frac{P_c V_c}{RT_c} = 0.375$ , with the experimental values, it has been found that the agreement is very poor.

**Critical constants of gases**

Gas	$P_c$ (atm)	$V_{m,c}$ (cm <sup>3</sup> mol <sup>-1</sup> )	$T_c$ (K)
He	2.26	57.9	5.2
Ne	26.9	41.7	44.4
Ar	48.1	75.2	150.7
Xe	58.0	119.0	289.7
H <sub>2</sub>	12.8	65.5	33.3
O <sub>2</sub>	50.1	78.2	154.8
N <sub>2</sub>	33.5	90.1	126.2
CO <sub>2</sub>	72.8	94.0	304.2
H <sub>2</sub> O	218.0	55.6	647.3
NH <sub>3</sub>	111.5	72.5	405.0
CH <sub>4</sub>	45.6	98.7	190.6
C <sub>2</sub> H <sub>6</sub>	48.2	148.0	305.4

**Ex.6** The critical temperature and pressure of CO<sub>2</sub> gas are 304.2 K and 72.9 atm respectively. What is the radius of CO<sub>2</sub> molecule assuming it to behave as vander Waal's gas ?

**Sol.**

$T_c = 304.2$  K     $P_c = 72.9$  atm

$T_c = \frac{8a}{27Rb}$                        $P_c = \frac{a}{27b^2}$

$\therefore \frac{T_c}{P_c} = \frac{\frac{8a}{27Rb}}{\frac{a}{27b^2}} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R}$  or  $b = \frac{RT_c}{8P_c} = \frac{1}{8} \times \frac{0.082 \times 304.2}{72.9} = 0.04277$  lit mol<sup>-1</sup>

$b = 4 N_A \times \frac{4}{3} \pi r^3 = 42.77$  cm<sup>3</sup>

or  $r = (4.24)^{1/3} \times 10^{-8}$  cm =  $1.62 \times 10^{-8}$  cm

$\therefore$  radius of CO<sub>2</sub> molecule =  $1.62$  Å

#### 4. THE LIQUID STATE

Liquid state is intermediate between gaseous and solid states. The liquids possess fluidity like gases but incompressibility like solids.

The behaviour of liquids explained above gives some characteristic properties to the liquids such as definite shape, incompressibility, diffusion, fluidity (or viscosity), evaporation (or vapour pressure), surface tension, etc.

The following general characteristics are exhibited by liquids :

(i) **Shape :**

Liquids have no shape of their own but assume the shape of the container in which they are kept. No doubt, liquids are mobile but they do not expand like gases as to fill up all the space offered to them but remain confined to the lower part of the container.

(ii) **Volume :**

Liquids have definite volume as the molecules of a liquid are closely packed and the cohesive forces are strong.

(iii) **Density :**

As the molecules in liquids are closely packed, the densities of liquids are much higher than in gaseous state. For example, density of water at 100° C and 1 atmospheric pressure is 0.958 g mL<sup>-1</sup> while that of water vapour under similar conditions as calculated from ideal gas law  $\left(d = \frac{MP}{RT}\right)$  is 0.000588 g mL<sup>-1</sup>.

(iv) **Compressibility :**

The molecules in a liquid are held in such close contact by their mutual attractive forces (cohesive forces) that the volume of any liquid decreases very little on increasing pressure. Thus, liquids are relatively incompressible compared to gases.

(v) **Diffusion :**

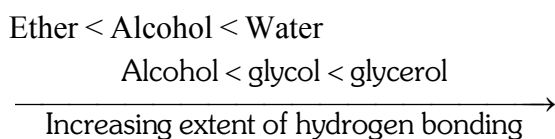
When two miscible liquids are put together, there is slow mixing as the molecules of one liquid move into the other liquid. As the space available for movement of molecules in liquids is much less and their velocities are small. Liquids diffuse slowly in comparison to gases.

(vi) **Evaporation :**

The process of changes of liquid into vapour state on standing is termed **evaporation**. Evaporation may be explained in terms of motion of molecules. At any given temperature all the motion of molecules do not possess the same kinetic energy (average kinetic energy is, however same). Some molecules move slowly, some at intermediate rates and some move very fast. A rapidly moving molecule near the surface of the liquid may possess sufficient kinetic energy to overcome the attraction of its neighbours and escape. Evaporation depends on the following factor.



(a) **Nature of the liquid :** The evaporation depends on the strength of intermolecular forces (cohesive forces). The liquids having low intermolecular forces evaporate faster in comparison to the liquids having high intermolecular forces. For example, ether evaporates more quickly than alcohol, and alcohol evaporates more quickly than water, as the intermolecular forces in these liquids are in the order :



(b) **Surface area :** Evaporation is a surface phenomenon. Larger the surface area, greater is the opportunity of the molecules to escape. Thus, rate of evaporation increases with increase of surface area.

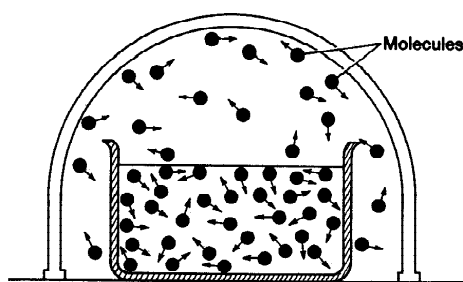
(c) **Temperature :** Rate of evaporation increases with the increase of temperature as the kinetic energy of the molecules increases with the rise of temperature.

(d) **Flow of air current over the surface :** Flow of air helps the molecules to go away from the surface of liquid and, therefore, increases the evaporation of liquid in open vessel.

(vii) **Heat of vaporisation :**

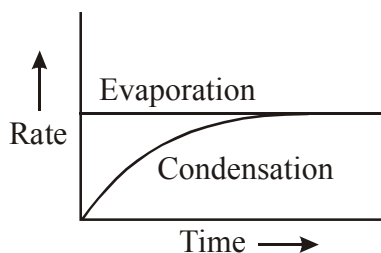
The quantity of heat required to evaporate a unit mass of a given liquid at constant temperature is known as heat of vaporisation. The heat of vaporisation depends on the strength of the intermolecular forces within the liquid. The value of heat of vaporisation generally decreases with increase in temperature. It becomes zero at the critical temperature. When the vapour is condensed into a liquid, heat is evolved. This is called **heat of condensation**. It is numerically equal to the heat of vaporisation at the same temperature.

(viii) **Vapour pressure :**



When the space above the liquids is closed, the molecules cannot escape into open but strike the walls of the container, rebound and may strike the surface of the liquid, where they may be trapped. The return of the molecules from the vapour state to the liquid state is known as **condensation**. As evaporation proceeds, the number of molecules in the vapour state increases and, in turn, the rate of condensation increases.

The rate of condensation soon becomes equal to the rate of the evaporation, i.e., the vapour in the closed container is in equilibrium with the liquid.



At equilibrium the concentration of molecules in the vapour phase remains unchanged. The pressure exerted by the vapour in equilibrium with liquid, at a given temperature, is called the **vapour pressure**. Mathematically, it may be given by ideal gas equation, assuming ideal behaviour.

$$P = \frac{n}{V} RT = CRT$$

where  $C$  is the concentration of vapour, in mol/litre.

Since the rate of evaporation increases and rate of condensation decreases with increasing temperature, vapour pressure of liquids always increases as temperature increases. At any given temperature, the vapour pressures of different liquids are different because their cohesive forces are different. Easily vaporisable liquids are called **volatile liquids** and they have relatively high vapour pressure. Vapour pressure values (in mm of Hg) for water, alcohol and ether at different temperatures are given in the following table :

Substance	Temperatures				
	0° C	20° C	40° C	80° C	100° C
Water	4.6	17.5	55.0	355.5	760.3
Ethyl alcohol	12.2	43.9	812.6	1693.3	
Diethyl ether	185.3	442.2	921.1	2993.6	4859.4

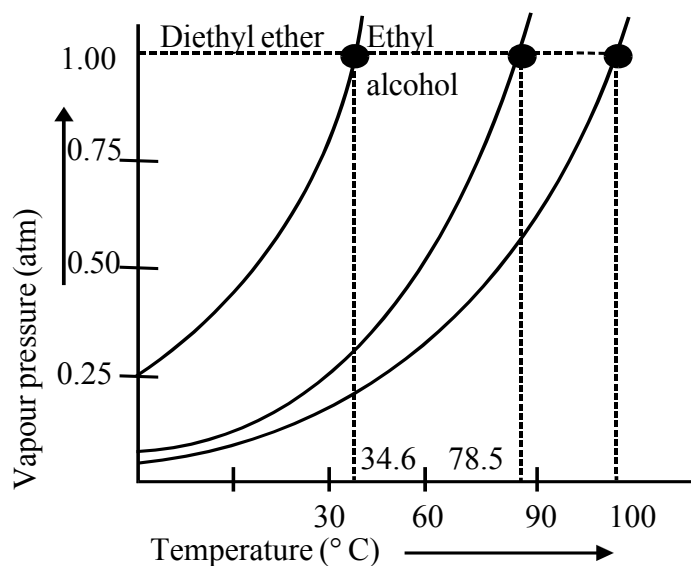
The vapour pressure of a given liquid at two different temperatures can be compared with the help of **Clausius-Clapeyron equation**.

$$\log \times \frac{P_2}{P_1} = \frac{\Delta H}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Where  $\Delta H$  is the latent heat of vaporisation and  $R$  is the molar gas constant.

**(ix) Boiling point :**

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the **boiling point** of the liquid. When a liquid is heated under a given applied pressure, bubbles of vapour begin to form below the surface of the liquid. They rise to the surface and burst releasing the vapour into the air. This process is called **boiling**. The normal boiling point is the temperature at which the vapour pressure of a liquid is equal to exactly one atmospheric pressure (760 mm of Hg). Figure shows that normal boiling points of di-ethyl ether, ethyl alcohol and water are 34.6° C, 78.5° C and 100° C respectively.



The temperature of the liquid remains constant until all the liquid has been vaporised. Heat must be added to the boiling liquid to maintain the temperature because in the boiling process, the high energy molecules are lost by the liquid.

The boiling point of a liquid changes with the change in external pressure. A liquid may boil at temperatures higher than normal under external pressures greater than one atmosphere; conversely, the boiling point of a liquid may be lowered than normal below one atmosphere. Thus, at high altitudes where the atmospheric pressure is less than 760 mm, water boils at temperatures below its normal boiling water.

Boiling and evaporation are similar processes (conversion of liquid into vapour) but differ in following respects :

- Evaporation takes place spontaneously at all temperatures but boiling occurs at a particular temperature at which the vapour pressure is equal to the atmospheric pressure.
- Evaporation is surface phenomenon. It occurs only at the surface of the liquid whereas boiling involves formation of bubbles below the surface of the liquid.

**Note. :** Boiling does not occur when liquid is heated in a closed vessel.

(x) **Freezing point :**

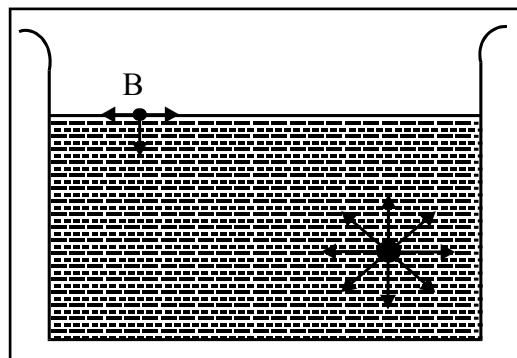
When a liquid is cooled, the kinetic energy of the molecules goes on decreasing. A stage comes when the intermolecular forces become stronger and the rotational motion is siezed. At this stage, the formation of solid begins and the liquid is seen to freeze out. The point (temperature) at which the vapour pressure of solid and liquid forms of a substance become equal is termed as **freezing point**.

**Normal freezing point** of a liquid is the temperature at which is liquid and solid forms are in equilibrium with each other under a pressure of one atmosphere. The freezing point of a liquid is the same as the melting point of its solid. The amount of heat that must be removed to freeze a unit mass of the liquid at the freezing point, which is called the **heat of fusion**.

The freezing point of a liquid is affected by the change of external pressure. With increased external pressure, the freezing point of some liquids rises while of others falls. But the effect of pressures is very small because solid as well as liquid are almost incompressible.

**(xi) Surface tension :**

It is the property of liquids caused by the intermolecular attractive forces. A molecule within the bulk of the liquid is attracted equally in all the directions by the neighbouring molecules. The resultant force on any one molecule in the centre of the liquid is, therefore, zero. However, the molecules on the surface of the liquid are attracted only inward and sideways. This unbalanced molecular attraction pulls some of the molecules into the bulk of the liquid, i.e., are pulled inward and the surface area is minimized.



**Surface tension is a measure of this inward force on the surface of the liquid. It acts downwards perpendicular to the plane of the surface.** The unit of surface tension is  $\text{dyne cm}^{-1}$ . Surface tension is, thus, defined as **the force acting on the surface at right angles to any line of unit length.**

As the intermolecular forces of attraction decreases with the rise of temperature, the surface tension of a liquid, thus, decreases with increase in temperature. Similarly, addition of chemicals to a liquid may reduce its surface tension. For example, addition of chemicals like soaps, detergents, alcohol, camphor, etc., lowers the surface tension of water.

Many common phenomenon can be explained with the help of surface tension. Some are described here :

**(a) Small droplets are spherical in shape :**

The surface tension acting on the surface of the liquid tries to minimise the surface area of a given mass of a liquid. It is known that for a given volume, a sphere has the minimum surface area. On account of this, drops of liquids acquire a spherical shape.

**(b) Insects can walk on the surface of water :**

Many insects can walk on the surface of water without drowning. This is due to the existence of surface tension. The surface tension makes the water surface to behave like an elastic membrane and prevents the insects from drowning.

**(c) Cleaing action of soap and detergents :**

Soap and detergent solutions due to their lower surface tensions penetrate into the fibre and surround the greasy substances and wash them away.

**(d) Capillary action :**

The tendency of a liquid to rise into narrow pores and tiny openings is called capillary action. The liquids rise in the capillary tubes due to the surface tension.

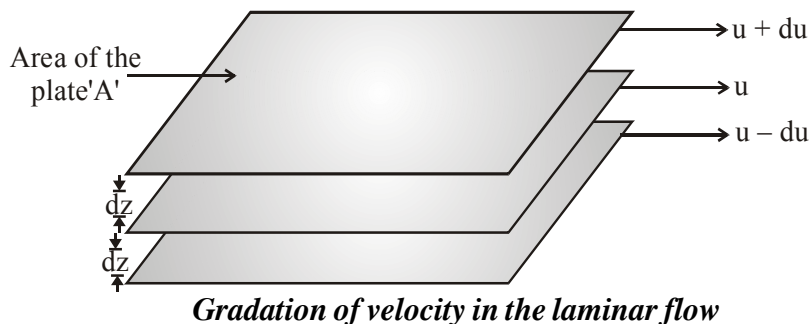
**(e) Surface Energy :**

The work required to be done to increase or extend surface area by unit area is called surface energy. The units of surface energy are, therefore, erg per sq. cm (or joule per sq. metre, i.e.  $\text{J m}^{-2}$  in S.I. system)

**(xii) Viscosity :**

It is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another.

When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increase as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called **laminar flow**. If we choose any layer in the flowing liquid, the layer above it accelerates its flow and the layer below this retards its flow.



If the velocity of the layer at a distance  $dz$  is changed by a value  $du$  then velocity gradient is given by the amount  $\frac{du}{dz}$ . A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$$F \propto A \text{ (A is the area of contact)}$$

$$F \propto A \frac{du}{dz} \text{ (where, } \frac{du}{dz} \text{ is velocity gradient; the change in velocity with distance)}$$

$$F \propto A \frac{du}{dz} \Rightarrow F = \eta A \frac{du}{dz}$$

' $\eta$ ' is proportionality constant and is called **coefficient of viscosity**. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus ' $\eta$ ' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre ( $\text{N s m}^{-2}$ ) = pascal second ( $\text{Pa s} = 1\text{kg m}^{-1}\text{s}^{-1}$ ). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

$$1 \text{ poise} = 1 \text{ g cm}^{-1}\text{s}^{-1} = 10^{-1}\text{kg m}^{-1}\text{s}^{-1}$$

Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids. However, property of flow of glass can be experienced by measuring the thickness of windowpanes of old buildings. These become thicker at the bottom than at the top.

Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.

### SOME MISCELLANEOUS SOLVED EXAMPLES

1. Calculate the temperature of gas if it obeys vander waal's equation from the following data. A flask of 25 litre contains 10 moles of a gas under 50 atm. Given  $a = 5.46 \text{ atm litre}^{-2}$  and  $b = 0.31 \text{ litre mol}^{-1}$ .

**Sol.** Given,  $P = 50 \text{ atm}$ ,  $V = 25 \text{ litre}$ ,  $n = 10$

$$a = 5.46 \text{ atm litre}^2\text{mol}^{-2}, b = 0.031 \text{ litre mol}^{-1}$$

Now vander waal's equation for  $n$  mole of gas.

$$\left[ P + \frac{n^2 a}{V^2} \right] [V - nb] = nRT$$

$$\left[ 50 + \frac{100 \times 5.46}{625} \right] [25 - 10 \times 0.031] = 10 \times 0.0821 \times T$$

$$\therefore T = 1529.93 \text{ K} = 1256.93^\circ\text{C}$$

2. The molar volume of He at 10.135 MPa and 273 K is 0.011075 of its molar volume of 101.325 kPa at 273K. Calculate the radius of helium atom. The gas is assumed to show real gas nature. Neglect the value of  $a$  for He.

**Sol.** For real gas :  $\left[ P + \frac{a}{V^2} \right] [V - b] = RT$

$$P [V - b] = RT \text{ (neglecting } a)$$

$$\therefore \frac{10.1325 \times 10^6}{101325} [V_1 - b] = 0.0821 \times 273$$

$$\text{or } 100 [V_1 - b] = 0.0821 \times 273 = 22.41 \quad \dots(1)$$

$$\frac{101.325 \times 10^3}{101325} [V_2 - b] = 0.0821 \times 273$$

$$\text{or} \quad [V_2 - b] = 22.41 \quad \dots(2)$$

$$\text{by eq. (1)} \quad V_1 - b = 0.2241 + b \quad \dots(3)$$

$$\text{by eq. (2)} \quad V_2 - b = 22.41 + b \quad \dots(4)$$

$$\text{By eqs. (3) and (4),} \quad \frac{V_1}{V_2} = \frac{0.2241 + b}{22.41 + b}$$

$$\frac{0.011075 V_2}{V_2} = \frac{0.2241 + b}{22.41 + b}$$

$$(V_1 = 0.011075 V_2 \text{ is given})$$

$$\therefore b = 0.024 \text{ litre mol}^{-1} = 24 \text{ cm}^3\text{mol}^{-1}$$

$$\therefore b = 4N \times v = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \pi r^3$$

$$\text{or } 24 = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \times \frac{22}{7} \times r^3$$

$$\therefore r = 1.33 \times 10^{-8} \text{ cm}$$

3. Calculate vander waal's constant a and b if critical temperature and critical pressure are 30°C and 72 atm respectively.

Sol.  $T_C = \frac{8a}{27Rb}$  and  $P_C = \frac{a}{27b^2}$

$$\therefore \frac{T_C}{P_C} = \frac{8b}{R} \text{ or } b = \frac{RT_C}{8P_C}$$

$$\therefore b = \frac{0.0821 \times 303}{8 \times 72} = 0.043 \text{ litre mol}^{-1}$$

$$\alpha = 27P_C \times b^2 = 27 \times 72 \times (0.043)^2 = 3.59 \text{ litre}^2 \text{ atm mol}^{-2}$$

4. Using vander waal's equation, calculate the constant, 'a' when two mole of a gas confined in a four litre temperature of 300K. The value of 'b' is 0.05 litre mol<sup>-1</sup>.

Sol. Vander waal's equation for n mole of gas is

$$\left[ P + \frac{n^2 a}{V^2} \right] [V - nb] = nRT$$

Given V = 4 litre ; P = 11.0 atm, T = 300 K

b = 0.05 litre mol<sup>-1</sup> ; n = 2

$$\text{Thus, } \left[ 11 + \frac{2^2 a}{4^2} \right] [4 - 2 \times 0.05] = 2 \times 0.082 \times 300.$$

$$\therefore a = 6.46 \text{ atm litre}^2 \text{ mol}^2$$

5. One way of writing the equation for state for real gases is,

[JEE 1997]

$$P \bar{V} = RT \left[ 1 + \frac{B}{\bar{V}} + \dots \right] \text{ where } B \text{ is a constant.}$$

Derive an approximate expression for 'B' in terms of van der Waals' constants 'a' & 'b'.

Ans.  $B = \left( b - \frac{a}{RT} \right)$

Sol.  $\left[ P + \frac{a}{V_m^2} \right] [V_m - b]$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$$

$$Z = \left( 1 - \frac{b}{V_m} \right)^{-1} - \frac{a}{V_m RT}$$

$$= 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \dots - \frac{a}{V_m RT}$$

$$= 1 + \left[ b - \frac{a}{RT} \right] \frac{1}{V_m} + \frac{b^2}{V_m^2} + \dots \quad \dots (1)$$

$$\text{Also, } p\bar{V} = RT \left[ 1 + \frac{B}{V} + \dots \right]$$

$$\Rightarrow \frac{p\bar{V}}{RT} = \left[ 1 + \frac{B}{V} + \dots \right] \quad \dots (2)$$

$\Rightarrow$  Comparing equation (1) & (2), we get

$$B = b - \frac{a}{RT}$$

6. Using Vander Waals equation, calculate the constant "a" when 2 moles of a gas confined in a 4 litre flask exerts a pressure of 11.0 atm at a temperature of 300 K. The value of "b" is 0.05 litre mol<sup>-1</sup>.

[JEE 1998]

**Ans. 6.52 atm L<sup>2</sup> mol<sup>-2</sup>**

**Sol.**  $\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$

$$\left[ 11 + \frac{2^2 \times a}{4 \times 4} \right] [4 - 2 \times 0.05] = 2 \times 0.0821 \times 300$$

$$\Rightarrow a = 6.52 \text{ atm L}^2 \text{ mol}^{-2}$$

7. A gas will approach ideal behaviour at :

[JEE 1999]

- (A) low temperature and low pressure  
 (B) low temperature and high pressure  
 (C) low pressure and high temperature  
 (D) high temperature and high pressure .

**Ans. (C)**

**Sol.** A gas approaches ideal behavior at High T & low P

8. The compressibility of a gas is less than unity at STP. Therefore ,

[JEE 2000]

- (A)  $V_m > 22.4 \text{ L}$  (B)  $V_m < 22.4 \text{ L}$   
 (C)  $V_m = 22.4 \text{ L}$  (D)  $V_m = 44.8 \text{ L}$

**Ans. (B)**

**Sol.**  $Z = \frac{(V_m)_{\text{real}}}{(V_m)_{\text{ideal}}} ; Z < 1$

$$\Rightarrow (V_m)_{\text{real}} < (V_m)_{\text{ideal}}$$

$$\therefore (V_m)_{\text{real}} < 22.4 \text{ L}$$



9. The compression factor (compressibility factor) for one mole of a Van der Waals' gas at 0° C and 100 atmosphere pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the Van der Waals' constant 'a'. [JEE 2001]

**Ans. 1.256 atm L<sup>2</sup> mol<sup>-2</sup>**

**Sol.**  $Z = 1 - \frac{a}{V_m RT}$

$$Z = \frac{PV_m}{RT} \Rightarrow V_m = \frac{RTZ}{P}$$

$$Z = 1 - \frac{a}{(RT)^2} \times \frac{P}{Z}$$

$$0.5 = 1 - \frac{a \times 100}{(273 \times 0.0821)^2 \times 0.5}$$

$$a = 1.256 \text{ atm L}^2 \text{ mol}^{-2}$$

10. The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 Kg m<sup>-3</sup>. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.

Determine

[JEE 2002]

- (i) mol. wt.; (ii) molar volume; (iii) compression factor z of the vapour and (iv) which forces among the gas molecules are dominating, the attractive or the repulsive

**Ans. (i) 18 g/mol, (ii) 50 L mol<sup>-1</sup>, (iii) 1.218, (iv) repulsive**

**Sol.** (i)  $\frac{r_{\text{gas}}}{r_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{gas}}}}$

$$\Rightarrow \frac{4}{3} = \sqrt{\frac{32}{M_{\text{gas}}}}$$

$$\Rightarrow M_{\text{gas}} = 18$$

(ii)  $V_m = \frac{18}{0.36} = 50 \text{ L mol}^{-1}$

(iii)  $Z = \frac{PV_m}{RT} = \frac{1 \times 50}{0.0821 \times 500} = 1.218$

(iv) since,  $Z > 1$  = Repulsive forces are operative

11. Positive deviation from ideal behaviour takes place because of [JEE 2003]

(A) molecular attractions between atoms and  $\frac{PV}{nRT} > 1$

(B) molecular attractions between atoms and  $\frac{PV}{nRT} < 1$

(C) finite size of atoms and  $\frac{PV}{nRT} > 1$

(D) finite size of atoms and  $\frac{PV}{nRT} < 1$

**Ans. (C)**

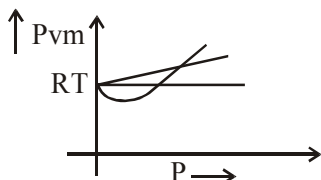
**Sol.** Positive deviation from ideal behavior takes place because of finite size of atoms & compressibility factor  $Z > 1$ .

12. For a real gas obeying van der Waals' equation a graph is plotted between  $PV_m$  (y-axis) and  $P$  (x-axis) where  $V_m$  is molar volume. Find y-intercept of the graph. [JEE 2004]

Ans.  $RT$

Sol.  $\lim_{P \rightarrow 0} PV_m = RT$

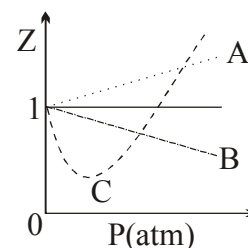
Since, at very low  $P$ , all gases behave ideally.



13. The given graph represents the variation of  $Z$

(compressibility factor =  $\frac{PV}{nRT}$ ) versus  $P$ , for three real

gases A, B and C. Identify the only **INCORRECT** statement.



(A) for the gas A,  $a = 0$  and its dependence on  $P$  is linear at all pressure

(B) for the gas B,  $b = 0$  and its dependence on  $P$  is linear at all pressure

(C) for the gas C, which is typical real gas for which neither  $a$  nor  $b = 0$ . By knowing the minima and the point of intersection, with  $Z = 1$ ,  $a$  and  $b$  can be calculated.

(D) At high pressure, the slope is positive for all real gases A, B and C.

[JEE 2006]

Ans. (D)

Sol. (A) In case of A, repulsion dominate because  $Z > 1$

$$\text{So, } Z = 1 + \frac{Pb}{RT} \Rightarrow a = 0$$

(B) In case of B, attraction dominate because  $Z < 1$

$$\text{So, } z = 1 - \frac{a}{V_m RT} \Rightarrow b = 0$$

(C) In case of C, a typical real gas :

We can calculate the minima of curve to given equation (1) in terms of  $a$  &  $b$ .

Similarly, at intersection point of the curve with  $Z = 1$ , we get another equation (2) in terms of  $a$  &  $b$ . Solving the two equation we can calculate  $a$  &  $b$ .

(D) At high  $P$ , a Slope is negative for gas B.

SO, (D) is incorrect.

14. Match gases under specific conditions listed in Column I with their properties / laws in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

**Column I**

- (A) Hydrogen gas ( $P = 200 \text{ atm}$ ,  $T = 273 \text{ K}$ )
- (B) Hydrogen gas ( $P \sim 0$ ,  $T = 273 \text{ K}$ )
- (C)  $\text{CO}_2$  ( $P = 1 \text{ atm}$ ,  $T = 273 \text{ K}$ )
- (D) Real gas with very large molar volume

**Column II**

- (P) Compressibility factor  $\neq 1$
- (Q) Attractive forces are dominant
- (R)  $PV = nRT$
- (S)  $P(V - nb) = nRT$

[JEE 2007]

Ans. (A) - P, S ; (B) - R ; (C) - P, Q ; (D) - R

- Sol.** (A)  $\text{H}_2$  gas at high P,  
Repulsions dominate  
So,  $Z \neq 1$   
&  $P(V - nb) = nRT$
- (B)  $\text{H}_2$  gas at  $P \rightarrow 0$ , will exhibit ideal behaviour  $PV = nRT$
- (C)  $\text{CO}_2$  at  $P = 1 \text{ atm}$ ,  $T = 273 \text{ K}$   
 $\text{CO}_2$  is easily liquefiable gas.  
 $Z < 1$ , So attraction forces dominate.
- (D) If volume is very large, no intermolecular force exists. Moreover, molecular volume can also be neglected.  
So,  $PV = nRT$

15. A gas described by van der Waals' equation [JEE 2008]

- (A) behaves similar to an ideal gas in the limit of large molar volumes
- (B) behaves similar to an ideal gas in the limit of large pressures
- (C) is characterised by van der Waals' coefficients that are dependent on the identity of the gas but are independent of the temperature
- (D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

Ans. (A,C,D)

- Sol.** (A)  $PV_m \rightarrow RT$  as  $V_m \rightarrow \infty$
- (B)  $PV_m \rightarrow RT$  as  $P \rightarrow 0$  So (B) is incorrect
- (C)  $\left( P + \frac{a}{V_m^2} \right) (V_m - b) = RT$   
where, a & b are vander waals, coefficients independent of temperature

- (D)  $P_{\text{real}} < P_{\text{ideal}}$  

## EXERCISE # S-I

- Calculate the pressure exerted by 22 g of carbon dioxide in 0.5 dm<sup>3</sup> at 300 K using:
  - the ideal gas law and
  - Van der Waal's equation respectively.

**Given : [a = 3.6 atm litre<sup>2</sup>mol<sup>-2</sup>, b = 0.04 litre mol<sup>-1</sup>, R = 0.08 L-atm/K-mol]**

**RG0001**
- Calculate from the Van der Waals equation, the temperature at which 192 g of SO<sub>2</sub> would occupy a volume of 6 dm<sup>3</sup> at 15 atm pressure. [a = 5.68 atm L<sup>2</sup> mol<sup>-2</sup>, b = 0.06 L mol<sup>-1</sup>]

**RG0002**

- The density of water vapour at 328.4 atm and 800 K is 135.0 g/dm<sup>3</sup>. Determine the molar volume, V<sub>m</sub> and the compression factor of water vapour .

**RG0003**

- At 300 K and under a pressure of 10.1325 MPa, the compressibility factor of O<sub>2</sub> is 0.9. Calculate the mass of O<sub>2</sub> necessary to fill a gas cylinder of 45 dm<sup>3</sup> capacity under the given conditions.  
[R = 0.08L-atm/K-mol]

**RG0004**

- 1 mole of CCl<sub>4</sub> vapours at 27°C occupies a volume of 40 L. If Van der Waals constants are 24.6 L<sup>2</sup> atm mol<sup>-2</sup> and 0.125 Lmol<sup>-1</sup>, then, calculate compressibility factor in
  - Low pressure region
  - High Pressure region [R = 0.082 L -atm/K-mol]

**RG0005**
- If at 200 K & 500 atm, density of CH<sub>4</sub> is 0.246 gm/ml then its compressibility factor (Z) is approx 2.0 × 10<sup>x</sup>. 'x' is:

**RG0006**

- Certain mass of a gas occupy 500 ml at 2 atm and 27°C. Calculate the volume occupied by same mass of the gas at 0.3 atm and 227°C. The compressibility factors of gas at the given condition are 0.8 and 0.9, respectively.

**RG0007**

## BOYLE TEMPERATURE

- The vander waal's constant for a gas are a = 1.92 atm L<sup>2</sup> mol<sup>-2</sup>, b = 0.06L mol<sup>-1</sup>. If R = 0.08 L atm K<sup>-1</sup>mol<sup>-1</sup>, what is the Boyle's temperatrue of this gas.

**RG0008**

- The Van der Waals constant for O<sub>2</sub> are a = 1.642 atm L<sup>2</sup> mol<sup>-2</sup> and b = 0.04 L mol<sup>-1</sup>. Calculate the temperature at which O<sub>2</sub> gas behaves ideally for longer range of pressure.

**RG0009**

## LIQUIFICATION OF GASES, CRITICAL PHENOMENON

10. The Van der Waals constants for gases A, B and C are as follows

Gas	a[atm L <sup>2</sup> mol <sup>-2</sup> ]	b[L mol <sup>-1</sup> ]
A	8.21	0.050
B	4.105	0.030
C	1.682	0.040

Which gas has (i) the highest critical temperature, (ii) the largest molecular volume, and (iii) most ideal behaviour around 500 K?

**RG0010**

11. For a real gas, if at critical conditions molar volume of gas is 8.21 litre at 3 atm, then critical temperature (in K) will be :

**RG0011**

12. An unknown gas behaves ideally at 540K in low pressure region, then calculate the temperature (in K) below which it can be liquified by applying pressure.

**RG0012**

## EXERCISE # S-II

1. The density of mercury is  $13.6 \text{ g/cm}^3$ . Estimate the value of 'b' (in  $\text{cm}^3/\text{mole}$ ).  
RG0013
2. The molarity of  $\text{O}_2$  gas at 72 atm and 300K is 6M. Calculate the value of Z for  $\text{O}_2$ .  
(Use :  $R = 0.08 \text{ atm-litre/K-mole}$ ).  
RG0014
3. Calculate the amount of He (in gm) present in the 10 litre container at 240 atm and 300K. Given value of "b" for He is  $0.08 \text{ dm}^3 \text{ mol}^{-1}$  ;  $R = 0.08 \text{ atm lit mol}^{-1} \text{ K}^{-1}$ .  
RG0015
4. For a real gas (mol. mass = 30) if density at critical point is  $0.40 \text{ g/cm}^3$  and its  $T_c = \frac{2 \times 10^5}{821} \text{ K}$ , then calculate Van der Waals constant a (in  $\text{atm L}^2 \text{ mol}^{-2}$ ).  
RG0016
5. Calculate the volume occupied by 0.2 mole of a Vander waal gas at  $27^\circ\text{C}$  and 0.0821 atm.  
[ $a = 4.105 \text{ L}^2 \text{ atm mol}^{-2}$ ,  $b = \frac{1}{6} \text{ Lmol}^{-1}$ ]  
RG0017
6. At what pressure and  $127^\circ\text{C}$ , the density of  $\text{O}_2$  gas becomes  $1.6 \text{ g/L}$  ?  
[ $a = 4.0 \text{ atm L}^2 \text{ mol}^{-2}$ ,  $b = 0.4 \text{ Lmol}^{-1}$ ,  $R = 0.08 \text{ L - atm/ K-mol}$ ]  
RG0018

EXERCISE # O-I

1. The correct expression for the Van der Waals equation of state is :

- (A)  $\left(P + \frac{a}{n^2V^2}\right)(V - nb) = nRT$                       (B)  $\left(P + \frac{an^2}{V^2}\right)(V - nb) = \Delta nRT$   
 (C)  $\left(P + \frac{an^2}{V^2}\right)(V - b) = nRT$                       (D)  $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

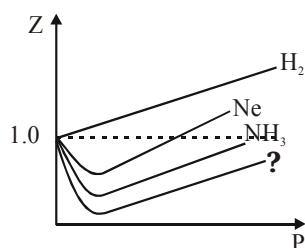
RG0019

2. At relatively high pressure, Van der Waals equation reduces to :

- (A)  $PV_m = RT$                       (B)  $PV_m = RT + \frac{a}{V_m}$                       (C)  $PV_m = RT + Pb$                       (D)  $PV_m = RT - \frac{a}{V_m^2}$

RG0020

3. Observe the following Z vs P graph.



The missing gas in the above graph can be :

- (A) He                      (B) Ar                      (C)  $C_5H_{12}$                       (D) All are correct

RG0021

4. Correct option regarding a container containing 1 mol of a gas in 22.4 litre container at 273 K is

- (A) If compressibility factor ( $Z$ ) > 1 then 'P' will be less than 1 atm.  
 (B) If compressibility factor ( $Z$ ) > 1 then 'P' will be greater than 1 atm.  
 (C) If 'b' dominates, pressure will be less than 1 atm.  
 (D) If 'a' dominates, pressure will be greater than 1 atm.

RG0022

5. If 'V' is actual volume of 1 molecule of gas then, excluded volume (b) of 1 mole of gaseous molecule is -

- (A)  $4 N_A V$                       (B)  $N_A V$                       (C)  $V/N_A$                       (D) V

RG0023

6. Consider the equation  $Z = \frac{PV}{RT}$ , Which of the following statements is correct :

- (A) When  $Z > 1$  real gases are easier to compress  
 (B) When  $Z = 1$  real gases are easier to compress  
 (C) When  $Z > 1$  real gases are difficult to compress  
 (D) When  $Z < 1$  real gases are difficult to compress

RG0024

7. Compressibility factor of ideal gas is :-

- (A)  $z > 1$                       (B)  $z > 1$                       (C)  $z = 1$                       (D)  $z = \infty$

RG0025

8. The density of a gaseous substance at 1 atm pressure and 750 K is 0.30 g/lit. If the molecular weight of the substance is 27, the dominant forces existing among gas molecules is -

- (A) Attractive                      (B) Repulsive                      (C) Both (A) and (B)                      (D) None of these

RG0026

9. The third virial coefficient of a He gas is  $4 \times 10^{-2} \text{ (lit/mol)}^2$ , then what will be volume of 2 mole He gas at 1 atm 273K ( $273\text{K} > T_B$ )

- (A) 22.0 lit                      (B) 44.0 lit                      (C) 44.8 lit                      (D) 45.3 lit

RG0027

10. At low pressure the vander waals equation is reduced to -

(A)  $Z = \frac{pV_m}{RT} = 1 - \frac{a}{RTV_m}$                       (B)  $Z = \frac{pV_m}{RT} = 1 + \frac{a}{RT}p$

(C)  $pV_m = RT$                       (D)  $Z = \frac{pV_m}{RT} = 1 - \frac{a}{RT}$

RG0028

11. The values of Van der Waals constant 'a' for the gases  $O_2$ ,  $N_2$ ,  $NH_3$  and  $CH_4$  are 1.360, 1.390, 4.170 and 2.253 L atm mol<sup>-2</sup> respectively. The gas which can most easily be liquefied is :

- (A)  $O_2$                       (B)  $N_2$                       (C)  $NH_3$                       (D)  $CH_4$

RG0029

12. The values of critical temperatures of few gases are given gases :

Gases :	$H_2$	He	$O_2$	$N_2$
$T_c$ (K)	33.2	5.2	154.3	126

From the above data arrange the given gases in the increasing order of ease of their liquification.

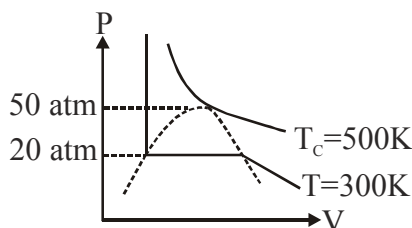
- (A)  $O_2, N_2, H_2, He$                       (B) He,  $N_2, O_2, H_2$   
 (C) He,  $H_2, N_2, O_2$                       (D)  $H_2, N_2, O_2, He$

RG0030



EXERCISE # O-II

1. For real gas the P–V curve was experimentally plotted and it had the following appearance. With respect to liquification, choose the incorrect statement :



- (A) At  $T = 500\text{ K}$ ,  $P = 40\text{ atm}$ , the state will be liquid
- (B) At  $T = 300\text{ K}$ ,  $P = 50\text{ atm}$ , the state will be gas
- (C) At  $T < 300\text{ K}$ ,  $P = 20\text{ atm}$ , the state will be gas
- (D) At  $300\text{ K} < T < 500\text{ K}$ ,  $P > 50\text{ atm}$ , the state will be liquid

RG0031

2. Select the incorrect statement (s)

- (A) The critical constant for a Vander Waal's gas is  $V_c = 3b$ ,  $P_c = \frac{a}{27b^2}$  and  $T_c = \frac{a}{27Rb}$
- (B) At  $56\text{ K}$  a gas may be liquified if its critical temperature is  $-156^\circ\text{C}$ .
- (C)  $U_{\text{avg}}$  of gas in a rigid container can be doubled when the pressure is quadrupled by pumping in more gas at constant temperature
- (D) At extremely low pressure, all real gases behave ideally.

RG0032

3. A 1 litre vessel contains 2 moles of a vanderwaal's gas.

Given data :  $a = 2.5\text{ atm}\cdot\text{L}^2\text{ mole}^{-2}$        $T = 240\text{ K}$   
 $b = 0.4\text{ L}\cdot\text{mole}^{-1}$        $RT = 20\text{ L}\cdot\text{atm}\text{ mole}^{-1}$

Identify the correct options about the gas sample :

- (A) Pressure of gas = 190 atm
- (B) Compressibility factor = 4.75
- (C) Attraction forces are dominant in the gaseous sample
- (D)  $T_B$  (Boyle temperature) = 75 K

RG0033

4. Choose the correct statement(s) among the following -

- (A) A gas having higher value  $T_c$  is easy to liquify
- (B) The radius of molecules of gas having same value of  $T_c/P_c$  is same
- (C) Hydrogen gas can be liquified at its boyle temperature by application of pressure.
- (D) Real gas show negative deviation from ideal behaviour at low pressure condition.

RG0034

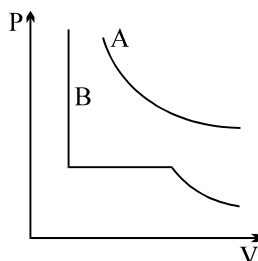
5. Select the **INCORRECT** statement(s):

- (A) At Boyle's temperature a real gas behaves like an ideal gas irrespective of pressure.  
 (B) At critical condition, a real gas behaves like an ideal gas.  
 (C) On increasing the temperature four times, collision frequency ( $Z_1$ ) becomes double at constant volume.  
 (D) At high pressure Van der Waals constant 'b' dominates over 'a'.

RG0035

**Question No. 6 & 7 (2 questions)**

For two gases A and B, P v/s V isotherms are shown at same temperature, T K.  $T_A$  &  $T_B$  are critical temperatures of A & B respectively



6. Which of the following is true?

- (A)  $T_A < T < T_B$  (B)  $T_A > T > T_B$   
 (C)  $T_A > T_B > T$  (D) none of above

RG0036

7. The correct statement(s) is/are

- (I) Pressure correction term will be more negligible for gas B at T K.  
 (II) The curve for gas 'B' will be of same shape as for gas A if  $T > T_B$   
 (III) Gas 'A' will show same P v/s V curve as of gas 'B' if  $T > T_A$   
 (A) III only (B) II and III (C) II only (D) All

RG0037

**Match the column:**

8. Match the column :

**Column-I**

- (A) Boyle's temperature  
 (B) Compressibility factor  
 (C) Real gas with very large molar volume  
 (D) Critical temperature

**Column-II**

- (P) Depends on 'a' and 'b'  
 (Q) Depends on identity of real gas  
 (R) The temperature at which  $\frac{dZ}{dP} = 0$  at low pressure region.  
 (S)  $PV = nRT$   
 (T)  $\frac{8a}{27R.b}$

RG0038

## EXERCISE # JEE-MAINS

1. 'a' and 'b' are Van der Waals constants for gases. Chlorine is more easily liquefied than ethane because :- [AIIEE-2011]

- (1)  $a$  for  $\text{Cl}_2 < a$  for  $\text{C}_2\text{H}_6$  but  $b$  for  $\text{Cl}_2 > b$  for  $\text{C}_2\text{H}_6$   
 (2)  $a$  for  $\text{Cl}_2 > a$  for  $\text{C}_2\text{H}_6$  but  $b$  for  $\text{Cl}_2 < b$  for  $\text{C}_2\text{H}_6$   
 (3)  $a$  and  $b$  for  $\text{Cl}_2 > a$  and  $b$  for  $\text{C}_2\text{H}_6$   
 (4)  $a$  and  $b$  for  $\text{Cl}_2 < a$  and  $b$  for  $\text{C}_2\text{H}_6$

RG0039

2. When does a gas deviate the most from its ideal behaviour ? [JEE-MAINS(ONLINE)-2015]

- (1) At high pressure and low temperature  
 (2) At high pressure and high temperature  
 (3) At low pressure and low temperature  
 (4) At low pressure and high temperature

RG0040

3. If  $Z$  is the compressibility factor, Van der Waals equation at low pressure can be written as :

[JEE-MAINS-2014]

- (1)  $Z = 1 - \frac{Pb}{RT}$       (2)  $Z = 1 + \frac{Pb}{RT}$       (3)  $Z = 1 + \frac{RT}{Pb}$       (4)  $Z = 1 - \frac{a}{V_m RT}$

RG0041

4. Among the following, the incorrect statement is : [JEE-Mains-2017(ONLINE)]

- (1) At low pressure, real gases show ideal behaviour  
 (2) At very large volume, real gases show ideal behaviour  
 (3) At Boyle's temperature, real gases show ideal behaviour  
 (4) At very low temperature, real gases show ideal behaviour

RG0042

5. The volume of gas A is twice that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressures of the gases for equal number of moles are :

[JEE-MAINS-2019]

- (1)  $2P_A = 3P_B$       (2)  $P_A = 3P_B$       (3)  $P_A = 2P_B$       (4)  $3P_A = 2P_B$

RG0043

6. At a given temperature  $T$ , gases Ne, Ar, Xe and Kr are found to deviate from ideal gas behaviour.

Their equation of state is given as  $p = \frac{RT}{V-b}$  at  $T$ .

[JEE-MAINS-2019]

Here,  $b$  is the van der Waals constant. Which gas will exhibit steepest increase in the plot of  $Z$  (compression factor) vs  $p$ ?

- (1) Ne      (2) Ar      (3) Xe      (4) Kr

RG0044

7. Consider the van der Waals constants,  $a$  and  $b$ , for the following gases.

Gas	Ar	Ne	Kr	Xe
$a/(\text{atm dm}^6 \text{ mol}^{-2})$	1.3	0.2	5.1	4.1
$b/(10^{-2} \text{ dm}^3 \text{ mol}^{-1})$	3.2	1.7	1.0	5.0

[JEE-MAINS-2019]

Which gas is expected to have the highest critical temperature?

- (1) Kr                      (2) Ne                      (3) Ar                      (4) Xe

RG0045

8. Consider the following table :

[JEE-MAINS-2019]

Gas	$a/(\text{k Pa dm}^6 \text{ mol}^{-1})$	$b/(\text{dm}^3 \text{ mol}^{-1})$
A	642.32	0.05196
B	155.21	0.04136
C	431.91	0.05196
D	155.21	0.4382

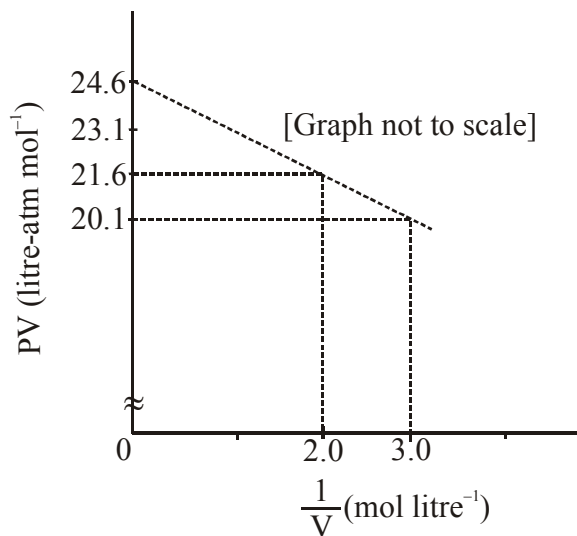
$a$  and  $b$  are vander waals constant. The correct statement about the gases is :

- (1) Gas C will occupy lesser volume than gas A; gas B will be lesser compressible than gas D  
 (2) Gas C will occupy more volume than gas A; gas B will be lesser compressible than gas D  
 (3) Gas C will occupy more volume than gas A; gas B will be more compressible than gas D  
 (4) Gas C will occupy lesser volume than gas A; gas B will be more compressible than gas D

RG0046

## EXERCISE # JEE-ADVANCED

1. For one mole of a Van der Waals gas when  $b = 0$  and  $T = 300$  K, the  $PV$  vs.  $1/V$  plot is shown below. The value of the Van der Waals constant  $a$  ( $\text{atm. litre}^2 \text{mol}^{-2}$ ) is [JEE 2012]



(A) 1.0

(B) 4.5

(C) 1.5

(D) 3.0

RG0047

**ANSWER KEY****EXERCISE # S-I**

- |   |                            |
|---|----------------------------|
| 1. (a) 24.0 atm, (b) 21.4 atm             | 2. 388 K                   |
| 3. Molar vol. = 0.1333 L/mol; $Z = 0.667$ | 4. 6.67 kg                 |
| 5. (a) 0.975 ; (b) 1.003                  | 6. Ans. 0                  |
| 7. 6.25 L                                 | 8. Ans. 400 K              |
| 9. 500 K                                  | 10. (i) A, (ii) A, (iii) C |
| 11. Ans. 800                              | 12. Ans. 160 K             |

**EXERCISE # S-II**

- |           |               |
|-----------|---------------|
| 1. 58.82  | 2. 0.5        |
| 3. 222.22 | 4. 1.6875     |
| 5. 60 L   | 6. 1.622 atm. |

**EXERCISE # O-I**

- |            |             |             |             |
|------------|-------------|-------------|-------------|
| 1. Ans.(D) | 2. Ans.(C)  | 3. Ans.(C)  | 4. Ans.(B)  |
| 5. Ans.(A) | 6. Ans.(C)  | 7. Ans.(C)  | 8. Ans.(B)  |
| 9. Ans.(D) | 10. Ans.(A) | 11. Ans.(C) | 12. Ans.(C) |

**EXERCISE # O-II**

- |   |               |                 |                 |
|---|---------------|-----------------|-----------------|
| 1. Ans. (A,B,C)   | 2. Ans. (A,C) | 3. Ans. (A,B,D) | 4. Ans. (A,B,D) |
| 5. Ans.(A,B)  | 6. Ans.(A)    | 7. Ans. (C)     |                 |
| 8. (A) - P,Q,R,S ; (B) - P, Q ; (C) - S ; (D) - P, Q, T |               |                 |                 |

**EXERCISE # JEE-MAINS**

- |             |             |             |             |
|-------------|-------------|-------------|-------------|
| 1. Ans. (2) | 2. Ans. (1) | 3. Ans. (4) | 4. Ans. (4) |
| 5. Ans. (1) | 6. Ans.(3)  | 7. Ans. (1) | 8. Ans.(3)  |

**EXERCISE # JEE-ADVANCED**

1. Ans.(C)



# Chapter Contents

## 03

## ATOMIC STRUCTURE

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## ATOMIC STRUCTURE

### 1. INTRODUCTION :

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word 'atom' has been derived from the Greek word 'a-tomio' which means 'uncuttable' or 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century. The atomic theory of matter was first proposed on a firm scientific basis by **John Dalton**, a British school teacher in 1808. His theory, called **Dalton's atomic theory**, regarded the atom as the ultimate particle of matter.

### 2. DALTON ATOMIC THEORY :

- (i) Atom is the smallest particle of any substance which cannot be divided further.
- (ii) Atoms can never be created nor be destroyed. Only the rearrangement of atoms occurs in chemical reactions.
- (iii) All the atoms are hard and dense.
- (iv) All the atoms of an element are identical but the atoms of different elements will be different.
- (v) A compound is formed by the combinations of atoms of different elements in a fixed ratio by mass.

We start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms can be further divided into subatomic particles, i.e., electrons, protons and neutrons. a concept very different from that of Dalton. The major problems before the scientists at that time were:

- to account for the stability of atom after the discovery of sub-atomic particles,
- to compare the behaviour of one element from other in terms of both physical and chemical properties,
- to explain the formation of different kinds of molecules by the combination of different atoms and,
- to understand the origin and nature of the characteristics of electromagnetic radiation absorbed or emitted by atoms.

### 3. SUB-ATOMIC PARTICLES

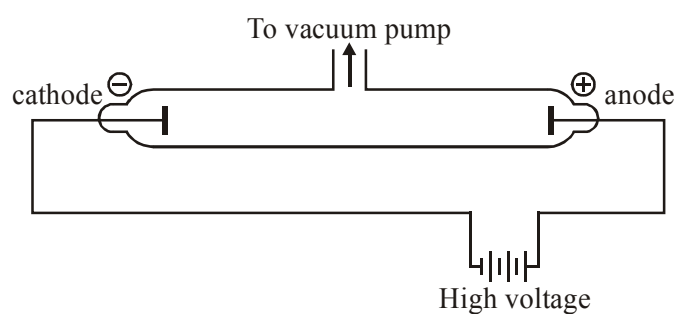
Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur generate electricity. Many different kinds of sub-atomic particles were discovered in the twentieth century.

### 3.1 Discovery of Electron :

In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. These results suggested the particulate nature of electricity.

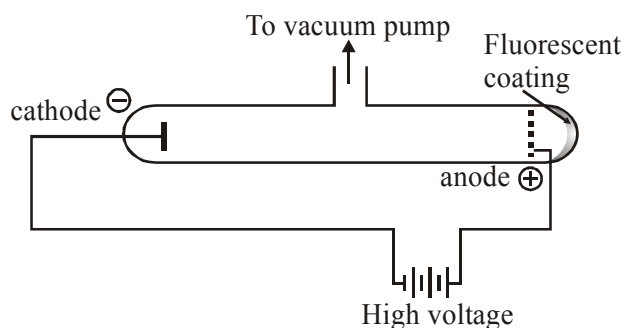
An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles: "Like charges repel each other and unlike charges attract each other".

In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as **cathode ray discharge tubes**.



*A cathode ray discharge tube*

A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called **cathode rays or cathode ray particles**. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot on the coating is developed (same thing happens in a television set)



*A cathode ray discharge tube with perforated anode*

The results of these experiments are summarised below.

- (i) The cathode rays start from cathode and move towards the anode.
- (ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

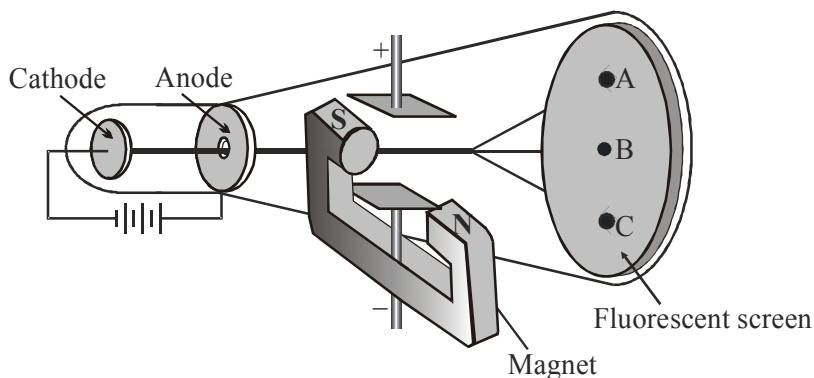
- (iii) In the absence of electrical or magnetic field, these rays travel in straight lines.
- (iv) In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called **electrons**.
- (v) The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.

Thus, we can conclude that electrons are basic constituent of all the atoms.

### 3.1.1 Charge to Mass Ratio of Electron :

In 1897, British physicist J.J. Thomson measured the ratio of electrical charge ( $e$ ) to the mass of electron ( $m_e$ ) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons. Thomson argued that the amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon :

- (i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection.
- (ii) the mass of the particle lighter the particle, greater the deflection.
- (iii) the strength of the electrical or magnetic field . the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field.



*The apparatus to determine the charge to the mass ratio of electron*

When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A. Similarly when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path followed as in the absence of electric or magnetic field and they hit the screen at point B. By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of  $e/m_e$  as:

$$\frac{e}{m_e} = 1.758820 \times 10^{11} \text{ C kg}^{-1}$$

where  $m_e$  is the mass of the electron in kg and  $e$  is the magnitude of the charge on the electron in coulomb (C). Since electrons are negatively charged, the charge on electron is  $-e$ .

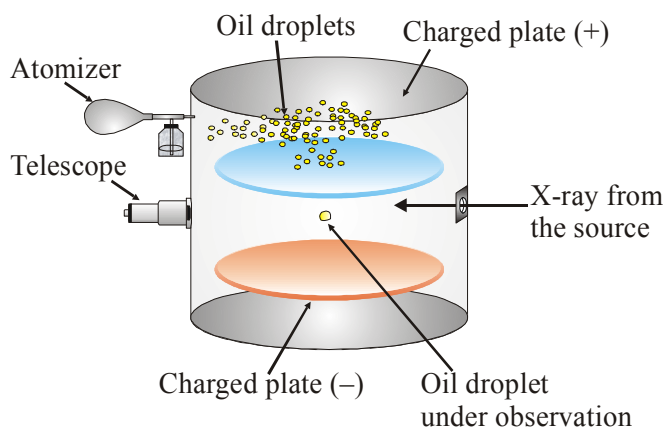
### 3.1.2 Charge on the Electron :

R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons. He found that the charge on the electron to be  $-1.6 \times 10^{-19}$  C. The present accepted value of electrical charge is  $-1.6022 \times 10^{-19}$  C. The mass of the electron ( $m_e$ ) was determined by combining these results with Thomson's value of  $e/m$  ratio.

$$m_e = \frac{e}{e/m_e} = \frac{1.6022 \times 10^{-19} \text{ C}}{1.758820 \times 10^{11} \text{ C kg}^{-1}} = 9.1094 \times 10^{-31} \text{ kg}$$

### Millikan's Oil Drop Method

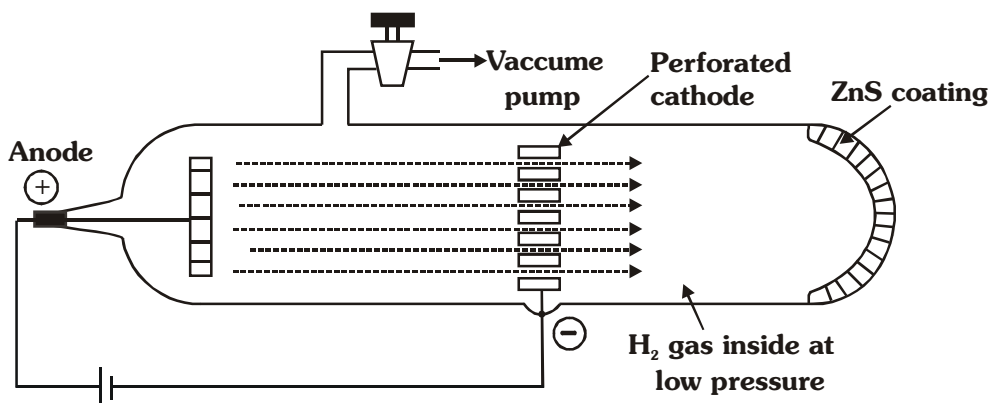
In this method, oil droplets in the form of mist, produced by the atomiser, were allowed to enter through a tiny hole in the upper plate of electrical condenser. The downward motion of these droplets was viewed through the telescope, equipped with a micrometer eye piece. By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets. The air inside the chamber was ionized by passing a beam of X-rays through it. The electrical charge on these oil droplets was acquired by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the magnitude of electrical charge,  $q$ , on the droplets is always an integral multiple of the electrical charge,  $e$ , that is,  $q = n e$ , where  $n = 1, 2, 3 \dots$ . The highest common factor (HCF) of charges on oil droplet was taken as charge on electron.



*The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electrical field and a viscous drag force when the oil drop is moving.*

### 3.2 CANAL RAYS (OR ANODE RAYS) – DISCOVERY OF PROTON :

Atoms are electrically neutral. Hence after the discovery of the negatively charged constituent (electron) of an atom, attempts were made to discover the positively charged counterpart of electrons. By using a discharge tube containing a perforated cathode, **Goldstein (1886)** found that some rays passed through these holes in a direction opposite to that of the cathode rays.



### Positive Rays or Canal Rays

Electrical discharge carried out in the modified cathode ray tube led to the discovery of particles carrying positive charge, also known as **canal rays**. The characteristics of these positively charged particles are listed below.

- unlike cathode rays, the positively charged particles depend upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.
- The charge to mass ratio of the particles is found to depend on the gas from which these originate.
- Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.
- The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

The smallest and lightest positive ion was obtained from hydrogen and was called proton. This positively charged particle was characterised in 1919.

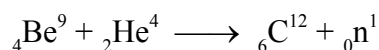
The lightest positively charged particle is called a proton (P or P<sup>+</sup>). Positive rays are atomic or molecular cations from which some electrons have been removed. The removed electrons constitute the cathode rays and the positive cations form the positive or canal rays.

### 3.3 DISCOVERY OF NEUTRON :

After the discovery of electron and proton **Rutherford (1920)** predicted the existence of a neutral fundamental particle. In **1932, Chadwick** bombarded the element Beryllium with  $\alpha$ -particles and noticed the emission of a radiation having the following characteristics.

- The radiation was highly penetrating.
- The radiation was unaffected by magnetic and electric fields which shows that it is electrically neutral.
- It was found to have approximately the same mass as the protons.

The name 'neutron' was given to this sub-atomic particle. It is denoted by  $n$  or  ${}_0n^1$ . Bombardment of beryllium by  $\alpha$ -particles results in the formation of carbon and neutrons are emitted.



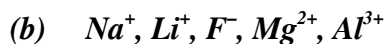
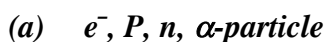
Mass of a neutron is 1.00867 amu ( $1.67493 \times 10^{-24}$  g or  $1.67493 \times 10^{-27}$  kg)

## 3.4 PROPERTIES OF FUNDAMENTAL PARTICLES :

Atoms are made up-essentially, of three fundamental particles, which differ in mass and electric charge as follows :

	Electron	Proton	Neutron
Symbol	e or e <sup>-</sup>	p	n
Approximate relative mass	1/1836	1	1
Approximate relative charge	-1	+1	0
Mass in kg	9.10939 × 10 <sup>-31</sup>	1.67262 × 10 <sup>-27</sup>	1.67493 × 10 <sup>-27</sup>
Mass in amu	0.00054	1.00727	1.00867
Actual charge/C	-1.6022 × 10 <sup>-19</sup>	+1.6022 × 10 <sup>-19</sup>	0

**Ex.1.** Arrange the particle in their increasing order of specific charge ratio.



$$\text{Sol. (a)} \quad \left(\frac{e}{m}\right)_e = \frac{1e}{\left(\frac{1}{1836}\right)\text{amu}}$$

$$\left(\frac{e}{m}\right)_p = \frac{1}{1} = 1 = \frac{1e}{1\text{amu}}$$

$$\left(\frac{e}{m}\right)_n = \frac{0}{1} = 0 = \frac{0e}{1\text{amu}}$$

$$\left(\frac{e}{m}\right)_\alpha = \frac{2}{4} = \frac{1}{2} = \frac{2e}{4\text{amu}}$$

**Ans.** n < α < p < e<sup>-</sup>

$$(b) \quad Na^+ = \frac{1}{23}; Li^+ = \frac{1}{7}; F^- = \frac{1}{19}; Mg^{2+} = \frac{2}{24} = \frac{1}{12}; Al^{3+} = \frac{3}{27} = \frac{1}{9}$$

$$Na^+ < F^- < Mg^{2+} < Al^{3+} < Li^+$$

**Ex.2.** Which of the following pairs have same specific charge  $\left(\frac{e}{m}\right)$  ?

(a) electron &amp; proton

(b) electron &amp; positron

(c) proton &amp; positron

(d) proton &amp; deuteron

(e) α-particle &amp; deuteron

**Answer.** b, e

**Ex.3.** Through what potential difference an  $\alpha$ -particle should be accelerated to have speed  $5 \times 10^6$  m/s.

**Sol. :**  $qV = \frac{1}{2}mv^2$

$$(2 \times 1.6 \times 10^{-19} \times V) = \frac{1}{2} \times 4 \times 1.66 \times 10^{-27} \times (5 \times 10^6)^2$$

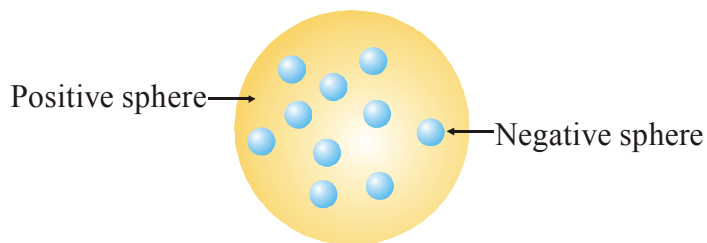
#### 4. ATOMIC MODELS :

Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is composed of sub-atomic particles carrying positive and negative charges. Different atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, proposed by J. J. Thomson and Ernest Rutherford are discussed below.

##### 4.1 Thomson Model of Atom :

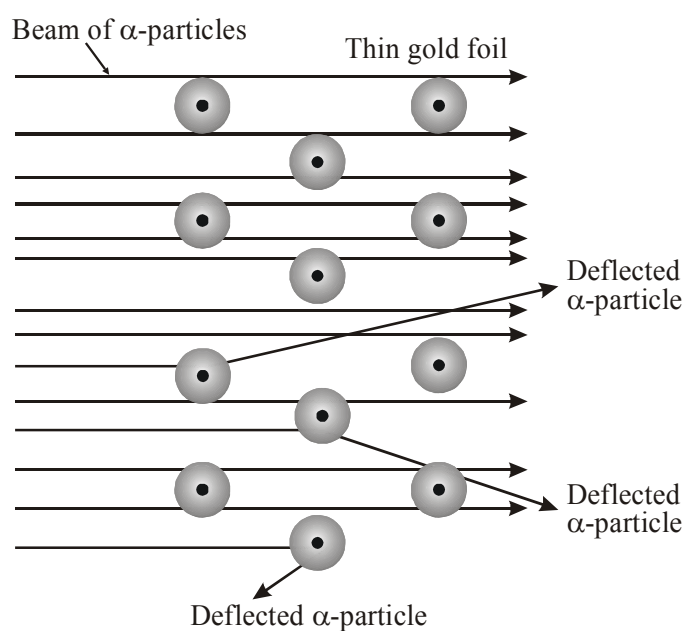
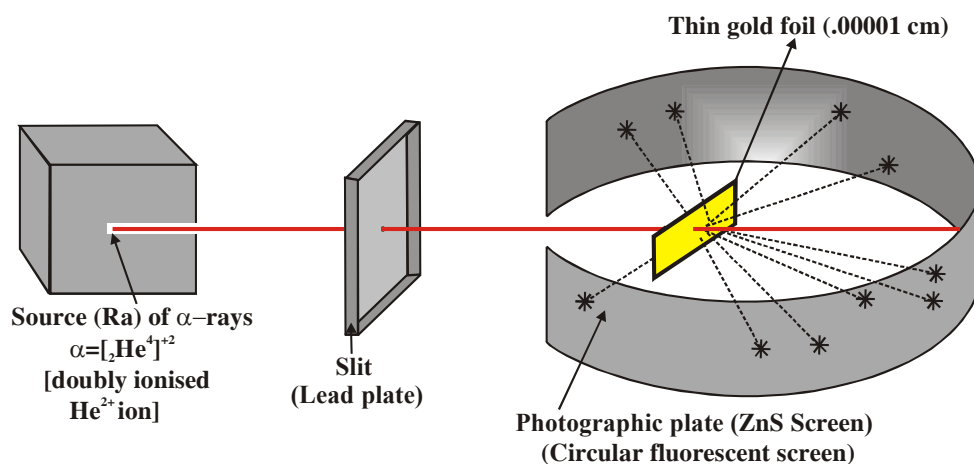
J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately  $10^{10}$  m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement. Many different names are given to this model, **for example, plum pudding, raisin pudding or watermelon**. This model can be visualised as a pudding or watermelon of positive charge with plums or seeds (electrons) embedded into it. An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom. Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments.

Thomson was awarded Nobel Prize for physics in 1906, for his theoretical and experimental investigations on the conduction of electricity by gases.



*Thomson model of atom*

## 4.2 Rutherford's model :

Rutherford's  $\alpha$ -scattering experiment

B. Schematic molecular view of the gold foil

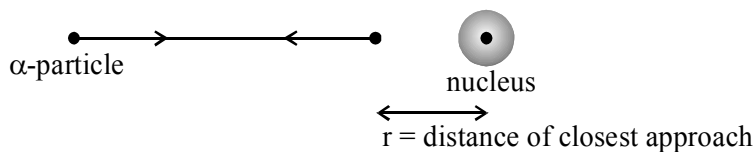
## ❖ Observations and conclusions :

- (i) Most of the  $\alpha$ -particles passed through the gold foil undeflected. Hence, most of the space in the atom is empty.
- (ii) A small fraction of  $\alpha$ -particles was deflected by small angles. A very few  $\alpha$ -particles ( $\sim 1$  in 20,000) bounced back, that is, were deflected by nearly  $180^\circ$ .

The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged  $\alpha$ -particles. Rutherford given the name **nucleus** to this positively charged center of atom.



- (iii) The volume occupied by the nucleus is negligibly small as compared to the total volume of atom. The radius of the atom is about  $10^{-10}$  m, while that of nucleus is  $10^{-15}$  m. Rutherford estimated the size of nucleus by calculating the distance of closest approach.



The initial kinetic energy of  $\alpha$ -particle must be equal to potential energy at distance of closest approach.

$$\text{K.E.} = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_1 \cdot q_2}{r} = \frac{1}{4\pi\epsilon_0} \cdot \frac{(2e) \cdot (Ze)}{r}$$

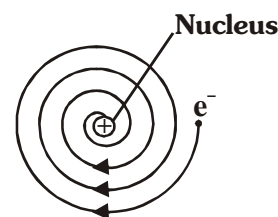
$$r = \frac{2Ze^2}{(4\pi\epsilon_0)(\text{K.E.})}$$

where  $Z$  = atomic number of element used in foil.

- (iv) Almost all mass of the atom is densely concentrated in extremely small region (nucleus).  
 (v) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Electrons and the nucleus are held together by electrostatic forces of attraction.

#### 4.2.1 Drawbacks of Rutherford model :

- (i) According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation. Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink.



Calculations show that it should take an electron only  $10^{-8}$  s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom.

- (ii) It does not explain the arrangement of electrons revolving round nucleus.  
 (iii) It does not explain the stability of nucleus against strong repulsive forces.  
 (iv) It does not explain atomic spectrum.

**Ex.4** An  $\alpha$ -particles of kinetic energy of 5.4 MeV is projected towards gold nucleus. Calculate the distance of closet approach. (Atomic number of gold = 79,  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ )

$$\text{Sol: K.E.} = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_1 q_2}{r}$$

$$\text{or } 5.4 \times 10^6 \times 1.6 \times 10^{-19} = 9 \times 10^9 \times \frac{(2 \times 1.6 \times 10^{-19}) \times (79 \times 1.6 \times 10^{-19})}{r}$$

$$\therefore r = 4.21 \times 10^{-14} \text{ m}$$

**Ex.5** An  $\alpha$ -particles is projected towards the following nucleus with same kinetic energy in different experiement the distance of closet approach is maximum for

(A) Na (Z = 11)

(B) Ca (Z = 20)

(C) Ag (Z = 47)

(D) Au (Z = 79)

Answer.(A)

**Ex.6.** An  $\alpha$ -particle, a proton, a deuteron and a neutron are projected towards the same nucleus with the same kinetic energy in different experiement. The distance of closet approach is minimum for

(A)  $\alpha$

(B) P

(C) d

(D) n

Answer.(D)

**Ex.7** An  $\alpha$ -particle having K.E. = 7.7 MeV is scattered by gold (Z = 79) nucleus through  $180^\circ$ . Find distance of closest approach.

$$\text{K.E.} = 7.7 \text{ MeV}$$

$$= 7.7 \times 10^6 \times 1.6 \times 10^{-19} \text{ J}$$

$$= 1.23 \times 10^{-12} \text{ J}$$

$$\frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \text{ Nm}^2\text{C}^{-2}$$

$$\text{Using we get: } \frac{9 \times 10^9 \times 2 \times 79 \times (1.6 \times 10^{-19})^2}{1.23 \times 10^{-12}}$$

$$r_0 = 3 \times 10^{-14} \text{ m}$$

From the above example it is clear that nuclear dimension cannot be greater than  $3 \times 10^{-14} \text{ m}$ .

## 5. WAVE THEORY :

A wave is defined as a periodic disturbance in space or in a medium that involves elastic displacement of material particles or a periodic change in some physical quantities such as T, P, V etc. Thus, wave motion represents propagation of a periodic disturbance carrying energy. The wave travels at right angles to the vibratory motion of the object.

When an object moves up and down or vibrates continuously, energy in the form of waves is transmitted by a vibrating object to a distant place. For example, when a stone is thrown in a still water of a pond, a disturbance is produced at a place where the stone strikes the water.

This disturbance advances outwards in the same form and reaches the edges of the pond. Such a disturbance is called a **mechanical wave**. The mechanical waves transmit only in a material medium. Besides the mechanical waves, there are waves which do not require any medium for their transmission. These waves are called **electromagnetic waves** or **electromagnetic radiations**.

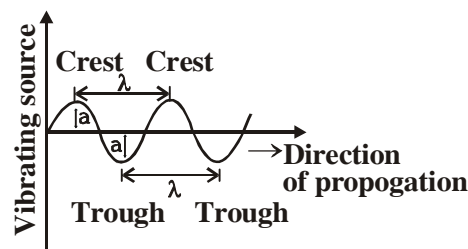
5.1 WAVE CHARACTERISTICS :

I. Wavelength ( $\lambda$ ) :

It is defined as the distance between two nearest crests or nearest troughs.

It is measured in terms of a Å (Angstrom), pm (Picometre), nm (nanometer), cm (centimetre), m (metre)

$$1 \text{ \AA} = 10^{-10} \text{ m}, \quad 1 \text{ pm} = 10^{-12} \text{ m}, \quad 1 \text{ nm} = 10^{-9} \text{ m}, \quad 1 \text{ cm} = 10^{-2} \text{ m}$$



II. Frequency ( $\nu$ ) :

Frequency of a wave is defined as the number of waves which pass through a point in 1 sec.

- It is measured in terms of Hertz (Hz),  $\text{sec}^{-1}$ , or cycle per second (cps)

$$1 \text{ Hertz} = 1 \text{ sec}^{-1}$$

III. Time period (T) : Time taken by a wave to pass through one point.

$$T = \frac{1}{\nu} \text{ sec.}$$

IV. Velocity (c) :

Velocity of a wave is defined as distance covered by a wave in 1 sec.

$$c = \lambda / T = \lambda \nu \quad \nu = c / \lambda \quad c = \nu (\text{sec}^{-1}) \times \lambda (\text{m}) \quad c = \nu \lambda (\text{m sec}^{-1})$$

Since c is constant for em-waves.

i.e. frequency is inversely proportional to  $\lambda$

V. Wave number ( $\bar{\nu}$ ) :

It is defined as number of waves per unit length. It is denoted by  $\bar{\nu}$  & is expressed in  $\text{cm}^{-1}$ .

$$\lambda \text{ m} \rightarrow 1 \text{ wave}$$

$$1 \text{ m} \rightarrow 1/\lambda \text{ waves}$$

$$\bar{\nu} = \frac{1}{\lambda} \quad (1 \text{ cm}^{-1} = 100 \text{ m}^{-1})$$

- It is measured in terms of  $\text{cm}^{-1}$ ,  $\text{m}^{-1}$  etc.

VI. Amplitude (a) :

It is the height of the crest or depth of the trough of a wave and is denoted by 'a'. It is half the vertical distance from the top of the wave to the bottom of the wave. It determines the intensity or brightness of the beam of light.

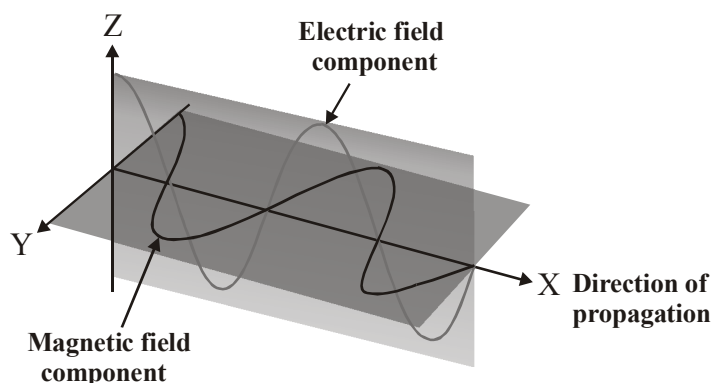
The amplitude of a wave in stretched string is the maximum displacement of the string from its normal position that of water waves is the maximum height of the water surface relative to its normal level, That of a sound wave is the maximum change in pressure relative to the normal pressure.

## 5.2 ELECTRO MAGNETIC (EM) WAVES :

**James Maxwell (1870)** suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted by it. These fields are transmitted in the forms of waves called electromagnetic waves or electromagnetic radiations.

### ❖ Main assumptions of Maxwell EM theory :

- (i) The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.



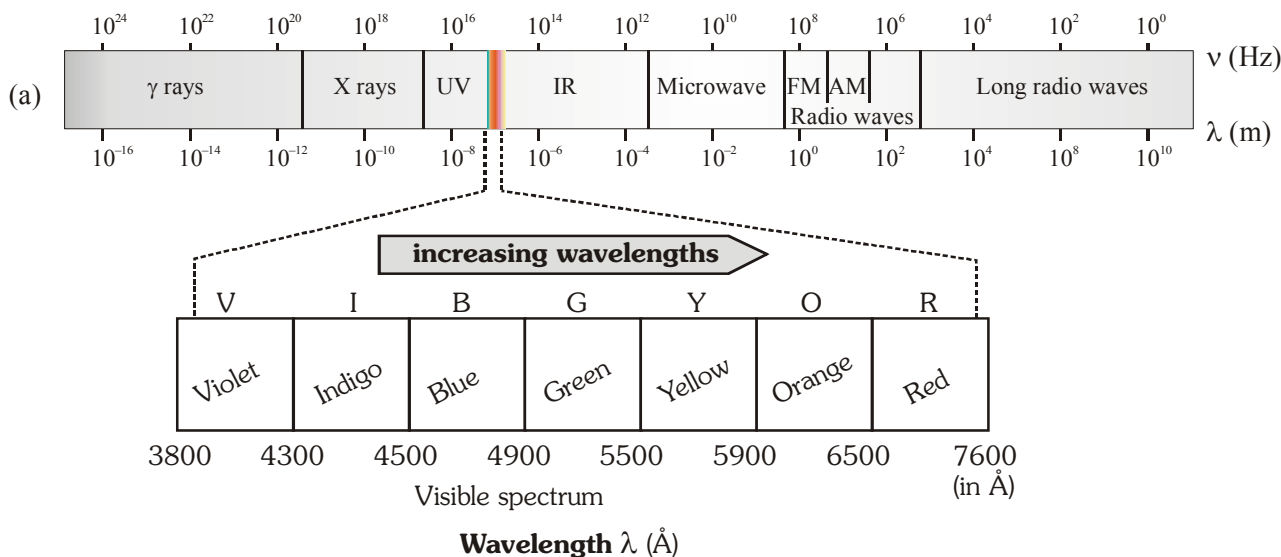
(The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.)

- (ii) Unlike sound waves or water waves, electromagnetic waves do not require medium and can move in vacuum.  
(However speed changes in different mediums)
- (iii) The EM waves travel with the velocity of light ( $3 \times 10^8$  m/sec) in vacuum.
- (iv) Energy of EM waves depends on its amplitude not on its frequency or wavelength.  
(This assumptions was later proved to be wrong in some situations).

5.3 ELECTRO MAGNETIC SPECTRUM :

The arrangement of various types of electromagnetic radiations in the order of their increasing or decreasing wavelength or frequencies is known as electromagnetic spectrum. The wavelength decreases in the following order.

Radio waves > microwaves > Infrared > Television waves > Visible > Ultraviolet > X-rays >  $\gamma$ -rays > cosmic rays



Ex.8. Calculate the frequency of EMR (Electromagnetic radiation) of wave number  $10^4 \text{ cm}^{-1}$ .

Sol:  $\nu = \frac{c}{\lambda} = c\bar{\nu} = (3 \times 10^8 \text{ m/s})(10^4 \text{ cm}^{-1}) = (3 \times 10^{10} \text{ cm/s})(10^4 \text{ cm}^{-1}) = 3 \times 10^{14} \text{ Hz}$ .

Ex.9. A radio station radiate the radiowaves of frequency 20kHz. What is meter band of that radio station?

Sol:  $20\text{kHz} = \frac{3 \times 10^8}{\lambda} \Rightarrow \lambda = 1.5 \times 10^4 \text{ m}$

6. PARTICLE NATURE OF ELECTROMAGNETIC RADIATIONS (PLANCK'S QUANTUM THEORY OF RADIATION)

Max Planck in 1901, put forward a theory known as "Planck's Quantum Theory". It regards electromagnetic radiations made up of particles. This was further extended by Einstein in 1905. The main points of the theory are :

- (i) The radiant energy is emitted or absorbed by atoms or molecules discontinuously in the form of small energy packets called quanta. In case of light , these energy packets are known as photons.
- (ii) The energy of each quantum is directly proportional to the frequency of the radiation i.e.

$$E \propto \nu \quad \text{or} \quad E = h\nu = \frac{hc}{\lambda}$$

Here h is a constant known as **Planck's constant**. Its value is  $6.626 \times 10^{-34}$  Joules sec.

(iii) The total amount of energy emitted or absorbed by a body is some whole number multiple of quantum i.e.,

$$E = nh\nu \quad (\text{Here } n \text{ is a positive integer : } 1, 2, 3, 4 \dots \text{ etc.})$$

Thus, Planck for the first time has given a relationship between the frequency (or wavelength) of the radiations and the energy associated with them. Cosmic rays, gamma rays and X-rays are high energy radiations since they have very high frequency. At the same time, microwaves and radiowaves with small frequency are regarded as low energy radiations.

#### ❖ Important features of Photon :

- Source of energy (light) emits radiation in the form photons, which travel with speed of light.
- Energy of single photon,  $E = h\nu = \frac{hc}{\lambda}$ .
- All the photons in vacuum travel with speed  $3 \times 10^8$  m/s but their speed is changed in different medium, however frequency remains same. Speed does not depend on energy.
- Photons travel as waves but are absorbed or emitted as particles.

**Ex.10. Calculate the energy per quanta of an EMR of frequency 400 MHz.**

**Sol :**  $E = 6.626 \times 10^{-34} \times 4 \times 10^6 \text{ J/quanta}$

**Ex.11. Calculate the energy per quanta of an EMR of wavelength 662.6 nm.**

**Sol :**  $E = n \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{662.6 \times 10^{-9} \text{ m}} = 3 \times 10^{-19} \text{ J/quanta}$

**Ex.12. Calculate the wavelength (in Å) of an EMR of energy 3.1 eV/quanta.**

**Sol :**  $E = h\nu = h \frac{c}{\lambda} \Rightarrow E(\text{eV}) \times 1.602 \times 10^{-19} = \frac{1 \times 6.62 \times 10^{-34} \times 3 \times 10^8}{\lambda(\text{Å})}$

$$E(\text{eV}) \approx \frac{12400}{\lambda(\text{Å})} = \frac{1240}{\lambda(\text{nm})}$$

**Ex.13. In order to see an object,  $10^{-19}$  J must be received by our eyes. How many photons of green light must be received by our eyes for its visibility. ( $\lambda = 550 \text{ nm}$ ,  $h = 6.6 \times 10^{-34} \text{ J}$ )**

**Sol :**  $E = n \frac{hc}{\lambda}$

$$10^{-19} = n \times \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{5500 \times 10^{-9}}$$

$$n = \frac{5}{18} \approx 1$$

**Ex.14.** A bulb is rated as 110 watt. If it emits 25% of absorbed energy as red light ( $\lambda = 6626\text{\AA}$ ), how many photons are emitted out by the bulb per second.

$$\text{Sol: } 110 \times \frac{25}{100} = n \times \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{6626 \times 10^{-10}}$$

**Ex.15.** The wavelength of microwave radiation is 0.08 m. How many moles of photons is needed to increase the temperature of 400 gm water from  $25^\circ$  to  $45^\circ\text{C}$ , assuming 25% efficiency.  
Specific heat capacity = 4.2 J/K-gm

$$\text{Sol: } \left( \frac{nhc}{\lambda} \right) \times \frac{25}{100} = ms\Delta t$$

$$n \times \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{0.08} \times \frac{25}{100} = 400 \times 4.2 \times 20$$

$$\therefore \text{ Number of moles of photon} = \frac{n}{N_A}$$

**Ex.16.** A dye absorbs the radiation of  $4000\text{\AA}$  and fluoresces the radiation of  $5000\text{\AA}$ . If only 40% of the absorbed energy is emitted out, calculate the ratio of number of quanta emitted out and the number of quanta absorbed.

$$\text{Sol: } E_a \times \frac{40}{100} = E_e$$

$$n_a \times \frac{hc}{4000\text{\AA}} \times \frac{40}{100} = n_e \times \frac{hc}{5000\text{\AA}}$$

$$\frac{n_e}{n_a} = \frac{40}{100} \times \frac{5000}{4000} = \frac{1}{2}$$

**Ex.17.** The bond dissociation energy of Cl–Cl bond in chlorine gas is 240 kJ/mol. Calculate the longest wavelength of EMR needed to dissociate bond. Assume one photon may dissociate only one bond.

$$\text{Sol: } \frac{240 \times 10^3}{6 \times 10^{23}} = \frac{1 \times 6.626 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

**Ex.18** A near ultra violet photon of wavelength 300 nm is absorbed by a gas and then emitted as two photons. One photon is of red light with wavelength 760 nm. What would be the wave length of the second photon ?

**Sol.** It may noted that energy of photon which adsorbed is emitted as sum of the energy of two photons.

$$\text{Energy absorbed } h\nu = \frac{hc}{\lambda}$$

According to available information,

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}; \frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}; \frac{1}{\lambda_2} = \left[ \frac{1}{\lambda} - \frac{1}{\lambda_1} \right]$$

Now,  $\lambda = 300 \text{ nm}$  ;  $\lambda_1 = 760 \text{ nm}$  ;  $\lambda_2$  can be calculated as :

$$\frac{1}{\lambda_2} = \left[ \frac{1}{300} - \frac{1}{760} \right] = \frac{760 - 300}{300 \times 760} (\text{nm}^{-1})$$

$$\frac{1}{\lambda_2} = \frac{460}{760 \times 300} (\text{nm}^{-1})$$

or  $\lambda_2 = 496 \text{ nm}$

## 7. PHOTOELECTRIC EFFECT :

**Hertz** in **1887** observed that when a light of certain frequency strikes the surface of a metal, electrons are ejected from the metal. This phenomenon is known as **photoelectric effect** and the ejected **electrons** are called **photoelectrons**.

A few metals, which are having low ionisation energy like Cesium, show this effect under the action of visible light but many more show it under the action of more energetic ultraviolet light.

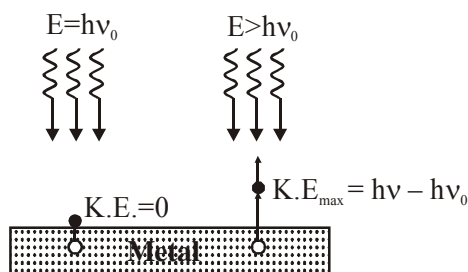
### 7.1 The experimental findings are summarized as below :

- Electrons come out as soon as the light (of sufficient energy) strikes the metal surface. There is no time lag between the two events.
- The light of any frequency will not be able to cause ejection of electrons from a metal surface. There is a minimum frequency, called the **threshold (or critical) frequency**, which can just cause the ejection. This frequency varies with the nature of the metal. The higher the frequency of the light, the more energy the photoelectrons have. Blue light results in faster electrons than red light.
- Photoelectric current is increased with increase in intensity of light of same frequency, if emission is permitted, i.e. a bright light yields more photoelectrons than a dim one of the same frequency, but the electron energies remain the same.



### 7.2 Einstein's explanation :

Light must have stream of energy particles or quanta of energy ( $h\nu$ ). Suppose, the threshold frequency of light required for ejecting electrons from a metal is  $\nu_0$ , when a photon of light of this frequency strikes a metal it imparts its entire energy ( $h\nu_0$ ) to the electron.



This energy enables the electron to break away from the surface by overcoming the attractive influence of the nucleus. Thus each photon can eject one electron. If the frequency of light is less than  $\nu_0$ , there is no ejection of electron. If the frequency of light is higher than  $\nu_0$  (let it be  $\nu$ ), the photon of this light having higher energy ( $h\nu$ ), will impart some energy to the electron that

is needed to remove it away from the atom. Einstein proposed that light consisted of quanta, which we call photons with a frequency over a certain threshold would have sufficient energy to eject a single electron, producing the photoelectric effect.

### 7.3 Einstein's Equation for the Photoelectric Effect :

Einstein's interpretation of the photoelectric effect results in equation :

Energy of photon = Energy needed to remove an electron + Max. Kinetic energy of the emitted electron

The excess energy would give a certain velocity (i.e. kinetic energy) to the electron.

$$h\nu = h\nu_0 + K.E._{max.}$$

$$h\nu = h\nu_0 + \frac{1}{2} mu^2$$

$$\frac{1}{2} mv^2 = h\nu - h\nu_0$$

where  $\nu$  = frequency of the incident light,  $\nu_0$  = threshold frequency

$v$  = max. speed of photoelectron.

$h\nu_0$  is the **threshold energy** (or) the **work function** denoted by  $\phi = h\nu_0$  (minimum energy of the photon to liberate electron). It is constant for particular metal.

The maximum kinetic energy of the photoelectrons increases linearly with the frequency of incident light. This, if the energy of the ejected electrons is plotted as a function of frequency, it results in a straight line whose slope is equal to Planck's constant 'h' and whose intercept is  $h\nu_0$ .



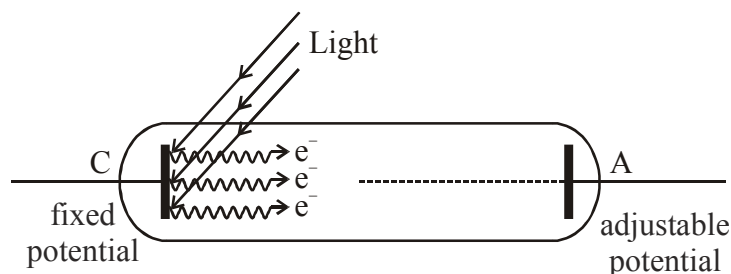
Albert Einstein (1879 - 1955)

Albert Einstein, a German born American physicist, is regarded by many as one of the two great physicists the world has known (the other is Isaac Newton). His three research papers (on special relativity, Brownian motion and the photoelectric effect) which he published in 1905, **Albert Einstein (1879 - 1955)** while he was employed as a technical assistant in a Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.

#### 7.4 Important conclusions from photoelectric effect :

- Photoelectric effect demonstrates particle nature of radiation.
- A photon is quanta of energy. Its rest mass is zero. This is why photon can give up its all energy to the particle it strikes.
- There is no effect of frequency of incident light on the number of the emitted photoelectrons.
- There is no effect of intensity of incident light on the K.E. of the emitted photoelectrons.

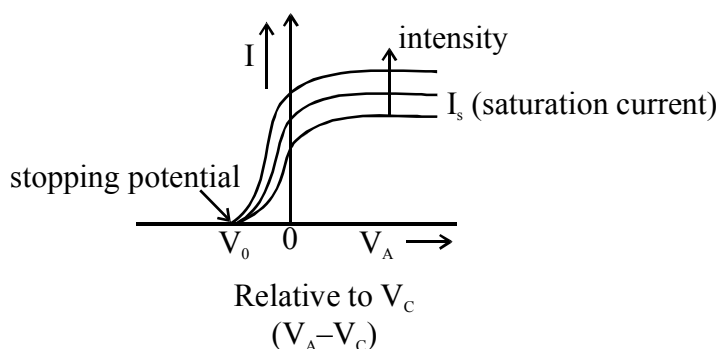
#### 7.5 SATURATION CURRENT & STOPPING POTENTIAL



**Case-I :**  $V_C = V_A$   
Some of the ejected electrons reach at electrode A resulting photocurrent.

**Case-II :**  $V_C < V_A$   
As electrode (A) is at high potential it attracts the electron & even a slower electron will reach at electrode A. It will result in increase in photocurrent. Further increase in the potential difference, a situation may result when the slowest photocurrent electron reach at electrode. It results maximum called **saturation current**. Further increase in potential will not increase photocurrent.

**Case-III :**  $V_C > V_A$   
As electrode (A) is at low potential. It will repel electron resulting decrease in photocurrent. Further decrease in potential at electrode (A) may result a situation when the fastest electron just fails to reach at (A) and the photocurrent drops to zero. The potential of (A) relative to C to just stop photocurrent is called **stopping potential**.



On increasing the intensity of light the stopping potential does not change because the maximum K.E. of photoelectron does not change. But the photocurrent increases, because the number of photon falling on the surface increase.

If the frequency of light is changed, the stopping potential will change.

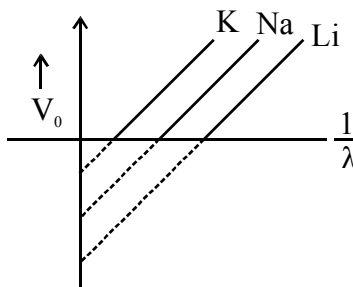
$$(KE)_{\max} = eV_0$$

$$(KE)_{\max} = h\nu - h\nu_0$$

$$eV_0 = \frac{hc}{\lambda} - \phi$$

$$V_0 = \frac{hc}{e} \frac{1}{\lambda} - \frac{\phi}{e}$$

y                      x



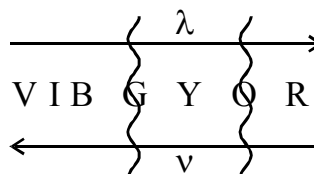
**Ex.19.** From a metal surface, photoelectron never comes out by orange light but comes from green light. Predict about the injection of photoelectron from the same metal by

- (i) Red    (ii) Blue    (iii) Yellow light

**Sol:** (i) Red light = No

(ii) Blue light = Yes

(iii) Yellow light = Can't say



**Ex.20.** The work function of a metal is 3 eV. If EMR of 200 nm fall on the metal surface, calculate the maximum speed of photoelectron ejected.

**Sol:**  $E = \frac{1240}{200} = 6.2\text{eV}$

$$(KE)_{\max} = h\nu - \phi$$

$$\frac{1}{2}mv^2 = (6.2 - 3)\text{eV}$$

$$\frac{1}{2} \times 9.1 \times 10^{-31} v_{\max}^2 = 3.2 \times 1.6 \times 10^{-19}$$

**Ex.21.** When EMR of frequency  $5 \times 10^{15}$  Hz fall on a metal surface, the maximum kinetic energy of photoelectron is double than the photoelectron which emits when EMR of frequency  $3 \times 10^{15}$  Hz fall on the same metal. The threshold frequency for the metal is

**Sol:**  $(K.E.)_1 = h \times 5 \times 10^{15} - h\nu_0$

$$(K.E.)_2 = h \times 3 \times 10^{15} - h\nu_0$$

$$2E_1 = E_2$$

$$\nu_0 = 1 \times 10^{15} \text{ Hz.}$$

**Ex.22** A photon of wavelength  $3000 \text{ \AA}$  strikes a metal surface, the work function of the metal being  $2.20 \text{ eV}$ . Calculate (i) the energy of the photon in eV (ii) the kinetic energy of the emitted photo electron and (iii) the velocity of the photo electron.

**Sol.** (i) Energy of the photon

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.6 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ ms}^{-1})}{3 \times 10^{-7} \text{ m}} = 6.6 \times 10^{-19} \text{ J}$$

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

$$\text{Therefore } E = \frac{6.6 \times 10^{-19} \text{ J}}{1.6 \times 10^{-19} \text{ J/eV}} = 4.125 \text{ eV}$$

(ii) Kinetic energy of the emitted photo electron

$$\text{Work function} = 2.20 \text{ eV}$$

$$\text{Therefore, KE} = 2.475 - 2.20$$

$$= 1.925 \text{ eV} = 3.08 \times 10^{-19} \text{ J}$$

(iii) Velocity of the photo electron

$$\text{KE} = \frac{1}{2}mv^2 = 3.08 \times 10^{-19} \text{ J}$$

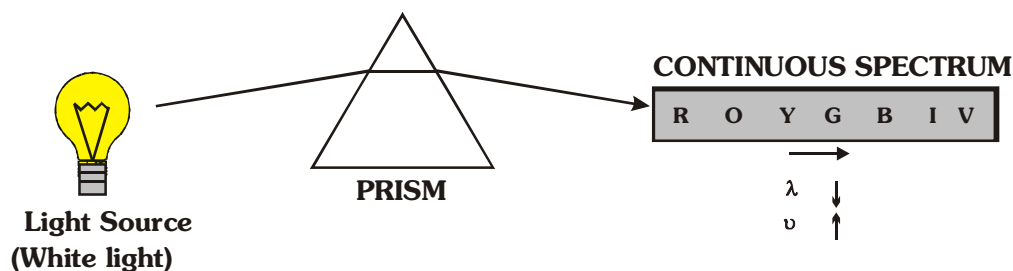
$$\text{Therefore, velocity (v)} = \sqrt{\frac{2 \times 3.08 \times 10^{-19}}{9.1 \times 10^{-31}}} = 8.22 \times 10^5 \text{ ms}^{-1}$$

## 8. SPECTRUM

It is the impressions produced on any screen when a light falls on it after passing through prism or prism like material.

**Classification of spectrum :**

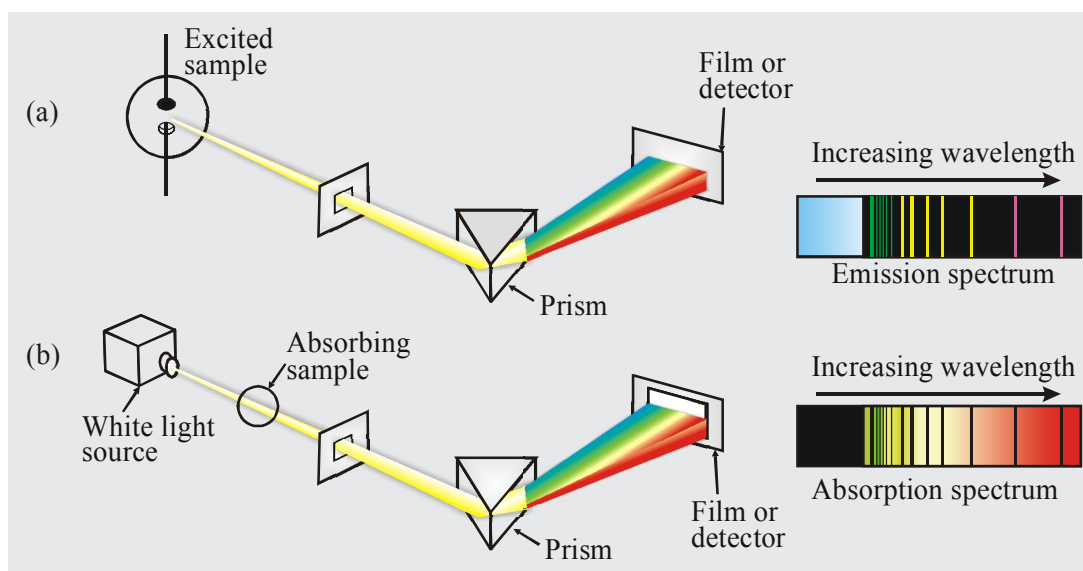
- (i) **Continuous and discontinuous spectrum :** In continuous spectrum, the impression produced on screen overlap each other, but in discontinuous spectrum, same gap exist between the impression. The spectrum of white light that we can see ranges from violet at  $7.50 \times 10^{14} \text{ Hz}$  to red at  $4 \times 10^{14} \text{ Hz}$ . This spectrum is called *continuous spectrum* because violet merges into blue, blue into green, and so on. A similar spectrum is produced when a rainbow forms in the sky. In a continuous spectrum, radiations corresponding to all the wavelengths are present.



(ii) **Emission and Absorption Spectra :** The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be '**excited**'. To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called **line spectra** or **atomic spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig)



**Fig. (a) Atomic emission.** The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum. **(b) Atomic absorption.** When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.

**Line emission spectra** are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as finger prints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements.

Elements like rubidium (Rb), caesium (Cs) thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

## 9. BOHR'S ATOMIC MODEL

Bohr's model for hydrogen atom is based on the following postulates:

- (i) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called **orbits**, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.
- (ii) The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state. The energy change does not take place in a continuous manner.
- (iii) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by  $\Delta E$ , is given by :

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

Where  $E_1$  and  $E_2$  are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

- (iv) The angular momentum of an electron in a given stationary state can be expressed as in equation

$$m_e v r = n \cdot \frac{h}{2\pi} \quad n = 1, 2, 3$$

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of  $h/2\pi$  that is why only certain fixed orbits are allowed.

### 9.1 APPLICATION OF BOHR'S MODEL

When electron revolves in fixed circular orbit than electrostatic force of attraction and centrifugal force are equal.

$$\text{Electrostatic force} = \frac{Kq_1q_2}{r^2} = \frac{K.Ze.e}{r^2} = \frac{KZe^2}{r^2}$$



**Niels Bohr  
(1885-1962)**

Niels Bohr, was a Danish physicist. After first world war, Bohr worked for peaceful uses of atomic energy. He was awarded the Nobel Prize in physics in 1922.

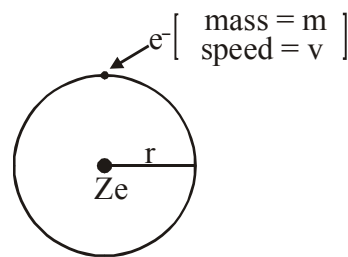
Where, constant  $K = 9 \times 10^9 \text{ Nm}^2/\text{C}^2$  (MKS) = 1 (CGS)

$$\text{Centrifugal force} = \frac{mv^2}{r}$$

In balanced condition

Electrostatic force = Centrifugal force

$$\frac{KZe^2}{r^2} = \frac{mv^2}{r} \text{ or } \frac{KZe^2}{r} = mv^2 \text{ or } \frac{Ze^2}{r} = mv^2 \text{ (CGS)}$$



.....(i)

### 9.1.1 Radius of various orbits (shell) :

According to Bohr model,  $mvr = \frac{nh}{2\pi}$

$$v = \frac{nh}{2\pi mr} \quad \text{.....(ii)}$$

Now putting the value of v from eq.(ii) into eq.(i)

$$\frac{KZe^2}{r} = m \left( \frac{nh}{2\pi mr} \right)^2$$

$$\frac{KZe^2}{r} = \frac{mn^2h^2}{4\pi^2 m^2 r^2}$$

$$r = \frac{n^2h^2}{4\pi^2 mKZe^2} \text{ or } r = \frac{n^2h^2}{4\pi^2 mZe^2} \text{ (CGS } \because K = 1) \text{ .....(iii)}$$

Putting the value of  $\pi$ , h, m, K, & e (Constants) in the above eq .(iii)

$$r = 0.529 \times 10^{-10} \times \frac{n^2}{Z} \text{ m} \quad \{ \text{\AA} = 10^{-10} \text{ m} = 10^{-8} \text{ cm} \}$$

$$\text{or } \boxed{r_n = 0.529 \times \frac{n^2}{Z} \text{\AA}}$$

This formula is only applicable for hydrogen and hydrogen like species i.e. species containing single electron.

### 9.1.2. Velocity of electron in Bohr orbit :

According to Bohr postulate

$$mvr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\pi mr} = \frac{nh}{\frac{2\pi m \times n^2 h^2}{4\pi^2 mKZe^2}}$$

$$v = \frac{2\pi KZe^2}{nh} \text{ (MKS) .....(iv)}$$

$$v = \frac{2\pi Ze^2}{nh} \text{ (CGS)}$$

Putting the value of  $\pi$ , h, K, & e (Constants) in the above eq (iv)

$$v = 2.18 \times 10^6 \frac{Z}{n} \text{ m/s}$$

### 9.1.3. Total energy of electron in Bohr orbit :

Total energy of an electron is the sum of kinetic and potential energy.

i.e.  $T.E. = K.E. + P.E.$

(i) Potential energy :  $P.E. = -\frac{Kq_1q_2}{r} = -\frac{KZe^2}{r} = -\frac{KZe^2}{r}$

(ii) Kinetic energy :  $K.E. = \frac{1}{2}mv^2$

But  $\frac{KZe^2}{r} = mv^2$  (By eq. i)

$K.E. = \frac{KZe^2}{2r}$

(iii) Total energy :  $T.E. = K.E. + P.E.$

$T.E. = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$

Now putting the value of r from eq. (iii)

$T.E. = -\frac{KZe^2 \times 4\pi^2 m KZe^2}{2n^2 h^2} \Rightarrow -\frac{2\pi^2 m \times K^2 Z^2 e^4}{n^2 h^2}$

Now putting the value of  $\pi$ , K, e, m, h, we get :

$$\begin{aligned} T.E. &= -2.18 \times 10^{-18} \times \frac{Z^2}{n^2} \text{ J/atom} = -1312 \times \frac{Z^2}{n^2} \text{ kJ/mol} \\ &= -2.18 \times 10^{-11} \times \frac{Z^2}{n^2} \text{ erg/atom} = -313.6 \times \frac{Z^2}{n^2} \text{ Kcal/mol} \\ &= -13.6 \times \frac{Z^2}{n^2} \text{ eV/atom} \Rightarrow E_n = -\frac{13.6Z^2}{n^2} \text{ eV/atom} \end{aligned}$$

### 9.1.4 Some extra points :

- (i)  $K.E. = \frac{KZe^2}{2r}$  i.e.  $K.E. \propto \frac{1}{r}$  On increasing radius, K.E. decreases.
- (ii)  $P.E. = -\frac{KZe^2}{r}$  i.e.  $P.E. \propto -\frac{1}{r}$  On increasing radius, P.E. increases.
- (iii)  $T.E. = -\frac{KZe^2}{2r}$  i.e.  $E. \propto -\frac{1}{r}$  On increasing radius, total energy increases.
- (iv) Relation between T.E., P.E. and K.E.
- $P.E. = -2 KE$
- $KE = -T.E.$
- $P.E. = 2 T.E.$



### 9.1.5 Important Definitions :

(i) **Ionization energy :**

Minimum energy required to liberate an electron from the ground state of an isolated atom is called the ionization energy.

(ii) **Separation energy :**

Minimum energy required to remove an electron from its excited state is called as separation energy.

(iii) **Excitation energy :**

Amount of energy required to shift an electron from ground state to any excited state.

**Note :** All these kinds of energy are always positive.

**Ex.23. Calculate the radius of 1<sup>st</sup> 4 orbits of hydrogen atom**

**Sol:**  $r_1 = 0.529 \times \frac{1^2}{1} = 0.529 \text{ \AA}$

$$r_2 = 0.529 \times \frac{2^2}{1} = 2.116 \text{ \AA} = r_1 \times 2^2$$

$$r_3 = 0.529 \times \frac{3^2}{1} = 4.761 \text{ \AA} = r_1 \times 3^2$$

$$r_4 = 0.529 \times \frac{4^2}{1} = 8.464 \text{ \AA}$$

From this, for same  $Z$  :  $r_n = r_1 \times n^2$

**Ex.24 Calculate the ratio of radius of 2<sup>nd</sup> orbits of  $\text{Li}^{2+}$  atom & 3<sup>rd</sup> orbits  $\text{He}^+$  ion.**

**Sol:** 
$$\frac{r_{2, \text{Li}^{2+}}}{r_{3, \text{He}^+}} = \frac{0.529 \times \frac{4}{3}}{0.529 \times \frac{9}{2}} = \frac{8}{27}$$

**Ex.25 Calculate the radius ratio of 3<sup>rd</sup> & 5<sup>th</sup> orbit of  $\text{He}^+$ .**

**Sol.**  $r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$

At. Number of He = 2

$$\therefore r_3 = 0.529 \times \frac{(3)^2}{2} = 0.529 \times \frac{9}{2}$$

$$r_5 = 0.529 \times \frac{(5)^2}{2} = 0.529 \times \frac{25}{2}$$

Therefore 
$$\frac{r_3}{r_5} = \frac{0.529 \times \frac{(3)^2}{2}}{0.529 \times \frac{(5)^2}{2}}$$

$$\frac{r_3}{r_5} = \frac{9}{25}$$

**Ex.26** Calculate the energy of  $\text{Li}^{+2}$  atom for 2<sup>nd</sup> excited state.

**Sol.**  $E = -13.6 \times \frac{Z^2}{n^2}$

$\therefore Z = 3$  and  $e^-$  exist in 2<sup>nd</sup> excited state, means  $e^-$  present in 3<sup>rd</sup> shell i.e.  $n = 3$

$\therefore E = -13.6 \times \frac{(3)^2}{(3)^2} = -13.6 \text{ eV/atom}$

**Ex.27** If the P.E. of an electron is  $-6.8 \text{ eV}$  in hydrogen atom then find out K.E.,  $E$  of orbit where electron exist & radius of orbit.

**Sol.** (i) P.E. =  $-2\text{K.E.}$

$-6.8 = -2\text{K.E.}$

$\frac{6.8}{2} = \text{K.E.} \quad \text{K.E.} = 3.4 \text{ eV}$

(ii)  $E = -\text{K.E.}$

$= -3.4 \text{ eV}$

(iii) Orbit = 2<sup>nd</sup>

$\therefore E = -13.6 \times \frac{Z^2}{n^2}$

$\therefore 3.4 = -13.6 \times \frac{1^2}{n^2}$

$\Rightarrow n^2 = \frac{-13.6}{-3.4} = 4$

i.e.  $n = 2$

(iv)  $r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$

$r = 0.529 \times \frac{(2)^2}{1} \text{ \AA}$

$= 0.529 \times 4 \text{ \AA} = 2.16 \text{ \AA}$

**Ex.28** The ionization energy for the hydrogen atom is  $13.6 \text{ eV}$  then calculate the required energy in  $\text{eV}$  to excite it from the ground state to 1<sup>st</sup> excited state.

**Sol.** Ionization energy =  $13.6 \text{ eV}$

i.e. 1<sup>st</sup> energy state =  $-13.6 \text{ eV}$

Energy of 1<sup>st</sup> excited state

i.e. 2<sup>nd</sup> orbit =  $-3.4 \text{ eV}$

so,  $E_2 - E_1 = -3.4 + 13.6 = 10.2 \text{ eV}$

**Ex.29** Calculate the amount of energy absorbed in the transition  $n = 1$  to  $n = 3$  in  $\text{Li}^{2+}$  ion.

**Sol.**  $n_1$  orbit  $\longleftrightarrow$   $n_2$  orbit

$$\Delta E = E_{n_2} - E_{n_1} = \left(-13.6 \frac{Z_1^2}{n_2^2}\right) - \left(-13.6 \frac{Z_2^2}{n_1^2}\right)$$

$$\Delta E = 13.6 Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{eV}$$

$$\Delta E = 13.6 \times 3^2 \left(\frac{1}{1^2} - \frac{1}{3^2}\right) = 108.8 \text{eV}$$

**Ex.30** Calculate the excitation energy of  $\text{Be}^{3+}$  ion in ground state.

**Sol.**  $\Delta E = 13.6 \times 16 \left(\frac{1}{1} - \frac{1}{4}\right) = 163.2 \text{eV}$

**Ex.31** The ionisation energy of  $\text{He}^+$  ion is  $x$  kJ/mole. Calculate ionisation energy of  $\text{Li}^{2+}$  ion.

**Sol.** For I.E.  $\Rightarrow n = 1 \longrightarrow n = \infty$

$$IE = 13.6 Z^2 \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = 13.6 Z^2 \text{eV}$$

$$\frac{(\text{I.E.})_{\text{Li}^{2+}}}{(\text{I.E.})_{\text{He}^+}} = \frac{3^2}{2^2} \Rightarrow (\text{I.E.})_{\text{Li}^{2+}} = \frac{9}{4} x \text{ kJ/mol}$$

**Ex.32** The ionisation energy for a single electron system is 14.4 eV. Calculate the amount of energy released when electron jumps from 3<sup>rd</sup> orbits to 2<sup>nd</sup> orbit.

**Sol.**  $\Delta E = (\text{IE}) \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 14.4 \times \left(\frac{1}{4} - \frac{1}{9}\right) = 2 \text{eV}$

**Ex.33** Calculate the speed of an electron in the 3<sup>rd</sup> orbit of the  $\text{Li}^{2+}$  ion. Also calculate the number of revolutions per second that it makes around the nucleus.

**Sol.** Radius of 2<sup>nd</sup> orbit =  $r_1 \times \frac{(n)^2}{Z} = 0.529 \times \frac{(3)^2}{3} = 1.587 \text{\AA}$

Velocity of electron in 2<sup>nd</sup> orbit,  $v = 2.18 \times 10^6 \frac{Z}{n} \text{ m/sec} = 2.18 \times 10^6 \text{ m/sec}$

$$\begin{aligned} \text{No. of revolutions/sec} &= \frac{1}{2\pi r/v} = \frac{v}{2\pi r} = \frac{2.18 \times 10^6 \text{ m/sec}}{2 \times 3.14 \times 1.587 \times 10^{-10} \text{ m}} \\ &= 2.187 \times 10^{15} \text{ rev/sec} \end{aligned}$$

## 9.2 RYDBERG FORMULA

If an electron shows transition from  $n_2$  to  $n_1$  energy level then energy change  $\Delta E$  will be.

$$\Delta E = E_{n_2} - E_{n_1}$$

$$\Delta E = \frac{-2\pi^2 m K^2 Z^2 e^4}{n_2^2 h^2} - \left[ \frac{-2\pi^2 m K^2 Z^2 e^4}{n_1^2 h^2} \right] = \frac{2\pi^2 m K^2 Z^2 e^4}{n_1^2 h^2} - \frac{2\pi^2 m K^2 Z^2 e^4}{n_2^2 h^2}$$

But  $\Delta E = h\nu = \frac{hc}{\lambda}$

$$\therefore \frac{hc}{\lambda} = \frac{2\pi^2 m K^2 Z^2 e^4}{h^2} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\frac{1}{\lambda} = \frac{2\pi^2 m K^2 e^4 Z^2}{ch^3} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where  $\frac{2\pi^2 m K^2 e^4}{ch^3}$  is a constant called Rydberg constant (R) (Assume nucleus is stationary)

$$\text{So, } \bar{\nu} = \frac{1}{\lambda} = RZ^2 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\text{value of } R = 109677 \text{ cm}^{-1} = 10967700 \text{ m}^{-1}$$

$$\approx 109700 \text{ cm}^{-1} \approx 10970000 \text{ m}^{-1}$$

$$\frac{1}{R} = 912 \text{ \AA}$$

**Ex.34** What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from the energy level with  $n = 4$  to the energy level with  $n = 1$  ?

**Sol.** According to Rydberg's formula,  $\bar{\nu}(\text{cm}^{-1}) = 109,677 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

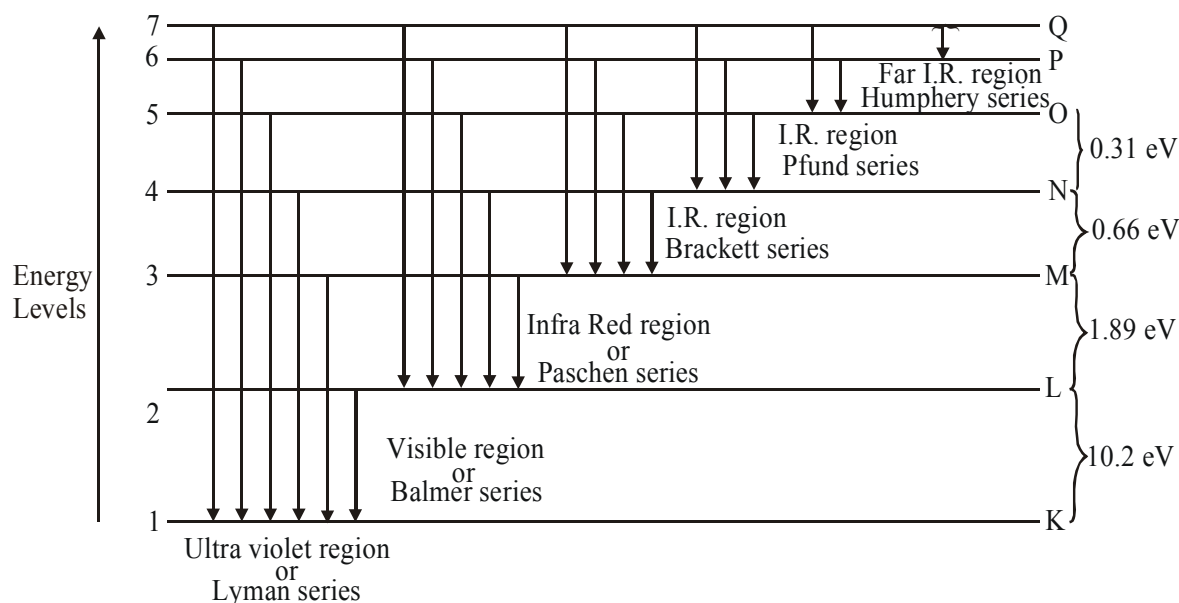
In the present case  $n_2 = 4$  and  $n_1 = 1$

$$\bar{\nu} = 109,677 \left( \frac{1}{(1)^2} - \frac{1}{(4)^2} \right) = 109,677 \times \frac{15}{16} = 102822 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{102822} \text{ cm} = 9.7 \times 10^{-6} \text{ cm} = 9.7 \times 10^{-6} \times 10^7 \text{ nm} = \mathbf{97 \text{ nm.}}$$

9.3 HYDROGEN LINE SPECTRUM :

When an electric excitation is applied on atomic hydrogen gas at low pressure, a bluish light is emitted. When a ray of this light is passed through a prism, a spectrum of several isolated sharp lines is obtained. The wavelength of various lines show that spectrum lines lie in visible, Ultraviolet and Infra red region. These lines are grouped into different series.



Series	Discovered by	Regions	n <sub>2</sub>	n <sub>1</sub>
Lyman	Lyman	U.V. region	n <sub>2</sub> = 2, 3, 4 ...	n <sub>1</sub> = 1
Balmer	Balmer	Visible region	n <sub>2</sub> = 3, 4, 5 ...	n <sub>1</sub> = 2
Paschen	Paschen	Infra red (I.R.)	n <sub>2</sub> = 4, 5, 6 ...	n <sub>1</sub> = 3
Brackett	Brackett	I.R. region	n <sub>2</sub> = 5, 6, 7 ...	n <sub>1</sub> = 4
Pfund	Pfund	I.R. region	n <sub>2</sub> = 6, 7, 8 ...	n <sub>1</sub> = 5
Humphery	Humphery	Far I.R. region	n <sub>2</sub> = 7, 8, 9 ...	n <sub>1</sub> = 6

KEY POINTS :

- First line / Starting line / Initial line (λ<sub>max</sub> and ν<sub>min</sub>)
- Last line / limiting line / Series limit (λ<sub>min</sub> and ν<sub>max</sub>.)
- First line of any series = α line  
Second line of any series = β line  
Third line of any series = γ line
- Total no. of emission lines between n<sub>2</sub> & n<sub>1</sub> =  $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$ , (n<sub>2</sub> > n<sub>1</sub>)
- For transition from any orbit 'n' to n = 1, total no. of emission lines =  $\frac{n(n-1)}{2}$

**Ex.35** In a hydrogen spectrum if electron moves from 6<sup>th</sup> to 2<sup>nd</sup> by transition in multi steps then find out the number of lines in spectrum

**Sol.** Total number of line = 4 + 3 + 2 + 1 + 0 = 10

$$\text{Total number of lines} = \frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(6 - 2)(4 + 1)}{2} = 10$$

**Ex.36** In the spectrum of He<sup>+</sup> ion the wavelength of  $\alpha$  line of Balmer series is  $x \text{ \AA}$ . What is the wavelength of  $\alpha$  line of Paschen series.

**Sol.**  $\frac{1}{\lambda_1} = RZ^2 \left( \frac{1}{2^2} - \frac{1}{3^2} \right)$

$$\frac{1}{\lambda_2} = RZ^2 \left( \frac{1}{3^2} - \frac{1}{5^2} \right)$$

$$\frac{\lambda_2}{\lambda_1} = \frac{\frac{1}{2^2} - \frac{1}{3^2}}{\frac{1}{3^2} - \frac{1}{5^2}} \Rightarrow \frac{\lambda_2}{x \text{ \AA}} = \frac{5}{16} \times \frac{25}{4}$$

**Ex.37** A sample of He<sup>+</sup> ions in ground state absorbs the radiation of  $x \text{ \AA}$ . subsequently, the sample emit radiation of 6 different wavelength. Calculate the value of  $x$ .

**Sol.**  $\frac{1}{x} = R \left( \frac{1}{1^2} - \frac{1}{4^2} \right) \times 2^2$

$$x = \frac{16}{15} \times \frac{912}{4} \text{ \AA}$$

**Ex.38** In a hydrogen spectrum if electron moves from 6<sup>th</sup> to 2<sup>nd</sup> by transition in multi steps then find out the number of lines in spectrum

**Sol.** Total number of line = 4 + 3 + 2 + 1 + 0  
= 10

$$\text{Total number of lines} = \frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(6 - 2)(4 + 1)}{2} \Rightarrow \frac{4 \times 5}{2} = 10$$

#### 9.4 Limitation of the Bohr's model

- Bohr's theory does not explain the spectrum of multi electron atom.
- Why the Angular momentum of the revolving electron is equal to  $\frac{nh}{2\pi}$ , has not been explained by Bohr's theory.
- Bohr inter-related quantum theory of radiation and classical law of physics without any theoretical explanation. This was the biggest drawback of this model.
- Bohr's theory does not explain the fine structure of spectral lines. Fine structure of the spectral line is obtained when spectrum is viewed by a spectroscopy of high resolving power.
- Bohr's theory does not explain the splitting of spectral lines in the presence of magnetic field (**Zeeman effect**) or electric field (**Stark effect**)

10. DUAL BEHAVIOUR OF MATTER & DE BROGLIE WAVELENGTH :

In 1923, a French physicist, *Louis de Broglie* suggested that, like light, matter also has dual character. It exhibits wave as well as particle nature. According to de Broglie, the wavelength  $\lambda$  of an electron is inversely proportional to its momentum  $p$ .



de Broglie'  
(1892-1987)

A French physicist, studied history as an undergraduate in the early 1910,s. His interest turned to science as a result of his assignment to radio communications in world war 1. He was awarded the Nobel Prize in physics in 1929.

$$\lambda \propto \frac{1}{p} \quad \text{or} \quad \lambda \propto \frac{1}{mv}$$

$$\lambda = \frac{h}{p} \quad \text{Here } h = \text{Planck's constant}$$

$p = \text{momentum of electron}$

$$\therefore \text{Momentum } (p) = \text{Mass } (m) \times \text{Velocity } (v)$$

The above relation can be derived for a photon as follows by using Einstein's equation, Planck's quantum theory and wave theory of light.

$$E = mc^2 \text{ (Einstein's equation)} \quad \dots\dots(i)$$

Where  $E$  is energy,  $m$  is mass of a body and  $c$  is its velocity.

$$E = hv = h \times \frac{c}{\lambda} \text{ (Planck's equation)} \quad \left( v = \frac{c}{\lambda} \right) \quad \dots\dots(ii)$$

Combining (i) and (ii)

$$E = mc^2 = h \times \frac{c}{\lambda} \quad \text{or} \quad mc = \frac{h}{\lambda} \quad \text{or} \quad \lambda = \frac{h}{mc}$$

$$\boxed{\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda = \frac{h}{p}}$$

It is clear from the above equation that the value of  $\lambda$  decreases on increasing either  $m$  or  $v$  or both. The wavelength of many fast-moving objects like an aeroplane or a cricket ball, is very low because of their high mass. Thus wave nature of macroscopic objects can be neglected but for microscopic particles like electrons, protons, atoms etc. wave nature is significant & cannot be neglected.

10.1 DERIVATION OF BOHR'S ANGULAR MOMENTUM QUANTIZATION RULE :

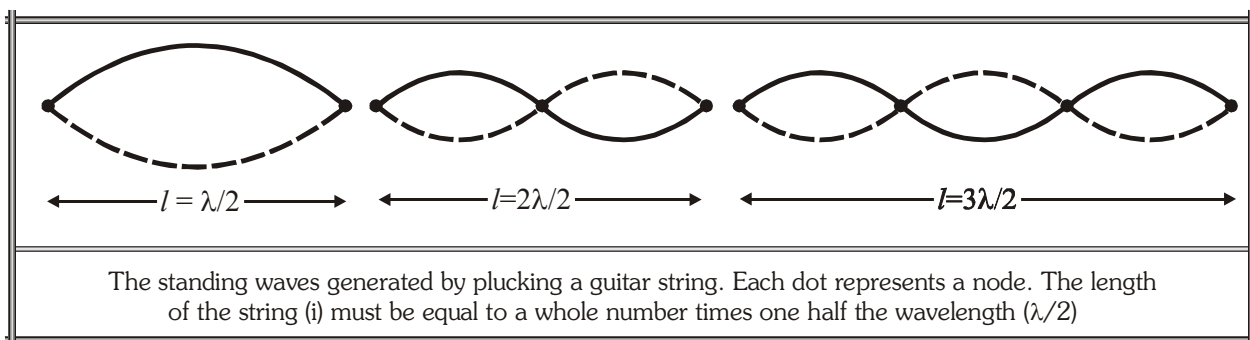
We know that according to Bohr theory,  $mvr = \frac{nh}{2\pi}$

$$\text{or} \quad 2\pi r = \frac{nh}{mv} \quad (\because mv = p \text{ momentum})$$

$$\text{or} \quad 2\pi r = \frac{nh}{p} \quad \left( \because \frac{h}{p} = \lambda \text{ de-Broglie equation} \right)$$

According to de Broglie, an electron bound to the nucleus behaves like a standing wave.

A standing wave – also known as a stationary wave – is a wave that remains in a constant position. Two opposing waves combine to form a standing wave. This phenomenon can occur because the medium is moving in the opposite direction to the wave, or it can arise in a stationary medium as a result of interference between two waves travelling in opposite directions.



For a circular standing wave to persist, a whole number of wavelength must fit into the circumference of the circle ( $2\pi$ ).

And if  $n$  number of waves of  $\lambda$  wavelength are present in this circle total circumference will be  $n\lambda$ .

$$2\pi r = n\lambda$$

$n$  = Number of wave made by electron in one complete revolution.

According to de Broglie

$$\lambda = \frac{h}{mv}$$

$$2\pi r = n \frac{h}{mv}$$

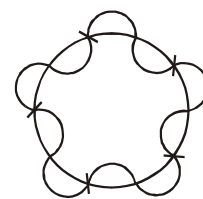
$$mvr = \frac{nh}{2\pi}$$

Therefore in  $2\pi r = n\lambda$   $n$  = Number of shell

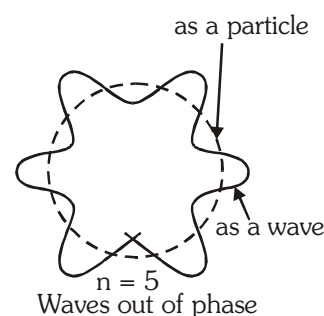
i.e., 2<sup>nd</sup> shell  $2\pi r = 2\lambda$

3<sup>rd</sup> shell  $2\pi r = 3\lambda$

Electron in  $n^{\text{th}}$  orbit of any unielectron system can create 'n' waves in one complete revolution.



$\therefore$  Waves made = 5



**Ex.39 Calculate the de Broglie wavelength of a ball of mass 0.1 kg moving with a speed of  $30 \text{ ms}^{-1}$ .**

**Sol.**  $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{0.1 \times 30} = 2.2 \times 10^{-34} \text{ m}$

This is apparent that this wavelength is too small for ordinary observation.

Although the de Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles.



**Ex.40** What should be the mass of the sodium photon if its wavelength is  $5894 \text{ \AA}$ , the velocity of light is  $3 \times 10^8 \text{ metre/second}$  and the value of  $h$  is  $6.652 \times 10^{-34} \text{ kg m}^2/\text{sec}.$

- (A)  $3.746 \times 10^{-26}$  (B)  $3.746 \times 10^{-30}$   
 (C)  $3.746 \times 10^{-34}$  (D)  $3.746 \times 10^{-36}$

**Sol.**  $\lambda = \frac{h}{m \times c} \Rightarrow m = \frac{h}{c\lambda}$   
 $(\because \lambda = 5894 \text{ \AA} = 5894 \times 10^{-10} \text{ m})$   
 $m = \frac{6.652 \times 10^{-34}}{3 \times 10^8 \times 5894 \times 10^{-10}} \quad \text{or} \quad \frac{6.652}{17682} \times 10^{-32}$   
 $= 0.0003746 \times 10^{-32} = 3.746 \times 10^{-36} \text{ kg}$

**Ex.41** Calculate the de-Broglie wavelength when  $e^-$  is accelerated by the following voltage.

- (i) 750 V (ii) 300 volt

**Sol.** (i)  $\lambda = \sqrt{\frac{150}{V}} \text{ \AA} = \sqrt{\frac{150}{750}} \text{ \AA} = \frac{1}{\sqrt{5}} \text{ \AA}$  (ii)  $\lambda = \sqrt{\frac{150}{300}} \text{ \AA} = \frac{1}{\sqrt{2}} \text{ \AA}$

**Ex.42** Find de-Broglie wavelength of electron with  $KE = 9.6 \times 10^{-19} \text{ J}$ .

**Sol.**  $KE = \frac{9.6 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} = 6 \text{ eV}$

$\lambda = \sqrt{\frac{150}{6}} \text{ \AA} = 5 \text{ \AA}$

KE of 6 eV means  $e^-$  is accelerated by 6 volt.

**Ex.43** Calculate the ratio of de-Broglie wavelength of electron and  $\alpha$ -particle.

- (i) Moving at same speed  
 (ii) Moving at same momentum  
 (iii) Having same K.E.  
 (iv) Accelerated from rest through the same P.D.

**Sol.** (i)  $\lambda = \frac{h}{mv}$   
 $\lambda \propto \frac{1}{m}$   
 $\frac{\lambda_{\text{electron}}}{\lambda_{\alpha}} = \frac{m_{\alpha}}{m_e} = \frac{4 \times 1836}{1}$   
 (ii)  $\frac{\lambda_{\text{electron}}}{\lambda_{\alpha}} = \frac{1}{1}$   
 (iii)  $\frac{h}{\sqrt{2mE}}$   
 $\lambda = \frac{h}{\sqrt{2mE}} = \frac{\lambda_e}{\lambda_{\alpha}} = \sqrt{\frac{m_{\alpha}}{m_e}} = \sqrt{\frac{1836 \times 4}{1}}$   
 (iv)  $\lambda = \frac{h}{\sqrt{2mqV}} = \frac{\lambda_e}{\lambda_{\alpha}} = \sqrt{\frac{(mq)_{\alpha}}{(mq)_e}} = \sqrt{\frac{4 \times 2}{1/1836 \times 1}}$

**Ex.44** In  $\text{Li}^{2+}$  ion electron jumps from  $2^{\text{nd}}$  to  $1^{\text{st}}$  orbit. If the emitted radiation is absorbed by H atom. Calculate the de-Broglie wavelength of the ejected electron.

**Sol.**  $\Delta E = 13.6 \times 9 \left(1 - \frac{1}{4}\right) = 91.8 \text{ eV}$

Excess energy =  $91.8 - 13.6 = 78.2 \text{ eV}$

$$\lambda = \sqrt{\frac{150}{78.2}} \text{ \AA} = 1.38 \text{ \AA}$$

**Ex.45** Photoelectrons are liberated by ultra violet light of wavelength  $2000 \text{ \AA}$  from a metallic surface for which the photoelectric threshold is  $4000 \text{ \AA}$ . Calculate the de-Broglie wavelength of electrons emitted with maximum kinetic energy.

**Solution :**  $K.E. = \text{Quantum Energy} - \text{Threshold energy}$

$$\begin{aligned} &= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{2000 \times 10^{-10}} - \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}} \\ &= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{10^{-10}} \left( \frac{1}{2000} - \frac{1}{4000} \right) = 4.969 \times 10^{-19} \text{ Joule.} \end{aligned}$$

$$\frac{1}{2}mv^2 = 4.969 \times 10^{-19} \Rightarrow m^2v^2 = 2 \times 4.969 \times 10^{-19} \times 9.1 \times 10^{-31}$$

$$mv = 9.51 \times 10^{-25} \Rightarrow \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.51 \times 10^{-25}} = 0.696 \times 10^{-9} \text{ m}$$

**Ex.46** Calculate the de-Broglie wavelength when proton is accelerated by the 750 V.

**Sol.** (i)  $\lambda = \sqrt{\frac{150}{V \times 1836}} \text{ \AA} = \sqrt{\frac{150}{750 \times 1836}} \text{ \AA}$

## 10.2 Justification of dual nature of electrons :

### I. Particle character :

- (a) If an  $e^-$  strikes a screen coated with ZnS, it produces a spot of light called scintillation. On  $e^-$  produces only one scintillation point which means  $e^-$  are localised not spread out like wave : Photoelectric effect also proves its particle nature.
- (b) Electron possess definite mass, momentum & KE proving their particle nature.

### II. Wave character :

- It was confirmed by phenomenon of diffraction, interference, reflection.
- Davisson and Germer showed that when high speed  $e^-$  strike Ni crystal a diffraction pattern (having number of rings) is obtained like X-rays of electromagnetic spectrum.

## 11 HEISENBERG UNCERTAINTY PRINCIPLE :

Bohr's theory considers an electron as a material particle. Its position and momentum can be determined with accuracy. But, when an electron is considered in the form of wave as suggested by de-Broglie, it is not possible to ascertain simultaneously the exact position and velocity of the electron more precisely at a given instant since the wave is extending throughout a region of space.

In 1927, **Werner Heisenberg** presented a principle known as Heisenberg uncertainty principle which states as : "*It is impossible to measure simultaneously the exact position and exact momentum of a body as small as an electron*".

The uncertainty of measurement of position,  $\Delta x$ , and the uncertainty of momentum  $\Delta p$  or  $m\Delta v$ , are related by Heisenberg's relationship as : ( $p = mv$ ,  $\Delta p = m\Delta v$ )

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \cdot m\Delta v \geq \frac{h}{4\pi}$$

$$\text{or} \quad \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

where  $h$  is Planck's constant.

$\Delta x \Delta v =$  uncertainty product

For an electron of mass  $m$  ( $9.10 \times 10^{-28}$  g), the product of uncertainty is quite large.

$$\begin{aligned} \Delta x \cdot \Delta v &\geq \frac{6.624 \times 10^{-27}}{4\pi m} \geq \frac{6.624 \times 10^{-27}}{4 \times 3.14 \times 9.10 \times 10^{-28}} \\ &= 0.57 \text{ erg sec per gram approximately} \end{aligned}$$

When,  $\Delta x = 0$ ,  $\Delta v = \infty$  and vice-versa.

In the case of bigger particles (having considerable mass), the value of uncertainty product is negligible. If the position is known quite accurately, i.e.,  $\Delta x$  is very small,  $\Delta v$  becomes large and vice-versa.

**Ex.47** A golf ball has a mass of 40 g and a speed of 45 m/s. If the speed can be measured within accuracy of 2 %, calculate the uncertainty in the position.

**Sol.** Mass of the ball = 40 g =  $40 \times 10^{-3}$  kg

The uncertainty in the speed,

$$\Delta v = 45 \times \frac{2}{100} = 0.9 \text{ ms}^{-1}$$

$$\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times (40 \times 10^{-3} \text{ kg})(0.9 \text{ ms}^{-1})} = 1.46 \times 10^{-33} \text{ m.}$$

**Ex.48** Calculate the uncertainty in the velocity of a cricket ball of mass 150 g, if the uncertainty in its position is of the order of 1 Å.

( $h = 6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$ )

**Sol.** Mass of ball ,

$$m = 150 \text{ g} = 150 \times 10^{-3} \text{ kg} = 0.150 \text{ kg}$$

Uncertainty in position,  $\Delta x = 1 \text{ Å} = 10^{-10} \text{ m}$

$$\Delta x \times m \Delta v = \frac{h}{4\pi}$$

$$\Delta v = \frac{h}{4\pi \times \Delta x \times m}$$

$$= \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 10^{-10} \text{ m} \times 0.150 \text{ kg}}$$

$$= 3.52 \times 10^{-24} \text{ m s}^{-1}.$$

## 12 QUANTUM MECHANICAL MODEL OF ATOM

Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone, orbiting planets etc., which have essentially a particle-like behaviour as shown in the previous section. However it fails when applied to microscopic objects like electrons, atoms, molecules etc. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the uncertainty principle. The branch of science that takes into account this dual behaviour of matter is called **quantum mechanics**.

Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties. It specifies the laws of motion that these objects obey. When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrodinger. Here, however, we shall be discussing the quantum mechanics which is based on the ideas of wave motion. The fundamental equation of quantum mechanics was developed by Schrodinger and it won him the Nobel Prize in Physics in 1933. This equation which incorporates wave-particle duality of matter as proposed by de Broglie is quite complex and knowledge of higher mathematics is needed to solve it. You will learn its solutions for different systems in higher classes.

For a system (such as an atom or a molecule whose energy does not change with time) the Schrodinger equation is written as

$$\hat{H}\psi = E\psi$$

$\hat{H}$  is a mathematical operator called Hamiltonian. Schrodinger gave a recipe of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives  $E$  and  $\psi$ .

### 12.1 Hydrogen Atom and the Schrodinger Equation

When Schrodinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) ( $\psi$ ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (**principal quantum number  $n$ , azimuthal quantum number  $l$  and magnetic quantum number  $m_l$** ) arise as a natural consequence in the solution of the Schrodinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron.

*Erwin Schrodinger, an Austrian physicist received his Ph.D. in theoretical physics from the University of Vienna in 1910. In 1927 Schrodinger succeeded Max Planck at the University of Berlin at Planck's request. In 1933, Schrodinger left Berlin because of his opposition to Hitler and Nazi policies and returned to Austria in 1936. After the invasion of Austria by Germany, Schrodinger was forcibly removed from his professorship. He then moved to Dublin, Ireland where he remained for seventeen years. Schrodinger shared the Nobel Prize for Physics with P.A.M. Dirac in 1933.*



**Erwin Schrodinger (1887-1961)**

The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called **atomic orbitals**.

Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the  $|\psi|^2$  at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

Application of Schrodinger equation to multi-electron atoms presents a difficulty: the Schrodinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above.

The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later, unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number  $n$ , the energies of the orbitals in multi-electron atoms depend on quantum numbers  $n$  and  $l$ .

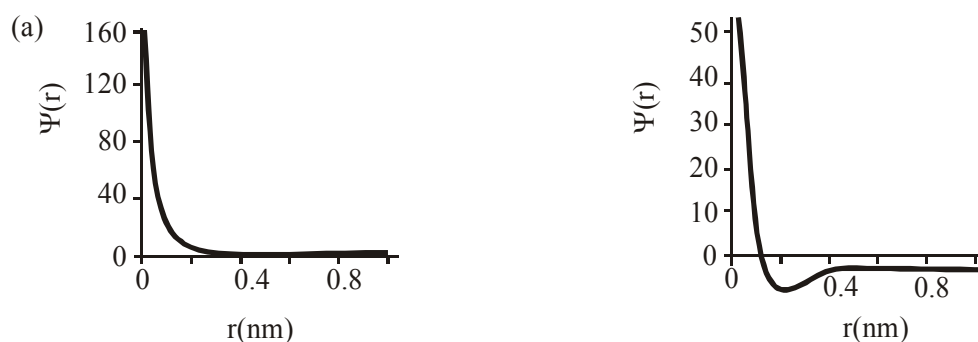
### 12.2 Important Features of the Quantum Mechanical Model of Atom–

Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrodinger equation to atoms. The following are the important features of the quantummechanical model of atom:

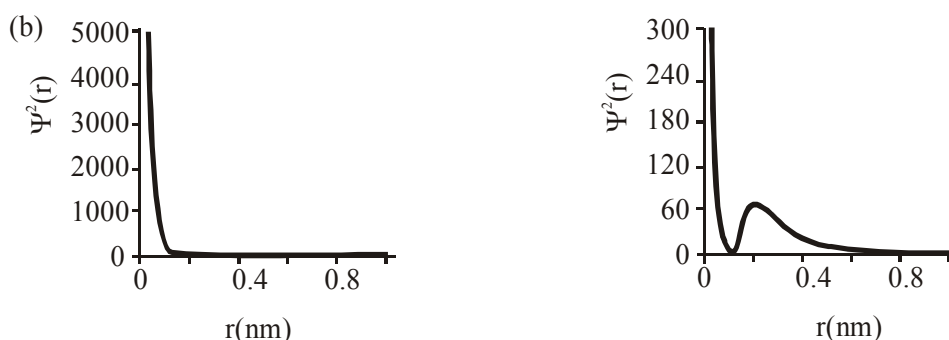
1. The energy of electrons in atoms is quantized (i.e., can only have certain specific values), for example when electrons are bound to the nucleus in atoms.
2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons and are allowed solutions of Schrodinger wave equation.
3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom therefore, can never be determined or known accurately. That is why, as you shall see later on, one talks of only probability of finding the electron at different points in an atom.
4. **An atomic orbital is the wave function  $\psi$  for an electron in an atom.** Whenever an electron is described by a wave function, we say that the electron occupies that orbital. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. These “one electron orbital wave functions” or orbitals form the basis of the electronic structure of atoms. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For each electron of a multi-electron atom, there shall, therefore, be an orbital wave function characteristic of the orbital it occupies. All the information about the electron in an atom is stored in its orbital wave function  $\psi$  and quantum mechanics makes it possible to extract this information out of  $\psi$ .
5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e.,  $|\psi|^2$  at that point.  $|\psi|^2$  is known as **probability density** and is always positive. **From the value of  $|\psi|^2$  at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.**

### 12.3 Shapes of Atomic Orbitals

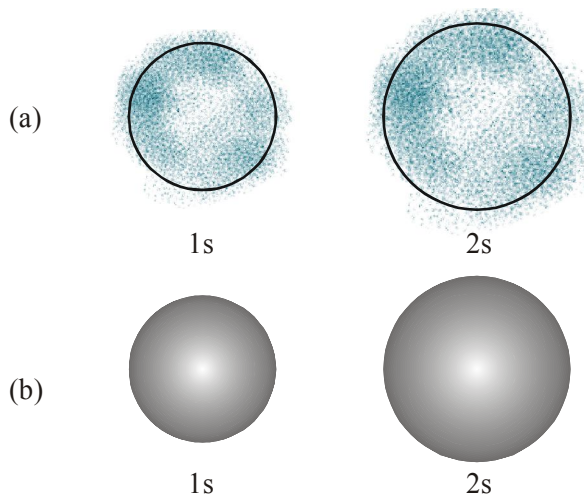
The orbital wave function or  $\psi$  for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of corresponding wave functions as a function of  $r$  (the distance from the nucleus) are different. Such plots for  $1s$  ( $n = 1, l = 0$ ) and  $2s$  ( $n = 2, l = 0$ ) orbitals are



According to the German physicist, Max Born, the square of the wave function (i.e.,  $\psi^2$ ) at a point gives the probability density of the electron at that point. The variation of  $\psi^2$  as a function of  $r$  for 1s and 2s orbitals is given in fig. Here again, you may note that the curves for 1s and 2s orbitals are different.



It may be noted that for 1s orbital the probability density is maximum at the nucleus and it decreases sharply as we move away from it. On the other hand, for 2s orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maxima it decreases again and approaches zero as the value of  $r$  increases further. The region where this probability density function reduces to zero is called **nodal surfaces** or simply **nodes**. In general, it has been found that ns-orbital has  $(n - 1)$  nodes, that is, number of nodes increases with increase of principal quantum number  $n$ . In other words, number of nodes for 2s orbital is one, two for 3s and so on. These probability density variation can be visualised in terms of charge cloud diagrams. In these diagrams, the density of the dots in a region represents electron probability density in that region.

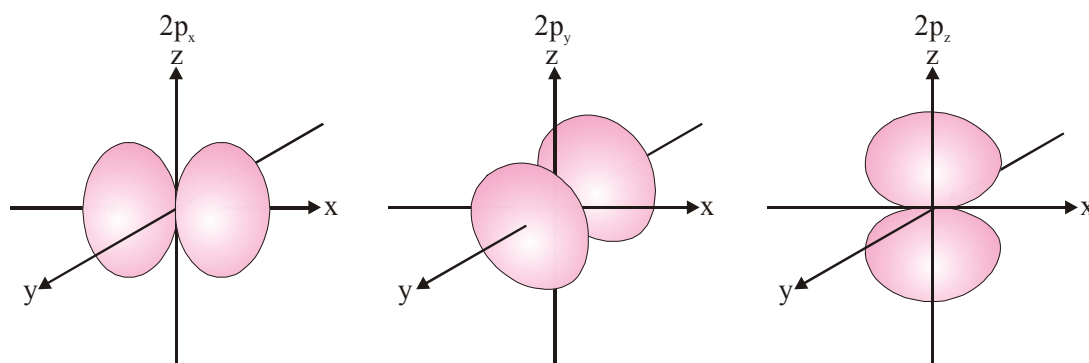


**(a) Probability density plots of 1s and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region. (b) Boundary surface diagram for 1s and 2s orbitals.**

**Boundary surface diagrams** of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of probability density  $|\psi|^2$  is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%.

The boundary surface diagram for 1s and 2s orbitals are given in fig. One may ask a question : Why do we not draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is, 100 %? The answer to this question is that the probability density  $|\psi|^2$  has always some value, however small it may be, at any finite distance from the nucleus. It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for a s orbital is actually a sphere centred on the nucleus. In two dimensions, this sphere looks like a circle. It encloses a region in which probability of finding the electron is about 90%.

Thus we see that 1s and 2s orbitals are spherical in shape. In reality all the s-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in n, that is,  $4s > 3s > 2s > 1s$  and the electron is located further away from the nucleus as the principal quantum number increases. Boundary surface diagrams for three 2p orbitals ( $l = 1$ ) are

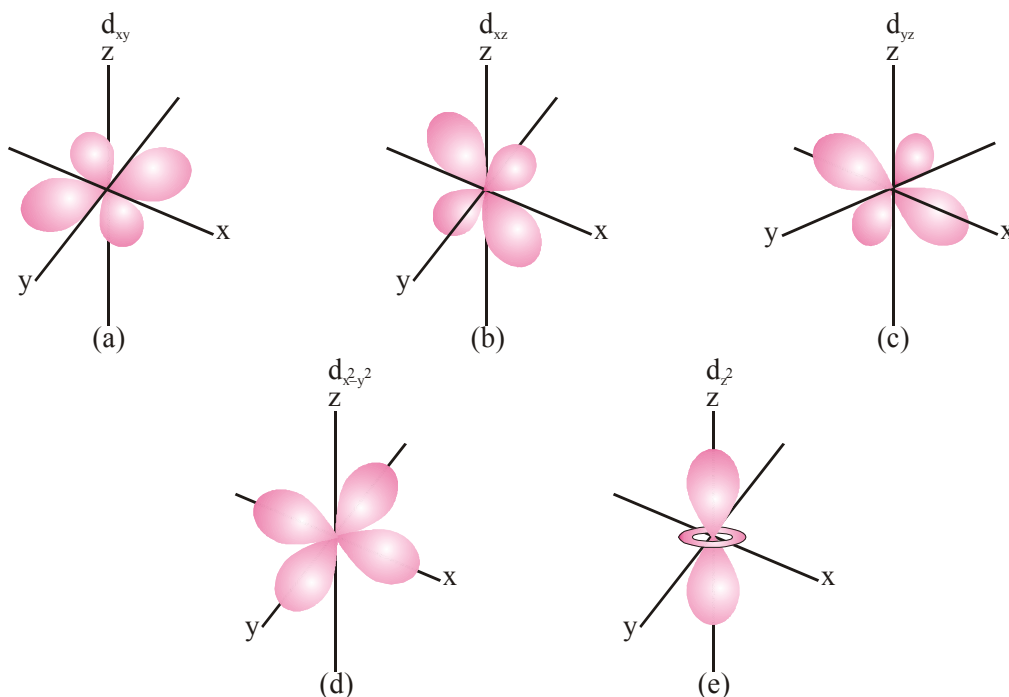


*Boundary surface diagrams of the three 2p orbitals.*

In these diagrams, the nucleus is at the origin. Here, unlike s-orbitals, the boundary surface diagrams are not spherical. Instead each p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density function is zero on the plane where the two lobes touch each other. The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations  $2p_x$ ,  $2p_y$ , and  $2p_z$ . It should be understood, however, that there is no simple relation between the values of  $m_l$  ( $-1, 0$  and  $+1$ ) and the x, y and z directions. For our purpose, it is sufficient to remember that, because there are three possible values of  $m_l$ , there are, therefore, three p orbitals whose axes are mutually perpendicular. Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is  $4p > 3p > 2p$ . Further, like s orbitals, the probability density functions for p-orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases. The number of nodes are given by the  $n - 2$ , that is number of radial node is 1 for 3p orbital, two for 4p orbital and so on.

For  $l = 2$ , the orbital is known as d-orbital and the minimum value of principal quantum number (n) has to be 3, as the value of  $l$  cannot be greater than  $n - 1$ . There are five  $m_l$  values  $-2, -1, 0, +1$  and  $+2$ ) for  $l = 2$  and thus there are five d orbitals. The boundary surface diagram of d orbitals are





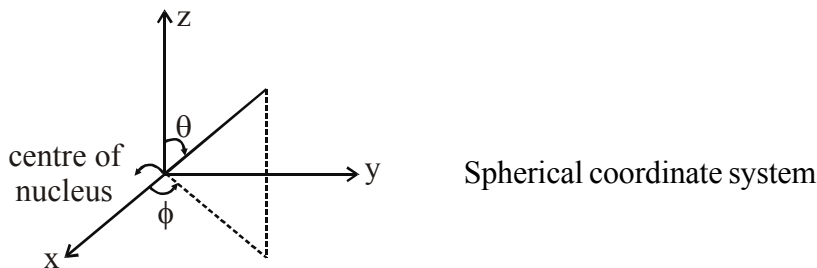
Boundary surface diagrams of the five 3d orbitals.

The five d-orbitals are designated as  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ . The shapes of the first four d-orbitals are similar to each other, whereas that of the fifth one,  $d_{z^2}$ , is different from others, but all five 3d orbitals are equivalent in energy. The d orbitals for which  $n$  is greater than 3 (4d, 5d...) also have shapes similar to 3d orbital, but differ in energy and size.

Besides the radial nodes (i.e., probability density function is zero), the probability density functions for the  $np$  and  $nd$  orbitals are zero at the plane(s), passing through the nucleus (origin). For example, in case of  $p_z$  orbital,  $xy$ -plane is a nodal plane, in case of  $d_{xy}$  orbital, there are two nodal planes passing through the origin and bisecting the  $xy$  plane containing  $z$ -axis. These are called **angular nodes** and number of angular nodes are given by ' $l$ ', i.e., one angular node for  $p$  orbitals, two angular nodes for 'd' orbitals and so on.

**The total number of nodes are given by  $(n-1)$ , i.e., sum of  $l$  angular nodes and  $(n - l - 1)$  radial nodes.**

**12.4 SOLUTION OF SCHRODINGER EQUATION :**



The solution in spherical coordinates may be represented as :

$$\psi = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$$

$R(r)$  : Radial function depends on  $n$  and  $l$

$\Theta(\theta) \cdot \Phi(\phi)$  : Angular function depends on  $l$  and  $m$ .

## 12.4.1 Radical part of solution :

$$1s \quad (n = 1, \ell = 0) : \quad R_{1s}(r) = 2 \cdot \left( \frac{Z}{a_0} \right)^{3/2} \cdot e^{-\sigma/2}$$

$$\text{where } \sigma = \frac{2Zr}{na_0} \quad a_0 = \text{1st Bohr's radius} = 0.529 \text{ \AA}$$

$$2s \quad (n = 2, \ell = 0) : \quad R_{2s}(r) = \frac{1}{2\sqrt{2}} \cdot \left( \frac{Z}{a_0} \right)^{3/2} \cdot (2 - \sigma) e^{-\sigma/2}$$

$$2p \quad (n = 2, \ell = 1) : \quad R_{2p}(r) = \frac{1}{2\sqrt{6}} \cdot \left( \frac{Z}{a_0} \right)^{3/2} \cdot \sigma \cdot e^{-\sigma/2}$$

$$3s \quad (n = 3, \ell = 0) : \quad R_{3s}(r) = \frac{1}{9\sqrt{3}} \cdot \left( \frac{Z}{a_0} \right)^{3/2} \cdot (6 - 6\sigma + \sigma^2) e^{-\sigma/2}$$

$$3p \quad (n = 3, \ell = 1) : \quad R_{3p}(r) = \frac{1}{9\sqrt{6}} \cdot \left( \frac{Z}{a_0} \right)^{3/2} \cdot \sigma(4 - \sigma) e^{-\sigma/2}$$

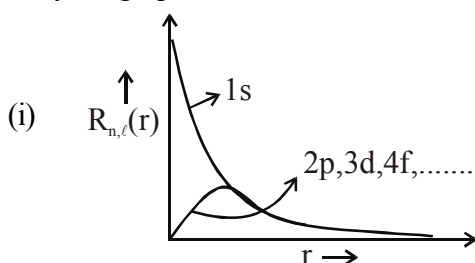
$$3d \quad (n = 3, \ell = 2) : \quad R_{3d}(r) = \frac{1}{9\sqrt{30}} \cdot \left( \frac{Z}{a_0} \right)^{3/2} \cdot \sigma^2 \cdot e^{-\sigma/2}$$

## General form :

$$R_{n\ell}(r) = K \cdot e^{-\sigma/2} \cdot \sigma^\ell \quad (\text{Polynomial of order } n - \ell - 1)$$

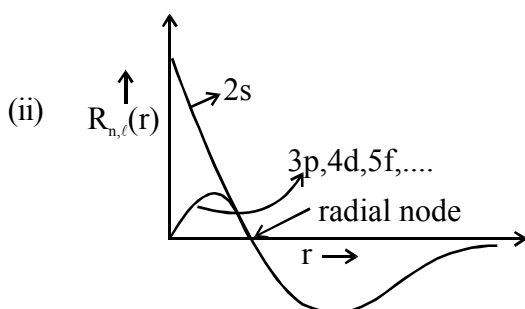
12.4.2 Graph of radial function [R(r) or  $\Psi(r)$ ]:

Only the graph of s-orbital does not start from origin.



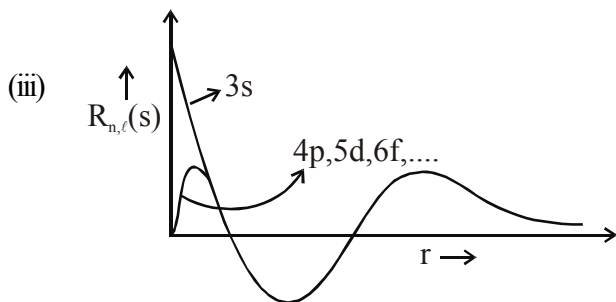
$$n - \ell - 1 = 0$$

1s, 2p, 3d, 4f ..... orbitals



$$n - \ell - 1 = 1$$

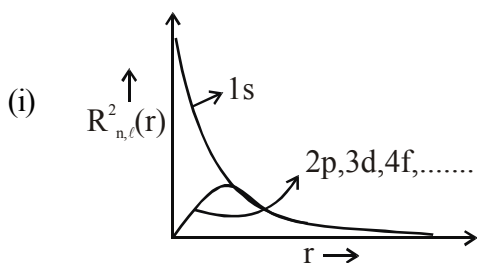
2s, 3p, 4d, 5f ..... orbitals



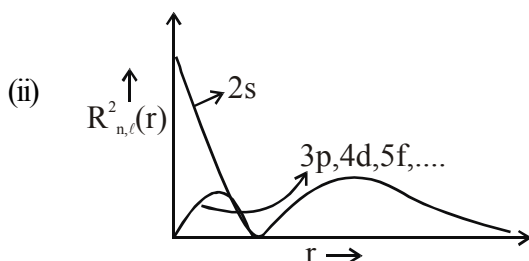
$$n - \ell - 1 = 2$$

3s, 5p, 5d, 6f ..... orbitals

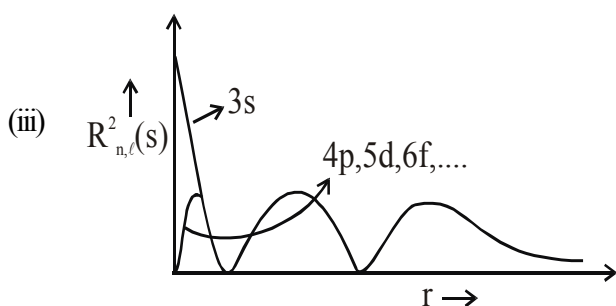
### 12.4.3 GRAPH OF RADIAL PROBABILITY DENSITY FUNCTION [ $R^2(r)$ or $\psi^2(r)$ ] :



$$n - \ell - 1 = 0, \quad (1s, 2p, 3d, 4f \dots \text{orbitals})$$



$$n - \ell - 1 = 1 \quad (2s, 3p, 4d, 5f \dots \text{orbitals})$$



$$n - \ell - 1 = 2 \quad (3s, 5p, 5d, 6f \dots \text{orbitals})$$

### 12.4.3 RADIAL PROBABILITY DISTRIBUTION FUNCTION (RPDF), $4\pi r^2 \psi^2(r)$

It is often useful to know the likelihood of finding the electron in an orbital at any given distance away from the nucleus. This enables us to say at what distance from the nucleus the electron is most likely to be found, and also how tightly or loosely the electron is bound in a particular atom. This is expressed by the radial probability distribution function,  $4\pi r^2 \psi^2(r)$ .

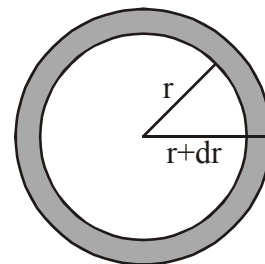
Radial distribution function is the measure of the probability of finding the electron in a spherical shell between thickness  $r$  and  $(r + dr)$  from the nucleus, irrespective of the direction.

## ❖ Volume of radial shell :

$$dV = \left[ \text{Volume of sphere with radius } (r + dr) \right] - \left[ \text{Volume of sphere with radius } r \right]$$

$$= \frac{4}{3}\pi(r + dr)^3 - \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi(r^3 + 3r^2 dr + 3r dr^2 + dr^3) - \frac{4}{3}\pi r^3 = \frac{4}{3}\pi[r^3 + 3r^2 dr - r^3]$$



(As  $dr$  represents an extremely small thickness, the higher powers of  $dr$  such as  $dr^2$  and  $dr^3$  may be neglected.)

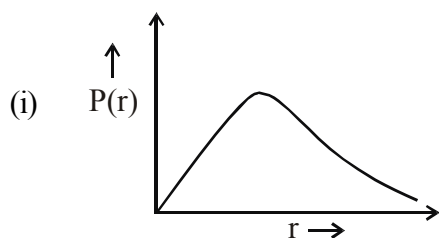
$$\therefore \text{Volume of shell, } dV = \frac{4}{3}(\pi \times 3r^2 dr) = 4\pi r^2 dr$$

$$\text{Now, radial probability density, } R^2(r) = \frac{P}{dV}$$

$\therefore$  Probability of finding electron in the volume element,

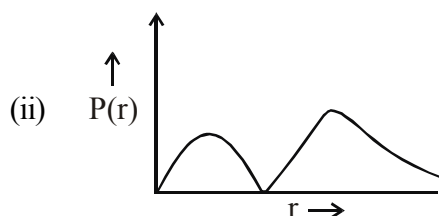
$$P = R^2(r) \cdot dV = R^2(r) \cdot 4\pi r^2 \cdot dr$$

$$\text{Now radial probability distribution function, } P(r) = \frac{P}{dr} = 4\pi r^2 \cdot R^2(r)$$



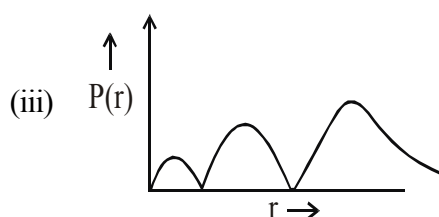
$$n - l - 1 = 0$$

1s, 2p, 3d, 4f ..... orbitals



$$n - l - 1 = 1$$

2s, 3p, 4d, 5f ..... orbitals



$$n - l - 1 = 2$$

3s, 5p, 5d, 6f ..... orbitals

❖ **Characteristics of radial distribution function :**

- (i) The number of maxima in radial distribution function plot are  $(n - \ell)$ .
- (ii) The maximum probability of finding the electron, for the ground state hydrogen atom (1s) is found to be at  $a_0$  (first Bohr radius).
- (iii) For 2s, 3s, 3p orbitals, the number of maxima is more than one, indicating that there is maximum probability of finding the electron at the distance corresponding to the highest value of peak. However, there is lesser probability of finding the electron at the other peaks. It shows that in a certain state, the electron spends some portion of its time very close to the nucleus.

**12.5 ANGULAR PART OF SOLUTION :**

**(1) s-orbital :**

$$\ell = 0, m = 0 \qquad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{1}{4\pi}}$$

As the probability of finding electron is not depending on angle (direction) then it must be same. In all direction and hence the shape of s-orbital is sphere.

**(2) p-orbital :**

$$p_x \text{-orbital : } \ell = 1, m = +1 \qquad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{3}{4\pi}} \cdot \sin \theta \cos \phi$$

$$p_y \text{-orbital : } \ell = 1, m = -1 \qquad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{3}{4\pi}} \cdot \sin \theta \sin \phi$$

$$p_z \text{-orbital : } \ell = 1, m = 0 \qquad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{3}{4\pi}} \cdot \cos \theta$$

**(3) d-orbital :**

$$d_{z^2} \text{-orbital : } \ell = 2, m = 0 \qquad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$d_{x^2-y^2} \text{-orbital : } \ell = 2, m = -2 \qquad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin^2 \theta \cos 2\phi$$

$$d_{xy} \text{-orbital : } \ell = 2, m = +2 \qquad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin^2 \theta \sin 2\phi$$

$$d_{xz} \text{-orbital : } \ell = 2, m = +1 \qquad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin \theta \cos \theta \sin 2\phi$$

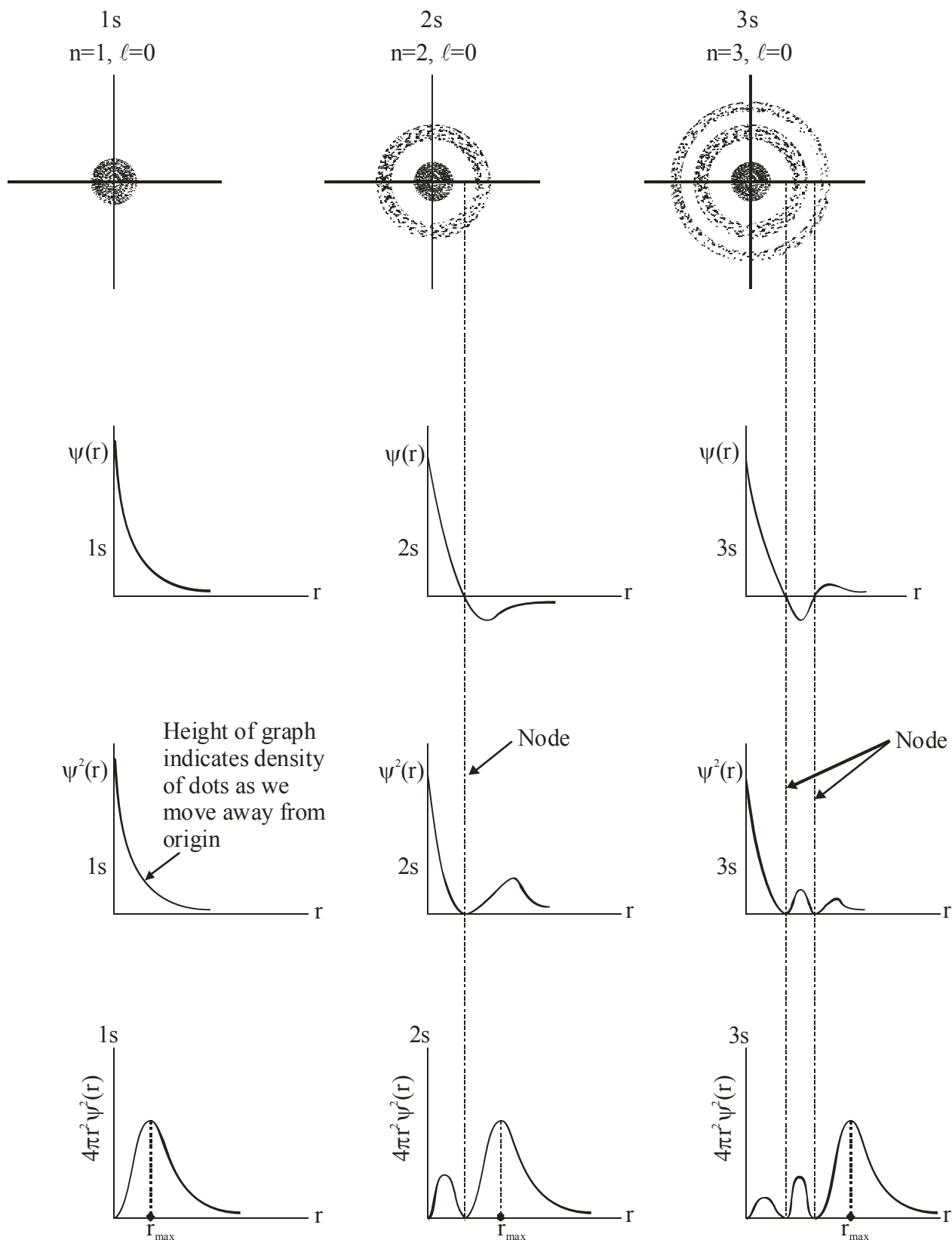
$$d_{yz} \text{-orbital : } \ell = 2, m = -1 \qquad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin \theta \cos \theta \cdot \sin \phi$$

**Note :** Number of radial nodes =  $n - \ell - 1$

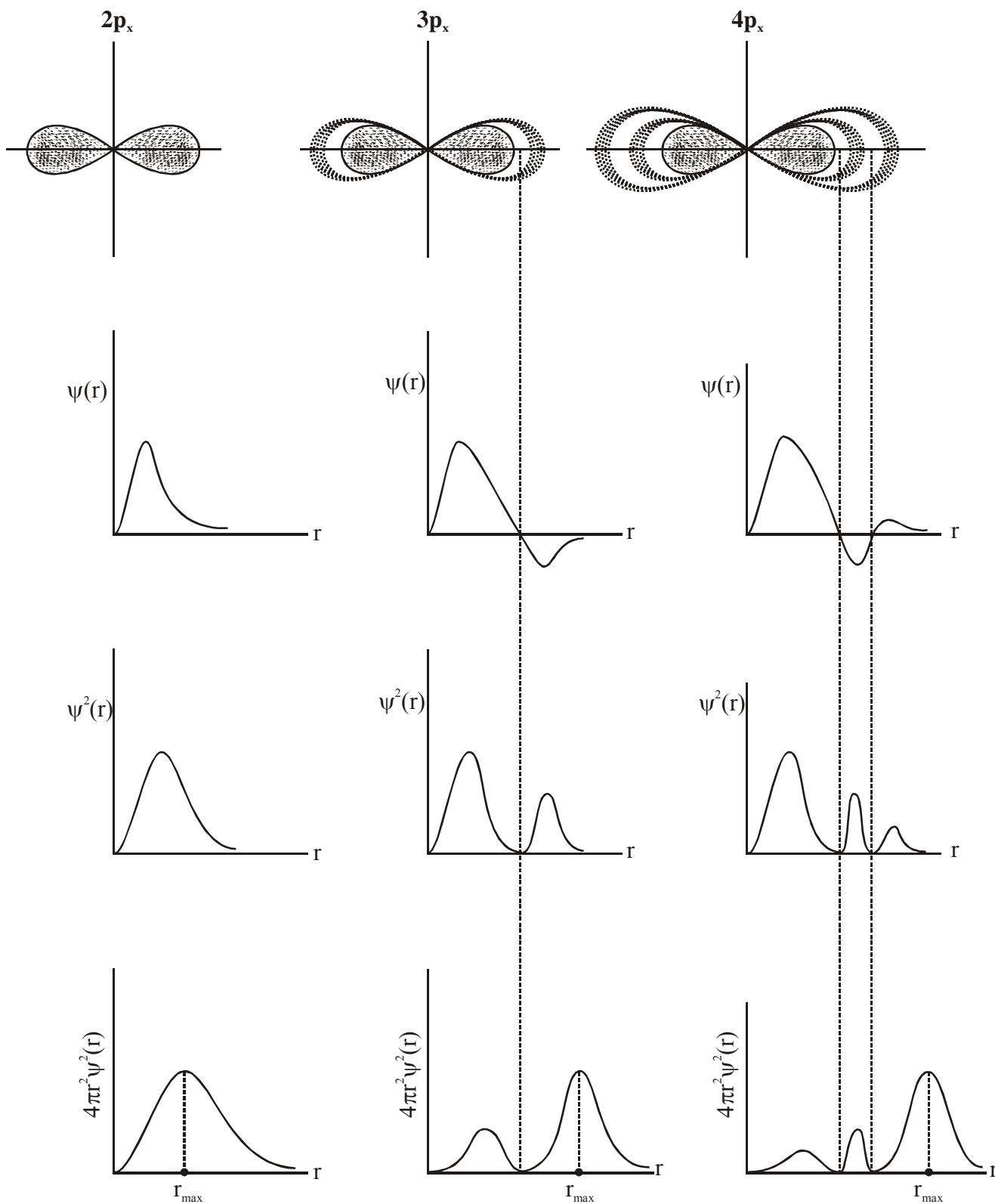
Number of angular nodes =  $\ell$

Total of number nodes =  $n - 1$

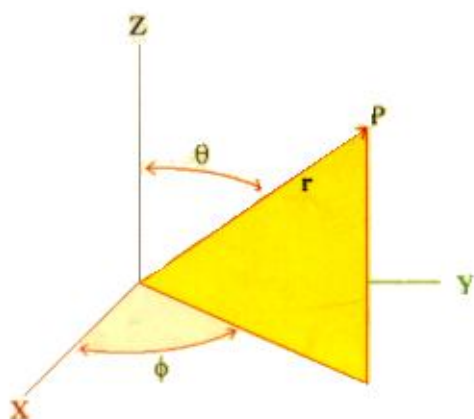
**12.6 Electron-density distribution in 1s, 2s and 3s-orbitals.** The lower part of the fig. shows how the electron density, represented by  $\psi^2$  varies as a function of distance from the nucleus. In the 2s and 3s - orbitals, the electron-density function drops to zero at certain distances from the nucleus. The spherical surfaces around the nucleus at which  $\psi^2$  is zero are called nodes.



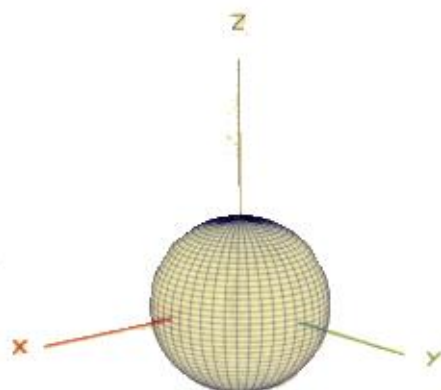
12.7 Electron-density distribution in  $2p_x$ ,  $3p_x$  and  $4p_x$ -orbitals :



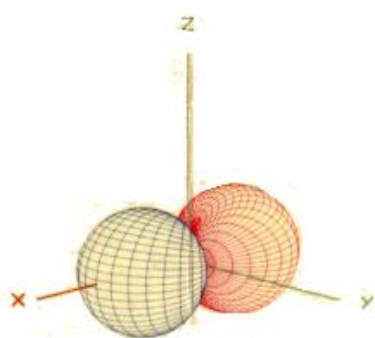
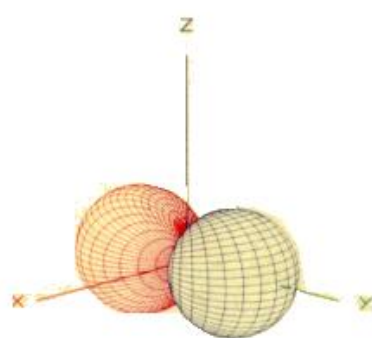
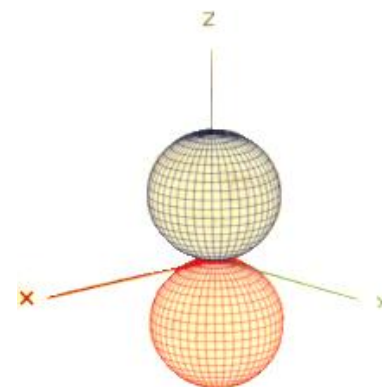
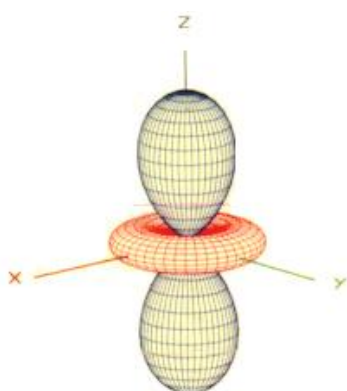
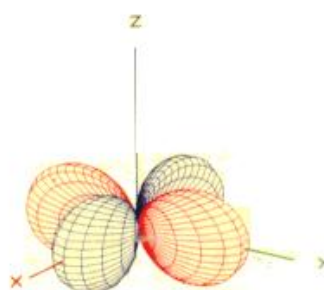
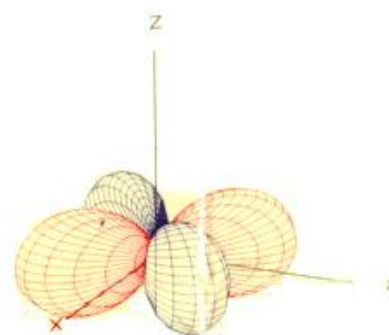
## 12.8 SHAPES OF ATOMIC ORBITALS



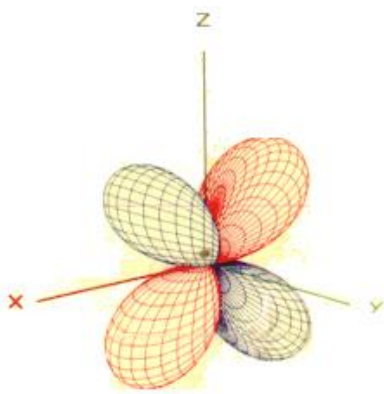
The spherical Polar Coordinates



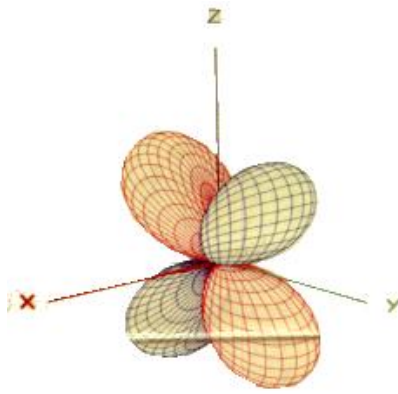
S

 $p_x$  $p_y$  $p_z$  $d_{z^2}$  $d_{x^2-y^2}$  $d_{xy}$

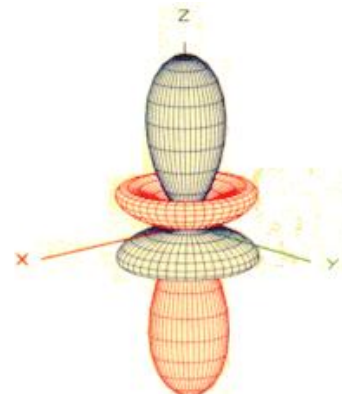




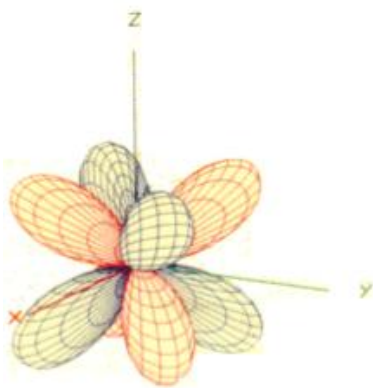
$d_{xz}$



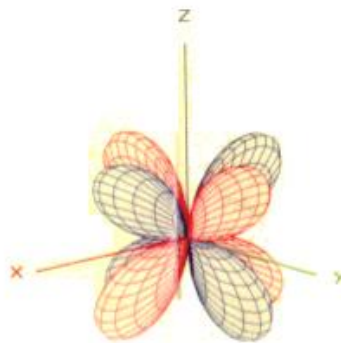
$d_{yz}$



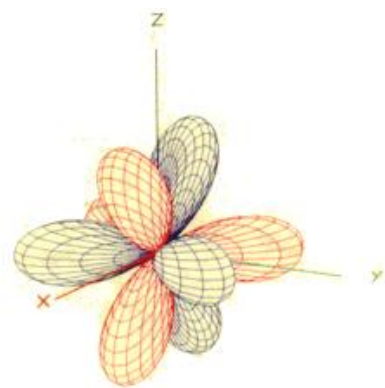
$f_z^3$



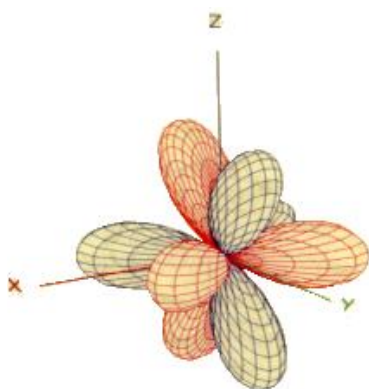
$f_{xyz}$



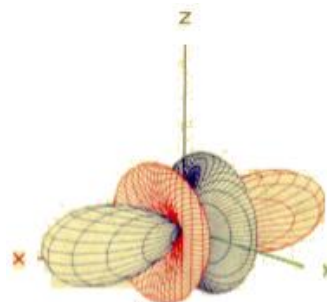
$f_{z(x^2-y^2)}$



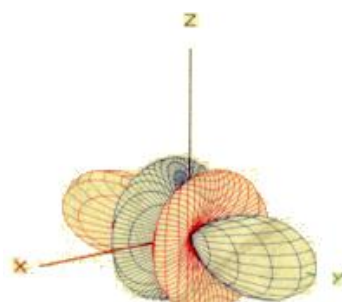
$f_{x(y^2-z^2)}$



$f_{y(z^2-x^2)}$



$f_x^3$



$f_y^3$

**Ex.49** Find the distance at which probability of finding electron is maximum for 1s orbital in a He atom.

The wave function of orbital is given as.

$$\psi_{1s} = \frac{4}{a_0^{3/2}} \cdot e^{-\frac{2r}{a_0}}$$

**Sol.** Probability distribution function is  $P(r) = \psi^2 \cdot 4\pi r^2 = \left(\frac{16}{a_0^3}\right) e^{-\left(\frac{4r}{a_0}\right)} \cdot 4\pi r^2$

$$\Rightarrow P(r) = k \cdot r^2 \cdot e^{-\frac{4r}{a_0}}$$

$$\text{differentiating } \frac{dP(r)}{dr} = 2r \cdot e^{-\frac{4r}{a_0}} - \left(\frac{4}{a_0}\right) r^2 \cdot e^{-\frac{4r}{a_0}} = 0$$

$$\Rightarrow 1 = \frac{2r}{a_0} \Rightarrow r = \frac{a_0}{2}$$

$\Rightarrow$  probability of finding electron is maximum at distance  $\frac{a_0}{2}$  from nucleus.

**Ex.50** Consider  $\psi$  (wave function) of 2s atomic orbital of H-atom is -

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left[ 2 - \frac{r}{a_0} \right] e^{-\frac{r}{2a_0}}$$

Find distance of radial node from nucleus in terms of  $a_0$ .

**Sol.**  $R(r) = 0$

$$\left[ 2 - \frac{r}{a_0} \right] e^{-\frac{r}{2a_0}} = 0 \Rightarrow 2 - \frac{r}{a_0} = 0 \Rightarrow r = 2 a_0$$

## SOME PREVIOUS YEARS QUESTION

1. With what velocity should an  $\alpha$ -particle travel towards the nucleus of a Cu atom so as to arrive at a distance  $10^{-13}$  m. [JEE 1997]

Ans.  $6.3 \times 10^6$  m/s

Sol.  $\frac{1}{2}mv^2 = \frac{kq_1q_2}{r}$

$$v^2 = \frac{2kq_1q_2}{mr}$$

$$= \frac{2 \times 9 \times 10^9 \times 2e \times 29e}{(10^{-13})(1.67 \times 10^{-27})}$$

$$= \frac{18 \times 2 \times 29 \times 10^9 \times (1.6)^2 \times 10^{-38}}{1.67 \times 10^{-23} \times 10^{-27}}$$

$$= \frac{36 \times 29 \times 2.56 \times 10^{-29+40}}{1.67}$$

$$= 1600.3 \times 10^{11}$$

2. A compound of Vanadium has magnetic moment of 1.73 BM work out electronic configuration of Vanadium Ion in the compound. [JEE 1997]

Ans. [Ar]  $3d^1$

Sol.  $r = \sqrt{n(n+2)} \quad n = 1$

$$= \sqrt{3}$$

$$= 1.73 \quad [\text{Ar}] 3d^2$$

3. The energy of an electron in the first Bohr orbit of H atom is  $-13.6$  eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is/are :

(A)  $-3.4$  eV      (B)  $-4.2$  eV      (C)  $-6.8$  eV      (D)  $+6.8$  eV [JEE 1998]

Ans. (A)

Sol.  $E = -13.6$

$$E = \frac{-13.6}{4} = -3.4 \text{ eV}$$

4. The number of nodal planes in a  $p_x$  orbital is: [JEE 2000]

(A) one      (B) two      (C) three      (D) zero

Ans. (A)

Sol. One

5. Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298K to the first excited state of atomic hydrogen. The energy for the dissociation of H-H is  $436 \text{ kJ mol}^{-1}$ .

Ans. 97.819 KJ

Sol.  $E = 436$

$T = 298 \text{ K}$

$$p = 1 \text{ atm} \quad \text{Energy req.} = 436 \times \frac{1}{298 \times R}$$

$$u = 1\ell \quad E = \left( 10.2 \times 96.47 \times \frac{2}{R \times 298} \right) + \left( \frac{436}{R \times 298} \right)$$

$$n = \frac{1}{298R} = \frac{2 \times 04 \times 96.47 \times 436}{298 \times R}$$

6. The quantum numbers  $+1/2$  and  $-1/2$  for the electron spin represent: [JEE 2001]

- (A) rotation of the electron in clockwise and anticlockwise direction respectively.  
 (B) rotation of the electron in anticlockwise and clockwise direction respectively.  
 (C) magnetic moment of the electron pointing up and down respectively.  
 (D) two quantum mechanical spin states which have no classical analogue.

Ans. (D)

Sol. Two quantum mechanical spin states which have no classical analogue.

7. Rutherford's experiment, which established the nuclear model of atom, used a beam of:—

- (A)  $\beta$  - particles, which impinged on a metal foil and get absorbed. [JEE 2002]  
 (B)  $\gamma$  - rays, which impinged on a metal foil and ejected electron.  
 (C) Helium atoms, which impinged on a metal foil and got scattered.  
 (D) Helium nuclei, which impinged on a metal foil and got scattered.

Ans. (D)

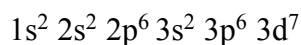
Sol. Helium nuclei, which impinged on a metal foil and got scattered.

8. The magnetic moment of cobalt of the compound  $\text{Hg}[\text{Co}(\text{SCN})_4]$  is [Given :  $\text{Co}^{+2}$ ]

- (A)  $\sqrt{3}$  (B)  $\sqrt{8}$  (C)  $\sqrt{15}$  (D)  $\sqrt{24}$  [JEE 2004]

Ans. (C)

Sol.  $\text{Co}^{+2}$



$$n = 3$$

$$r = \sqrt{n(n+2)}$$

$$= \sqrt{3 \times 5} = \sqrt{15}$$

9. The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom?

- (A)  $\text{He}^+$  ( $n=2$ ) (B)  $\text{Li}^{2+}$  ( $n=2$ ) (C)  $\text{Li}^{2+}$  ( $n=3$ ) (D)  $\text{Be}^{3+}$  ( $n=2$ ) [JEE 2004]

Ans. (D)

Sol.  $r = 0.529 \times \frac{n^2}{Z} \quad r_{\text{H}} = 0.529$

$$r_{\text{He}^+} = 0.529 \times \frac{4}{2} \quad r_{\text{Li}^{2+}} = 0.529 \times \frac{9}{3}$$

$$r_{\text{Li}^{2+}} = 0.529 \times \frac{4}{3} \quad r_{\text{Be}^{3+}} = 0.529 \times \frac{4}{4} = r_{\text{H}}$$

10. (a) The Schrodinger wave equation for hydrogen atom is

[IIT-2004]

$$\Psi_{2s} = \frac{1}{4(2\pi)^{1/2}} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r_0}{a_0} \right) e^{-r/a}$$

Where  $a_0$  is Bohr's radius. Let the rdial node in 2s be at  $r_0$ . Then find  $r_0$  in terms of  $a_0$ .

(b) A base ball having mass 100 g moves with velocity 100 m/s. Find out the value of wavelength of base ball.

Ans. (a)  $r_0 = 2a_0$ , (b)  $6.626 \times 10^{-25} \text{ \AA}$

Sol. 
$$\Psi_{2s} = \frac{1}{4(2\pi)^{1/2}} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r_0}{a_0} \right) e^{-r/a}$$

(b)  $\lambda = \frac{h}{mv}$                       (a)  $2 - \frac{r_0}{a_0} = 0$

$= \frac{6.626 \times 10^{-34}}{(0.1)(100)}$                        $\frac{r_0}{a_0} = 2$

$= 6.626 \times 10^{-35} \text{ m}$                        $r_0 = 2a_0$

$= 6.626 \times 10^{-35} \times 10^{10}$

$= 6.626 \times 10^{-25} \text{ \AA}$

11. (a) Calculate velocity of electron in first Bohr orbit of hydrogen atom (Given  $r = a_0$ ) [IIT-2005]

(b) Find de-Broglie wavelength of the electron in first Bohr orbit.

(c) Find the orbital angular momentum of 2p-orbital in terms of  $h/2\pi$  units.

Ans. (a)  $2.197 \times 10^6 \text{ m/s}$     (b)  $3.31 \text{ \AA}$     (c)  $\sqrt{2} \cdot \frac{h}{2\pi}$

Sol. (a)  $v = 2.188 \times 10^6 \times \frac{1}{1} \text{ m/s}$                       (b)  $\lambda = \frac{h}{mv}$

$= \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.188 \times 10^6}$

$= 0.332 \times 10^{-9} \text{ m}$

$= 3.31 \times 10^{-10} \text{ m}$

$= 3.31 \text{ \AA}$

(c)  $\sqrt{\ell(\ell+1)} \frac{h}{2\pi}$

$= \sqrt{1(1+1)} \frac{h}{2\pi} = \frac{\sqrt{2}h}{2\pi}$

12. Given in hydrogenic atom  $r_n, V_n, E, K_n$  stand for radius, potential energy, total energy and kinetic energy in  $n^{\text{th}}$  orbit. Find the value of  $U, v, x, y$ . [JEE 2006]

- (A)  $U = \frac{V_n}{K_n}$  (P) 1  
 (B)  $\frac{1}{r_n} \propto E^x$  (Q) -2  
 (C)  $r_n \propto Z^y$  (R) -1  
 ( $Z = \text{Atomic number}$ )  
 (D)  $v = (\text{Orbital angular momentum of electron in its lowest energy})$  (S) 0

Ans. (A) - Q ; (B) - P ; (C) - R ; (D) - S

Sol. (A)  $U = \frac{V_n}{K_n}$   
 $= \frac{-27.2}{13.6} = -2$

(B)  $\frac{1}{r_n} \propto E^x$

(C)  $r_n \propto Z^y$   
 $0.529 n^2/z = (z)^y$

13. Match the entries in **Column I** with the correctly related quantum number(s) in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS. [JEE 2008]

- | Column I   | Column II                        |
|--|----------------------------------|
| (A) Orbital angular momentum of the electron in a hydrogen-like atomic orbital | (P) Principal quantum number     |
| (B) A hydrogen-like one-electron wave function obeying Pauli principle         | (Q) Azimuthal quantum number     |
| (C) Shape, size and orientation of hydrogen like atomic orbitals               | (R) Magnetic quantum number      |
| (D) Probability density of electron at the nucleus in hydrogen-like atom       | (S) Electron spin quantum number |

Ans. (A) - Q,R ; (B) - P,Q,R,S ; (C) - P,Q,R ; (D) - P,Q

- Sol. (A) (Q) Azimuthal quantum number  
 (R) Magnetic quantum number  
 (B) (P) Principal quantum number  
 (Q) Azimuthal quantum number  
 (R) Magnetic quantum number  
 (S) spin quantum number  
 (C) (P) Principal quantum number  
 (Q) Azimuthal quantum number  
 (R) Magnetic quantum number  
 (D) (P) Principal quantum number  
 (Q) Azimuthal quantum number

## EXERCISE # S-I

## FUNDAMENTAL PARTICLES

- Find the ratio of specific charges  $\left(\frac{q}{m}\right)$  of an  $\alpha$ -particle and a deuteron  
AS0001
- Specific charges of two particles A and B are in ratio 2 : 3. If their mass ratio  $m_A : m_B$  is 2 : 3, then find ratio of their charges  $\left(\frac{q_A}{q_B}\right)$ ?  
AS0002
- Arrange electron (e), proton (p), neutron (n) and  $\alpha$ -particles ( $\alpha$ ), in the increasing order of their e/m ratio.  
AS0003
- In oil drop experiment, the following charges were experimentally determined for five oil droplets  $1.2 \times 10^{-18}$  unit,  $3.0 \times 10^{-18}$  unit,  $6.0 \times 10^{-18}$  unit,  $2.4 \times 10^{-18}$  unit and  $3.6 \times 10^{-18}$  unit (unit is arbitrary). What should be the charge on electron in this arbitrary unit?  
AS0004
- The kinetic energy of a charged particle (charge = q) accelerated by a potential difference of 10000 volt is  $1.6 \times 10^{-15}$  Joule. The value of 'q' is.  
AS0005

## RUTHERFORD'S ATOMIC MODEL

- If the radius of an atom is  $2\text{\AA}$  and the radius of its nucleus is  $4 \times 10^{-15}$  m. The ratio of volume of nucleus to that of atom is.  
AS0006
- Radius of nucleus may be given as  $R_N = R_0 A^{1/3}$ , where A = mass number and  $R_0 = \text{constant}$ . Calculate the density of nucleus of an atom if  $R_0 = 1.2 \times 10^{-15}$ .  
[ $N_A = 6 \times 10^{23}$ ,  $23 \times 8\pi \times (1.2)^3 = 1000$ ]  
AS0007
- The ratio of distances of closest approach of a proton and an  $\alpha$ -particle projected towards the same nucleus with the same initial kinetic energy is.  
AS0008
- An  $\alpha$ -particle of K.E. 5.4 MeV is projected towards Cr-nucleus ( $Z = 24$ ). What is its distance of closest approach? ( $e = 1.6 \times 10^{-19}\text{C}$ )  
AS0009
- With what speed an  $\alpha$ -particle should be projected towards stationary krypton nucleus ( $Z = 36$ ) such that it approaches upto  $2.4 \times 10^{-14}\text{m}$  from the nucleus? ( $N_A = 6 \times 10^{23}$ ,  $e = 1.6 \times 10^{-19}\text{C}$ ).  
AS0010

## WAVE CHARACTERISTICS

11. Calculate the wave length of an electromagnetic radiation of frequency  $2 \times 10^{15}$  Hz. AS0011
12. A radiostation emits the radiations of wavelength 2000 m (meter band of station). What is the frequency band of that station (Frequency of emitted radio waves) ? AS0012
13. The wave numbers of two electromagnetic radiations are  $4 \times 10^6 \text{ m}^{-1}$  and  $2 \times 10^5 \text{ cm}^{-1}$ . The ratio of their frequencies is. AS0013
14. An electromagnetic radiation makes 5000 waves in 20 cm. The frequency of radiation is. AS0014

## PLANCK'S QUANTUM THEORY

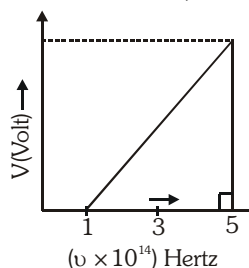
15. Calculate the energy in Joule of a photon of wave length 4000 Å. AS0015
16. The eyes of certain member of the reptile family pass a single visual signal to the brain when the visual receptors are struck by photons of wavelength 662 nm . If a total energy of  $3.0 \times 10^{-14}$  J is required to trip the signal, what is the minimum number of photons that must strike the receptor.  
( $h = 6.62 \times 10^{-34} \text{ J} \times \text{s}$ ) AS0016
17. Find the number of photons of radiation of frequency  $5 \times 10^{13} \text{ s}^{-1}$  that must be absorbed in order to melt one gm ice when the latent heat of fusion of ice is 330 J/g. ( $h = 6.6 \times 10^{-34} \text{ J} \times \text{sec.}$ ) AS0017
18. A certain dye absorbs 4000 Å and fluoresces at 5000 Å these being wavelengths of maximum absorption that under given conditions 40% of the absorbed energy is emitted. Calculate the ratio of the number of quanta emitted to the number absorbed. AS0018
19. The reaction between  $\text{H}_2$  and  $\text{Br}_2$  to form HBr in presence of light is initiated by the photo decomposition of  $\text{Br}_2$  into free Br atoms (free radicals) by absorption of light. The bond dissociation energy of  $\text{Br}_2$  is 192 KJ/mole. What is the longest wavelength (in Å) of the photon that would initiate the reaction.  

$$\left( 1 \frac{\text{eV}}{\text{atom}} = 96 \text{kJ} / \text{mol} ; hc = 1240 \text{ eV} \times \text{nm} \right)$$
AS0019
20. The quantum yield for decomposition of HI is 0.2. In an experiment 0.01 moles of HI are decomposed. Find the number of photons absorbed. ( $N_A = 6 \times 10^{23}$ ) AS0020



## PHOTOELECTRIC EFFECT

21. The minimum energy required for the emission of a metal electron is  $13.24 \times 10^{-19}$  J. Calculate the critical frequency and the corresponding wavelength of the photon (threshold wavelength) required to eject the electron ?
- AS0021**
22. A light source of wavelength  $\lambda$  illuminates a metal and ejects photo electron with  $(KE)_{\max} = 1$  eV. Another light source of wave length  $\frac{\lambda}{3}$ , ejects photoelectrons from same metal with  $(KE)_{\max} = 5$  eV. Find the value of work function (eV) of metal.
- AS0022**
23. The dissociation energy of  $H_2$  is 482.5 KJ/mol. If  $H_2$  is exposed to radiant energy of wavelength 124 nm, what % of radiant energy will be converted into K.E. ( $1 \frac{eV}{\text{atom}} = 96.5$  kJ/mol.)
- AS0023**
24. The K.E. of an electron emitted from tungstan surface is 3.06 eV. What voltage would be required to bring the electron to rest.
- AS0024**
25. Stopping potential [V volts] is plotted against frequency of light used [ $\nu$ ]. Find work function (eV). ( $h = 6.62 \times 10^{-34}$  J  $\times$  s)

**AS0025**

## BOHR'S MODEL

26. If the mass of electron is doubled, then find the new radius (in Å) of 1<sup>st</sup> orbit of H-atom ?
- AS0026**
27. If an electron in H-atom jumps from one orbit to other its angular momentum doubles. If the new radius is 'x' times the old radius, then find x ?
- AS0027**
28. The radius of the an orbit of hydrogen atom is 0.85 nm. Calculate the velocity (in m/sec) of electron in this orbit.
- AS0028**
29. The velocity of  $e^-$  in a certain Bohr orbit of the hydrogen atom bears the ratio 1:275 to the velocity of light. What is the quantum no. "n" of the orbit and the wave no. of the radiation emitted for the transition from the quatnum state (n+1) to the ground state.

**AS0029**

30. If the average life time of an excited state of H atom is of order  $10^{-8}$  sec, estimate how many orbits an  $e^{-}$  makes when it is in the state  $n = 2$  and before it suffers a transition to  $n = 1$  state.

AS0030

31. Calculate the frequency of  $e^{-}$  in the first Bohr orbit in a H-atom.

AS0031

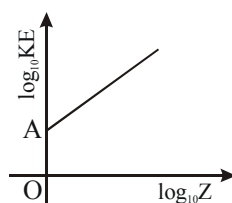
32. Calculate energy (in J) of electron which is moving in the orbit of a hydrogen atom that has its radius, sixteen times the radius of first Bohr orbit for H-atom.

AS0032

33. The energy of an excited H-atom is  $-3.4$  eV. Calculate angular momentum of  $e^{-}$  in the given orbit.

AS0033

34. In a H-like atom for an electron revolving in  $n^{\text{th}}$  orbit, the variation of  $\log_{10} \text{KE}$  versus  $\log_{10} Z$  is plotted as following -



where  $Z$  is atomic number & KE is kinetic energy of electron (in eV). If  $OA = \log_{10} 3.4$  then find the value of principle quantum number of the electron.

AS0034

35. The energy of the second stationary state in  $\text{Li}^{+2}$  ion is  $-11.025 \times 10^{-18}$  J. Find ionization energy (in J/mole) for  $\text{He}^{+}$  ions in its ground state :

AS0035

36. The energy of an electron in the first orbit of  $\text{He}^{+}$  is  $-871.6 \times 10^{-20}$  J. The energy of the electron in the first orbit of hydrogen would be :

AS0036

37. A single electron orbits around a stationary nucleus of charge  $+Ze$  where  $Z$  is atomic number and ' $e$ ' is the magnitude of the electric charge. The hydrogen like species required 47.2 eV to excite the electron from the second Bohr orbit to the third Bohr orbit. Find

- (i) the value of  $Z$  and give the hydrogen like species formed.
- (ii) the kinetic energy (in eV) and potential energy (in eV) of the electron in the first Bohr orbit.

AS0037

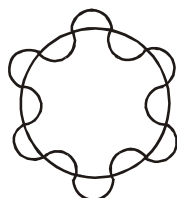
38. A hydrogen like atom with atomic number ' $Z$ ' is in higher excited state of quantum number ' $n$ '. This excited state atom can make a transition to the first excited state by successively emitting two photons of energies 10 eV and 68.2 eV respectively. Alternatively, the atom from the same excited state can make a transition to the 2nd excited state by emitting two photons of energies 4.25 eV and 5.95 eV respectively. Calculate the value of ' $Z$ '.

AS0038

39. H-atom is exposed to electromagnetic radiation of  $1026 \text{ \AA}$  and gives out induced radiations (radiations emitted when  $e^-$  returns to ground state). Calculate  $\lambda$  (in  $\text{\AA}$ ) of induced radiations. **AS0039**
40. Estimate the difference in energy (in eV) between I and II Bohr Orbit for a hydrogen atom. At what minimum atomic number a transition from  $n=2$  to  $n=1$  energy level would result in the emission of X-rays with  $\lambda = 3.0 \times 10^{-8} \text{ m}$ ? Which hydrogen like species does this atomic number correspond to. **AS0040**
41. A doubly ionised lithium atom is hydrogen like with atomic number  $z = 3$ . Find the wavelength (in  $\text{\AA}$ ) of the radiation required to excite the electron in  $\text{Li}^{2+}$  from the first to the third Bohr orbit. **AS0041**
42. If shortest wavelength of H-atom in Balmer series is X then.  
 (i) What is the shortest wave length in Lyman series.  
 (ii) What is the longest wave length in Paschen series. **AS0042**
43. Ionization energy of H-atom is 13.6 eV. If H-atoms in the ground state are excited by monochromatic light of energy 12.1 eV then the maximum number of spectral lines emitted according to Bohr's theory will be - **AS0043**
44. Find the number of spectral lines in Paschen series emitted by atomic H, when electron is excited from ground state to 7<sup>th</sup> energy level returns back. **AS0044**
45. A stationary  $\text{He}^+$  ion emitted a photon corresponding to a first line of the Lyman series. The photon liberated a photoelectron from a stationary H atom in ground state. What is the velocity (in cm/sec.) of photoelectron. **AS0045**

**DE-BROGLIE AND HEISENBERG EQUATION**

46. The figure shows a sample of H-atoms having electron revolving in higher orbit 'n'.



If this electron makes transition from this orbit 'n' to ground state, No. of paschen lines emtted are.

- AS0046**
47. deBroglie wavelength associated with an electron in 4<sup>th</sup> orbit of hydrogen atom is  $a \times (\pi r_0)$  where  $r_0$  is radius of 1<sup>st</sup> orbit of hydrogen atom, find value of 'a'. **AS0047**

48. The minimum number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number 3 will be -  
AS0048
49. Calculate the de-broglie wavelength (in m) associated with motion of earth (mass  $6 \times 10^{24}$  Kg) orbiting around the sun at a speed of  $3 \times 10^6$  m/s.  
AS0049
50. What is de Broglie wavelength (in pm) associated with an  $e^-$  accelerated through potential difference = 15 KV.  
AS0050
51. To what effective potential (in volt) a proton beam be subjected to give its protons a wavelength of  $1 \times 10^{-10}$  m.  
AS0051
52. A proton is accelerated to one-tenth of the velocity of light. If its velocity can be measured with a precision  $\pm 1\%$ . What must be its minimum uncertainty in position (in m). (Use :  $\frac{h}{4\pi} = 5.2 \times 10^{-35}$ )  
AS0052
53. The uncertainty in the position of an electron (mass  $9.1 \times 10^{-28}$  gm) moving with a velocity of  $3 \times 10^4$  cm  $\text{sec}^{-1}$ , uncertainty in velocity is 0.011% will be : ( $h = 6.6 \times 10^{-34}$  J  $\times$  s)  
AS0053
54. If uncertainties in measurement of position and momentum of an electron are equal, then the uncertainty in measurement of its velocity is  $x \times 10^{12}$ . The value of x (the closest whole number value) is  
 $m_e = 9.1 \times 10^{-31}$  kg, and  $h = 6.625 \times 10^{-34}$  Js.  
AS0054
55. With the help of Heisenberg's uncertainty principle, show that electron can never exist in the nucleus.  
AS0055

### SCHRODINGER EQUATION

56. Calculate the distance of spherical nodes for '3s' orbital from nucleus?

$$R_{3s} = \frac{1}{9\sqrt{3}a_0^{3/2}} (6 - 6\sigma + \sigma^2) e^{-\frac{\sigma}{2}} \quad \text{where } \sigma = \frac{2r}{na_0}$$

- AS0056
57. How many non-spherical subshell are possible that have atleast two maxima if a curve is plotted between radial probability distribution function versus radial distance for which principal quantum number :  $n \leq 4$ ?  
AS0057
58. The ratio of angular nodes of 3d orbital and radial nodes of 3p orbital is x : 1 what is the value of x.  
AS0058

59. For an orbital in  $B^{+4}$  radial function is :

$$R(r) = \frac{1}{9\sqrt{6}} \left( \frac{Z}{a_0} \right)^{\frac{3}{4}} (4 - \sigma) \sigma e^{-\sigma/2}$$

where  $\sigma = \frac{Zr}{a_0}$  and  $a_0 = 0.529 \text{ \AA}$  ;  $Z$  = atomic number,  $r$  = radial distance from nucleus.

The radial node of orbital is at distance from nucleus.

AS0059

60. Total nodes in 5f-orbital is.

AS0060

## EXERCISE # S-II

1. ' $\alpha$  particle' of 3.6 MeV are fired towards nucleus  ${}^A_Z X$ , at point of closest separation distance between ' $\alpha$  particle' and 'X' is  $1.6 \times 10^{-14}$  m. Calculate atomic number of 'X'

[Given :  $1/4\pi\epsilon_0 = 9 \times 10^9$  in S.I. units]

AS0061

2. Suppose the potential energy between electron and proton at a distance  $r$  is given by  $-\frac{ke^2}{3r^3}$ . Use Bohr's theory to obtain energy of such a hypothetical atom.

AS0062

3. In the Bohr's model, for unielectronic species following symbols are used

$r_{n,z}$   $\longrightarrow$  Radius of  $n^{\text{th}}$  orbit with atomic number "z"

$U_{n,z}$   $\longrightarrow$  Potential energy of electron in  $n^{\text{th}}$  orbit with atomic number "z"

$K_{n,z}$   $\longrightarrow$  Kinetic energy of electron in  $n^{\text{th}}$  orbit with atomic number "z"

$v_{n,z}$   $\longrightarrow$  Velocity of electron in  $n^{\text{th}}$  orbit with atomic number "z"

$T_{n,z}$   $\longrightarrow$  Time period of revolution of electron in  $n^{\text{th}}$  orbit with atomic number "z"

Calculate z in all in cases.

(i)  $U_{1,2} : K_{1,2} = -8 : 1$

(ii)  $r_{1,z} : r_{2,1} = 1 : 8$

(iii)  $v_{1,z} : v_{3,1} = 9 : 1$

(iv)  $T_{1,2} : T_{2,z} = 9 : 32$

AS0063

4. In a hypothetical H-atom the mass of electron & its charge is double of what we consider then calculate the total energy (in eV) of electron in the 1<sup>st</sup> orbit of such a hypothetical H-atom ?

[Assuming all others concepts and parameter to be same as we considered in Bohr's model.]

AS0064

5. In H-spectrum, longest wavelength of Lyman is 120 nm and shortest wavelength of Balmer is 360 nm. From this data, find longest wavelength of photon, that can ionize this H-atom

AS0065

6. A proton and an electron, both at rest initially, combine to form a H-atom in ground state. A single photon is emitted in this process. Find the wavelength (in nm) of this photon (use :  $hc = 1237.6 \text{ eV} \times \text{nm}$ )

AS0066

7. A H-like ion is observed to emit six different wavelengths originating from all possible transitions between a group of levels. These levels have energies between  $-0.85 \text{ eV}$  (Min) and  $-0.544 \text{ eV}$  (Max).

(a) Find atomic number (z) of element

(b) Find quantum numbers of levels between which transitions occur.

(c) Calculate largest wavelength emitted in transitions between the levels.

AS0067

8. The angular momentum of an electron in a Bohr's orbit of H-atom is  $3.1652 \times 10^{-34} \text{ kg-m}^2/\text{sec}$ . Calculate the wavenumber in terms of Rydberg constant (R) of the spectral line emitted when an electron falls from this level to the ground state. [Use  $h = 6.626 \times 10^{-34} \text{ Js}$ ]

AS0068

9. The ionisation energy of the hydrogen atom is given to be 13.6 eV. A photon falls on a hydrogen atom which is initially in the ground state and excites it to the ( $n = 4$ ) state.  
 (a) show this transition in the energy-level diagram &  
 (b) calculate the wavelength (in Å) of the photon.

AS0069

10. The ionisation energy of a H-like Bohr atom is 4 Rydbergs  
 (i) What is the wavelength (in Å) of radiation emitted when the  $e^-$  jumps from the first excited state to the ground state.  
 (ii) What is the radius (in cm) of first Bohr orbit for this atom. [1 Rydberg =  $2.18 \times 10^{-18} \text{ J}$ ]

AS0070

11. Photon having wavelength 12.4 nm was allowed to strike a metal plate having work function 25 eV. Calculate the  
 (a) Maximum kinetic energy (in eV) of photoelectrons emitted in eV.  
 (b) Wavelength (in Å) of electron with maximum kinetic energy in Å.  
 (c) Calculate the uncertainty in wavelength (in m) of emitted electron if the uncertainty in the momentum is  $6.62 \times 10^{-28} \text{ Kg m/sec}$ .

AS0071

12. The diameter of a dust particle of mass  $10^{-3} \text{ gm}$  is  $2\text{Å}$ . If uncertainty in speed of this particle is  $\frac{3.31}{\pi} \times 10^{-3} \text{ m/s}$ , then find minimum uncertainty in its position

AS0072

13. The vapours of Hg absorb some electrons accelerated by a potential diff. of 4.5 volt as a result of which light is emitted. If the full energy of single incident  $e^-$  is supposed to be converted into light emitted by single Hg atom, find the wave no. (in  $\text{m}^{-1}$ ) of the light.

AS0073

14. A photon having  $\lambda = 960 \text{ Å}$  causes the ionization of a nitrogen atom. Give the I.E. per mole of nitrogen in KJ. (Use :  $hc = 1240 \text{ eV} \times \text{nm}$  and  $1 \frac{\text{eV}}{\text{atom}} = 96.0 \text{ kJ/mol}$ .)

AS0074

15. Mr. Santa has to decode a number "ABCDEF" where each alphabet is represented by a single digit. Suppose an orbital whose radial wave function is represented as

$$\Psi_{(r)} = k_1 \cdot e^{-r/k_2} (r^2 - 5k_3r + 6k_3^2)$$

From the following information given about each alphabet then write down the answers in the form of "ABCDEF", for above orbital.

Info A = Value of n where "n" is principal quantum number

Info B = No. of angular nodes

Info C = Azimuthal quantum number of subshell to orbital belongs

Info D = No. of subshells having energy between  $(n + 5)s$  to  $(n + 5)p$  where n is principal quantum number

Info E = Orbital angular momentum of given orbital.

Info F = Radial distance of the spherical node which is farthest from the nucleus

(Assuming  $k_3 = 1$ )

AS0075



## EXERCISE # O-I

1. Anode rays are made up of :  
(A) only protons (B) only nucleus of atom  
(C) Positive residue of atoms (D) only electrons  
**AS0076**
2. When Lithium ( ${}^7_3\text{Li}$ ) vapours were filled in discharge tube for anode ray experiment, the anode rays were found to contain only  $\text{Li}^+$  ions. Thus the anode ray particle contains :  
(A) 1 proton only (B) 3 proton and 4 neutron only  
(C) 3 proton, 4 neutron and 2 electrons (D) 3 proton, 3 neutrons and 3 electrons  
**AS0077**
3. The specific charge is maximum for  
(A)  $\text{Na}^+$  (B)  $\text{Al}^{+3}$  (C)  $\text{H}^+$  (D)  $\text{Mg}^{+2}$   
**AS0078**
4. Which of the following particle is not deflected in the magnetic field  
(A) Electron (B) proton (C) Neutron (D) Deuteron  
**AS0079**
5. E/m ratio of a particle of charge 2 unit and mass 4 amu is  
(A)  $4.8 \times 10^7 \text{ C/kg}$  (B)  $0.5 \text{ C/kg}$  (C)  $4.8 \times 10^4 \text{ C/kg}$  (D)  $8 \times 10^{-20} \text{ C/kg}$   
**AS0080**
6.  $\alpha$ -particles are projected towards the nucleus of following metals, with the same kinetic energy. The distance of closest approach will be minimum for which metal?  
(A) Cu (B) Ag (C) Au (D) Ca  
**AS0081**
7. Which of the following is not a conclusion of Rutherford's atomic model -  
(A) Most of the part inside an atom is empty  
(B) Almost all mass of an atom is concentrated in the nucleus.  
(C) The size of nucleus is very small in comparison to the size of atom  
(D) Electron revolves around the nucleus in definite orbits.  
**AS0082**
8. In the different experiments,  $\alpha$ -particles, proton, deuteron and neutron are projected towards gold nucleus with the same kinetic energy. The distance of closest approach will be minimum for  
(A)  $\alpha$ -particle (B) proton (C) dueteron (D) neutron  
**AS0083**

9. The ratio of the energy of a photon of 2000 Å wavelength radiation to that of 4000 Å radiation is  
(A) 1 / 4 (B) 4 (C) 1 / 2 (D) 2 **AS0084**
10. Small packets of light is called  
(A) proton (B) quanta (C) photon (D) spectrum **AS0085**
11. Which of the following electromagnetic radiation have greater frequency ?  
(A) X - rays (B) Ultraviolet rays (C) Radio waves (D) Visible rays **AS0086**
12. Two electromagnetic radiations have wave numbers in the ratio 2 : 3. Their energies per quanta will be in the ratio  
(A) 3 : 2 (B) 9 : 4 (C) 4 : 9 (D) 2 : 3 **AS0087**
13. A radio station is emitting the radiations of frequency  $2 \times 10^4$  Hz. If its frequency is doubled,  
(A) wavelength will be doubled (B) energy per quanta will be doubled  
(C) wave number will be halved (D) all of these **AS0088**
14. A photon of 400 nm is absorbed by a gas molecule and then the molecule re-emits two photons. One re-emitted photon has wavelength 500 nm. Assuming that there is no change in the energy of molecule, the wavelength of second re-emitted photon is  
(A) 100 nm (B) 2000 nm (C) -100 nm (D) 900 nm **AS0089**
15. A green bulb and a red bulb are emitting the radiations with equal power. The correct relation between numbers of photons emitted by the bulbs per second is  
(A)  $n_g = n_r$  (B)  $n_g < n_r$  (C)  $n_g > n_r$  (D) unpredictable **AS0090**
16. The threshold wavelength for ejection of electrons from a metal is 330 nm. The work function for the photoelectric emission from the metal is ( $h = 6.6 \times 10^{-34}$  J-s)  
(A)  $1.2 \times 10^{-18}$  J (B)  $6.0 \times 10^{-19}$  J (C)  $1.2 \times 10^{-20}$  J (D)  $6.0 \times 10^{-12}$  J **AS0091**
17. In the emission of photoelectrons, the number of photoelectrons emitted per unit time depends upon  
(A) energy of the incident radiation (B) intensity of the incident radiation  
(C) frequency of the incident radiation (D) wavelength of the incident radiation **AS0092**
18. Radiations of frequency,  $\nu$ , are incident on a photosensitive metal. The maximum kinetic energy of photoelectrons is 'E'. When the frequency of the incident radiations is doubled, what is the maximum kinetic energy of the photoelectrons ?  
(A) 2E (B) E/2 (C) E +  $h\nu$  (D) E -  $h\nu$

AS0093

19. Radiation of  $\lambda = 155 \text{ nm}$  was irradiated on Li (work function = 5 eV) plate. The stopping potential (in V) is \_\_\_\_\_.
- (A) 3 V                      (B) 8 V                      (C) 9 V                      (D) 5 V

AS0094

20. Electromagnetic radiations having  $\lambda = 310 \text{ \AA}$  are subjected to a metal sheet having work function = 12.8 eV. What will be the velocity of photoelectrons with maximum Kinetic Energy..
- (A) 0, no emission will occur                      (B)  $2.18 \times 10^6 \text{ m/s}$
- (C)  $2.18\sqrt{2} \times 10^6 \text{ m/s}$                       (D)  $8.72 \times 10^6 \text{ m/s}$

AS0095

21. Bohr's model may be applied to
- (A)  $\text{Na}^{10+}$  ion                      (B) He atom                      (C)  $\text{Be}^{2+}$  ion                      (D)  $\text{C}^{6+}$  ion

AS0096

22. If the radius of 3<sup>rd</sup> Bohr's orbit of H is x, then radius of 4<sup>th</sup> orbit of  $\text{Li}^{2+}$  ion would be :-
- (A)  $\frac{27}{16}x$                       (B)  $\frac{16}{27}x$                       (C)  $\frac{9}{16}$                       (D) None of these

AS0097

23. What would be the approximate quantum number, n, for a circular orbit of hydrogen,  $1 \times 10^{-5} \text{ cm}$  in diameter?
- (A) 31                      (B) 43                      (C) 40                      (D) 39

AS0098

24. If the mass of electron is doubled, the radius of first orbit of H-atom become about
- (A)  $0.529 \text{ \AA}$                       (B)  $0.265 \text{ \AA}$                       (C)  $1.058 \text{ \AA}$                       (D)  $0.32 \text{ \AA}$

AS0099

25. The speed of electron revolving in the 4th orbit of a hydrogen like atom or ion is 1094 km/s. The atom or ion is
- (A) H                      (B)  $\text{He}^+$                       (C)  $\text{Li}^{2+}$                       (D)  $\text{Be}^{3+}$

AS0100

26. How much distance an electron revolving in 3rd orbit of  $\text{He}^+$  ion will travel in one second
- (A)  $1.458 \times 10^6 \text{ m}$                       (B)  $3.28 \times 10^6 \text{ m}$
- (C)  $4.862 \times 10^5 \text{ m}$                       (D)  $2.917 \times 10^6 \text{ m}$

AS0101

27. The ratio of time taken by electron in revolutions round the H-nucleus in 2nd and 3rd orbits, are
- (A) 2 : 3                      (B) 4 : 8                      (C) 8 : 27                      (D) 27 : 8

AS0102

28. Which of the following is not a permissible value of angular momentum of electron in H-atom?

- (A)  $1.5 \frac{h}{\pi}$                       (B)  $0.5 \frac{h}{\pi}$                       (C)  $1.25 \frac{h}{\pi}$                       (D) all of these

AS0103

29. Angular momentum for P-shell electron :-

- (A)  $\frac{3h}{\pi}$                       (B) Zero                      (C)  $\frac{\sqrt{2}h}{2\pi}$                       (D) None

AS0104

30. Angular momentum in 2<sup>nd</sup> Bohr orbit of H-atom is x. Then find out angular momentum in 1<sup>st</sup> excited state of  $Li^{+2}$  :-

- (A) 3x                      (B) 9x                      (C) x/2                      (D) x

AS0105

31. The orbit from which when electron will jump in other orbit, energy may be absorbed but not emitted out, will be

- (A) 1<sup>st</sup> orbit                      (B) 2<sup>nd</sup> orbit                      (C) 7<sup>th</sup> orbit                      (D) infinite orbit

AS0106

32. The potential energy of electron revolving in the ground state of H-atom is

- (A) -13.6 eV                      (B) -6.8 eV                      (C) -27.2 eV                      (D) Zero

AS0107

33. If the potential energy (PE) of hydrogen electron is -3.02 eV then in which of the following excited level is electron present :-

- (A) 1<sup>st</sup>                      (B) 2<sup>nd</sup>                      (C) 3<sup>rd</sup>                      (D) 4<sup>th</sup>

AS0108

34. A single electron is revolving in orbits around a stationary nucleus ( $z = 5$ ). The energy required to excite the electron from third to fourth Bohr orbit will be :-

- (A) 4.5 eV                      (B) 8.53 eV                      (C) 25 eV                      (D) 16.53 eV

AS0109

35. A photon of energy 12.75 eV is completely absorbed by a hydrogen atom initially in ground state. The principle quantum number of the excited state is

- (A) 1                      (B) 3                      (C) 4                      (D)  $\infty$

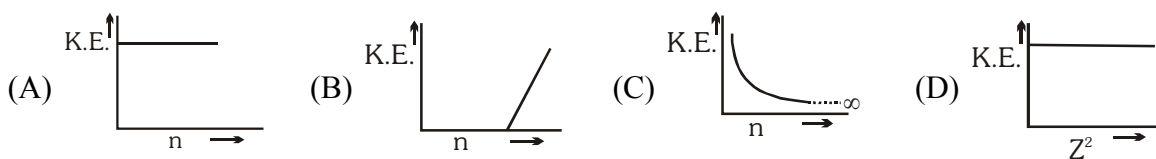
AS0110

36. An hydrogen atom (ionisation energy 13.6 eV) jumps from third excited state to first excited state. The energy of photon emitted in the process is

- (A) 1.89 eV                      (B) 2.55 eV                      (C) 12.09 eV                      (D) 12.75 eV

AS0111

37. Which is correct graph :-



AS0112

38. The energy required to remove an electron from the surface of sodium metal is 3.3 eV. What is the longest wavelength of radiation with which it can show photoelectric effect?

Use  $h = 6.6 \times 10^{-34}$  J.s

- (A)  $1.75 \times 10^{-7}$  m      (B)  $3.75 \times 10^{-5}$  m      (C)  $1.75 \times 10^{-5}$  m      (D)  $3.75 \times 10^{-7}$  m

AS0113

39. Which is correct for any H like species :-

- (A)  $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3)$       (B)  $(E_2 - E_1) < (E_3 - E_2) < (E_4 - E_3)$   
 (C)  $(E_2 - E_1) = (E_3 - E_2) = (E_4 - E_3)$       (D)  $(E_2 - E_1) = 1/4 (E_3 - E_2) = 1/9 (E_4 - E_3)$

AS0114

40. A single electron orbits a stationary nucleus of charge  $+Ze$ , where  $Z$  is a constant. It requires 47.2 eV to excite electron from second Bohr orbit to third Bohr orbit, find the value of  $Z$  :-

- (A) 1      (B) 3      (C) 5      (D) 4

AS0115

41. The energy of H-atom in  $n^{\text{th}}$  orbit is  $E_n$  then energy in  $n^{\text{th}}$  orbit of singly ionised helium atom will be:

- (A)  $4E_n$       (B)  $E_n/4$       (C)  $2E_n$       (D)  $E_n/2$

AS0116

42. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon

- (A) 3s      (B) 2p      (C) 2s      (D) 1s

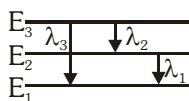
AS0117

43. The third line in Balmer series corresponds to an electronic transition between which Bohr's orbits in hydrogen

- (A)  $5 \rightarrow 3$       (B)  $5 \rightarrow 2$       (C)  $4 \rightarrow 3$       (D)  $4 \rightarrow 2$

AS0118

44. In the following transition which statement is correct



- (A)  $E_{3-1} = E_{3-2} - E_{2-1}$       (B)  $\lambda_3 = \lambda_1 + \lambda_2$   
 (C)  $\nu_3 = \nu_2 + \nu_1$       (D) All of these

AS0119

45. The first Lyman transition in the hydrogen spectrum has  $\Delta E = 10.2$  eV. The same energy change is observed in the second Balmer transition of :-

(A)  $\text{Li}^{2+}$  (B)  $\text{Li}^+$  (C)  $\text{He}^+$  (D)  $\text{Be}^{3+}$

AS0120

46. In a sample of H-atoms, electron transits from 6<sup>th</sup> orbit to 2<sup>nd</sup> orbit in multi step. Then total spectral lines (without Balmer series) will be :-

(A) 6 (B) 10 (C) 4 (D) 0

AS0121

47. What is the shortest wavelength in the Pfund series of  $\text{He}^+$  ion :-

(A)  $\frac{25}{R}$  (B)  $\frac{4}{R}$  (C)  $\frac{4R}{25}$  (D)  $\frac{25}{4R}$

AS0122

48. The shortest wavelength of  $\text{He}^+$  ion in Balmer series is x, then longest wavelength in the Paschene series of  $\text{Li}^{+2}$  is

(A)  $\frac{36x}{5}$  (B)  $\frac{16x}{7}$  (C)  $\frac{9x}{5}$  (D)  $\frac{5x}{9}$

AS0123

49. The ratio of wave length of photon corresponding to the  $\alpha$ -line of Lyman series in H-atom and  $\beta$ -line of Balmer series in  $\text{He}^+$  is

(A) 1 : 1 (B) 1 : 2 (C) 1 : 4 (D) 3 : 16

AS0124

50. Three energy levels P, Q, R of a certain atom are such that  $E_P < E_Q < E_R$ . If  $\lambda_1, \lambda_2$  and  $\lambda_3$  are the wave length of radiation corresponding to transition  $R \rightarrow Q$ ;  $Q \rightarrow P$  and  $R \rightarrow P$  respectively. The correct relationship between  $\lambda_1, \lambda_2$  and  $\lambda_3$  is

(A)  $\lambda_1 + \lambda_2 = \lambda_3$  (B)  $\frac{1}{\lambda_3} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$  (C)  $\lambda_3 = \sqrt{\lambda_1 \lambda_2}$  (D)  $\frac{2}{\lambda_3} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$

AS0125

51. Number of possible spectral lines which may be emitted in bracket series in H atom, if electrons present in 9<sup>th</sup> excited level returns to ground level, are

(A) 21 (B) 6 (C) 45 (D) 5

AS0126

52. The value of  $(n_2 + n_1)$  and  $(n_2^2 - n_1^2)$  for  $\text{He}^+$  ion in atomic spectrum are 4 and 8 respectively. The wavelength of emitted photon when electron jump from  $n_2$  to  $n_1$  is

(A)  $\frac{32}{9} R_H$  (B)  $\frac{9}{32} R_H$  (C)  $\frac{9}{32} R_H$  (D)  $\frac{32}{9} R_H$

AS0127

53. An electron, a proton and an alpha particle have kinetic energies of  $16E$ ,  $4E$  and  $E$  respectively. What is the qualitative order of their de Broglie wavelengths?

- (A)  $\lambda_e > \lambda_p = \lambda_\alpha$       (B)  $\lambda_p = \lambda_\alpha > \lambda_e$       (C)  $\lambda_p > \lambda_e > \lambda_\alpha$       (D)  $\lambda_\alpha < \lambda_e \gg \lambda_p$

AS0128

54. The wavelength associated with a golf weighing  $200\text{g}$  and moving at a speed of  $5\text{m/h}$  is of the order

- (A)  $10^{-10}\text{m}$       (B)  $10^{-20}\text{m}$       (C)  $10^{-30}\text{m}$       (D)  $10^{-40}\text{m}$

AS0129

55. An electron has kinetic energy  $2.8 \times 10^{-23}\text{J}$ . de-Broglie wavelength will be nearly :-

( $m_e = 9.1 \times 10^{-31}\text{kg}$ )

- (A)  $9.28 \times 10^{-24}\text{m}$       (B)  $9.28 \times 10^{-7}\text{m}$       (C)  $9.28 \times 10^{-8}\text{m}$       (D)  $9.28 \times 10^{-10}\text{m}$

AS0130

56. What will be de-Broglie wavelength of an electron moving with a velocity of  $1.2 \times 10^5\text{ms}^{-1}$ :-

- (A)  $6.068 \times 10^{-9}\text{m}$       (B)  $3.133 \times 10^{-37}\text{m}$       (C)  $6.626 \times 10^{-9}\text{m}$       (D)  $6.018 \times 10^{-7}\text{m}$

AS0131

57. For a valid Bohr orbit, its circumference should be:

- (A)  $= n\lambda$       (B)  $= (n-1)\lambda$       (C)  $> n\lambda$       (D)  $< n\lambda$

AS0132

58. The number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number  $+2$  :

- (A) 3      (B) 4      (C) 2      (D) 1

AS0133

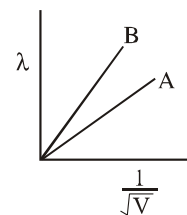
59. How fast is an electron moving if it has a wavelength equal to distance travelled in one second -

- (A)  $\sqrt{\frac{m}{h}}$       (B)  $\sqrt{\frac{h}{m}}$       (C)  $\sqrt{\frac{h}{p}}$       (D)  $\sqrt{\frac{h}{2 \times \text{K.E.}}}$

AS0134

60. De-Broglie wavelength of two particles A & B are plotted against  $\left(\frac{1}{\sqrt{V}}\right)$ ; where  $V$  is potential on the particles. Which of the following relation is correct about mass of particle (charge is same)

- (A)  $M_A = M_B$   
 (B)  $M_A > M_B$   
 (C)  $M_A < M_B$   
 (D)  $M_A \leq M_B$



AS0135

61. An  $\alpha$ -particle is accelerated through a potential difference of V volts from rest. The de-Broglie's wavelength associated with it is -

- (A)  $\sqrt{\frac{150}{V}} \text{ \AA}$       (B)  $\frac{0.286}{\sqrt{V}} \text{ \AA}$       (C)  $\frac{0.101}{\sqrt{V}} \text{ \AA}$       (D)  $\frac{0.983}{\sqrt{V}} \text{ \AA}$

AS0136

62. Which quantum number is not related with Schrodinger equation

- (A) Principal      (B) Azimuthal      (C) Magnetic      (D) Spin

AS0137

63. Which is true about  $\psi$  :-

- (A)  $\psi$  represents the probability of finding an electron around the nucleus  
 (B)  $\psi$  represent the amplitude of the electron wave  
 (C) Both A and B  
 (D) None of these

AS0138

64. According to Schrodinger model nature of electron in an atom is as :-

- (A) Particles only      (B) Wave only  
 (C) Both simultaneously      (D) Sometimes waves and sometimes particle

AS0139

65. The orbital angular momentum of an electron in 2s orbital is:

- (A)  $+\frac{1}{2} \cdot \frac{h}{2\pi}$       (B) Zero      (C)  $\frac{h}{2\pi}$       (D)  $\sqrt{2} \cdot \frac{h}{2\pi}$

AS0140

66. In an excited state, a calcium atom has the electronic configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 4d^1$ . What is

the orbital angular momentum for d electron :-  $\left( \hbar = \frac{h}{2\pi} \right)$

- (A)  $\sqrt{4}\hbar$       (B)  $\sqrt{16}\hbar$       (C)  $\sqrt{6}\hbar$       (D)  $\sqrt{10}\hbar$

AS0141

67. Which orbital has two angular nodal planes :-

- (A) s      (B) p      (C) d      (D) f



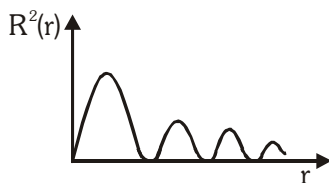
AS0142

68. From the following observations predict the type of orbital :

**Observation 1 :** x y plane acts as nodal plane

**Observation 2 :** The angular function of the orbital intersect the three axis at origin only.

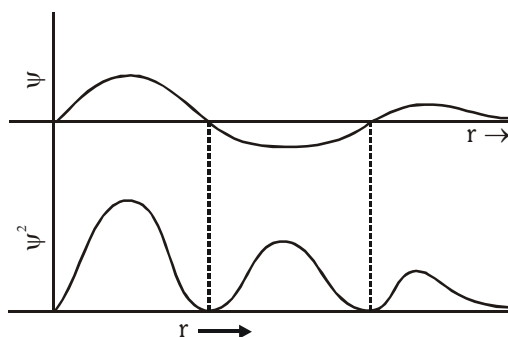
**Observation 3 :**  $R^2(r)$  v/s  $r$  curve is obtained for the orbital is



- (A)  $5p_z$                       (B)  $6d_{xy}$                       (C)  $6d_{x^2-y^2}$                       (D)  $6d_{yz}$

AS0143

69. The wave function  $\psi$  vs radial distance ( $r$ ) and square of wave function ( $\psi^2$ ) vs radial distance ( $r$ ) graph of certain orbital is given. Identify the orbital.



- (A) 3s                      (B) 4d                      (C) 3p                      (D) 4p

AS0144

70. The distance of spherical nodes from nucleus for the given orbital are

$$\psi_{\text{radial}} = \frac{1}{9\sqrt{2}} \left( \frac{Z}{a_0} \right)^{3/2} [\sigma^2 - 4\sigma + 3] \exp(-\sigma/2)$$

where  $a_0$  &  $Z$  are the constants and  $\sigma = \frac{2Zr}{a_0}$

- (A) Zero, infinity                      (B)  $\frac{a_0}{Z}, \frac{1}{2} \frac{a_0}{Z}$                       (C)  $\frac{3}{2} \frac{a_0}{Z}, \frac{1}{2} \frac{a_0}{Z}$                       (D)  $\frac{a_0}{Z}, \frac{3}{2} \frac{a_0}{Z}$

71. The radial function for an orbitals is :

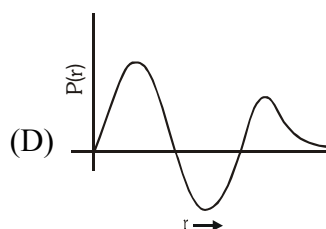
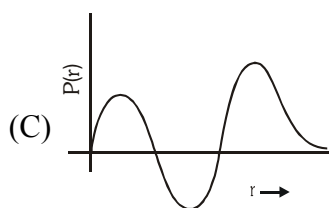
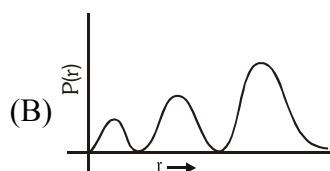
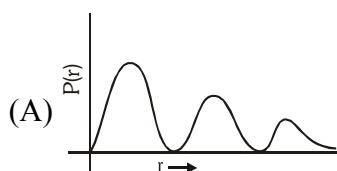
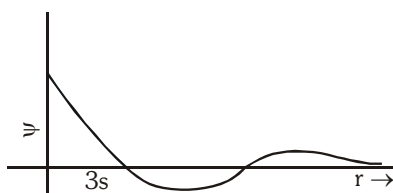
$$R(r) = \frac{1}{9\sqrt{6}} \left( \frac{1}{a_0} \right) \cdot (4 - \sigma) \sigma e^{-\frac{\sigma}{3}}; \sigma = \frac{r}{a_0}$$

Pick out the incorrect statement :

- (A) orbital must be 3p
- (B) orbital must be  $3p_x$
- (C) the orbital has one radial node
- (D) the orbital must have one angular node

AS0146

72. The wave function ( $\psi$ ) versus radial distance ( $r$ ) curve for certain orbital is given. Predict the shape of  $\psi^2 \cdot 4\pi r^2$  (radial probability distribution function) versus  $r$  graph.



AS0147

## EXERCISE # O-II

## SINGLE CORRECT :

1. In a hydrogen like sample electron is in 2<sup>nd</sup> excited state, the energy of 4<sup>th</sup> state of this sample is -13.6 eV, then incorrect statement is :
- (A) Atomic number of element is 4.  
 (B) 3 different types of spectral line will be observed if electrons make transition upto ground state from the 2<sup>nd</sup> excited state.  
 (C) A 25 eV photon can set free the electron from the 2<sup>nd</sup> excited state of this sample  
 (D) 2<sup>nd</sup> line of Balmer series of this sample has same energy value as 1<sup>st</sup> excitation energy of H-atoms.

AS0148

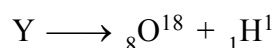
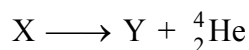
2. An electron in a hydrogen atom in its ground state absorbs energy equal to the ionisation energy of Li<sup>2+</sup>. The wavelength of the emitted electron is:
- (A)  $3.32 \times 10^{-10}$  m      (B) 1.17 Å      (C)  $2.32 \times 10^{-9}$  nm      (D) 3.33 pm

AS0149

3. Given  $\Delta H$  for the process  $\text{Li(g)} \longrightarrow \text{Li}^{3+}(\text{g}) + 3\text{e}^-$  is 19800 kJ/mole &  $\text{IE}_1$  for Li is 520 then  $\text{IE}_2$  &  $\text{IE}_3$  of Li are respectively (approx, value)
- (A) 7505, 11775      (B) 520, 19280      (C) 11775, 19280      (D) Data insufficient

AS0150

4. Consider the following nuclear reactions involving X & Y.



If both neutrons as well as protons in both the sides are conserved in nuclear reaction then moles of neutrons in 4.6 gm of X

- (A)  $2.4 N_A$       (B) 2.4      (C) 4.6      (D)  $0.2 N_A$

AS0151

## Assertion and Reason :

5. **Statement-1:** Energy emitted when an electron jump from 5  $\rightarrow$  2 (energy level) is less than when an electron jump from 2  $\rightarrow$  1 in all 'H' like atom.

**Statement-2:** The |total energy difference| between 1<sup>st</sup> & 2<sup>nd</sup> energy level is greater than that of any two energy level provided level '1' is not part of those two energy levels.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

AS0152

6. **Statement-1** : Emitted radiations will fall in visible range when an electron jump from higher level to  $n = 2$  in  $\text{Li}^{+2}$  ion.  
**Statement-2** : Balmer series radiations belong to visible range in all H-atoms.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.

AS0153

**More than one may be correct :**

7. Which of the following could be derived from Rutherford's  $\alpha$ -particle scattering experiment-  
(A) Most of the space in the atom is empty  
(B) The radius of the atom is about  $10^{-10}$  m while that of nucleus is  $10^{-15}$  m  
(C) Electrons move in a circular path of fixed energy called orbits  
(D) Electrons and the nucleus are held together by electrostatic forces of attraction.

AS0154

8. In a H-like sample electrons make transition from 5<sup>th</sup> excited state to 2<sup>nd</sup> excited state  
(A) 10 different spectral lines will be emitted  
(B) 6 different spectral lines will be emitted  
(C) Number of lines belonging to Balmer series will be 4  
(D) Number of lines belonging to paschen series will be 3

AS0155

9. The kinetic energy of photoelectron emitted on irradiating a metal surface with frequency  $\nu$  is related by  $\text{KE} = h\nu - \phi$ . The plots of KE vs. incident frequency  $\nu$  shows :  
(A) A straight line with slope equal to Planck's constant.  
(B) A straight line with intercept on x-axis equal to the product of threshold frequency and Planck's constant.  
(C) A straight line with extrapolated intercept on y-axis equal to threshold energy.  
(D) A straight line with intercept on x-axis equal to threshold frequency.

AS0156

10. Select the correct statement(s):  
(A) All electromagnetic radiation travel with speed of light in vacuum.  
(B) Energy of photon of UV light is lower than that of yellow light.  
(C)  $\text{He}^+$  and H have identical spectrum.  
(D) The total energy of an electron in unielectronic specie is greater than zero

AS0157

11. Choose the incorrect statement(s):

(A) Increasing order of wavelength is

Micro waves > Radio waves > IR waves > visible waves > UV waves

(B) The order of Bohr radius is ( $r_n$  : where n is orbit number for a given atom)  $r_1 < r_2 < r_3 < r_4$

(C) The order of total energy is ( $E_n$  : where n is orbit number for a given atom)  $E_1 > E_2 > E_3 > E_4$

(D) The order of velocity of electron in H,  $\text{He}^+$ ,  $\text{Li}^+$ ,  $\text{Be}^{3+}$  species in second Bohr orbit is  $\text{Be}^{3+} > \text{Li}^{+2} > \text{He}^+ > \text{H}$

AS0158

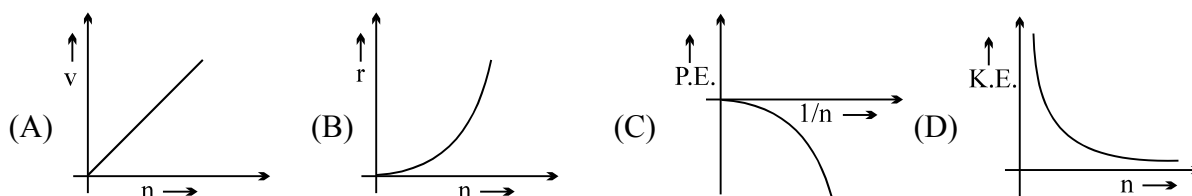
12. Select the correct curve(s):

If v = velocity of electron in Bohr's orbit

r = Radius of electron in Bohr's orbit

P.E. = Potential energy of electron in Bohr's orbit

K.E. = Kinetic energy of electron in Bohr's orbit.



AS0159

13. Which is / are correct statement.

(A) The difference in angular momentum associated with the electron present in consecutive orbits of

$$\text{H-atom is } (n-1) \frac{h}{2\pi}.$$

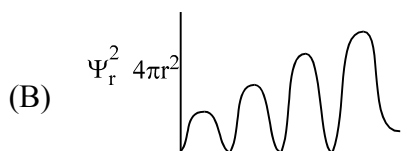
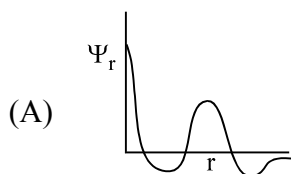
(B) Energy difference between energy levels will be changed if, P.E. at infinity assigned value other than zero.

(C) Frequency of spectral line in a H-atom is in the order of  $(2 \rightarrow 1) < (3 \rightarrow 1) < (4 \rightarrow 1)$ .

(D) On moving away from the nucleus, kinetic energy of electron decreases.

**Match the column :**

14. Column I & Column II contain data on Schrodinger Wave-Mechanical model, where symbols have their usual meanings. Match the columns.

**Column I**

(C)  $\Psi(\theta, \phi) = K$  (independent of  $\theta$  &  $\phi$ )

(D) at least one angular node is present

**Column II (Type of orbital)**

(P) 4s

(Q) 5p<sub>x</sub>

(R) 3s

(S) 6d<sub>xy</sub>

AS0161

15. **Column-I**

(A) Electron moving in 2<sup>nd</sup> orbit in He<sup>+</sup> ion electron is

(B) Electron moving in 3<sup>rd</sup> orbit in H-atom

(C) Electron moving in 1<sup>st</sup> orbit in Li<sup>+2</sup> ion

(D) Electron moving in 2<sup>nd</sup> orbit is Be<sup>+3</sup> ion

**Column-II**

(P) Radius of orbit in which moving is 0.529 Å

(Q) Total energy of electron is (-)13.6 × 9eV

(R) Velocity of electron is  $\frac{2.188 \times 10^6}{3}$  m/sec

(S) De-broglie wavelength of

electron is  $\sqrt{\frac{150}{13.6}}$  Å

AS0162

## COMPREHENSION :

## Question No. 16 to 18 (3 questions)

The French physicist Louis de Broglie in 1924 postulated that matter, like radiation, should exhibit a dual behaviour. He proposed the following relationship between the wavelength  $\lambda$  of a material particle, its linear momentum  $p$  and planck constant  $h$ .

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

The de Broglie relation implies that the wavelength of a particle should decrease as its velocity increases. It also implies that for a given velocity heavier particles should have shorter wavelength than lighter particles. The waves associated with particles in motion are called matter waves or de Broglie waves. These waves differ from the electromagnetic waves as they

- (i) have lower velocities
- (ii) have no electrical and magnetic fields and
- (iii) are not emitted by the particle under consideration.

The experimental confirmation of the de Broglie relation was obtained when Davisson and Germer, in 1927, observed that a beam of electrons is diffracted by a nickel crystal. As diffraction is a characteristic property of waves, hence the beam of electron behaves as a wave, as proposed by de Broglie.

Werner Heisenberg considered the limits of how precisely we can measure properties of an electron or other microscopic particle like electron. He determined that there is a fundamental limit of how closely we can measure both position and momentum. The more accurately we measure the momentum of a particle, the less accurately we can determine its position. The converse is also true. This is summed up in what we now call the "Heisenberg uncertainty principle: It is impossible to determine simultaneously and precisely both the momentum and position of a particle. The product of uncertainty in the position,  $\Delta x$  and the uncertainty in the momentum  $\Delta(mv)$  must be greater than

or equal to  $\frac{h}{4\pi}$ . i.e.

$$\Delta x \Delta(mv) \geq \frac{h}{4\pi}$$

16. The correct order of wavelength of Hydrogen ( ${}_1\text{H}^1$ ), Deuterium ( ${}_1\text{H}^2$ ) and Tritium ( ${}_1\text{H}^3$ ) moving with same kinetic energy is  
 (A)  $\lambda_{\text{H}} > \lambda_{\text{D}} > \lambda_{\text{T}}$       (B)  $\lambda_{\text{H}} = \lambda_{\text{D}} = \lambda_{\text{T}}$       (C)  $\lambda_{\text{H}} < \lambda_{\text{D}} < \lambda_{\text{T}}$       (D)  $\lambda_{\text{H}} < \lambda_{\text{D}} > \lambda_{\text{T}}$
17. The transition, so that the de-Broglie wavelength of electron becomes 3 times of its initial value in  $\text{He}^+$  ion will be  
 (A)  $2 \rightarrow 5$       (B)  $3 \rightarrow 2$       (C)  $2 \rightarrow 6$       (D)  $1 \rightarrow 2$

AS0163

AS0164

18. If the uncertainty in velocity & position is same, then the uncertainty in momentum will be

(A)  $\sqrt{\frac{hm}{4\pi}}$       (B)  $m\sqrt{\frac{h}{4\pi}}$       (C)  $\sqrt{\frac{h}{4\pi m}}$       (D)  $\frac{1}{m}\sqrt{\frac{h}{4\pi}}$

AS0165

**Question No. 19 to 22 (4 questions)**

The only electron in the hydrogen atom resides under ordinary conditions on the first orbit. When energy is supplied, the electron moves to higher energy orbit depending on the amount of energy absorbed. When this electron returns to any of the lower orbits, it emits energy. Lyman series is formed when the electron returns to the lowest orbit while Balmer series is formed when the electron returns to second orbit. Similarly, Paschen, Brackett and Pfund series are formed when electron returns to the third, fourth and fifth orbits from higher energy orbits respectively.

Maximum number of lines produced when an electron jumps from  $n$ th level to ground level is equal to  $\frac{n(n-1)}{2}$ . For example, in the case of  $n = 4$ , number of lines produced is 6. ( $4 \rightarrow 3$ ,  $4 \rightarrow 2$ ,  $4 \rightarrow 1$ ,  $3 \rightarrow 2$ ,  $3 \rightarrow 1$ ,  $2 \rightarrow 1$ ). When an electron returns from  $n_2$  to  $n_1$  state, the number of lines in the spectrum will be equal to

$$\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

If the electron comes back from energy level having energy  $E_2$  to energy level having energy  $E_1$ , then the difference may be expressed in terms of energy of photon as:

$$E_2 - E_1 = \Delta E, \lambda = \frac{hc}{\Delta E}$$

Since  $h$  and  $c$  are constants,  $\Delta E$  corresponds to definite energy; thus each transition from one energy level to another will produce a light of definite wavelength. This is actually observed as a line in the spectrum of hydrogen atom.

Wave number of line is given by the formula  $\bar{\nu} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ .

where  $R$  is a Rydberg's constant ( $R = 1.1 \times 10^7 \text{ m}^{-1}$ )

19. The energy photon emitted corresponding to transition  $n = 3$  to  $n = 1$  is  $[h = 6 \times 10^{-34} \text{ J-sec.}]$   
 (A)  $1.76 \times 10^{-18} \text{ J}$       (B)  $1.98 \times 10^{-18} \text{ J}$       (C)  $1.76 \times 10^{-17} \text{ J}$       (D) None of these

AS0166

20. In a collection of H-atom, electrons make transition from 5<sup>th</sup> excited state to 2<sup>nd</sup> excited state then maximum number of different types of photons observed are  
 (A) 3      (B) 4      (C) 6      (D) 15



AS0167

21. The difference in the wavelength of the 1<sup>st</sup> line of Lyman series and 2<sup>nd</sup> line of Balmer series in a hydrogen atom is
- (A)  $\frac{9}{2R}$                       (B)  $\frac{4}{R}$                       (C)  $\frac{88}{15R}$                       (D) None

AS0168

22. The wave number of electromagnetic radiation emitted during the transition of electron in between two levels of  $Li^{2+}$  ion whose principal quantum numbers sum is 4 and difference is 2 is
- (A) 3.5 R                      (B) 4 R                      (C) 8 R                      (D)  $\frac{8}{9}R$

AS0169

1 TABLE (3Q)

Column-I	Column-II	Column-III
(A) Energy of electron in H-like atomic orbital	(P) Principal quantum number(n)	(I) Radial function [R(r)]
(B) Orientation and shape of H-like atomic orbital	(Q) Azimuthal quantum number ( <i>l</i> )	(II) Angular function
(C) Magnitude & direction of spin angular momentum	(R) Magnetic quantum number (m)	(III) Wave function [ $\Psi$ ]
(D) Probability density of electron in s-orbital of H-like atom/ion	(S) Spin quantum number(s)	(IV) Cannot be determined from Schrodinger equation

Assume no external electric or magnetic fields in Q.23 to Q.25

23. Which of the following option is incorrectly matched -
- (A) B – Q – II                      (B) B – R – II                      (C) B – P – I                      (D) B – Q – III
24. Which option is correctly matched ?
- (A) C – S – III                      (B) D – R – III                      (C) A – P – IV                      (D) C – S – IV
25. If option (A) is considered in presence of external electric or magnetic field then which option is incorrect -
- (A) A – P – III                      (B) A – Q – III                      (C) A – R – III                      (D) A – S – I

AS0170

AS0170

AS0170

## EXERCISE # J-MAINS

1. If the kinetic energy of an electron is increased four times, the wavelength of the de-Broglie wave associated with it would become :- [JEE-Main(online) 2012]  
 (1) Two times (2) Half (3) One fourth (4) Four times  
**AS0171**
2. If the radius of first orbit of H atom is  $a_0$ , the de-Broglie wavelength of an electron in the third orbit is :- [JEE-Main(online) 2012]  
 (1)  $6\pi a_0$  (2)  $8\pi a_0$  (3)  $2\pi a_0$  (4)  $4\pi a_0$   
**AS0172**
3. The wave number of the first emission line in the Balmer series of H-Spectrum is : (R = Rydberg constant) : [JEE-Main(online) 2013]  
 (1)  $\frac{3}{4}R$  (2)  $\frac{9}{400}R$  (3)  $\frac{5}{36}R$  (4)  $\frac{7}{6}R$   
**AS0173**
4. The de Broglie wavelength of a car of mass 1000 kg and velocity 36 km/hr is : [JEE-Main(online) 2013]  
 ( $h = 6.63 \times 10^{-34}$  Js)  
 (1)  $6.626 \times 10^{-31}$  m (2)  $6.626 \times 10^{-34}$  m  
 (3)  $6.626 \times 10^{-38}$  m (4)  $6.626 \times 10^{-30}$  m  
**AS0174**
5. For which of the following particles will it be most difficult to experimentally verify the de-Broglie relationship? [JEE-Main(online) 2014]  
 (1) a dust particle (2) an electron (3) a proton (4) an  $\alpha$ -particle.  
**AS0175**
6. If the binding energy of the electron in a hydrogen atom is 13.6 eV, the energy required to remove the electron from the first excited state of  $Li^{++}$  is : [JEE-Main(online) 2014]  
 (1) 13.6 eV (2) 30.6 eV (3) 122.4 eV (4) 3.4 eV  
**AS0176**
7. Based on the equation [JEE-Main(online) 2014]  

$$\Delta E = -2.0 \times 10^{-18} \text{ J} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$
 the wavelength of the light that must be absorbed to excite hydrogen electron from level  $n=1$  to level  $n=2$  will be ( $h = 6.625 \times 10^{-34}$  Js,  $C = 3 \times 10^8$  ms $^{-1}$ ) [JEE-Main(online) 2014]  
 (1)  $2.650 \times 10^{-7}$  m (2)  $1.325 \times 10^{-7}$  m  
 (3)  $1.325 \times 10^{-10}$  m (4)  $5.300 \times 10^{-10}$  m  
**AS0177**
8. If  $\lambda_0$  and  $\lambda$  be the threshold wavelength and wavelength of incident light, the velocity of photoelectron ejected from the metal surface is [JEE-Main(online) 2014]

(1)  $\sqrt{\frac{2hc}{m} \left( \frac{\lambda_0 - \lambda}{\lambda \lambda_0} \right)}$  (2)  $\sqrt{\frac{2h}{m} \left( \frac{1}{\lambda_0} - \frac{1}{\lambda} \right)}$  (3)  $\sqrt{\frac{2h}{m} (\lambda_0 - \lambda)}$  (4)  $\sqrt{\frac{2hc}{m} (\lambda_0 - \lambda)}$

AS0178

9. Ionization energy of gaseous Na atoms is  $495.5 \text{ kJ mol}^{-1}$ . The lowest possible frequency of light that ionizes a sodium atom is

$$(h = 6.626 \times 10^{-34} \text{ Js}, N_A = 6.022 \times 10^{23} \text{ mol}^{-1}) \quad [\text{JEE-Main(online) 2014}]$$

$$(1) 3.15 \times 10^{15} \text{ s}^{-1} \quad (2) 4.76 \times 10^{14} \text{ s}^{-1} \quad (3) 1.24 \times 10^{15} \text{ s}^{-1} \quad (4) 7.50 \times 10^4 \text{ s}^{-1}$$

AS0179

10. Which of the following is the energy of a possible excited state of hydrogen?

[JEE-Main(offline) 2015]

$$(1) -3.4 \text{ eV} \quad (2) +6.8 \text{ eV} \quad (3) +13.6 \text{ eV} \quad (4) -6.8 \text{ eV}$$

AS0180

11. At temperature  $T$ , the average kinetic energy of any particle is  $\frac{3}{2} kT$ . The de Broglie wavelength follows the order :

[JEE-Main(online) 2015]

$$(1) \text{ Visible photon} > \text{ Thermal electron} > \text{ Thermal neutron}$$

$$(2) \text{ Thermal proton} > \text{ Thermal electron} > \text{ Visible photon}$$

$$(3) \text{ Visible photon} > \text{ Thermal neutron} > \text{ Thermal electron}$$

$$(4) \text{ Thermal proton} > \text{ Visible photon} > \text{ Thermal electron}$$

AS0181

12. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference  $V$  volts. If  $e$  and  $m$  are charge and mass of an electron respectively, then the value of  $h/\lambda$  (where  $\lambda$  is wavelength associated with electron wave) is given by : [JEE-Main(online) 2016]

$$(1) \sqrt{2meV} \quad (2) meV \quad (3) 2meV \quad (4) \sqrt{meV}$$

AS0182

13. The radius of the second Bohr orbit for hydrogen atom is : [JEE-Main(offline) 2017]

(Planck's const.  $h = 6.6262 \times 10^{-34} \text{ Js}$  ; mass of electron =  $9.1091 \times 10^{-31} \text{ kg}$  ; charge of electron  $e = 1.60210 \times 10^{-19} \text{ C}$  ; permittivity of vacuum

$$\epsilon_0 = 8.854185 \times 10^{-12} \text{ kg}^{-1} \text{ m}^{-3} \text{ A}^2)$$

$$(1) 1.65 \text{ \AA} \quad (2) 4.76 \text{ \AA} \quad (3) 0.529 \text{ \AA} \quad (4) 2.12 \text{ \AA}$$

AS0183

14. If the shortest wavelength in Lyman series of hydrogen atom is  $A$ , then the longest wavelength in Paschen series of  $\text{He}^+$  is :

[JEE-Main(online) 2017]

$$(1) \frac{36A}{5} \quad (2) \frac{9A}{5} \quad (3) \frac{36A}{7} \quad (4) \frac{5A}{9}$$

AS0184

15. The electron in the hydrogen atom undergoes transition from higher orbitals to orbital of radius 211.6 pm. This transition is associated with:-

[JEE-Main(online) 2017]

- (1) Brackett series      (2) Balmer series      (3) Lyman series      (4) Paschen series

AS0185

16. The de-Broglie's wavelength of electron present in first Bohr orbit of 'H' atom is :-

[JEE-Main(online) 2018]

- (1)  $\frac{0.529}{2\pi} \text{Å}$       (2)  $2\pi \times 0.529 \text{Å}$       (3)  $0.529 \text{Å}$       (4)  $4 \times 0.529 \text{Å}$

AS0186

17. Ejection of the photoelectron from metal in the photoelectric effect experiment can be stopped by applying 0.5 V when the radiation of 250 nm is used. The work function of the metal is :

- (1) 5 eV      (2) 4 eV      (3) 5.5 eV      (4) 4.5 eV [JEE-Main(online) 2018]

AS0187

18. Which of the following statements is false ?

[JEE-Main(online) 2018]

- (1) Photon has momentum as well as wavelength.  
 (2) Splitting of spectral lines in electrical field is called Stark effect.  
 (3) Frequency of emitted radiation from a black body goes from a lower wavelength to higher wavelength as the temperature increases.  
 (4) Rydberg constant has unit of energy.

AS0188

19. If  $p$  is the momentum of the fastest electron ejected from a metal surface after the irradiation of light having wavelength  $\lambda$ , then for  $1.5 p$  momentum of the photoelectron, the wavelength of the light should be:

[JEE-Main(online) 2019]

(Assume kinetic energy of ejected photoelectron to be very high in comparison to work function)

- (1)  $\frac{1}{2}\lambda$       (2)  $\frac{3}{4}\lambda$       (3)  $\frac{2}{3}\lambda$       (4)  $\frac{4}{9}\lambda$

AS0189

20. The quantum number of four electrons are given below -

[JEE-Main(online) 2019]

I.  $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$

II.  $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$

III.  $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$

IV.  $n = 3, l = 1, m_l = 1, m_s = -\frac{1}{2}$

The correct order of their increasing energies will be -

- (1)  $IV < III < II < I$       (2)  $IV < II < III < I$       (3)  $I < II < III < IV$       (4)  $I < III < II < IV$

AS0190

21. For any given series of spectral lines of atomic hydrogen, let  $\Delta\bar{\nu} = \bar{\nu}_{\max} - \bar{\nu}_{\min}$  be the difference in maximum and minimum frequencies in  $\text{cm}^{-1}$ . The ratio  $\Delta\bar{\nu}_{\text{Lyman}} / \Delta\bar{\nu}_{\text{Balmer}}$  is :

- (1) 27 : 5      (2) 4 : 1      (3) 5 : 4      (4) 9 : 4

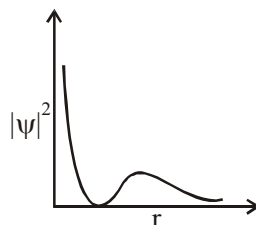
[JEE-Main(online) 2019]

AS0191

22. The ratio of the shortest wavelength of two spectral series of hydrogen spectrum is found to be about 9. The spectral series are: [JEE-Main(online) 2019]
- (1) Paschen and P fund (2) Lyman and Paschen  
 (3) Brackett and Piund (4) Balmer and Brackett

AS0192

23. The graph between  $|\psi|^2$  and  $r$ (radial distance) is shown below. This represents :-



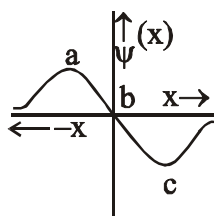
- (1) 3s orbital (2) 1s orbital [JEE-Main(online) 2019]  
 (3) 2p orbital (4) 2s orbital

AS0193

24. Among the following, the energy of 2s orbital is lowest in : [JEE-Main(online) 2019]
- (1) K (2) Na (3) Li (4) H

AS0194

25. The electrons are more likely to be found : [JEE-Main(online) 2019]



- (1) in the region a and b (2) in the region a and c  
 (3) only in the region c (4) only in the region a

AS0195

26. What is the work function of the metal if the light of wavelength  $4000 \text{ \AA}$  generates photoelectrons of velocity  $6 \times 10^5 \text{ ms}^{-1}$  form it ? [JEE-Main(online) 2019]
- (Mass of electron =  $9 \times 10^{-31} \text{ kg}$   
 Velocity of light =  $3 \times 10^8 \text{ ms}^{-1}$   
 Planck's constant =  $6.626 \times 10^{-34} \text{ Js}$   
 Charge of electron =  $1.6 \times 10^{-19} \text{ JeV}^{-1}$ )
- (1) 0.9 eV (2) 4.0 eV (3) 2.1 eV (4) 3.1 eV

AS0196

27. If the de Broglie wavelength of the electron in  $n^{\text{th}}$  Bohr orbit in a hydrogenic atom is equal to  $1.5 \pi a_0$  ( $a_0$  is Bohr radius), then the value of  $n/z$  is : [JEE-Main(online) 2019]
- (1) 1.0 (2) 0.75 (3) 0.40 (4) 1.50

AS0197

28. The upper stratosphere consisting of the ozone layer protects us from the sun's radiation that falls in the wavelength region of: [JEE-Main(online) 2019]

(1) 600-750 nm      (2) 0.8-1.5 nm      (3) 400-550 nm      (4) 200-315 nm

AS0198

29. Heat treatment of muscular pain involves radiation of wavelength of about 900 nm. Which spectral line of H-atom is suitable for this purpose? [JEE-Main(online) 2019]

$[R_H = 1 \times 10^5 \text{ cm}^{-1}, h = 6.6 \times 10^{-34} \text{ Js}, c = 3 \times 10^8 \text{ ms}^{-1}]$

(1) Paschen,  $5 \rightarrow 3$       (2) Paschen,  $\infty \rightarrow 3$       (3) Lyman,  $\infty \rightarrow 1$       (4) Balmer,  $\infty \rightarrow 2$

AS0199

30. The de Broglie wavelength ( $\lambda$ ) associated with a photoelectron varies with the frequency ( $\nu$ ) of the incident radiation as, [ $\nu_0$  is threshold frequency]: [JEE-Main(online) 2019]

(1)  $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{3}{2}}}$       (2)  $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{2}}}$       (3)  $\lambda \propto \frac{1}{(\nu - \nu_0)^{\frac{1}{4}}}$       (4)  $\lambda \propto \frac{1}{(\nu - \nu_0)}$

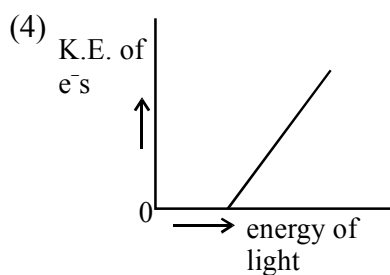
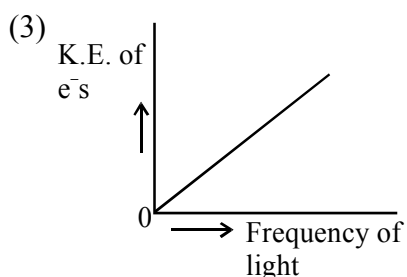
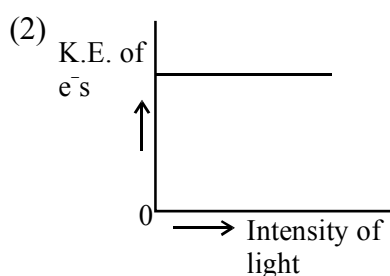
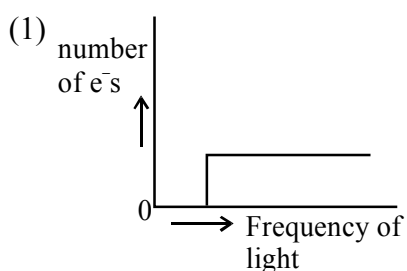
AS0200

31. The ground state energy of hydrogen atom is  $-13.6 \text{ eV}$ . The energy of second excited state  $\text{He}^+$  ion in eV is: [JEE-Main(online) 2019]

(1)  $-6.04$       (2)  $-27.2$       (3)  $-54.4$       (4)  $-3.4$

AS0201

32. Which of the graphs shown below does not represent the relationship between incident light and the electron ejected from metal surface? [JEE-Main(online) 2019]



AS0202

33. Which of the following combination of statements is true regarding the interpretation of the atomic orbitals ? [JEE-Main(online) 2019]

(a) An electron in an orbital of high angular momentum stays away from the nucleus than an electron in the orbital of lower angular momentum.

(b) For a given value of the principal quantum number, the size of the orbit is inversely proportional to the azimuthal quantum number.

(c) According to wave mechanics, the ground state angular momentum is equal to  $\frac{h}{2\pi}$ .

(d) The plot of  $\psi$  Vs  $r$  for various azimuthal quantum numbers, shows peak shifting towards higher  $r$  value.

(1) (b), (c)

(2) (a), (d)

(3) (a), (b)

(4) (a), (c)

AS0203

34. For emission line of atomic hydrogen from  $n_i = 8$  to  $n_f = n$  the plot of wave number ( $\bar{\nu}$ ) against

$\left(\frac{1}{n^2}\right)$  will be (The Rydberg constant,  $R_H$  is in wave number unit).

(1) Linear with slope -  $R_H$

[JEE-Main(online) 2019]

(2) Linear with intercept -  $R_H$

(3) Non linear

(4) Linear with slope  $R_H$

AS0204

35. The number of orbitals associated with quantum numbers  $n = 5$ ,  $m_s = +\frac{1}{2}$  is :

(1) 11

(2) 25

(3) 15

[JEE-Main(online) 2020]

(4) 50

AS0205

36. For the Balmer series in the spectrum of H atom,  $\bar{\nu} = R_H \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\}$ , the correct statements among

(I) and (IV) are :

[JEE-Main(online) 2020]

(I) As wavelength decreases, the lines in the series converge

(II) The integer  $n_1$  is equal to 2

(III) The lines of longest wavelength corresponds to  $n_2 = 3$

(IV) The ionization energy of hydrogen can be calculated from wave number of these lines

(1) (II), (III), (IV)

(2) (I), (II), (III)

(3) (I), (III), (IV)

(4) (I), (II), (IV)

AS0206

37. The radius of the second Bohr orbit, in terms of the Bohr radius,  $a_0$ , in  $\text{Li}^{2+}$  is :

[JEE-Main(online) 2020]

(1)  $\frac{4a_0}{9}$

(2)  $\frac{2a_0}{9}$

(3)  $\frac{2a_0}{3}$

(4)  $\frac{4a_0}{3}$

AS0207

38. The de Broglie wavelength of an electron in the 4<sup>th</sup> Bohr orbit is : [JEE-Main(online) 2020]

## EXERCISE # J-ADVANCED

## Paragraph for questions 1 to 3

The hydrogen-like species  $\text{Li}^{2+}$  is in a spherically symmetric state  $S_1$  with one radial node. Upon absorbing light the ion undergoes transition to a state  $S_2$ . The state  $S_2$  has one radial node and its energy is equal to the ground state energy of the hydrogen atom. [JEE 2010]

1. The state  $S_1$  is :-

- (A) 1s (B) 2s (C) 2p (D) 3s

AS0209

2. Energy of the state  $S_1$  in units of the hydrogen atom ground state energy is :-

- (A) 0.75 (B) 1.50 (C) 2.25 (D) 4.50

AS0210

3. The orbital angular momentum quantum number of the state  $S_2$  is :-

- (A) 0 (B) 1 (C) 2 (D) 3

AS0211

4. The maximum number of electrons that can have principal quantum number,  $n=3$ , and spin quantum number,  $m_s = -1/2$ , is [JEE 2011]

AS0212

5. The work function ( $\phi$ ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is : :- [JEE 2011]

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
$\phi(\text{eV})$	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

AS0213

6. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [ $a_0$  is Bohr radius] [JEE 2012]

- (A)  $\frac{h^2}{4\pi^2ma_0^2}$  (B)  $\frac{h^2}{16\pi^2ma_0^2}$  (C)  $\frac{h^2}{32\pi^2ma_0^2}$  (D)  $\frac{h^2}{32\pi^2ma_0^2}$

AS0214

7. The atomic masses of He and Ne are 4 and 20 a.m.u. respectively. The value of the de Broglie wavelength of He gas at  $-73^\circ\text{C}$  is "M" times that of the de Broglie wavelength of Ne at  $727^\circ\text{C}$ . M is. [JEE 2013]

AS0215

8. In an atom, the total number of electrons having quantum numbers  $n = 4$ ,  $|m_l| = 1$  and

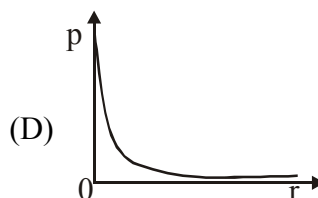
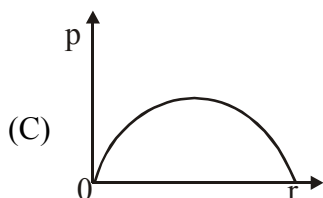
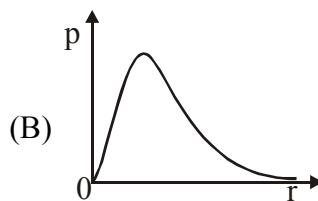
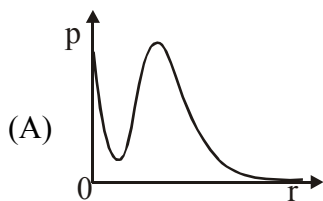
$$m_s = -\frac{1}{2} \text{ is}$$

[JEE 2014]

AS0216



9. P is the probability of finding the 1s electron of hydrogen atom in a spherical shell of infinitesimal thickness, dr, at a distance r from the nucleus. The volume of this shell is  $4\pi r^2 dr$ . The qualitative sketch of the dependence of P on r is - [JEE 2016]



AS0217

Answer Q.10, Q.11 and Q.12 by appropriately matching the information given in the three columns of the following table. [JEE 2017]

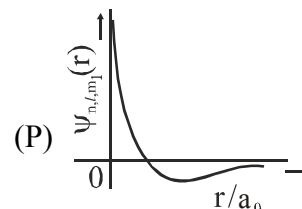
Column-1

Column-2

Column-3

(I) 1s orbital

(i)  $\Psi_{n,l,m_l} \propto \left(\frac{Z}{a_0}\right)^{3/2} e^{-\left(\frac{Zr}{a_0}\right)}$



(II) 2s orbital

(ii) One radial node

(Q) Probability density at nucleus  $\propto \frac{1}{a_0^3}$

(III) 2p<sub>z</sub> orbital

(iii)  $\Psi_{n,l,m_l} \propto \left(\frac{Z}{a_0}\right)^{5/2} re^{-\left(\frac{Zr}{2a_0}\right)} \cos\theta$

(R) Probability density is maximum at nucleus

(IV) 3d<sub>z<sup>2</sup></sub> orbital

(iv) xy - plane is a nodal plane

(S) Energy needed to excite electron from n = 2 state to n = 4 state is  $\frac{27}{32}$  times the energy needed to excite electron from n = 2 state to n = 6 state

10. For the given orbital in column 1, the only **CORRECT** combination for any hydrogen - like species is :

- (A) (IV) (iv) (R)      (B) (II) (ii) (P)      (C) (III) (iii) (P)      (D) (I) (ii) (S)

AS0218

11. For  $\text{He}^+$  ion, the only **INCORRECT** combination is

- (A) (II) (ii) (Q)      (B) (I) (i) (S)      (C) (I) (i) (R)      (D) (I) (iii) (R)

AS0219

12. For hydrogen atom, the only **CORRECT** combination is

- (A) (I) (iv) (R)      (B) (I) (i) (P)      (C) (II) (i) (Q)      (D) (I) (i) (S)

AS0220

13. The ground state energy of hydrogen atom is  $-13.6$  eV. Consider an electronic state  $\Psi$  of  $\text{He}^+$  whose energy, azimuthal quantum number and magnetic quantum number are  $-3.4$  eV, 2 and 0 respectively. Which of the following statement(s) is(are) true for the state  $\Psi$ ? [JEE 2019]

- (1) It has 2 angular nodes  
 (2) It has 3 radial nodes  
 (3) It is a 4d state  
 (4) The nuclear charge experienced by the electron in this state is less than  $2e$ , where  $e$  is the magnitude of the electronic charge.

AS0221

14. Answer the following by appropriately matching the lists based on the information given in the paragraph [JEE 2019]

Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following List-I contains some quantities for the  $n^{\text{th}}$  orbit of the atom and List-II contains options showing how they depend on  $n$ .

**List-I**

- (I) Radius of the  $n^{\text{th}}$  orbit  
 (II) Angular momentum of the electron in the  $n^{\text{th}}$  orbit  
 (III) Kinetic energy of the electron in the  $n^{\text{th}}$  orbit  
 (IV) Potential energy of the electron in the  $n^{\text{th}}$  orbit

**List-II**

- (P)  $\propto n^{-2}$   
 (Q)  $\propto n^{-1}$   
 (R)  $\propto n^0$   
 (S)  $\propto n^1$   
 (T)  $\propto n^2$   
 (U)  $\propto n^{1/2}$

Which of the following options has the correct combination considering List-I and List-II?

- (1) (II), (R)      (2) (I), (P)      (3) (I), (T)      (4) (II), (Q)

AS0222

15. Answer the following by appropriately matching the lists based on the information given in the paragraph [JEE 2019]

Consider the Bohr's model of a one-electron atom where the electron moves around the nucleus. In the following List-I contains some quantities for the  $n^{\text{th}}$  orbit of the atom and List-II contains options showing how they depend on  $n$ .

**List-I**

- (I) Radius of the  $n^{\text{th}}$  orbit  
(II) Angular momentum of the electron in the  $n^{\text{th}}$  orbit  
(III) Kinetic energy of the electron in the  $n^{\text{th}}$  orbit  
(IV) Potential energy of the electron in the  $n^{\text{th}}$  orbit

**List-II**

- (P)  $\propto n^{-2}$   
(Q)  $\propto n^{-1}$   
(R)  $\propto n^0$   
(S)  $\propto n^1$   
(T)  $\propto n^2$   
(U)  $\propto n^{1/2}$

Which of the following options has the correct combination considering List-I and List-II?

- (1) (III), (S)                      (2) (IV), (Q)                      (3) (IV), (U)                      (4) (III), (P)

AS0223

## ANSWER KEY

## EXERCISE # S-I

- |  |   |
|--|---|
| 1. Ans.(1 : 1)   | 2. Ans.(4 : 9)                                    |
| 3. Ans. $n < \alpha < p < e$                               | 4. Ans. $6.0 \times 10^{-19}$ unit.               |
| 5. Ans. $1.6 \times 10^{-19}$ Coulomb.                     | 6. Ans. $8 \times 10^{-15} : 1$                   |
| 7. Ans. $2.3 \times 10^{17}$ kg/m <sup>3</sup>             | 8. Ans. 1 : 2                                     |
| 9. Ans. $1.28 \times 10^{-14}$ m.                          | 10. Ans. $1.44 \times 10^7$ m/s                   |
| 11. Ans. 1500 Å  | 12. Ans. 150 KHz                                  |
| 13. Ans. 1 : 5   | 14. Ans. $7.5 \times 10^{12}$ Hz                  |
| 15. Ans. $4.96 \times 10^{-19}$ Joule                      | 16. Ans. $1.0 \times 10^5$                        |
| 17. Ans. $10^{22}$   | 18. Ans. 0.5                                      |
| 19. Ans. 6200 Å  | 20. Ans. $3 \times 10^{22}$                       |
| 21. Ans. ( $2 \times 10^{15}$ Hz , $1.5 \times 10^{-7}$ m) | 22. Ans. (1)                                      |
| 23. Ans. 50 %  | 24. Ans. 3.06 V                                   |
| 25. Ans. 0.41375 eV  | 26. Ans. (0.2645) Å                               |
| 27. Ans. (x = 4)   | 28. Ans. $5.44 \times 10^5$ m/s                   |
| 29. Ans. 2   | 30. Ans. $8 \times 10^6$                          |
| 31. Ans. $6530 \times 10^{12}$ Hz                          | 32. Ans. $-1.36 \times 10^{-19}$ Joules           |
| 33. $h/\pi$  | 34. Ans. (2)                                      |
| 35. Ans. $1.18 \times 10^7$                                | 36. Ans. ( $-217.9 \times 10^{-20}$ J)            |
| 37. Ans. 340 eV , - 680 eV                                 | 38. Ans. (6)                                      |
| 39. Ans. 6563 Å ; 1216 Å ; 1026 Å                          | 40. Ans. 10.2 eV , z = 2                          |
| 41. Ans. 113.74 Å  | 42. Ans. (i) $\frac{x}{4}$ ; (ii) $\frac{36x}{7}$ |
| 43. Ans. (3)   | 44. Ans. (4)                                      |
| 45. Ans. $3.09 \times 10^8$ cm/sec                         | 46. Ans. (3)                                      |
| 47. Ans. (8)   | 48. Ans. (4)                                      |
| 49. Ans. $3.68 \times 10^{-65}$ m                          | 50. Ans. 10 pm                                    |
| 51. Ans. 0.0826 volts                                      | 52. Ans. $1.05 \times 10^{-13}$ m                 |

53. Ans.(0.175 cm)

54. Ans (8)

56.  $\frac{9+3\sqrt{3}}{2} a_0, \frac{9-3\sqrt{3}}{2} a_0$

57. Ans.(3)

58. Ans.(2)

59. Ans.(0.423 Å)

60. Ans.(4)

**EXERCISE # S-II**

1. Ans. 20

2. Ans.  $E = \frac{n^6 h^6}{384 m^3 K^2 e^4 \pi^6}$

3. Ans. (i) 1, (ii) 2, (iii) 3, (iv) 3

4. Ans. - 435.2 eV

5. Ans. 90 nm

6. Ans. 91 nm

7. Ans. (a)  $Z = 3$  ; (b)  $n_1 = 12$  ,  $n_2 = 15$  ; (c)  $\lambda_{\max} = 15406$  nm

8. Ans. R  $\left(\frac{8}{9}\right)$

9. Ans. 973.5 Å

10. Ans. 303.89 Å ,  $2.645 \times 10^{-9}$  cm

11. Ans. (a) 75 eV;(b) 1.414 Å;(c)  $2 \times 10^{-14}$  m

12. Ans.  $5 \times 10^{-26}$  m

13. Ans.  $3.63 \times 10^6 m^{-1}$

14. Ans. 1240 kJ/mol.

15. Ans. 300303

**EXERCISE # O-I**

1. Ans.(C)

2. Ans.(C)

3. Ans.(C)

4. Ans.(C)

5. Ans.(A)

6. Ans.(D)

7. Ans.(D)

8. Ans.(D)

9. Ans.(D)

10. Ans.(C)

11. Ans.(A)

12. Ans.(D)

13. Ans.(B)

14. Ans.(B)

15. Ans.(B)

16. Ans.(B)

17. Ans.(B)

18. Ans.(C)

19. Ans.(A)

20. Ans.(C)

21. Ans.(A)

22. Ans.(B)

23. Ans.(A)

24. Ans.(B)

25. Ans.(B)

26. Ans.(A)

27. Ans.(C)

28. Ans.(C)

29. Ans.(A)

30. Ans.(D)

31. Ans.(A)

32. Ans.(C)

33. Ans.(B)

34. Ans.(D)

35. Ans.(C)

36. Ans.(B)

37. Ans.(C)

38. Ans.(D)

39. Ans.(A)

40. Ans.(C)

41. Ans.(A)

42. Ans.(D)

43. Ans.(B)

44. Ans.(C)

45. Ans.(C)

46. Ans.(A)

47. Ans.(D)

48. Ans.(B)

49. Ans.(A)

50. Ans.(B)

51. Ans.(B)

52. Ans.(C)

53. Ans.(A)

54. Ans.(C)

55. Ans.(C)

56. Ans.(A)

57. Ans.(A)

58. Ans.(A)

59. Ans.(B)

60. Ans.(B)

61. Ans.(C)

62. Ans.(D)

63. Ans.(B)

64. Ans.(C)

65. Ans.(B)

66. Ans.(C)

67. Ans.(C)

68. Ans.(D)

69. Ans.(D)

70. Ans.(C)

71. Ans.(B)

72. Ans.(B)

## EXERCISE # O-II

- |   |                                    |                |                 |
|---|------------------------------------|----------------|-----------------|
| 1. Ans.(D)                                  | 2. Ans.(B)                         | 3. Ans.(A)     | 4. Ans.(B)      |
| 5. Ans.(A)                                  | 6. Ans.(D)                         | 7. Ans.(A, B)  | 8. Ans. (B,D)   |
| 9. Ans (A,D)                                | 10. Ans.(A)                        | 11. Ans.(A, C) | 12. Ans.(B,C,D) |
| 13. Ans.(C,D)                               |                                    |                |                 |
| 14. Ans.(A) P, (B) P,Q,S, (C) P, R (D) Q, S | 15. Ans.(A) S, (B) R, (C) Q, (D) P |                |                 |
| 16. Ans.(A)                                 | 17. Ans.(C)                        | 18. Ans.(A)    | 19. Ans.(A)     |
| 20. Ans.(C)                                 | 21. Ans.(B)                        | 22. Ans.(C)    | 23. Ans.(C)     |
| 24. Ans.(D)                                 | 25. Ans.(D)                        |                |                 |

## EXERCISE # J-MAINS

- |             |             |             |             |
|-------------|-------------|-------------|-------------|
| 1. Ans.(2)  | 2. Ans.(1)  | 3. Ans.(3)  | 4. Ans.(3)  |
| 5. Ans.(1)  | 6. Ans.(2)  | 7. Ans.(2)  | 8. Ans.(1)  |
| 9. Ans.(3)  | 10. Ans.(1) | 11. Ans.(1) | 12. Ans.(1) |
| 13. Ans.(4) | 14. Ans.(3) | 15. Ans.(2) | 16. Ans.(2) |
| 17. Ans.(4) | 18. Ans.(3) | 19. Ans.(4) | 20. Ans.(2) |
| 21. Ans.(4) | 22. Ans.(2) | 23. Ans.(4) | 24. Ans.(1) |
| 25. Ans.(2) | 26. Ans.(3) | 27. Ans.(2) | 28. Ans.(4) |
| 29. Ans.(2) | 30. Ans.(2) | 31. Ans.(1) | 32. Ans.(3) |
| 33. Ans.(4) | 34. Ans.(4) | 35. Ans.(2) | 36. Ans.(2) |
| 37. Ans.(4) | 38. Ans.(1) |             |             |

## EXERCISE # J-ADVANCED

- |               |             |             |             |
|---------------|-------------|-------------|-------------|
| 1. Ans.(B)    | 2. Ans.(C)  | 3. Ans.(B)  | 4. Ans.(9)  |
| 5. Ans.(4)    | 6. Ans.(C)  | 7. Ans.(5)  | 8. Ans.(6)  |
| 9. Ans.(B)    | 10. Ans.(B) | 11. Ans.(D) | 12. Ans.(D) |
| 13. Ans.(1,3) | 14. Ans.(3) | 15. Ans.(4) |             |



# Chapter Contents

## 04

## CHEMICAL EQUILIBRIUM

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## CHEMICAL EQUILIBRIUM

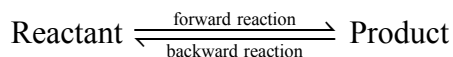
### I. TYPES OF CHEMICAL REACTION :

The chemical reactions are classified on the basis of the extent to which they proceed, into the following two classes ;

**I. Reversible reactions :** Reaction in which entire amount of the reactants is not converted into products is termed as reversible reaction.

**(i) Characteristics of reversible reactions :**

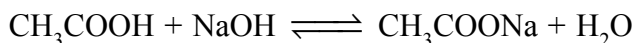
- (a) These reactions can be started from either side.
- (b) These reactions are never complete.
- (c) This sign ( $\rightleftharpoons$ ) represents the reversibility of the reaction.



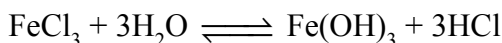
- (d) These reactions attain equilibrium and all the times, reaction mixture contains both reactant and product molecules. When reaction attains equilibrium the concentrations of reactants and product become constant (not same necessarily).

**(ii) Examples of reversible reactions :**

- (a) Neutralisation between an acid and a base either one or both are weak.



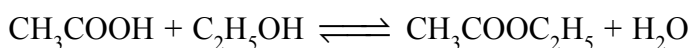
- (b) Salt hydrolysis



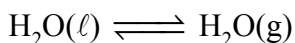
- (c) Thermal decomposition



- (d) Esterification



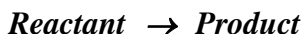
- (e) Evaporation of water in a closed vessel



**II. Irreversible reactions :** Reaction in which entire amount of the reactants is converted into products is termed as irreversible reaction.

**(i) Characteristics of irreversible reactions :**

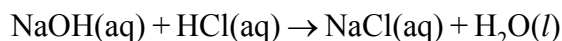
- (a) These reactions proceed only in one direction (forward direction)
- (b) These reactions can proceed to completion and reactant is completely converted into product.
- (c) The arrow ( $\rightarrow$ ) is placed between reactants and products



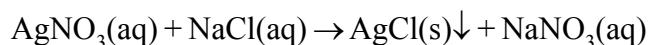
- (d) These reactions never attain equilibrium.

**(ii) Examples of irreversible reactions :**

- (a) Neutralisation between strong acid and strong base



- (b) Precipitation reactions

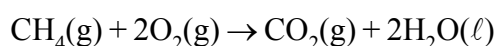


- (c) Thermal decomposition



However, if the above reaction is carried out in closed container, i.e., leaving no scope for gas to escape out, the reaction shows reversible nature.

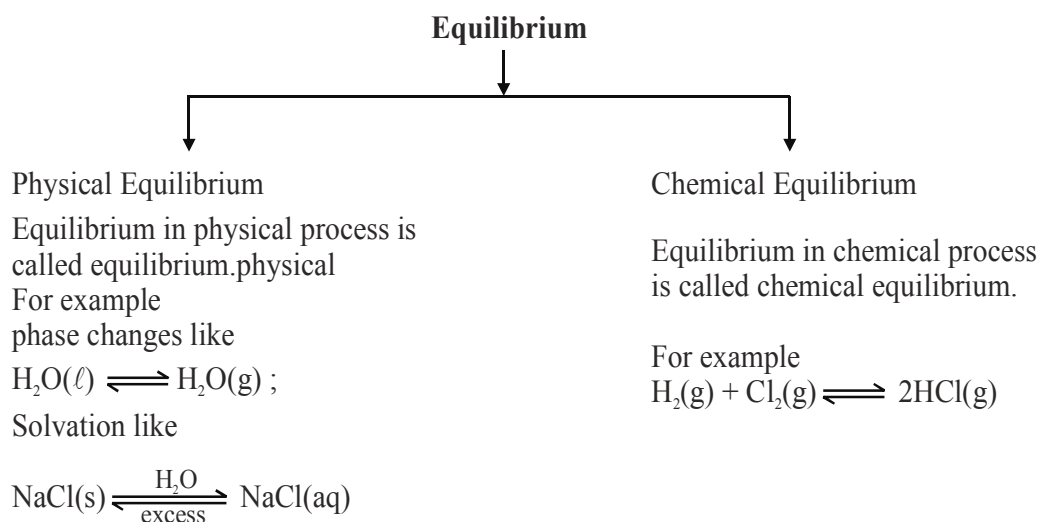
- (d) Combustion reactions

**2. EQUILIBRIUM :**

In the state of equilibrium, system loses its tendency for a change and all the properties associated with system like pressure, temperature, composition, etc become constant and do not vary without external stimulation. On the basis of nature of process in which state of equilibrium is attained, it may be of two types :

(A) Physical equilibrium

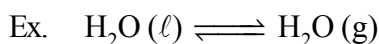
(B) Chemical equilibrium

**2.1 Physical equilibrium :**

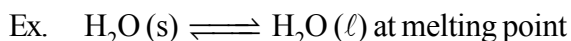
If in a system only physical state (phase) is changed and equilibrium is established, (i.e. there is no chemical change), the equilibrium is called **physical equilibrium**. Ex : Fusion of ice, evaporation of water, dissolution of salts, absorption of gases in liquid, etc.

Following are the types of common physical equilibria :

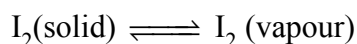
(i) **Liquid-Vapour equilibria** : In a closed vessel, the vapours above the liquid are in equilibrium at given temperature.



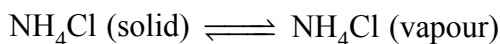
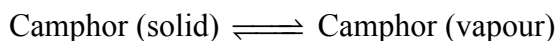
(ii) **Solid-Liquid equilibria** : This equilibrium can be established only at melting point of solid. At this stage solid and liquid phases exist simultaneously in equilibrium.



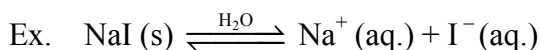
(iii) **Solid-Vapour equilibria** : Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as,



Other examples showing this kind of equilibrium are,



(iv) **(Solute-Solvent) Saturated solution equilibria** : If the rate of dissolution of solids in liquid is equal to the rate of crystallization of solid from solution i.e. solution is saturated with respect to solid then saturated solution equilibria established, provided temperature is constant.



(v) **(Gas + Solvent) Saturated solution equilibria** : In such equilibria, solvent is saturated with respect to gas i.e. rate of entering of gas molecules in solvent is equal to rate of escaping of gas molecules from solvents. Above phenomenon can be observed in closed container at definite temperature. Ex : Dissolved  $\text{CO}_2$  in cold drinks, dissolved  $\text{O}_2$  in water, etc.

**Note:** (i) The solubilities of gases in liquid is a function of pressure of gas over liquid.

(ii) **Henry's law** can be applied on such system, that states, the mass of gas dissolved in a given mass of solvent at any temperature is proportional to the pressure of the gas above the solvent.

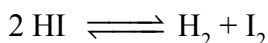
(iii) One should not compare it with liquid vapour equilibria.

## 2.2 Chemical equilibrium :

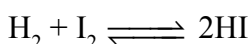
Analogous to the physical systems, chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products become constant. This is the stage of chemical equilibrium. This equilibrium consists of a forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants.

### 2.2.1 Characteristics of Chemical equilibrium :

- (i) It is attained in reversible chemical reactions only.
- (ii) Equilibrium is possible only in closed system.
- (iii) In this state, all the measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time, i.e. constant.
- (iv) Equilibrium is dynamic in nature i.e., at microscopic level reaction is not stopped. It appears that no change is occurring but both the opposing reactions are proceeding at the same rate. So there is no net change. Thus equilibrium is not static in nature.
- (v) Chemical equilibrium can be approached from both sides



or

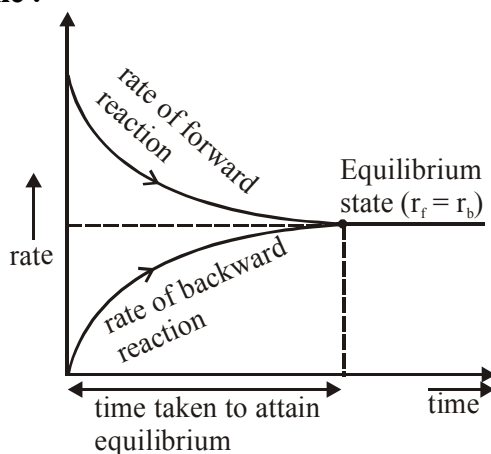


At equilibrium, reactants and products have fixed composition and this is independent of the fact whether the reaction start with the reactant or with the product.

- (vi) Equilibrium is not affected by the presence of catalyst. The catalyst only helps in attaining equilibrium rapidly.
- (vii) At equilibrium, opposing reactions (i.e., forward and backward) proceeds with equal rates. i.e., rate of forward reaction = rate of backward reaction.

- Note:**
- (i) Whenever question doesn't ask about direction, then we take forward direction only.
  - (ii) In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic and vice versa.

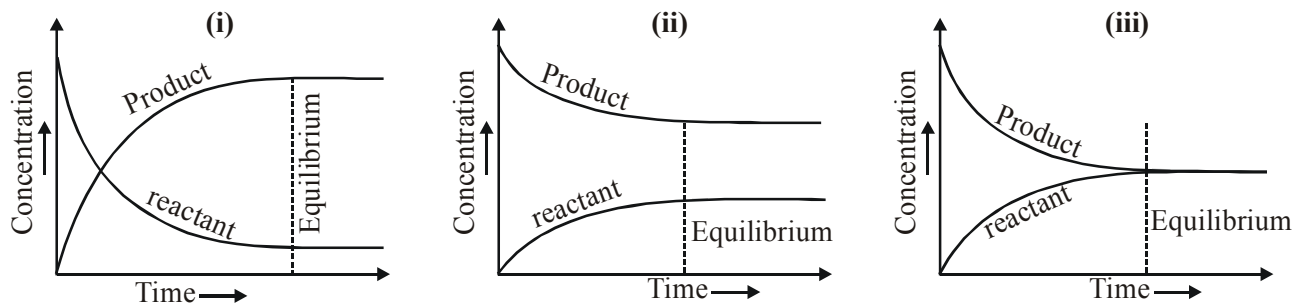
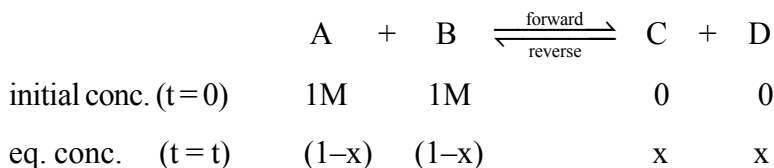
### 2.2.2 Variation of Rate v/s Time :



From above graph, initially rate of forward reaction decreases and the rate of backward reaction increases. At certain stage, rate of forward reaction becomes equal to rate of backward reaction called *equilibrium state*.

### 2.2.3 Variation of Concentration v/s Time :

Let us consider a reversible reaction,



In the beginning (at time  $t = 0$ ), the container has only the reacting molecules A and B while the products C and D are nil. With the passage of time, the reactants A and B will be used up or consumed to form the products, C and D. It means that the concentration or molar concentration of the reactants will decrease while those of the products will increase. A stage will be ultimately reached when their concentration becomes constant i.e., there will be no further change in concentration of either of the reactants A and B or of the products C and D. This represents a state of equilibrium.

**Note:** At equilibrium, the concentration of reactant and product will be constant. It means, it may be different as above graph (i) & (ii) or same as above graph (iii) but the rate of forward reaction and the backward reaction will be always same.

#### Ex.1 Chemical equilibrium is a condition :

- (A) where all species have same concentration
- (B) where all species have constant concentration with respect to time.
- (C) where all species have unit concentration
- (D) all of above

**Sol. (B)**

#### Ex.2 Example of physical equilibria, is :

- (A)  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- (B)  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
- (C)  $H_2O(s) \rightleftharpoons H_2O(l)$
- (D)  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

**Sol. (C)**

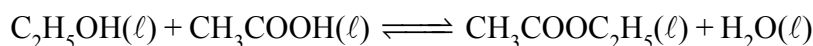
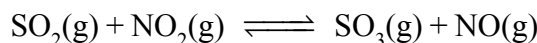
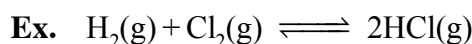
Physical equilibria does not include any chemical change.

### 3. TYPES OF CHEMICAL EQUILIBRIUM :

- I. Homogeneous equilibrium                      II. Heterogeneous equilibrium

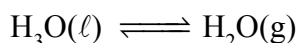
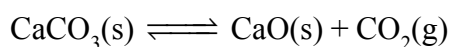
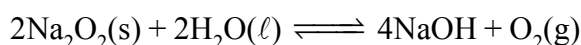
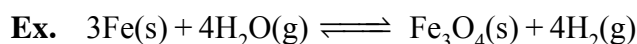
#### I. Homogeneous equilibrium :

It is the equilibrium when all reactants and products are in same phase.



#### II. Heterogeneous equilibrium :

It is the equilibrium the reactants and the products are present in different phases. All physical equilibria are heterogeneous.



### 4. ACTIVE MASS :

The mass of a substance which effect the rate of reaction i.e. mass of substance which take a part actively in a reaction. Active mass depends on state of substance.

- (i) **Solution state :** In this state, active mass of a substance is represented by concentration (molarity). Active mass is usually expressed in concentration by enclosing the symbol of the reactant in square bracket [ ].

$$\text{Active mass} = \frac{\text{moles}}{\text{Volume in litres}} = \frac{\text{grams(w)}}{\text{mol.wt.}(M_w) \times \text{Volume in litres}(V)} = \frac{w \times 1000}{M_w \times V(\text{mL})}$$

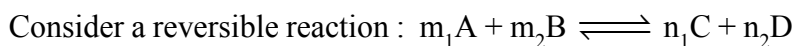
- (ii) **Gaseous state :** In this state, active mass of a substance may be represented as concentration (molarity) or partial pressure.
- (iii) **Pure solid & pure liquid :** In this state, active mass of solids , pure liquids and solvents in large excess is a constant quantity because there is no change in activity with the change in quantity or volume of system.

$$\text{Molar concentration (M)} = \frac{w}{M \times V} = \frac{d}{M} = \frac{\text{density of the substance}}{\text{molar mass of the substance}} = \text{constant}$$

as density of pure solids and liquids is constant and molar mass is also constant.

### 5. LAW OF MASS ACTION AND LAW OF EQUILIBRIUM CONSTANT :

The law of mass action is given by *Guldberg* and *Waage*. According to it, "the rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers equal to their stoichiometric coefficients".



According to law of mass action

rate of forward reaction ( $r_f$ )  $\propto (a_A)^{m_1} (a_B)^{m_2}$

$$r_f = k_f (a_A)^{m_1} (a_B)^{m_2}$$

rate of backward reaction ( $r_b$ )  $\propto (a_C)^{n_1} (a_D)^{n_2}$

$$r_b = k_b (a_C)^{n_1} (a_D)^{n_2}$$

At equilibrium  $r_f = r_b$

$$k_f (a_A)^{m_1} (a_B)^{m_2} = k_b (a_C)^{n_1} (a_D)^{n_2}$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{(a_C)^{n_1} (a_D)^{n_2}}{(a_A)^{m_1} (a_B)^{m_2}}$$

where,  $K_{eq}$  = equilibrium constant

$k_f$  = forward rate (velocity) constant

$k_b$  = backward rate (velocity) constant

$a_A, a_B$  = active mass of reactant A & B

$a_C, a_D$  = active mass of product C & D

$m_1, m_2$  = stoichiometry coefficient of reactant A & B

$n_1, n_2$  = stoichiometry coefficient of product C & D

At a given temperature, the product of molar concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of molar concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the *Equilibrium Law or Law of Chemical Equilibrium*.

#### 5.1 Types of equilibrium constant ( $K_{eq}$ ) :

- (i) **Equilibrium constant in terms of concentration ( $K_C$ ) :**  $K_C$  is defined for reactions in gas phase & solution phase. Molar concentrations are used to express amounts.
- (ii) **Equilibrium constant in terms of partial pressure ( $K_P$ ) :**  $K_P$  is defined for reactions in gas phase. Partial pressures are used to express amounts.

**Ex.** Consider a reversible reaction in gas phase :  $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$K_C = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}$$

$$K_P = \frac{(P_C)^{n_1} (P_D)^{n_2}}{(P_A)^{m_1} (P_B)^{m_2}}$$

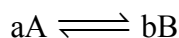
here,

$[A], [B], [C], [D]$  = Molar concentration of A, B, C, D respectively at equilibrium .

$(P_A), (P_B), (P_C), (P_D)$  = partial pressure of A, B, C, D respectively at equilibrium .

## 5.2 Units of equilibrium constant :

**5.2.1** The value of equilibrium constant  $K_c$  can be calculated by substituting the concentration terms in mol/L or M and for  $K_p$  partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same. For general reactions,



$$(i) \quad K_C = \frac{[B]^b}{[A]^a}$$

$$\text{unit of } K_C = \left(\frac{\text{mol}}{\text{L}}\right)^{b-a} = [M]^{b-a} = M^{\Delta n_g}$$

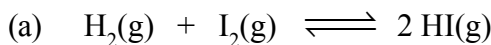
here,  $\Delta n_g = b - a = \text{moles of (Product - Reactant)}$

$$(ii) \quad K_p = \frac{(P_B)^b}{(P_A)^a}$$

$$\text{unit of } K_p = (\text{atm})^{b-a} = (\text{atm})^{\Delta n_g} \text{ or } (\text{Pa})^{\Delta n_g} \text{ or } (\text{bar})^{\Delta n_g}$$

here,  $\Delta n_g = b - a = \text{moles of (Product - Reactant)}$

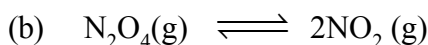
**Ex.3 Write down the expression and unit for following reaction :**



$$K_C = \frac{[HI]^2}{[H_2][I_2]} \quad \left(\frac{\text{mol}}{\text{L}}\right)^0$$

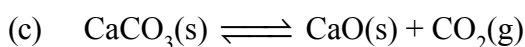
$$K_p = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} \quad (\text{atm})^0$$

$\therefore K_C$  and  $K_p$  have no unit.



$$K_C = \frac{[NO_2]^2}{[N_2O_4]} \quad \left(\frac{\text{mol}}{\text{L}}\right)^1$$

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}} \quad (\text{atm})^1$$

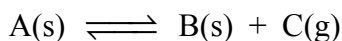


$$K_C = [CO_2] \quad \left(\frac{\text{mol}}{\text{L}}\right)^1$$

$$K_p = P_{CO_2} \quad (\text{atm})^1$$



**5.2.2** Equilibrium constants is expressed in standard state that is called standard state equilibrium constant or thermodynamic equilibrium constant, which is dimensionless quantity. It is denoted by  $K_c^0$  and  $K_p^0$ . For a pure gas, the standard state is 1 bar. Therefore a pressure of 4 bar in standard state can be expressed as  $4 \text{ bar}/1 \text{ bar} = 4$ , which is a dimensionless number and concentration of 3 M solution in standard state can be expressed as  $\frac{3\text{M}}{1\text{M}} = 3$ , which is a dimensionless number. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both  $K_c^0$  and  $K_p^0$  are dimensionless quantities but have different numerical values due to different standard states. For example,



$$K_c = [\text{C}] \quad (\text{mol/L})$$

$$\text{but } K_c^0 \text{ is a dimensionless quantity so } K_c^0 = \frac{[\text{C}]}{1\text{M}}$$

$$K_p = P_C \quad (\text{bar})^1$$

$$\text{but } K_p^0 \text{ is a dimensionless quantity so } K_p^0 = \frac{P_C}{1 \text{ bar}}$$

### 5.3 Relation between $K_p$ & $K_c$ :

For the reaction,  $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

we can write

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad \dots\dots\dots(\text{i})$$

Assuming the gaseous components to behave ideally,

$$P_i V_i = n_i RT$$

$$P_i = (n_i/V_i) RT = C_i RT = [i] RT$$

where  $[i]$  is the molar concentration of the species 'i'.

$$P_A = [\text{A}]RT, P_B = [\text{B}]RT, P_C = [\text{C}]RT, P_D = [\text{D}]RT$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} = \frac{([\text{C}]RT)^c ([\text{D}]RT)^d}{([\text{A}]RT)^a ([\text{B}]RT)^b} = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \times (RT)^{(c+d)-(a+b)}$$

from eq.(i)

$$K_p = K_c (RT)^{(c+d)-(a+b)}$$

$$\boxed{K_p = K_c (RT)^{\Delta n_g}}$$

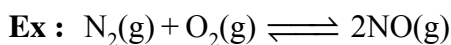
$\Delta n_g = (\text{Number of moles of gaseous products}) - (\text{Number of moles of gaseous reactants}).$

$$\Delta n_g = (c + d) - (a + b)$$

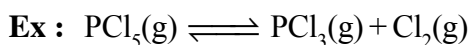
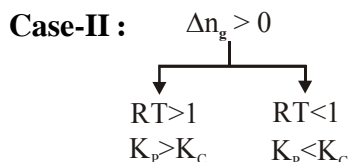
The units of  $K_p$  &  $K_c$  are not fixed and depend on stoichiometry of the reaction. In case the number of moles of the reactant & that of the product are same  $K_p$  &  $K_c$  do not have any unit.

#### 5.4 Different cases for $K_p = K_c(RT)^{\Delta n_g}$ :

**Case-I :** If  $\Delta n_g = 0$  then  $K_p = K_c$



$$K_p = \text{unit less} ; K_c = \text{unit less} ;$$

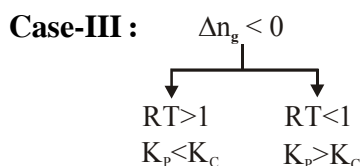


$$\Delta n_g = 2 - 1 = 1 \text{ then } K_p = K_c (RT)^1$$

$$\text{if } RT > 1 \text{ then } K_p > K_c$$

$$\text{if } RT < 1 \text{ then } K_p < K_c$$

$$\text{Unit: } K_p = \text{atm}^1 ; K_c = \text{conc.}^1$$



$$\Delta n_g = 2 - 4 = -2 \text{ then } K_p = K_c (RT)^{-2}$$

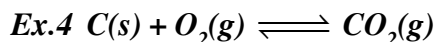
$$\text{if } RT > 1 \text{ then } K_p < K_c$$

$$\text{if } RT < 1 \text{ then } K_p > K_c$$

$$K_p = \text{atm}^{-2} ; K_c = \text{conc.}^{-2}$$

**Case-IV :** If  $T = \frac{1}{R} = \frac{1}{0.821} \approx 12.2 \text{ K}$

$$[K_p = K_c ; \text{for any value of } \Delta n_g]$$



Mole of  $O_2$  and  $CO_2$  are 5 mole and 10 mole at equilibrium respectively, then find  $K_p$  &  $K_c$  for above reaction.

**Sol.** Partial pressure = Mole fraction  $\times$  Total pressure

$$P_{CO_2} = X_{CO_2} \cdot P_T = \frac{n_{CO_2}}{n_T} \times P_T = \frac{10}{15} \times P_T$$

$$P_{O_2} = X_{O_2} \cdot P_T = \frac{n_{O_2}}{n_T} \times P_T = \frac{5}{15} \times P_T$$

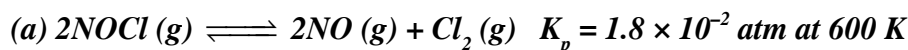
$$K_p = \frac{P_{CO_2}}{P_{O_2}}$$

$$K_p = \frac{\frac{10}{15} \times P_T}{\frac{5}{15} \times P_T} = 2$$

$$\therefore K_p = K_c (RT)^{\Delta n_g}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{2}{(RT)^0} = 2$$

**Ex.5** Find the values of  $K_c$  for each of the following equilibria from the value of  $K_p$ .



**Sol.** (a)  $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

$$K_p = 1.8 \times 10^{-2} \text{ atm} \quad \text{and} \quad \Delta n_g = 3 - 2 = 1$$

$$K_p = K_c (RT)^{\Delta n_g} = K_c \times (RT)$$

$$\therefore K_c = \frac{K_p}{RT} = \frac{1.8 \times 10^{-2}}{0.0821 \times 600} = 3.65 \times 10^{-4} \text{ M}$$

(b)  $K_p = 167 \text{ atm}$  and  $\Delta n_g = 1$

$$K_p = K_c (RT)^{\Delta n_g} = K_c \times (RT)$$

$$\therefore K_c = \frac{K_p}{RT} = \frac{167}{0.0821 \times 1173} = 1.734 \text{ M}$$

**Ex.6** In the reaction,  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$  the concentration of  $H_2$ ,  $I_2$  and  $HI$  at equilibrium are 10.0, 6.0 and 28 moles per litre respectively. What will be the equilibrium constant?

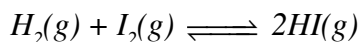
(A) 30.61

(B) 13.066

(C) 29.40

(D) 20.90

**Sol.(B)**



Applying law of mass action,

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$\begin{aligned} \text{Given } [H_2] &= 10 \text{ mol L}^{-1} \\ [I_2] &= 6.0 \text{ mol L}^{-1} \\ [HI] &= 28.0 \text{ mol L}^{-1} \end{aligned}$$

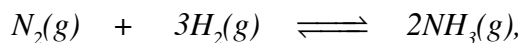
$$\text{So, } K_c = \frac{(28.0)^2}{(10) \times (6.0)} = 13.066$$

**Ex.7** For a gas phase reaction at equilibrium,

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ , the partial pressures of  $H_2$  and  $N_2$  are 0.4 and 0.8 atmosphere respectively. The total pressure of the entire system is 2.4 atmosphere. What will be the value of  $K_p$  if all the pressures are given in atmosphere ?

- (A)  $32 \text{ atm}^{-2}$       (B)  $20 \text{ atm}^{-2}$       (C)  $28.125 \text{ atm}^{-2}$       (D)  $80 \text{ atm}^{-2}$

**Sol.(C)**



Partial pressures at equilibrium

$$0.8 \quad 0.4 \quad [2.4 - (0.8 + 0.4) = 1.2]$$

Applying law of mass action,

$$K_p = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{1.2 \times 1.2}{0.8 \times 0.4 \times 0.4 \times 0.4} \Rightarrow K_p = 28.125 \text{ atm}^{-2}$$

**Ex.8.**  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$  ; Correct option for reaction is/are :

- (a)  $K_p = K_c$   
 (b)  $K_p > K_c$   
 (c)  $K_p < K_c$   
 (d) any of these, depending on temperature.

**Sol.(D)**

If (d) option is not given, then the answer is (b) because  $\frac{1}{R} \approx 12.2K$  which is very low relative to room temperature.

**Ex.9.** For which of the following reactions,  $K_p > K_c$  at  $25^\circ C$  (298K)

- (a)  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$   
 (b)  $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$   
 (c)  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$   
 (d)  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$   
 (e)  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

**Sol.** (b, d, e)

**Ex.10.** For a gaseous reaction  $K_p = 0.4 \text{ atm}^3$  at  $27^\circ\text{C}$ . Calculate  $K_c$ .

**Sol.**  $K_p = K_c (RT)^{\Delta n}$

$$0.4 = K_c (0.0821 \times 300)^3$$

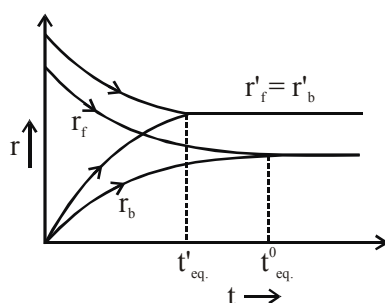
$$K_c = 2.6 \times 7 \times 10^{-8} \text{ M}^3$$

**6. Characteristics of equilibrium constant :**

- (i) The expression for equilibrium constant  $K$  is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.
- (ii) The value of equilibrium constant is independent of initial concentration of the reactants and product.
- (iii) Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.
- (iv) Value of equilibrium constant is not affected by catalyst. Catalyst simply helps in attaining equilibrium earlier.  
The relative increase in the rate of forward as well as backward reaction remain same on using the catalyst.

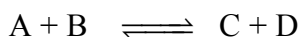
$$K_{\text{eq. uncatalyst}} = \frac{K_f}{K_b}$$

$$K_{\text{eq. catalyst}} = \frac{K_f \times x}{K_b \times x} = \frac{K_f}{K_b} = K_{\text{eq. (uncatalyst)}}$$



**6.1 Factor affecting the equilibrium constant :**

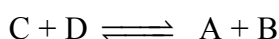
**(A) Mode of representation of the reaction :**



The equilibrium constant for the reaction

$$K_c = \frac{[C][D]}{[A][B]}$$

If the reaction is reversed



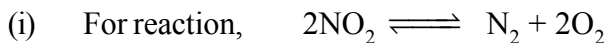
then,  $K'_c = \frac{[A][B]}{[C][D]}$

The two equilibrium constant related as ;  $K_c = \frac{1}{K'_c}$

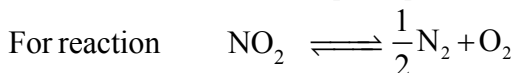
*If the reaction is reversed, the value of the equilibrium constant is inverted.*

**(B) Stoichiometry of the reaction :**

When a reversible reaction can be written with the help of two or more stoichiometric equation, the value of equilibrium constant will be numerically different.

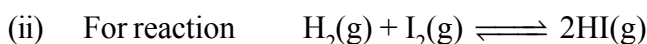


$$K_c = \frac{[\text{N}_2][\text{O}_2]^2}{[\text{NO}_2]^2}$$

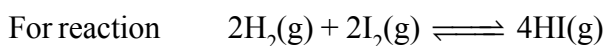


$$K'_c = \frac{[\text{N}_2]^{\frac{1}{2}}[\text{O}_2]}{[\text{NO}_2]}$$

The two constants are related as  $K'_c = \sqrt{K_c}$

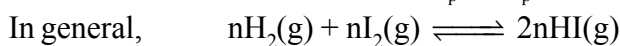


$$K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} \cdot P_{\text{I}_2}}$$



$$K'_p = \frac{P_{\text{HI}}^4}{P_{\text{H}_2}^2 \cdot P_{\text{I}_2}^2}$$

The two constants are related as  $K'_p = K_p^2$ .



$$K' = K^n$$

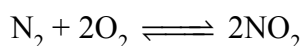
**When the coefficient of a balanced equation are multiplied by a common factor 'n', the equilibrium constant must be raised to the respective factor,  $K_{\text{eq}}^n$ .**

**(C) Addition the reaction :**

For the 1<sup>st</sup> step,  $K_1 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$

For the 2<sup>nd</sup> step,  $K_2 = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$

from eq. (i) + (ii)



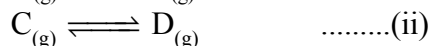
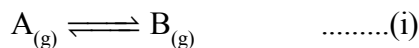
For this reaction,  $K = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2}$

the above reaction is related as

$$\therefore K_1 \times K_2 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2} = K$$

**If there is addition of two reaction then the equilibrium constant is multiplied.**

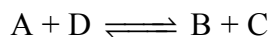
(D) Subtract the reaction :



For the (i) step,  $K_1 = \frac{[B]}{[A]}$

For the (ii) step,  $K_2 = \frac{[D]}{[C]}$

from eq. (i) – (ii)



For this reaction,  $K = \frac{[B][C]}{[A][D]}$

the above reaction is related as,  $K = \frac{K_1}{K_2} = \frac{[B]}{[A]} \times \frac{[C]}{[D]} = K$

**If we subtract of two reaction, then the equilibrium constant will be divided.**

**Ex.11** What should be the equilibrium constant for the reaction  $HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$  if the equilibrium constant for the reaction  $H_2 + I_2 \rightleftharpoons 2HI$  at  $444^\circ C$  is 64 ?

(A) 64

(B) 8

(C) 0.12

(D) 0.81



$$K_1 = \frac{[HI]^2}{[H_2][I_2]} \quad K_2 = \frac{[H_2]^{1/2}[I_2]^{1/2}}{[HI]}$$

Therefore,  $K_2 = \frac{1}{\sqrt{K_1}} = \frac{1}{\sqrt{64}} = \frac{1}{8} = 0.12$

**(E) Equilibrium constant depends upon the temperature.**

The equilibrium constant of a particularly balanced reaction depends only on temperature. It is independent from all other factor like amount of components, concentration, pressure, volume etc.

$$K_{eq.} = \frac{K_f}{K_b}$$

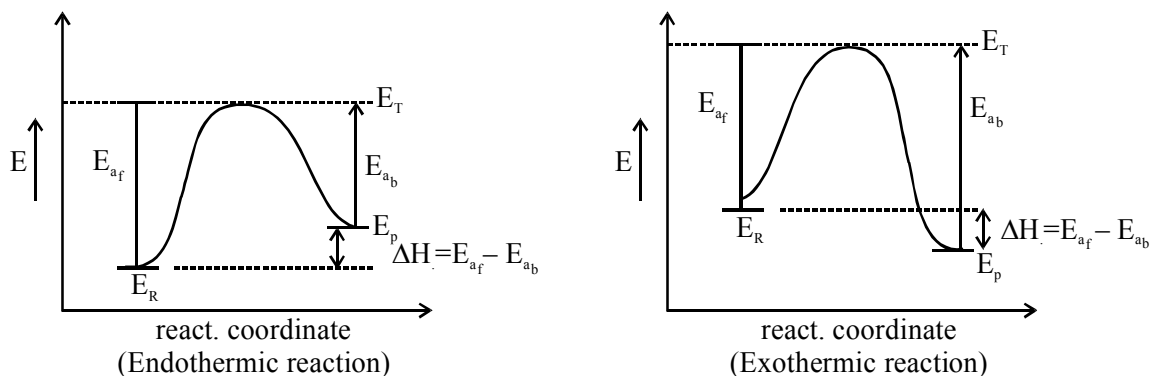
And rate constant,  $K = A \cdot e^{-E_a/RT}$

Now,  $K_{eq.} = \frac{K_f}{K_b} = \frac{A_f \cdot e^{-E_{af}/RT}}{A_b \cdot e^{-E_{ab}/RT}} = \frac{A_f}{A_b} \cdot e^{-(E_{af}-E_{ab})/RT}$

$$K_{eq.} = A \cdot e^{-\Delta H/RT} \quad (\text{Van't Hoff's equation})$$

where  $A = \frac{A_f}{A_b} = \text{constant}$

and  $\Delta H = E_{af} - E_{ab}$



If  $K_1$  and  $K_2$  be the equilibrium constants of a reaction at absolute temperatures  $T_1$  and  $T_2$ , then

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

On increasing the temperature the rate constant of reaction increases. But the reaction with higher activation energy is more sensitive towards temperature change. For the reaction of higher activation energy the value of rate constant increases largely on increasing temperature as well as the rate constant decreases largely as decrease in temperature.

For endothermic reaction

$$\Delta H = E_{a_f} - E_{a_b} = +ve$$

$$\Rightarrow T \uparrow ; K_{eq} = \frac{K_f \uparrow}{K_b \uparrow} \quad (K_f \text{ larger increasing and hence } K_{eq} \text{ increase})$$

For exothermic reaction

$$\Delta H = E_{a_f} - E_{a_r} = -ve$$

$$\Rightarrow T \uparrow ; K_{eq} = \frac{K_f \uparrow}{K_b \uparrow} \quad (K_b \text{ larger increasing and hence } K_{eq} \text{ decreases})$$

**Ex.12** The equilibrium constant for the reaction  $H_2(g) + S(s) \rightleftharpoons H_2S(g)$  is 18.5 at 925 K and 9.25 at 1000 K respectively. The enthalpy of the reaction will be :

(A)  $-68000.05 \text{ J mol}^{-1}$

(B)  $-71080.57 \text{ J mol}^{-1}$

(C)  $-80071.75 \text{ J mol}^{-1}$

(D)  $57080.75 \text{ J mol}^{-1}$

**Sol.(B)**

Using the relation,

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{9.25}{18.5} = \frac{\Delta H}{2.303 \times 8.314} \times \frac{75}{925 \times 1000}$$

$$-0.301 = \frac{\Delta H \times 75}{2.303 \times 8.314 \times 925 \times 1000} \Rightarrow \Delta H = -71080.57 \text{ J mol}^{-1}$$



**Ex.13.** The equilibrium  $2A + B_2 \rightleftharpoons 2AB$  involves the two component equilibria,

$A + B_2 \rightleftharpoons AB + B$  and  $A + B \rightleftharpoons AB$  with respective equilibrium constants  $K_1$  and  $K_2$ . How is the equilibrium constant,  $K$ , for the overall equilibrium related to  $K_1$  and  $K_2$ ?

- (A)  $K = K_1 + K_2$       (B)  $K = K_1 K_2$       (C)  $K = K_1 / K_2$       (D)  $K / 2 = K_1 K_2$

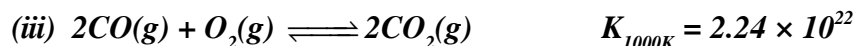
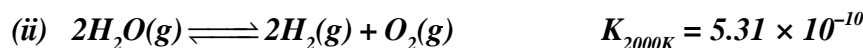
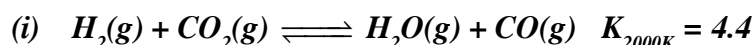
**Sol.** (B)

**Ex.14.** For the reactions :



**Sol.**  $9.04 \times 10^{-16}$

**Ex.15.** From the following data :



State whether the reaction (iii) is exothermic or endothermic?

**Sol.** Equation (iii) =  $-[2 \times (i) + (ii)]$

$$\therefore K_{2000(iii)} = \frac{1}{K_1^2 K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

$$\therefore T \uparrow K \downarrow \Rightarrow \text{reaction is exothermic.}$$

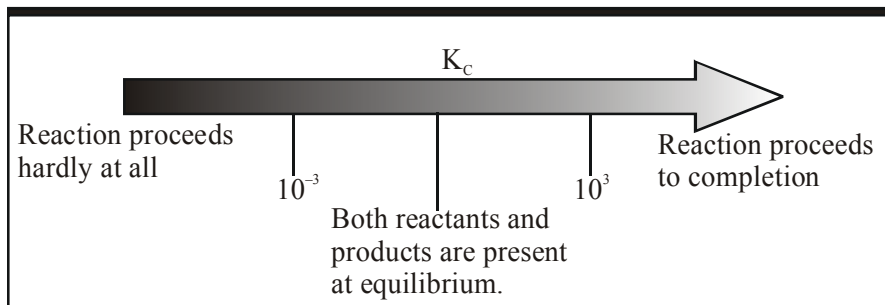
## 7. APPLICATION OF EQUILIBRIUM CONSTANT :

- (I) Predicting the extent of a reaction
- (II) Predicting the direction of the reaction and
- (III) Calculating equilibrium composition.

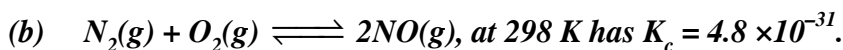
### 7.1 Predicting the extent of reaction :

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium does not give any information about the rate at which the equilibrium is reached. The magnitude of  $K_c$  or  $K_p$  is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of  $K$  is suggestive of a high concentration of products and vice-versa. We can make the following generalisations concerning the composition of equilibrium mixtures:

- (i) If  $K_c > 10^3$ , products predominate over reactants. If  $K_c$  is very large, the reaction proceeds almost all the way to completion.
- (ii) If  $K_c < 10^{-3}$ , reactants predominate over products. If  $K_c$  is very small, the reaction proceeds hardly at all.
- (iii) If  $K_c$  is in the range  $10^{-3}$  to  $10^3$ , appreciable concentration of both reactants and products are present.



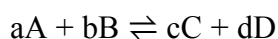
**Ex.16** In the following cases which is predominant (reactant or product) for the given value of  $K_c$ .



- Sol.** (a) If  $K_c > 10^3$ , products predominate over reactants. If  $K_c$  is very large, the reaction proceeds almost all the way to completion.
- (b) If  $K_c < 10^{-3}$ , reactants predominate over products. If  $K_c$  is very small, the reaction proceeds hardly at all.
- (c) Also, gas phase decomposition of  $N_2O_4$  to  $NO_2$  is another reaction with a value of  $K_c = 4.64 \times 10^{-3}$  at  $25^\circ C$  which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both  $N_2O_4$  and  $NO_2$ .

## 7.2 Predicting the direction of the Reaction :

The equilibrium constant is also used to find in which direction, the reaction mixture of reactants and products will proceed. For this purpose, we calculate the reaction quotient,  $Q$ . The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give  $Q_c$ , or with partial pressure to give  $Q_p$ ) at any stage of reaction. For a general reaction:



$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Then, if  $Q_c > K_c$ , the reaction will proceed in the direction of reactants (reverse reaction).

if  $Q_c < K_c$ , the reaction will move in the direction of the products

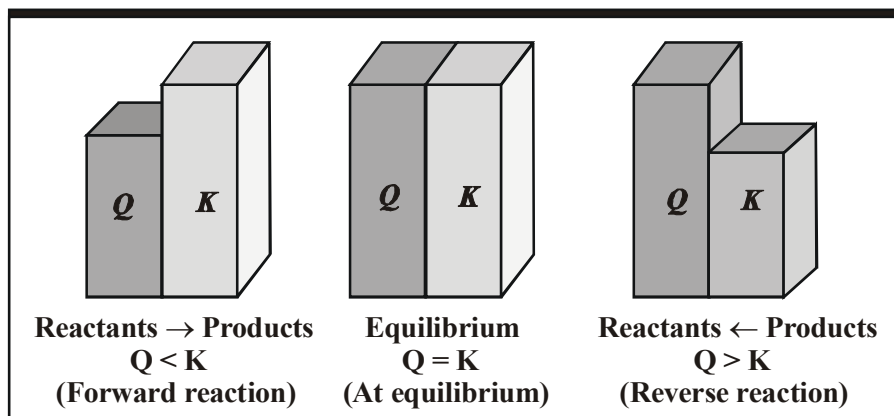
if  $Q_c = K_c$ , the reaction mixture is already at equilibrium.

In the reaction,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , if the molar concentrations of  $\text{H}_2$ ,  $\text{I}_2$  and  $\text{HI}$  are 0.1 M, 0.2 M and 0.4 M, respectively at 783 K, then reaction quotient at this stage of the reaction is

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

$K_c$  for this reaction at 783 K is 46 and we find that  $Q_c < K_c$ . The reaction, therefore, will move to right i.e. more  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$  will react to form more  $\text{HI}(\text{g})$  and their concentration will decrease till  $Q_c = K_c$ .

Thus, a reaction has a tendency to form products if  $Q < K$  and to form reactants if  $Q > K$ .



**Ex.17.** For the reaction  $\text{NOBr}(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \frac{1}{2}\text{Br}_2(\text{g})$

$K_p = 0.15$  atm at  $90^\circ\text{C}$ . If  $\text{NOBr}$ ,  $\text{NO}$  and  $\text{Br}_2$  are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 2.0 atm respectively, will  $\text{Br}_2$  be consumed or formed ?

**Sol.** 
$$Q_p = \frac{[\text{P}_{\text{Br}_2}]^{1/2}[\text{P}_{\text{NO}}]}{[\text{P}_{\text{NOBr}}]} = \frac{[0.20]^{1/2}[0.4]}{[0.50]} = 0.36$$

$\therefore K_p = 0.15$

Hence, reaction will shift in backward direction

$\therefore \text{Br}_2$  will be consumed

**Ex.18.** Predict whether 1%  $\text{CO}_2$  in air be sufficient to prevent any loss in weight of  $\text{MgCO}_3$  or not.

**Sol.**  $\text{MgCO}_3(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{CO}_2(\text{g}) \quad K_p = 0.095$  atm

$$Q = \frac{P_{\text{CO}_2}}{1} = P_{\text{CO}_2} = X_{\text{CO}_2} \cdot 1_{\text{total}}$$

$$\frac{1}{100} \times 1 \text{ atm} = 0.01 \text{ atm} < K_p$$

It will go in forward direction

0.1%  $\text{CO}_2$  is not sufficient

**Ex.19.** Predict whether  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$  be efflorescent or  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}(\text{s})$  be hygroscopic and vapour pressure of  $\text{H}_2\text{O}$  at  $25^\circ\text{C} = 0.04 \text{ atm}$ .

**Sol.**  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{g}) \quad K_p = 4 \times 10^{-4} \text{ atm}$

Partial pressure of  $\text{H}_2\text{O}$  at eq. =  $P_{\text{H}_2\text{O}}$

$$K_p = P_{\text{H}_2\text{O}}^2$$

$$P_{\text{H}_2\text{O}} = \sqrt{4 \times 10^{-4}} = 2 \times 10^{-2} \text{ atm}$$

$$Q = 4 \times 10^{-2} \text{ atm}$$

So,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  be hygroscopic in this condition.

**Ex.20.** In above problem what maximum humidity for which  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$  work as efflorescent.

**Sol.**  $\left(0.04 \times \frac{x}{100}\right)^2 < 4 \times 10^{-4}$

$$0.16 \times 10^{-4} \times \frac{x^2}{10000} < 4 \times 10^{-4}$$

$$x^2 < 50$$

$$x < 50\%$$

Max. R.H. = 50% Ans.

**Ex.21.** Study the following reaction



(i) Which of the following is best dehydrating drying agent.

(A) A.  $2\text{H}_2\text{O}(\text{g})$  (D) A(s)

(B) B.  $3\text{H}_2\text{O}(\text{g})$  (E) B(s)

(C) C.  $4\text{H}_2\text{O}(\text{g})$  (F) C(s)

$$\text{A} \rightarrow K_p = P_{\text{H}_2\text{O}}^2 \Rightarrow P_{\text{H}_2\text{O}} = 0.02 \text{ atm}$$

$$\text{B} \rightarrow K_p = P_{\text{H}_2\text{O}}^3 \Rightarrow P_{\text{H}_2\text{O}} = 0.03 \text{ atm}$$

$$\text{C} \rightarrow K_p = P_{\text{H}_2\text{O}}^4 \Rightarrow P_{\text{H}_2\text{O}} = 0.04 \text{ atm}$$

For the best dehydrating agent the moisture remained must be minimum.

(ii) If A(s), B(s) and C(s) are placed in a room where  $P_{\text{H}_2\text{O}}(\text{g}) = 0.025 \text{ atm}$ , which will act as dehydrating agent.

(A) A(s) (B) B(s) & C(s) (C) B(s) (D) All

(iii) Which of the following will be efflorescent at 7.5% R.H. if aqueous term = 0.04 atm.

(a) Only A.  $2\text{H}_2\text{O}(\text{s})$  (b) Only B.  $3\text{H}_2\text{O}(\text{s})$

(c) Only C.  $4\text{H}_2\text{O}(\text{s})$  (d) Only A.  $2\text{H}_2\text{O}(\text{s})$  & B.  $3\text{H}_2\text{O}(\text{s})$

(e) Only B.  $3\text{H}_2\text{O}(\text{s})$  & C.  $4\text{H}_2\text{O}(\text{s})$

**Sol.** (i) D (ii) A (iii) C

### 7.3 Calculating equilibrium concentrations :

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed :

**Step 1.** Write the balanced equation for the reaction.

**Step 2.** Under the balanced equation, make a table that lists for each substance involved in the reaction :

- (a) the initial concentration,
- (b) the change in concentration on going to equilibrium, and
- (c) the equilibrium concentration.

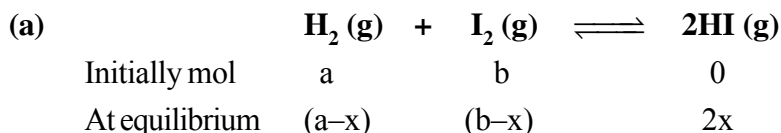
In constructing the table, define  $x$  as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of  $x$ .

**Step 3.** Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for  $x$ . If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

**Step 4.** Calculate the equilibrium concentrations from the calculated value of  $x$ .

**Step 5.** Check your results by substituting them into the equilibrium equation.

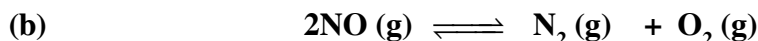
#### 7.3.1 Some General Equilibrium Expressions :



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_p = \frac{(p_{\text{HI}})^2}{p_{\text{H}_2} \times p_{\text{I}_2}} = \frac{\frac{(2x)^2}{(a+b)^2} P^2}{\left(\frac{a-x}{a+b} \cdot P\right)\left(\frac{b-x}{a+b} \cdot P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

So  $K_c = K_p$  ( $\Delta n_g = 0$ )



Initially mol	a	0	0
At equilibrium	(a-x)	x/2	x/2

$$K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2} = \frac{x/2 \times x/2}{(a-x)^2} = \frac{x^2}{4(a-x)^2} = K_p \quad (\Delta n_g = 0)$$



Initially mol	a	b	0	0
At equilibrium	(a-x)	(b-x)	x	x

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{x^2}{(a-x)(b-x)}$$

$K_p$  should not be given for this reaction ,



Initially mol	a	0	0
At equilibrium	(a-x)	x	x
Active mass	$\frac{(a-x)}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\frac{x}{v} \times \frac{x}{v}}{(a-x)} = \frac{x^2}{(a-x)v}$$

$$K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\left(\frac{x}{a+x} \cdot P\right) \times \left(\frac{x}{a+x} \cdot P\right)}{\left(\frac{a-x}{a+x}\right) P} = \frac{x^2 P}{(a+x)(a-x)} = \frac{x^2 P}{a^2 - x^2}$$

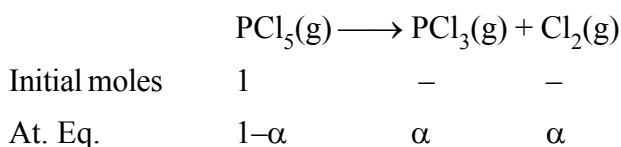


Initially mol	a	b	0
At equilibrium	(a-x)	(b-3x)	2x
Active mass	$\frac{(a-x)}{v}$	$\left(\frac{b-3x}{v}\right)$	$\left(\frac{2x}{v}\right)$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3} = \frac{4x^2 v^2}{(a-x)(b-3x)^3}$$

$$K_p = \frac{(p_{\text{NH}_3})^2}{p_{\text{N}_2} \times (p_{\text{H}_2})^3} = \frac{\left[\frac{2xP}{a+b-2x}\right]^2}{\left[\frac{(a-x)P}{a+b-2x}\right] \left[\frac{(b-3x)P}{a+b-2x}\right]^3} = \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3 P^2}$$

(g) Equilibrium constant expressions in term of 'α'



$$K_C = \frac{\alpha^2}{1-\alpha} \left( \frac{1}{V} \right) \quad \text{and} \quad K_P = \frac{\alpha^2}{1-\alpha^2} P_T$$

(h) Degree of dissociation in terms of molar mass and vapour density

(i)  $\text{A}(\text{g}) \rightleftharpoons n\text{B}(\text{g})$

$$\alpha = \frac{M_T - M_O}{M_O(n-1)} \quad \text{or} \quad \alpha = \frac{D_T - D_O}{D_O(n-1)}$$

$M_T$  = Theoretical molar mass of reactant

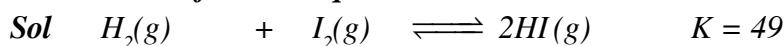
$M_O$  = Observed molar mass of mixture

$$D_T = \frac{M_T}{2} \quad \text{and} \quad D_O = \frac{M_O}{2}$$

(ii)  $n\text{A}(\text{g}) \rightleftharpoons \text{A}_n(\text{g})$

$$\alpha = \frac{M_T - M_O}{M_O \left( \frac{1}{n} - 1 \right)}$$

**Ex.22** 5 moles  $\text{H}_2$  gas and 5 moles iodine-vapours are taken in vessel of 10 L capacity. Determine the moles of each at equilibrium.



$$49 = \frac{(2x)^2 v^2}{(5-x)(5-x)v^2}$$

$$49 = \frac{(2x)^2}{(5-x)^2}$$

$$7 = \frac{2x}{5-x}$$

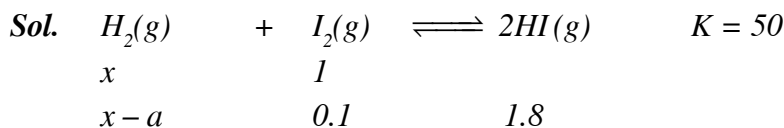
$$35 - 7x = 2x$$

$$35 = 9x$$

$$x = \frac{35}{9}$$

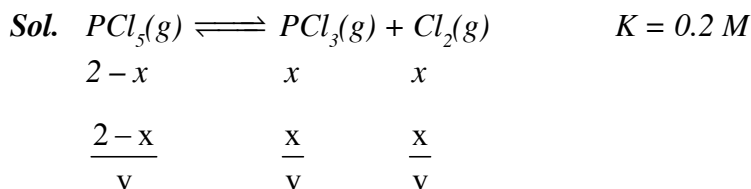
$$\text{Moles at equilibrium} = \frac{10}{9}, \frac{10}{9}, \frac{70}{9}$$

**Ex.23** How many moles of  $H_2(g)$  should be mixed with each mole  $I_2$  vapours in order to convert 90% of it into  $HI$ .



$$50 = \frac{3.24}{(x-0.9)(0.1)} \Rightarrow x = 1.548$$

**Ex.24** 2 moles of  $PCl_5(g)$  is taken in 10 l vessel. Calculate its concentration at equilibrium.



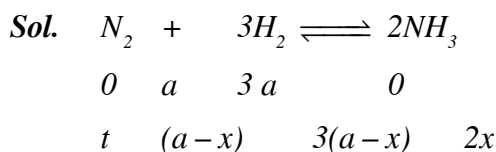
$$0.2 = \frac{\left(\frac{x}{v}\right)^2}{\left(\frac{2-x}{v}\right)} \Rightarrow x = 1.24$$

$$[PCl_5] = 0.076 M$$

$$[PCl_3] = 0.124 M$$

$$[Cl_2] = 0.124 M$$

**Ex.25** 1 : 3 molar ratio mixture of  $N_2$  and  $H_2$  yields 20% by mole  $NH_3$  at 30 atm; calculate  $K_p$  for the equilibrium represented by



$$\text{Total moles} = 4a - 2x$$

$$X_{NH_3} = 0.2 = \frac{2x}{4a - 2x} \Rightarrow 2x = 0.8a - 0.4x \Rightarrow x = a/3$$

$$P_{NH_3} = 0.2 \times 30 = 6 \text{ atm}$$

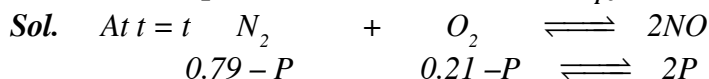
$$P_{N_2} = X_{N_2} \times P_T = \frac{a-x}{4a-2x} \times 30 = 0.2 \times 30 = 6 \text{ atm}$$

$$P_{H_2} = \frac{3(a-x)}{4a-2x} = 0.6 \times 30 = 18 \text{ atm}$$

$$\therefore K_p = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{6}{6 \times (18)^2} = 1.03 \times 10^{-3} \text{ atm}^{-2}$$



**Ex.27** An air sample containing 21:79 (mole ratio) of  $O_2$  &  $N_2$  is heated to  $2400^\circ C$ . If the mole percent of  $NO$  at equilibrium is 1.8%, calculate  $K_p$  for the reaction  $N_2 + O_2 \rightleftharpoons 2NO$ .



$$X_{NO} = 0.018$$

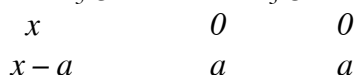
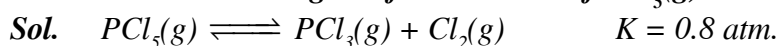
$$P_{NO} = 0.018 \times P_T$$

$$2P = 0.018 \times P_T \quad [\because \Delta n = 0 \Rightarrow P_T = 1 \text{ atm}]$$

$$P = \frac{0.018 \times 1}{2} = 0.009$$

$$K_p = \frac{[P_{NO}]^2}{P_{N_2} \times P_{O_2}} = \frac{(0.018)^2}{(0.781)(0.201)} = 2.06 \times 10^{-3}$$

**Ex.28** Calculate the degree of dissociation of  $PCl_5(g)$  at 20 atm.



$$\text{Total mole} = x + a$$

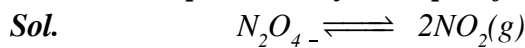
$$\frac{x-a}{x+a}(20) \quad \frac{a}{x+a}20 \quad \frac{a}{x+a}20$$

$$0.8 = \frac{\left(\frac{a}{x+a}\right)^2 (20)^2}{\left(\frac{x-a}{x+a}\right) 20} \Rightarrow 0.04 = \frac{a^2}{x^2 - a^2}$$

$$\frac{x}{a} = \frac{1}{\sqrt{26}} = 0.2$$

$$\alpha = 0.2$$

**Ex.28** The vapour density a sample of  $N_2O_4(g)$  is 40 at 10 atm. Calculate  $K_p$  for the reaction.



$$\text{Initial} \quad a \quad 0$$

$$a - x \quad 2x$$

$$\text{Total mole} = (a - x) + 2x = a + x$$

$$\frac{a-x}{a+x} P \quad \frac{2x}{a+x} P$$

$$V.D. = \frac{M_{avg}}{2}$$

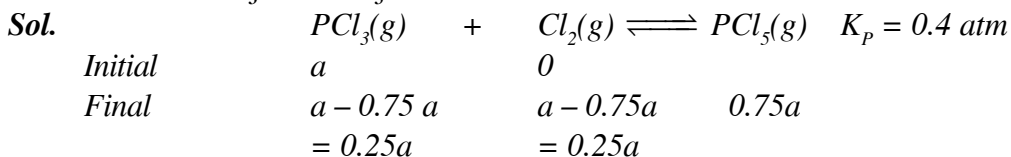
$$M_{avg} = 2 \times 40 = 80$$

$$M_{avg} = \frac{\text{Total mass}}{\text{Total moles}} = \frac{92a}{a+x} = 80$$

$$x = \frac{12}{80} a = 0.15a$$

$$K_p = \frac{4x^2}{a^2 - x^2} = 9.2 \times 10^{-2}$$

**Ex.29** At what pressure an equimolar mixture of  $\text{PCl}_3(\text{g})$  and  $\text{Cl}_2(\text{g})$  should be taken in order to convert 75% of  $\text{PCl}_3$  into  $\text{PCl}_5$ .



Total mole =  $1.25a$

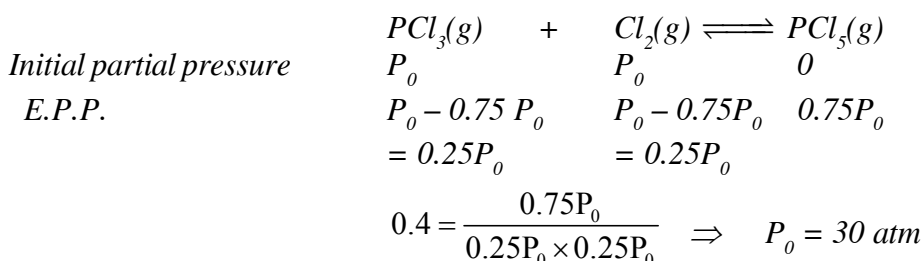
Equ. par. pr.	$\frac{0.25a \times P}{1.25a}$	$\frac{0.25a \times P}{1.25a}$	$\frac{0.75a \times P}{1.25}$
	$\frac{P}{5}$	$\frac{P}{5}$	$\frac{3P}{5}$

$$K_p = \frac{P_{\text{PCl}_5}}{P_{\text{PCl}_3} P_{\text{Cl}_2}} \Rightarrow 0.4 = \frac{\frac{3P}{5}}{\frac{P}{5} \times \frac{P}{5}} \Rightarrow P = 37.5$$

But this is pressure at equilibrium but we have to find initial pressure  
Now, from  $PV = nRT$

$$\frac{P_1}{P_2} = \frac{n_1}{n_2} \Rightarrow \frac{P_1}{37.5} = \frac{2}{1.25} \Rightarrow P = 60 \text{ atm}$$

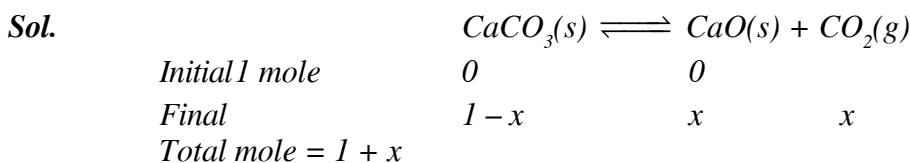
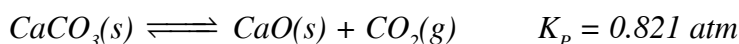
**Alternate method :**



$\therefore$  Initial total pressure of mixture =  $P_0 + P_0 = 60 \text{ atm}$

**Note :** In any problem related with relative extent of reaction, initial mole may be taken as 1 but the initial pressure or concentration should not be taken as 1.

**Ex.30** 100 gm  $\text{CaCO}_3$  is taken in 30 l empty vessel and the vessel is sealed and the sample is heated to  $627^\circ\text{C}$ . Calculate the mass % of  $\text{CaCO}_3$  decomposed.

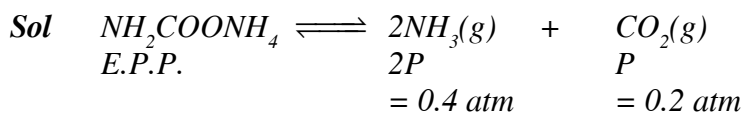


$$K_p = \frac{P_{\text{CO}_2}}{1} = P_{\text{CO}_2} \Rightarrow P_{\text{CO}_2} = \frac{n \cdot RT}{V}$$

$$0.821 = \frac{x \times 0.0821 \times 900}{30} \Rightarrow x = \frac{1}{3}$$

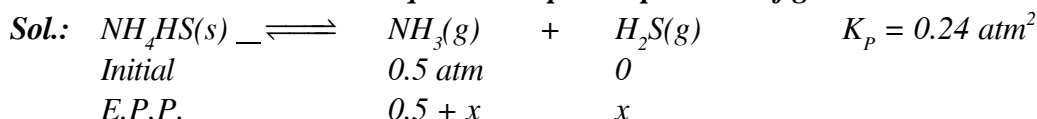
$$\% \text{ of } \text{CaCO}_3 \text{ decomposed} = \frac{1}{3} \times 100 = \frac{100}{3} \%$$

**Ex.31** Some solid ammonium carbamate  $NH_4COONH_4$  is taken in an evacuated vessel and the vessel is sealed after a very long time a constant pressure of 0.6 atm is observed due to dissociation of the solid into  $NH_3$  and  $CO_2$  gas. Calculate the dissociation constant of solid.



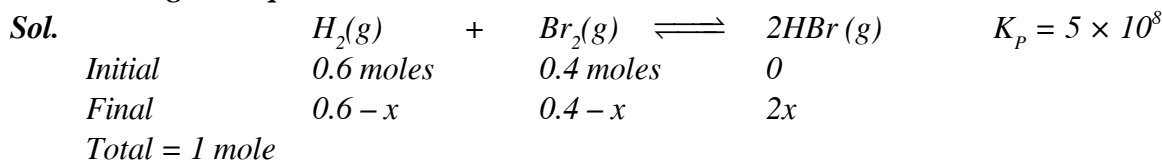
$$K_p = \frac{[0.4]^2 [0.2]}{1} = 0.032 \text{ atm}^3$$

**Ex.32** Some solid ammonium hydrogen sulphide  $NH_4HS$  is in a vessel containing ammonium gas at 0.5 atm. Calculate the equilibrium partial pressure of gas.



$$K_p = \frac{P_{NH_3} \cdot P_{H_2S}}{1} \Rightarrow 0.24 = (0.5 + x)x \Rightarrow x = 0.3 \text{ atm.}$$

**Ex.33** 0.6 moles of  $H_2(g)$  and 0.4 moles of  $Br_2$  vapour are allowed to react. Calculate the moles of each gas at equilibrium.



$$K = \frac{(2x)^2}{(0.6 - x)(0.4 - x)} = \frac{4x^2}{x^2 - x + 0.24}$$

$$(5 \times 10^8 - 4)x^2 - 5 \times 10^8 x + 1.2 \times 10^8 = 0$$

$$5 \times 10^8 x^2 - 5 \times 10^8 x + 1.2 \times 10^8 = 0$$

$$8x^2 - x + 0.24 = 0$$

$$x = 0.4, 0.6 \text{ (Not acceptable)}$$

As  $K_p$  is much larger than 1000 the reaction almost completes.

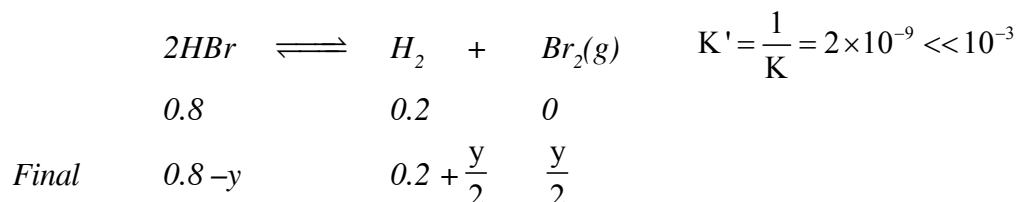
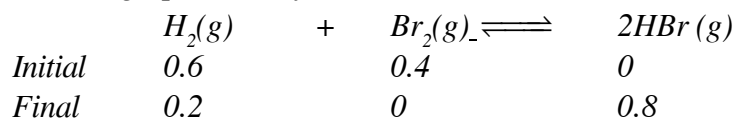
$$\text{Final moles of } HBr = 0.8$$

$$\text{Final moles of } H_2 = 0.2$$

But Final moles of  $Br_2 \neq 0$

**Note :**

The final moles of  $Br_2$  may be calculated by first completing the reaction in forwards direction and then achieving equilibrium from backward direction.



$$K' = \frac{[H_2][Br_2]}{[HBr]^2} = 2 \times 10^{-9} = \frac{\left(0.2 + \frac{y}{2}\right) \frac{y}{2}}{(0.8 - y)^2}$$

As  $K'$  is very small we may assume that  $0.8 - y \simeq 0.8$

and,  $0.2 + \frac{y}{2} \simeq 0.2$

$$\therefore 2 \times 10^{-9} = \frac{0.2 \times \frac{y}{2}}{0.64}$$

$$y = 1.28 \times 10^{-8}$$

Final moles  $HBr = 0.8 - y \simeq 0.8$

$$H_2 = 0.2 + \frac{y}{2} \simeq 0.2$$

$$Br_2 = \frac{y}{2} = 6.4 \times 10^{-9}$$

**Ex.34** Calculate concentration of A at equilibrium for a reaction,  $A(g) \rightleftharpoons B(g)$ ;  $K_C = 10^{50}$ , if the initial concentration of A is 2 M.

**Sol.**

	$A(g) \rightleftharpoons B(g)$	
initial conc.	2	0
Change in conc.	-x	x
equib. conc.	2-x	0+x

$K_C$  is very-very high so maximum reactant converted into product.

$$\therefore \frac{K_C}{\text{initial conc.}} \geq 10^3 \text{ then } \frac{10^{50}}{2} \geq 10^3.$$

So  $2-x \simeq 0 \Rightarrow x \simeq 2$  but reactant never zero.

equib. conc.  $2-x \simeq y$        $x \simeq 2$

$$K_C = \frac{[B]}{[A]}$$

$$10^{50} = \frac{x}{2-x}$$

$$10^{50} = \frac{2}{y} \Rightarrow y = 2 \times 10^{-50} \text{ M}$$

$$[A] = 2 \times 10^{-50} \text{ M}$$

## 8. LE CHATELIER'S PRINCIPLE :

Le Chatelier's principle is applicable for any system in equilibrium which states as :

When a system in equilibrium is disturbed by external agency, the system tends to attain again an equilibrium by adjusting itself. These are these some factors by which a system in equilibrium can be disturbed.

- (i) Changing the concentration of reactant and product.
- (ii) Changing the pressure (or volume) of the system.
- (iii) Changing the temperature.

For a chemical reaction in equilibrium, Le Chatelier's principle can be stated as,

**If we change concentration, pressure or temperature of a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimise the change.**

### 8.1 Effect of a change in concentration :

- (a) If more reactant is added or some product is removed from an equilibrium mixture having equilibrium constant  $K$  then the reaction moves in the forward direction (as  $Q_c < K_c$ ) to give a new equilibrium and more products are produced.
- (b) If more product are added to or some reactant are removed from an equilibrium mixture, the reaction moves in the reverse direction (as  $Q_c > K_c$ ) to give a new equilibrium and more reactant are produced.

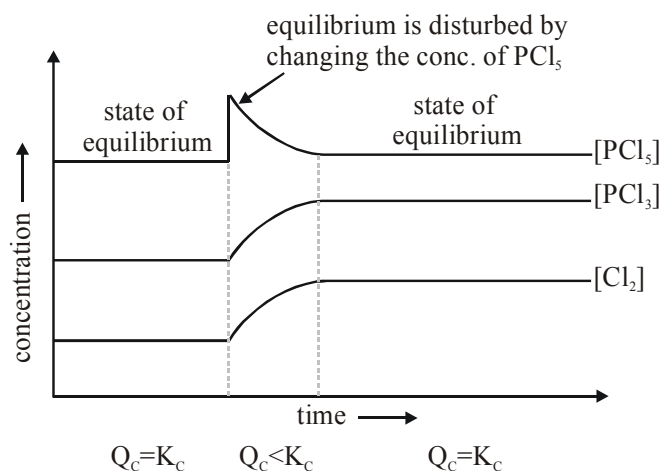
**Ex.** The decomposition of gaseous  $\text{PCl}_5$  is a reversible reaction,  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ . Let the equilibrium concentrations of  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  are respectively  $[\text{PCl}_5]$ ,  $[\text{PCl}_3]$  and  $[\text{Cl}_2]$ . The  $K_c$  for this reaction can be written as :

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \quad \text{Also we know that at equilibrium } K_c = Q_c.$$

**Case-I :** Let the concentration of  $\text{PCl}_5$  is doubled to disturb the equilibrium. This will change the reaction quotient,  $Q_c$  to :

$$Q_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[2\text{PCl}_5]} = \frac{1}{2} \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{K_c}{2}$$

After disturbing the equilibrium, the value of  $Q_c$  becomes less than  $K_c$ . In order to restore the  $Q_c$  value to  $K_c$ , the concentration of  $PCl_5$  must be decreased while the concentrations of  $PCl_3$  and  $Cl_2$  are to be increased. This is achieved by favoring the forward reaction.

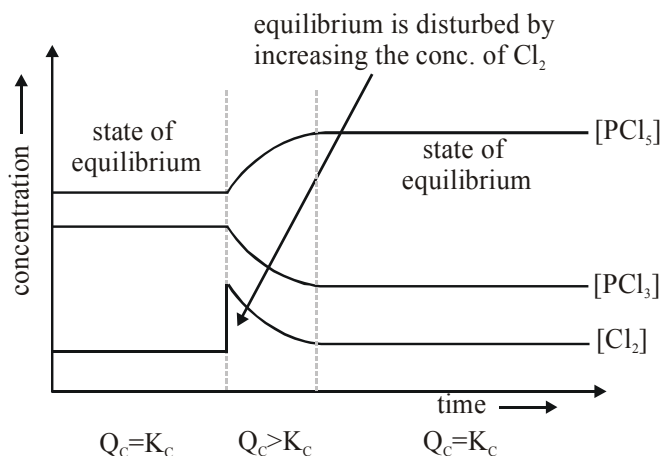


The forward reaction is also favored by removing the products from the reaction mixture (decrease in the concentration of products). Upon removal of products, the rate of forward reaction becomes greater than that of backward reaction momentarily. This will also decrease the reaction quotient. Hence the system tries to reestablish the equilibrium by converting more reactants to products so as to make the rates of both forward and backward reactions become equal again.

**Case-II :** For example, in case of the decomposition of  $PCl_5$ , if the concentration of  $Cl_2$  is increased by two times at equilibrium, the  $Q_c$  value becomes greater than the  $K_c$  value.

$$Q_c = \frac{[PCl_3][2Cl_2]}{[PCl_5]} = 2 \times \frac{[PCl_3][Cl_2]}{[PCl_5]} = 2K_c$$

Hence the system tries to restore the value of  $Q_c$  to  $K_c$  again. The backward reaction is favored to decrease the concentration of  $Cl_2$ . However the concentration of  $PCl_3$  also decreases automatically while the concentration of  $PCl_5$  increases while doing so.



### 8.2 Effect of a change in pressure :

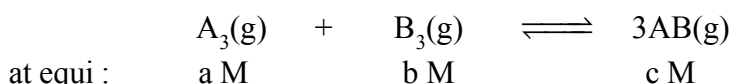
We know that, if we increase the volume of container then the pressure of the container decreases and if we decrease the volume of container then the pressure of the container increases.

$$\text{i.e., Pressure (P)} \propto \frac{1}{\text{Volume (V)}}$$

Hence, if the pressure is decreased by increasing the volume of a reaction mixture, the reaction shifts in the direction of more moles of gas while if the pressure is increased by decreasing the volume of a reaction mixture, the reaction shifts in the direction of fewer moles of gas.

Here moles of reactant or product means co-efficients of reactant or product.

(a) Suppose a general equation



For this reaction, moles of product > moles of reactant i.e.,  $[\Delta n = (3 - 2) > 0]$

$$K_c = \frac{(c)^3}{a \times b}$$

If we increase the pressure of the system from 0.5 atm pressure to 1 atm pressure by decreasing the volume of container from 5 litre to 2.5 litre. Hence, concentration of all the reactant and product will change and it will be greater than the initial value. Hence we can say that,

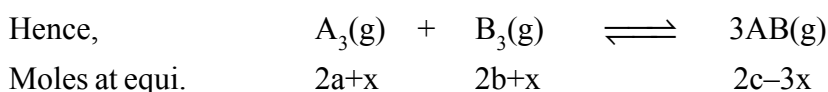
If pressure becomes double then volume becomes half and hence concentration becomes double as

$$\left( \text{Concentration} \propto \frac{\text{Moles}}{\text{Volume}} \right)$$

∴ Concentration  $\propto$  Pressure

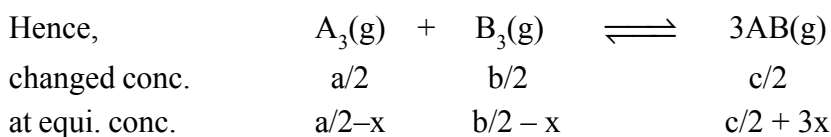
$$Q_c = 2 \times \frac{c^3}{a \times b} > K_c$$

Hence reaction will move from right to left i.e., in the backward direction.



It can be simply said that, reaction will move from right to left by increasing the pressure of the system as moles of product > moles of reactant i.e., move in the direction of fewer moles.

(b) If pressure decreases from 1 atm to 0.5 atm. Volume will increase by factor 2 concentration will decrease by factor 1/2



$$Q_c = \frac{(c/2)^3}{a/2 \times b/2} = \frac{1}{2} \frac{c^3}{a \times b} < K_c$$

i.e.,  $Q_c < K_c$

Therefore, reaction will move from left to right and as moles of product > moles of reactants, therefore reaction will move from left to right by decreasing the pressure of the system i.e. move in the direction of greater moles.

- (c) If moles of reactant = moles of product i.e.,  $\Delta n = 0$  then change in pressure of equilibrium mixture has no effect i.e. at this position  $Q_c = K_c$  will always exist.

### 8.3 Effect of a change in temperature :

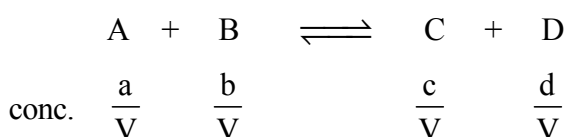
On increasing the temperature equilibrium shifts in the direction of absorption of heat (endothermic direction)

### 8.4 EFFECT OF INERT GAS AT THE EQUILIBRIUM :

#### (i) Effect of inert gas at constant volume :

When the addition of inert gas (non-reacting gas) is carried out at constant volume (V), the equilibrium remains unaffected for reactions whether they have  $\Delta n = 0$  or  $\Delta n \neq 0$ .

Let us consider a general equation at temperature T K, and a, b, c and d are the moles of A, B, C and D respectively,



Since, V = constant, so addition of inert gas has no effect on equilibrium

$\therefore \frac{a}{V}, \frac{b}{V}, \frac{c}{V}$  and  $\frac{d}{V}$  will not change

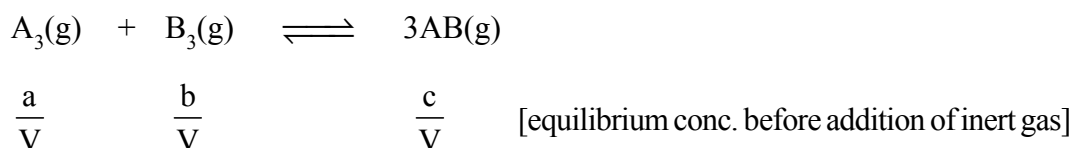
$$Q_c = K_c \quad \text{or} \quad Q_p = K_p$$

#### (ii) Effect of inert gas at constant pressure :

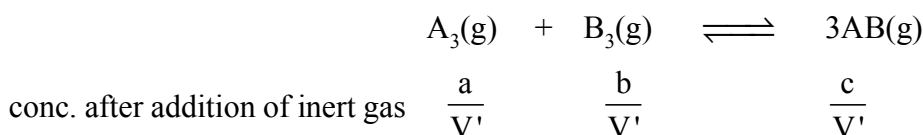
- (a) The addition of an inert gas at constant pressure to an equilibrium, the equilibrium shifts in the direction of greater number of moles.

At constant pressure, addition of inert gas or non-reacting gas means increase in volume of the system.

Suppose a reaction having  $\Delta n > 0$  and a, b, c and d are the moles of A, B, C and D respectively and V be the volume before addition of inert gas.



Let us consider V' be the total volume of the system after addition of inert gas So,  $V' > V$

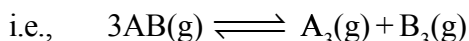


$\therefore \frac{a}{V'} < \frac{a}{V}, \frac{b}{V'} < \frac{b}{V}$  and  $\frac{c}{V'} < \frac{c}{V}$

$$\text{Now, } K_c = \frac{\left(\frac{c}{V}\right)^3}{\left(\frac{a}{V}\right)\left(\frac{b}{V}\right)} = \frac{1}{V} \times \frac{c^3}{a \times b} \quad \text{and} \quad Q_c = \frac{\left(\frac{c}{V'}\right)^3}{\left(\frac{a}{V'}\right)\left(\frac{b}{V'}\right)} = \frac{1}{V'} \times \frac{c^3}{a \times b}$$



$K_c > Q_c$ , hence reaction will move from left to right (forward direction) as  $\Delta n > 0$  and similarly we can prove that for a reaction having  $\Delta n < 0$

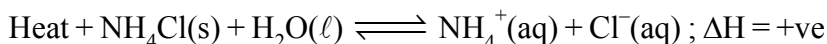


For this reaction  $K_c < Q_c$ , after addition of inert gas. Hence, reaction will move from right to left (reverse direction) as  $\Delta n < 0$ .

### 8.5 APPLICATION OF LE-CHATELIER'S PRINCIPLE :

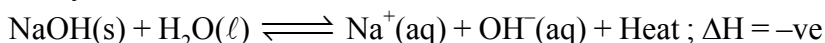
The principle is applicable not only to chemical equilibria but also to physical equilibria in similar way.

- (a) Dissolution of ammonium chloride in water



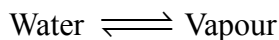
With rise in temperature, equilibrium will shift in direction which will lower the temperature counteract the effect. So, equilibrium shifts in forward direction which is endotherm reaction. Hence, solubility of  $\text{NH}_4\text{Cl}$  increases with rise in temperature.

- (b) Dissolution of sodium hydroxide in water



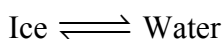
Sodium hydroxide dissolve in water with evolution of heat. Therefore, a rise in temperature will decrease its solubility. On the other hand, a decrease in temperature will increase the solubility of sodium hydroxide and reaction will shift in forward direction.

- (c) Effect of pressure on boiling point :



An increase in pressure will favour backward reaction i.e., the reaction in which volume decreases ( $V_{\text{vap.}} > V_{\text{w.}}$ ). thus more water will exist at equilibrium (B.pt of solvent increase with increase in pressure). So decrease in pressure will shift the reaction forward.

- (d) Effect of pressure on melting point :

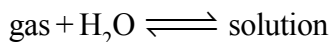


increase in pressure will favour forward reaction because  $V_{\text{ice}} > V_{\text{water}}$ . Thus more ice melt or the m.pt of ice is lowered with pressure.



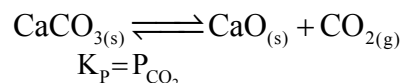
An increase in pressure will favour backward reaction because volume of liquid is more than solid thus more solid will exist at equilibrium (m.pt of solid increases with pressure).

- (e) Effect of pressure on solubility of gases :



increase in pressure favour forward reaction. [Henry's law]

- (f) In solid reactants equilibrium will not shift to the right side even if the more reactants an added.

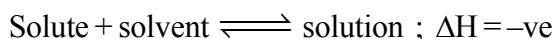


Equilibrium will not be affected by adding  $\text{CaO}$  or  $\text{CaCO}_3$  at that temperature. But if volume is increased the equilibrium will shift to the right side to keep the pressure of  $\text{CO}_2$  constant.

- (g) Effect of temperature on solubility



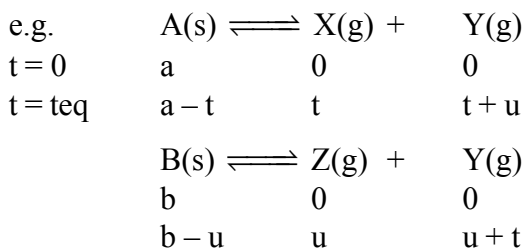
An increase in temperature favour endothermic or forward reaction i.e., solubility increases (urea, glucose).



In exothermic dissolution solubility decreases with temperature i.e., reaction will be in backward direction.

### 9. SIMULTANEOUS EQUILIBRIUM

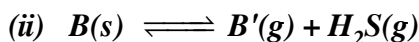
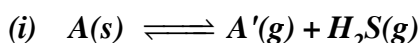
If in any container there are two or more equilibria existing simultaneously involving one or more than one common species, then in both/all the equilibrium, the concentration of common species is the total concentration of that species due to all the equilibria under consideration.



$$K_{C_1} = t(u + t)$$

$$K_{C_2} = (u + t)u$$

**Ex.35** Two solid compounds A and B dissociate into gaseous products at 20°C as

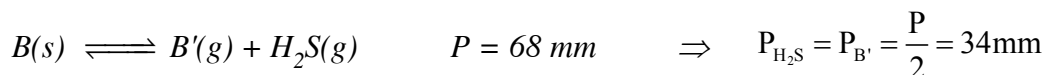
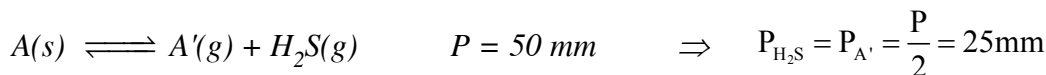
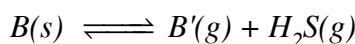
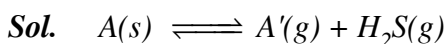


At 20°C, pressure over excess solid A is 50 mm and that over excess solid B is 68 mm find

(a) The dissociation constant of A and B

(b) Relative no. of moles of A and B in the vapour phase over a mixture of solid A and B.

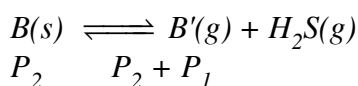
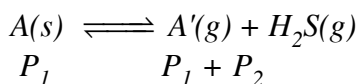
(c) Show that the total pressure of the gas over the solid mixture would be 84.4 mm



(i)  $K_{P_1} = (25)^2 = 625 \text{ mm}^2$

$K_{P_2} = (34)^2 = 1156 \text{ mm}^2$

(ii) Ratio of moles is same as that of partial pressure so,



$K_{P_1} = P_{A'} \times P_{H_2S} = P_1(P_1 + P_2) \quad \dots(i)$

$K_{P_2} = P_{B'} \times P_{H_2S} = P_2(P_1 + P_2) \quad \dots(ii)$

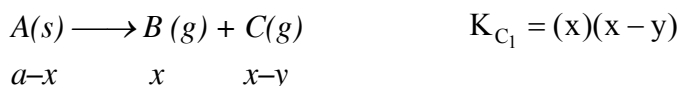
$$\frac{K_{P_1}}{K_{P_2}} = \frac{P_1}{P_2} = \frac{625}{1156}$$

(iii) total pressure =  $P_1 + P_2 + (P_1 + P_2) = 2(P_1 + P_2)$

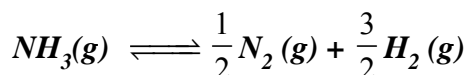
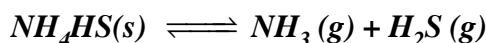
(i) + (ii) =  $(P_1 + P_2)^2$

$\sqrt{K_{P_1} + K_{P_2}} = P_1 + P_2 \quad \Rightarrow \quad P_T = 2\sqrt{K_{P_1} + K_{P_2}} = 84.4 \text{ mm}$

10. SEQUENTIAL EQUILIBRIUM

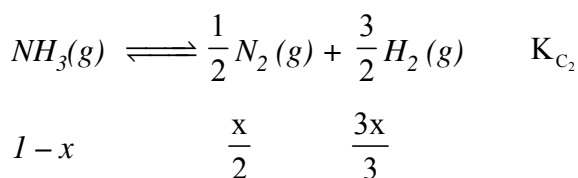
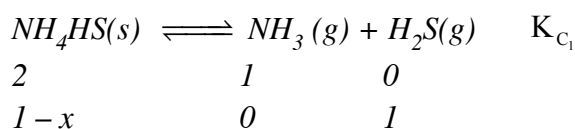


Ex36. 102 g of solid  $NH_4HS$  is taken in the 2L evacuated flask at  $57^\circ C$ . Following two equilibrium exist simultaneously



one mole of the solid decomposes to maintain both the equilibrium and 0.75 mole of  $H_2$  was found at the equilibrium then find the equilibrium concentration of all the species and  $K_C$  for both the reaction.

Sol. Moles of  $NH_4HS = \frac{102}{51} = 2$

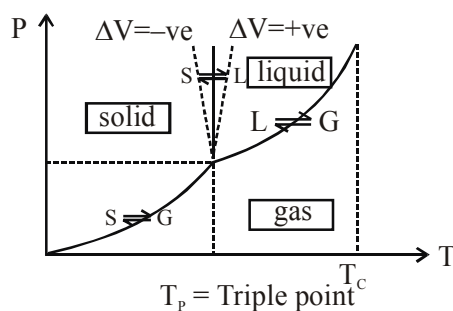


Given that moles of  $H_2 = \frac{3x}{3} = 0.75 \Rightarrow x = \frac{1}{2}$

$$K_{C_1} = \frac{1(1-x)}{2} = \frac{1}{8} \quad [Since V = 2L]$$

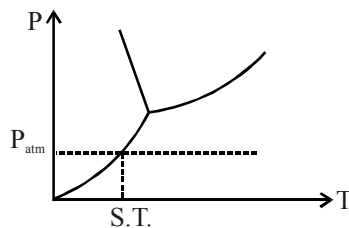
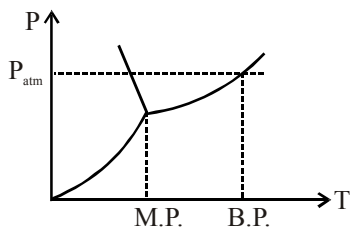
$$K_{C_3} = \frac{\left(\frac{3x}{4}\right)^{3/2} \left(\frac{x}{4}\right)^{1/2}}{\left(\frac{1-x}{2}\right)} = \frac{\left(\frac{3}{8}\right)^{3/2} \left(\frac{1}{4}\right)^{1/2}}{\left(\frac{1}{4}\right)} = (3)^{3/2} \frac{1}{64} \times \frac{4}{1} = \frac{(3)^{3/2}}{16}$$

## 11. PHYSICAL EQUILIBRIUM



- (i) The combination of temperature and pressure at which all the three physical state of matter co-exist is called triple point of that matter.
- (ii) The vapour pressure solid is minimum (0) at absolute zero and maximum at triple point.
- (iii) The vapour pressure of liquid is minimum at triple point and maximum at critical temperature.
- (iv) On each line in the graph, the matter exist in two physical states is equilibrium.
- (v) In between two lines, the matter exist in only one physical state.
- (vi) The melting point of solid and the triple point of matter differs slightly.
- (vii) Any solid may be directly converted into gaseous state or through liquid state by adjusting the external pressure relative to triple point pressure.

(viii)



### MISSLENIOUS PREVIOUS YEARS QUESTION

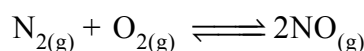
1. For the reaction  $\text{CO}_{(g)} + 2\text{H}_{2(g)} \rightleftharpoons \text{CH}_3\text{OH}_{(g)}$ ;  $\text{H}_2$  is introduced into a five litre flask at  $327^\circ\text{C}$ , containing 0.2 mole of  $\text{CO}_{(g)}$  and a catalyst till the pressure is 4.92 atmosphere. At this point 0.1 mole of  $\text{CH}_3\text{OH}_{(g)}$  is formed. Calculate  $K_c$  and  $K_p$ . [JEE 1990]

1.  $K_c = 279.64 \text{ litre}^2 \text{ mole}^{-2}$ ;  $K_p = 0.115 \text{ atm}^{-2}$

2. At temperature  $T$ , a compound  $\text{AB}_{2(g)}$  dissociates according to the reaction  $2\text{AB}_{2(g)} \rightleftharpoons 2\text{AB}_{(g)} + \text{B}_{2(g)}$ ; with a degree of dissociation 'x', which is small compared to unity. Deduce the expression for 'x' in terms of the equilibrium constant  $K_p$  and the total pressure  $P$ . [JEE 1994]

2.  $x = \sqrt[3]{\frac{2K_p}{P}}$

3. A sample of air consisting of  $\text{N}_2$  and  $\text{O}_2$  was heated to 2500 K until the equilibrium

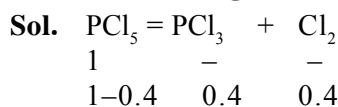


was established with an equilibrium constant  $K_c = 2.1 \times 10^{-3}$ . At equilibrium, the mole% of NO was 1.8. Estimate the initial composition of air in mole fraction of  $\text{N}_2$  and  $\text{O}_2$ . [JEE 1997]

3. **79%, 21%**

4. The degree of dissociation is 0.4 at 400K & 1.0 atm for the gasous reaction  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ . Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 400K & 1.0 atm pressure. [JEE 1999]

4. **Ans. 4.54 g dm<sup>-3</sup>**



$$M_{av} = \frac{208.5}{1.4}$$

$$PM = dRT$$

$$1 \times \frac{208.5}{1.4} = d \times 0.0821 \times 400$$

5. For the reversible reaction : [JEE 2000]

$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$  at  $500^\circ\text{C}$ . The value of  $K_p$  is  $1.44 \times 10^{-5}$ , when partial pressure is measured in atmospheres. The corresponding value of  $K_c$  with concentration in  $\text{mol L}^{-1}$  is :

(A)  $1.44 \times 10^{-5} / (0.082 \times 500)^2$

(B)  $1.44 \times 10^{-5} / (8.314 \times 773)^2$

(C)  $1.44 \times 10^{-5} / (0.082 \times 500)^2$

(D)  $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$

5. **Ans.(D)**

**Sol.**  $K_p = K_c (RT)^{-2}$

6. When two reactants A and B are mixed to give products C and D, the reaction quotient  $Q_c$  at the initial stages of the reaction : [JEE 2000]
- (A) is zero (B) decrease with time  
 (C) independent of time (D) increases with time

6. **Ans.(D)**

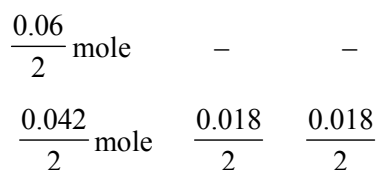
**Sol.**  $Q_c$  increases at initial steps

7. When 3.06g of solid  $\text{NH}_4\text{HS}$  is introduced into a two litre evacuated flask at  $27^\circ\text{C}$ , 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. [JEE 2000]

- (i) Calculate  $K_c$  &  $K_p$  for the reaction at  $27^\circ\text{C}$ .  
 (ii) What would happen to the equilibrium when more solid  $\text{NH}_4\text{HS}$  is introduced into the flask?

7. (i)  $K_c = 8.1 \times 10^{-5} \text{ mol}^2 \text{ L}^2$ ;  $K_p = 4.91 \times 10^{-2} \text{ atm}^2$  (ii) No effect;

- (i)  $\text{NH}_4\text{HS}(s) \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g)$



$$K_c = \frac{0.018}{2} \times \frac{0.018}{2}$$

$$K_c = 8.1 \times 10^{-5}$$

$$K_p = (8.1 \times 10^{-5}) \times (RT)^2$$

- (ii) When more of  $\text{NH}_4\text{HS}(s)$  is added then no-effect will occur on equilibrium
8. At constant temperature, the equilibrium constant ( $K_p$ ) for the decomposition reaction.  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  is expressed by  $K_p = 4x^2P/(1-x^2)$  where P is pressure, x is extent of decomposition. Which of the following statement is true ? [JEE 2001]
- (A)  $K_p$  increases with increase of P (B)  $K_p$  increases with increase of x  
 (C)  $K_p$  increases with decrease of x (D)  $K_p$  remains constant with change in P or x

8. **Ans.(D)**

**Sol.**  $K_p$  depends only on temperature.

9. Consider the following equilibrium in a closed container :  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ .

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant ( $K_p$ ) and degree of dissociation ( $\alpha$ ) : [JEE 2002]

- (A) Neither  $K_p$  nor  $\alpha$  changes (B) Both  $K_p$  and  $\alpha$  change  
 (C)  $K_p$  changes, but  $\alpha$  does not change (D)  $K_p$  does not change, but  $\alpha$  changes

9. **Ans.(D)**

**Sol.**  $K_p$  is independent of volume of container

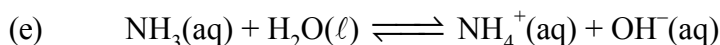
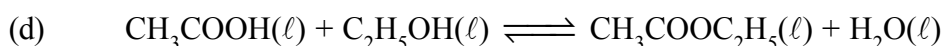
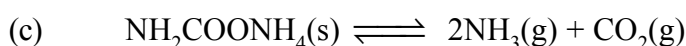
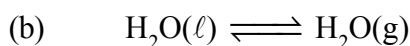
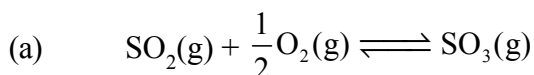
## EXERCISE # S-I

1. Which of the following reactions goes almost all the way to completion, and which proceeds hardly at all?

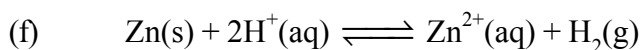


CE0001

2. Write down the expression for equilibrium constant  $K_c$  and  $K_p$  for the following reactions :

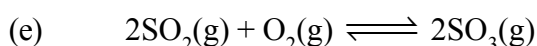


(excess)



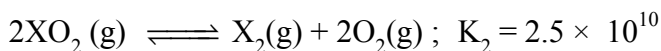
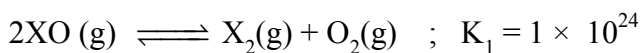
CE0002

3. Write the relationship between  $K_p$  and  $K_c$  for the following reactions :



CE0003

4. Find stability of reactants for the given equilibrium reaction :

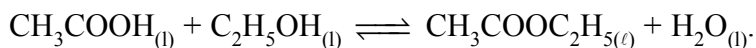


CE0004

5. The value of  $K_c$  for the reaction  $2\text{A} \rightleftharpoons \text{B} + \text{C}$  is  $2 \times 10^{-3}$ . At a given time, the composition of reaction mixture is  $[\text{A}] = [\text{B}] = [\text{C}] = 3 \times 10^{-4}$  M. In which direction the reaction will proceed?

CE0005

6. The ester or ethyl acetate is formed by the reaction between ethanol and acetic acid and equilibrium is represented as :



- (a) Write the concentration ratio (reaction quotient),  $Q_c$  for this reaction. (Note that water is not in excess and is not a solvent in this reaction).
- (b) At 293 K, if starts with 1.00 mole of acetic acid and 0.180 moles of ethanol, there is 0.171 moles of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.
- (c) Starting with 0.500 moles of ethanol and 1.000 mole of acetic acid and maintaining it at 293 K, 0.214 moles of ethyl acetate is found after some time. Has equilibrium been reached ?

CE0006

7. If  $K_c = 0.5 \times 10^{-9}$  at 1000 K for the reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ , what is  $K_c$  at 1000 K for the reaction  $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$ ?

CE0007

8. An equilibrium mixture of  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  at a certain temperature contains  $0.5 \times 10^{-3}$  M  $\text{PCl}_5$ ,  $1.5 \times 10^{-2}$  M  $\text{PCl}_3$ , and  $3 \times 10^{-2}$  M  $\text{Cl}_2$ . Calculate the equilibrium constant  $K_c$  for the reaction  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ .

CE0008

9. A sample of HI ( $9.6 \times 10^{-3}$  mol) was placed in an empty 2.00 L container at 1000 K. After equilibrium was reached, the concentration of  $\text{I}_2$  was  $4 \times 10^{-4}$  M. Calculate the value of  $K_c$  at 1000 K for the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ .

CE0009

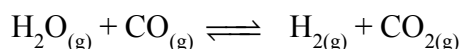
10. The vapour pressure of water at  $27^\circ\text{C}$  is 0.2463 atm. Calculate the values of  $K_p$  and  $K_c$  at  $27^\circ\text{C}$  for the equilibrium  $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ .

CE0010

11. The value of  $K_c$  for the reaction  $3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$  is  $8 \times 10^{-55}$  at  $25^\circ\text{C}$ . Do you expect pure air at  $25^\circ\text{C}$  to contain much  $\text{O}_3$  (ozone) when  $\text{O}_2$  and  $\text{O}_3$  are in equilibrium? If the equilibrium concentration of  $\text{O}_2$  in air at  $25^\circ\text{C}$  is  $8 \times 10^{-3}$  M, what is the equilibrium concentration of  $\text{O}_3$ ?

CE0011

12. One mole of  $\text{H}_2\text{O}$  and one mole of  $\text{CO}$  are taken in a 10 L vessel and heated to 725 K. At equilibrium 40 percent of water (by mass) reacts with carbon monoxide according to the equation.



Calculate the equilibrium constant for the reaction.

CE0012

13. A vessel at 1000 K contains  $\text{CO}_2$  with a pressure of 0.6 atm. some of the  $\text{CO}_2$  is converted into  $\text{CO}$  on addition of graphite. Calculate the value of  $K$ , if total pressure at equilibrium is 0.9 atm.

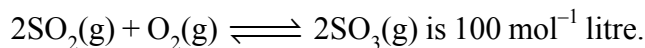
CE0013



14. Calculate the equilibrium concentration of  $H_2$ ,  $I_2$  and  $HI$  at 300 K if initially 2 mol of  $H_2$  and  $I_2$  are taken in a closed container of having volume 10 lit. [Given :  $H_2 + I_2 \rightleftharpoons 2HI$  ;  $K = 100$  at 300 K]

CE0014

15. A mixture of  $SO_3$ ,  $SO_2$  and  $O_2$  gases is maintained at equilibrium in 10 litre flask at a particular temperature in which  $K_c$  for the reaction,



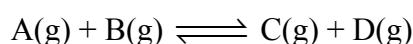
At equilibrium,

(a) If number of mole of  $SO_3$  and  $SO_2$  in flask are same, how many mole of  $O_2$  are present ?

(b) If number of mole of  $SO_3$  in flask are twice the number of mole of  $SO_2$ , how many mole of  $O_2$  are present ?

CE0015

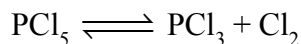
16. For the given reaction,



the number of moles at equilibrium was found to be 4, 4, 2 & 8 respectively in 1 L container. Find the new equilibrium concentration if 18 moles of D are added to above 1 L container.

CE0016

17. For the given reaction,



the number of moles at equilibrium was found to be 2, 6 & 4 respectively at 10 atm pressure. Find the new equilibrium moles & partial pressure, if it is reestablished at an equilibrium pressure 50 atm.

CE0017

18. For the dissociation reaction  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$  derive the expression for the degree of dissociation in terms of  $K_p$  and total pressure P.

CE0018

19. For the reaction  $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

Initially 5 moles of  $SO_3$  is taken and at equilibrium 4 moles of  $SO_3$  is dissociated then find out  $\alpha$  and the value of  $K_c$  (Volume = 2litre)

CE0019

20. 1.1 mole of A mixed with 2.2 mole of B and the mixture is kept in a 1 litre flask at the equilibrium,  $A + 2B \rightleftharpoons 2C + D$  is reached. At equilibrium 0.2 mole of C is formed then the value of  $K_c$  will be.

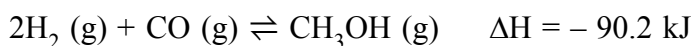
CE0020

21. The air pollutant NO is produced in automobile engines from the high temperature reaction  $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$  ;  $K_c = 16$  at 2300 K. If the initial concentrations of  $N_2$  and  $O_2$  at 2300 K are both 1.5 M, what are the concentrations of NO,  $N_2$ , and  $O_2$  when the reaction mixture reaches equilibrium?

CE0021

22. At 700 K,  $K_p = 0.2$  for the reaction  $\text{ClF}_3(\text{g}) \rightleftharpoons \text{ClF}(\text{g}) + \text{F}_2(\text{g})$ . Calculate the equilibrium partial pressure of  $\text{ClF}_3$ ,  $\text{ClF}$ , and  $\text{F}_2$  if only  $\text{ClF}_3$  is present initially, at a partial pressure of 0.150 atm. **CE0022**
23. The degree of dissociation of  $\text{N}_2\text{O}_4$  into  $\text{NO}_2$  at 1.5 atmosphere and  $40^\circ\text{C}$  is 0.25. Calculate its  $K_p$  at  $40^\circ\text{C}$ . Also report degree of dissociation at 10 atmospheric pressure at same temperature. **CE0023**
24. At  $46^\circ\text{C}$ ,  $K_p$  for the reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  is 0.667 atm. Compute the percent dissociation of  $\text{N}_2\text{O}_4$  at  $46^\circ\text{C}$  at a total pressure of 380 Torr. **CE0024**
25.  $2\text{NOBr}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$ . If nitrosyl bromide ( $\text{NOBr}$ ) is 33.33% dissociated at  $25^\circ\text{C}$  & a total pressure of 0.28 atm. Calculate  $K_p$  for the dissociation at this temperature. **CE0025**
26. The system  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  maintained in a closed vessel at  $60^\circ\text{C}$  & a pressure of 5 atm has an average (i.e. observed) molecular weight of 69, calculate  $K_p$ . At what pressure at the same temperature would the observed molecular weight be (230/3)? **CE0026**
27. In the esterification  $\text{C}_2\text{H}_5\text{OH}(\text{l}) + \text{CH}_3\text{COOH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$  an equimolar mixture of alcohol and acid taken initially yields under equilibrium, the water with mole fraction = 0.333. Calculate the equilibrium constant. **CE0027**
28. The equilibrium constant for the reaction is 9 at  $900^\circ\text{C}$   $\text{S}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons \text{CS}_2(\text{g})$ . Calculate the pressure of two gases at equilibrium, when 2 atm of  $\text{S}_2$  and excess of  $\text{C}(\text{s})$  come to equilibrium. **CE0028**
29. A sample of  $\text{CaCO}_3(\text{s})$  is introduced into a sealed container of volume 0.821 litre & heated to 1000K until equilibrium is reached. The equilibrium constant for the reaction  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  is  $4 \times 10^{-2}$  atm at this temperature. Calculate the mass of  $\text{CaO}$  present at equilibrium. **CE0029**
30. Anhydrous calcium chloride is often used as a desiccant. In the presence of excess of  $\text{CaCl}_2$ , the amount of the water taken up is governed by  $K_p = 6.4 \times 10^{85}$  for the following reaction at room temperature,  $\text{CaCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$ . What is the equilibrium vapour pressure of water in a closed vessel that contains  $\text{CaCl}_2(\text{s})$ ? **CE0030**
31. 20.0 grams of  $\text{CaCO}_3(\text{s})$  were placed in a closed vessel, heated & maintained at  $727^\circ\text{C}$  under equilibrium  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  and it is found that 75% of  $\text{CaCO}_3$  was decomposed. What is the value of  $K_p$ ? The volume of the container was 15 litres. **CE0031**

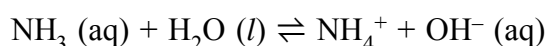
32. (a) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst. Write the expression for the equilibrium constant for the reversible reaction.



- (b) Assume that equilibrium has been established and predict how the concentration of  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CH}_3\text{OH}$  will differ at a new equilibrium if (1) more  $\text{H}_2$  is added. (2)  $\text{CO}$  is removed. (3)  $\text{CH}_3\text{OH}$  is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased. (6) more catalyst is added.

CE0032

33. Ammonia is a weak base that reacts with water according to the equation

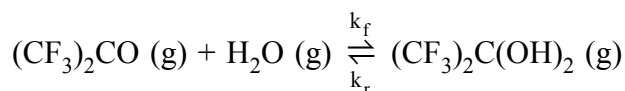


Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

- (a) Addition of  $\text{NaOH}$ . (b) Addition of  $\text{HCl}$ . (c) Addition of  $\text{NH}_4\text{Cl}$ .

CE0033

34. Consider the gas-phase hydration of hexafluoroacetone,  $(\text{CF}_3)_2\text{CO}$ :



At  $76^\circ\text{C}$ , the forward and reverse rate constants are  $k_f = 0.15 \text{ M}^{-1}\text{s}^{-1}$  and  $k_r = 6 \times 10^{-4}\text{s}^{-1}$ . What is the value of the equilibrium constant  $K_c$ ?

CE0034

35. Listed in the table are forward and reverse rate constants for the reaction  $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$

Temperature (K)	$k_f$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$k_r$ ( $\text{M}^{-1}\text{s}^{-1}$ )
1400	0.29	$1.1 \times 10^{-6}$
1500	1.3	$1.4 \times 10^{-5}$

Is the reaction endothermic or exothermic? Explain in terms of kinetics.

CE0035

## EXERCISE # S-II

1. One mole of  $N_2O_4(g)$  at 300 K is left in a closed container under one atm. It is heated to 600 K when 20 % by mass of  $N_2O_4(g)$  decomposes to  $NO_2(g)$ . Calculate resultant pressure.

CE0036

2. Solid Ammonium carbamate dissociates as:  $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$ . In a closed vessel solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium, ammonia is added such that the partial pressure of  $NH_3$  at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at new equilibrium to that of original total pressure.

CE0037

3. A definite amount of solid  $NH_4HS$  is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure.  $NH_4HS$  decomposes to give  $NH_3$  and  $H_2S$  and at equilibrium total pressure in flask is 0.84 atm. Calculate equilibrium constant for the reaction :

CE0038

4. For the reaction  $A(g) + 2B(g) \rightleftharpoons C(g) + D(g)$ ;  $K_c = 10^{12}$ . If the initial moles of A, B, C and D are 0.5, 1, 0.5 and 3.5 moles respectively in a one litre vessel. What is the equilibrium concentration of B?

CE0039

5. Calculate the equilibrium concentration of  $PCl_3$  and  $Cl_2$  at 300 K if initially 1 mol of  $PCl_5$  is taken in a closed container of having volume 10 lit.

[Given :  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ ;  $K_c = 10^{-2}$  at 300 K,  $\sqrt{41} = 6.4$ ]

CE0040

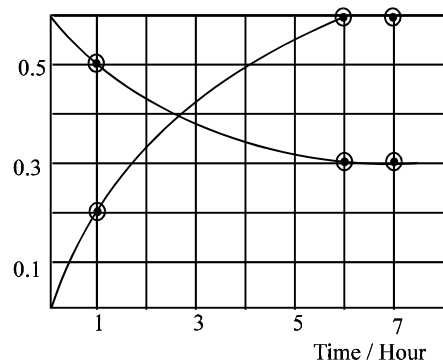
6. When 36.8g  $N_2O_4(g)$  is introduced into a 1.0-litre flask at  $27^\circ C$ . The following equilibrium reaction occurs :  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ ;  $K_p = 0.1642$  atm.

- (a) Calculate  $K_c$  of the equilibrium reaction.  
 (b) What are the number of moles of  $N_2O_4$  and  $NO_2$  at equilibrium?  
 (c) What is the total gas pressure in the flask at equilibrium?  
 (d) What is the percent dissociation of  $N_2O_4$ ?

CE0041

7. The progress of the reaction  $A \rightleftharpoons nB$  with time, is presented in figure. Determine

- (i) the value of n.  
 (ii) the equilibrium constant K.  
 (iii) the initial rate of conversion of A.

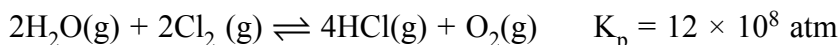


CE0042

8. A mixture of hydrogen & iodine in the mole ratio 1.5 : 1 is maintained at 450°C. After the attainment of equilibrium  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , it is found on analysis that the mole ratio of  $\text{I}_2$  to HI is 1 : 18. Calculate the equilibrium constant and the number of moles of each species present under equilibrium, if initially, 127 grams of iodine were taken.

CE0043

9. At certain temperature (T) for the gas phase reaction



If  $\text{Cl}_2$ , HCl &  $\text{O}_2$  are mixed in such a manner that the partial pressure of each is 2 atm and the mixture is brought into contact with excess of liquid water. What would be approximate partial pressure of  $\text{Cl}_2$  when equilibrium is attained at temperature (T)?

[Given : Vapour pressure of water is 380 mm Hg at temperature (T)]

CE0044

10. Two solids X and Y dissociate into gaseous products at a certain temperature as follows:  
 $\text{X}(\text{s}) \rightleftharpoons \text{A}(\text{g}) + \text{C}(\text{g})$ , and  $\text{Y}(\text{s}) \rightleftharpoons \text{B}(\text{g}) + \text{C}(\text{g})$ . At a given temperature, pressure over excess solid X is 40 mm and total pressure over solid Y is 60 mm. When they are preset in separate containers. Calculate
- the values of  $K_p$  for two reactions (in  $\text{mm}^2$ )
  - the ratio of moles of A and B in the vapour state over a mixture of X and Y.
  - the total pressure of gases over a mixture of X and Y.

CE0045

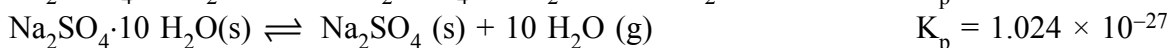
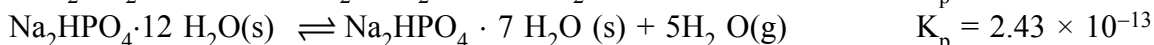
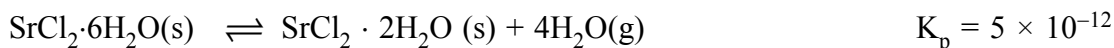
11. When 1 mole of A(g) is introduced in a closed rigid 1 litre vessel maintained at constant temperature the following equilibria are established.



The pressure at equilibrium is twice the initial pressure. Calculate the value of  $\frac{K_{C_2}}{K_{C_1}}$  if  $\frac{[\text{C}]_{\text{eq}}}{[\text{B}]_{\text{eq}}} = \frac{1}{5}$

CE0046

12. Equilibrium constants are given (in atm) for the following reactions at 0°C:



$$(\% \text{ Relative humidity} = \frac{P_{\text{H}_2\text{O}}}{\text{Vapour pressure of H}_2\text{O}} \times 100)$$

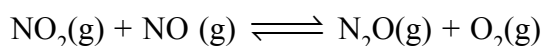
The vapor pressure of water at 0°C is 4.56 torr.

Out of  $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ ,  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$  and  $\text{Na}_2\text{SO}_4(\text{s})$ ,

Which is the most effective drying agent at 0°C?

CE0047

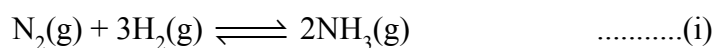
13. At certain temperature,  $K_c = 1.0$  for reaction :



equal moles of NO and  $\text{NO}_2$  are to be placed in 5 litre container until  $\text{N}_2\text{O}$  concentration at equilibrium is 0.5M. How many mole of  $(\text{NO} + \text{NO}_2)$  must be placed in the container.

CE0048

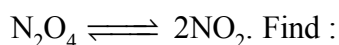
14. In a vessel, two equilibrium are simultaneously established at same temperature as follows,



Initially the vessel contains  $\text{N}_2$  and  $\text{H}_2$  in the molar ratio of 9 : 13. The equilibrium pressure is  $7 P_0$  in which pressure due to ammonia is  $P_0$  and due to hydrogen is  $2P_0$ . Find the values of equilibrium constants ( $K_p$ 's) for both the reactions.

CE0049

15. If vapour density of equilibrium mixture  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  is found to be 42 for the reaction,



- (a) Abnormal molecular weight  
(b) Degree of dissociation  
(c) Percentage of  $\text{NO}_2$  in the mixture

CE0050

## EXERCISE # O-I

Only one is correct

1.  $x \rightleftharpoons y$  reaction is said to be in equilibrium, when :-

- (A) Only 10% conversion of x to y takes place  
 (B) Complete conversion of x to y has taken place  
 (C) Conversion of x to y is only 50% complete  
 (D) The rate of change of x to y is just equal to the rate of change of y to x in the system

CE0051

2. For which reaction is  $K_p = K_c$  :-

- (A)  $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$       (B)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$   
 (C)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$       (D)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

CE0052

3. For the reaction



Which one is correct representation :-

- (A)  $K_p = (P_{\text{H}_2\text{O}})^2$       (B)  $K_c = [\text{H}_2\text{O}]^2$       (C)  $K_p = K_c(\text{RT})^2$       (D) All

CE0053

4.  $\log \frac{K_p}{K_c} + \log \text{RT} = 0$  is true relationship for the following reaction:-

- (A)  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$       (B)  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$   
 (C)  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$       (D) (B) and (C) both

CE0054

5. For a reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ , the value of  $K_c$  does not depend upon :-

- (a) Initial concentration of the reactants      (b) Pressure  
 (c) Temperature      (d) Catalyst  
 (A) Only c      (B) a, b, c      (C) a, b, d      (D) a, b, c, d

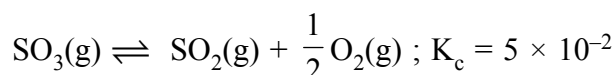
CE0055

6. If some He gas is introduced into the equilibrium  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$  at constant pressure and temperature then equilibrium constant of reaction:

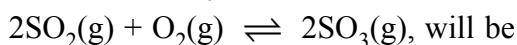
- (A) Increase      (B) Decrease      (C) Unchange      (D) Nothing can be said

CE0056

7. The equilibrium constant for the given reaction :



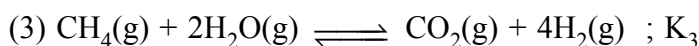
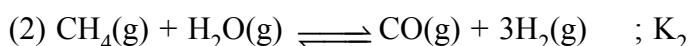
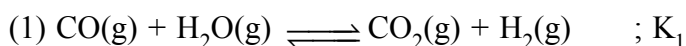
The value of  $K_c$  for the reaction :



- (A) 400 (B)  $2.40 \times 10^{-3}$  (C)  $9.8 \times 10^{-2}$  (D)  $4.9 \times 10^{-2}$

CE0057

8. For the following three reactions, 1, 2 and 3 equilibrium, constants are given :



Which of the following relations is correct ?

- (A)  $K_1\sqrt{K_2} = K_3$  (B)  $K_2K_3 = K_1$  (C)  $K_3 = K_1K_2$  (D)  $K_3 = K_2^3 K_1^2$

CE0058

9. Sulfide ion in alkaline solution reacts with solid sulfur to form polysulfide ions having formulas  $\text{S}_2^{2-}$ ,  $\text{S}_3^{2-}$ ,  $\text{S}_4^{2-}$  and so on. The equilibrium constant for the formation of  $\text{S}_2^{2-}$  is 12 ( $K_1$ ) & for the formation of  $\text{S}_3^{2-}$  is 132 ( $K_2$ ), both from S and  $\text{S}^{2-}$ . What is the equilibrium constant for the formation of  $\text{S}_3^{2-}$  from  $\text{S}_2^{2-}$  and S?

- (A) 11 (B) 12 (C) 132 (D) None of these

CE0059

10. If 0.5 mole  $\text{H}_2$  is reacted with 0.5 mole  $\text{I}_2$  in a ten-litre container at  $444^\circ \text{C}$  and at same temperature value of equilibrium constant  $K_c$  is 49, the ratio of  $[\text{HI}]$  and  $[\text{I}_2]$  will be :-

- (A) 7 (B)  $\frac{1}{7}$  (C)  $\sqrt{\frac{1}{7}}$  (D) 49

CE0060

11. In the reaction,  $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ , the moles/litre of  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{NO}$  respectively 0.25, 0.05 and 1.0 at equilibrium. The initial concentrations of  $\text{N}_2$  and  $\text{O}_2$  will respectively be

- (A) 0.75 mole/lit., 0.55 mole/lit. (B) 0.50 mole/lit., 0.75 mole/lit.  
(C) 0.25 mole/lit., 0.50 mole/lit. (D) 0.25 mole/lit., 1.0 mole/lit.

CE0061

12. How many moles per litre of  $\text{PCl}_5$  has to be taken to obtain 0.1 mole  $\text{Cl}_2$ , if the value of equilibrium constant  $K_c$  is 0.04 ?

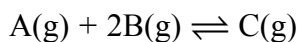
- (A) 0.15 (B) 0.25 (C) 0.35 (D) 0.05

CE0062



13. In the beginning of the reaction,  $A \rightleftharpoons B + C$ , 2 moles of A are taken, out of which 0.5 mole gets dissociated. What is the degree of dissociation of A ?  
 (A) 0.5 (B) 1 (C) 0.25 (D) 4.2  
**CE0063**
14. In the reaction,  $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ , the amount of each  $PCl_5$ ,  $PCl_3$  and  $Cl_2$  is 2 mole at equilibrium and total pressure is 3 atmosphere. The value of  $K_p$  will be  
 (A) 1.0 atm. (B) 3.0 atm. (C) 2.9 atm. (D) 6.0 atm.  
**CE0064**
15. 4 moles of  $PCl_5$  are heated at constant temperature in closed container. If degree of dissociation for  $PCl_5$  is 0.5 calculate total number of moles at equilibrium :-  
 (A) 4.5 (B) 6 (C) 3 (D) 4  
**CE0065**
16. For the reaction  $A + 2B \rightleftharpoons 2C + D$ , initial concentration of A is a and that of B is 1.5 times that of A. Concentration of A and D are same at equilibrium. What should be the concentration of B at equilibrium ?  
 (A)  $\frac{a}{4}$  (B)  $\frac{a}{2}$  (C)  $\frac{3a}{4}$  (D) All of the above.  
**CE0066**
17. For the reaction  $3A(g) + B(g) \rightleftharpoons 2C(g)$  at a given temperature,  $K_c = 9.0$ . What must be the volume of the flask, if a mixture of 2.0 mol each of A, B and C exist in equilibrium?  
 (A) 6L (B) 9L (C) 36 L (D) None of these  
**CE0067**
18. For the following gases equilibrium.  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$   
 $K_p$  is found to be equal to  $K_c$ . This is attained when temperature is  
 (A)  $0^\circ C$  (B) 273 K (C) 1 K (D) 12.19 K  
**CE0068**
19. The degree of dissociation of  $SO_3$  is  $\alpha$  at equilibrium pressure  $p^0$ .  
 $K_p$  for  $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$   
 (A)  $\frac{p^0 \alpha^3}{2(1-\alpha)^3}$  (B)  $\frac{p^0 \alpha^3}{(2+\alpha)(1-\alpha)^2}$  (C)  $\frac{p^0 \alpha^2}{2(1-\alpha)^2}$  (D) None of these  
**CE0069**
20. For the reaction :  $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ , the degree of dissociated ( $\alpha$ ) of  $HI(g)$  is related to equilibrium constant  $K_p$  by the expression  
 (A)  $\frac{1+2\sqrt{K_p}}{2}$  (B)  $\sqrt{\frac{1+2K_p}{2}}$  (C)  $\sqrt{\frac{2K_p}{1+2K_p}}$  (D)  $\frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$   
**CE0070**

21. The equilibrium constant for the reaction



is  $0.25 \text{ dm}^6 \text{ mol}^{-2}$ . In a volume of  $5 \text{ dm}^3$ , what amount of A must be mixed with 4 mol of B to yield 1 mol of C at equilibrium.

- (A) 3 moles (B) 24 moles (C) 26 moles (D) None of these

CE0071

22. A 20.0 litre vessel initially contains 0.50 mole each of  $\text{H}_2$  and  $\text{I}_2$  gases. These substances react and finally reach an equilibrium condition. Calculate the equilibrium concentration of HI if  $K_{\text{eq}} = 49$  for the reaction  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ .

- (A) 0.78 M (B) 0.039 M (C) 0.033 M (D) 0.021 M

CE0072

23. At 675 K,  $\text{H}_2(g)$  and  $\text{CO}_2(g)$  react to form  $\text{CO}(g)$  and  $\text{H}_2\text{O}(g)$ ,  $K_p$  for the reaction is 0.16. If a mixture of 0.25 mole of  $\text{H}_2(g)$  and 0.25 mol of  $\text{CO}_2$  is heated at 675 K, mole % of  $\text{CO}(g)$  in equilibrium mixture is :

- (A) 7.14 (B) 14.28 (C) 28.57 (D) 33.33

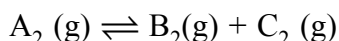
CE0073

24. The vapour density of  $\text{N}_2\text{O}_4$  at a certain temperature is 30. What is the % dissociation of  $\text{N}_2\text{O}_4$  at this temperature?

- (A) 53.3% (B) 106.6% (C) 26.7% (D) None

CE0074

25. The equilibrium constant  $K_p$  (in atm) for the reaction is 9 at 7 atm and 300 K.



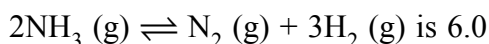
Calculate the average molar mass (in gm/mol) of an equilibrium mixture.

**Given :** Molar mass of  $A_2$ ,  $B_2$  and  $C_2$  are 70, 49 & 21 gm/mol respectively.

- (A) 50 (B) 45 (C) 40 (D) 37.5

CE0075

26. Vapour density of the equilibrium mixture of the reaction



is 6.0. Percent dissociation of ammonia gas is:

- (A) 13.88 (B) 58.82 (C) 41.66 (D) None of these

CE0076

27. The equilibrium concentration of B  $[(B)_e]$  for the reversible reaction  $A \rightleftharpoons B$  can be evaluated by the expression:-

- (A)  $K_c [A]_e^{-1}$  (B)  $\frac{k_f}{k_b} [A]_e^{-1}$  (C)  $k_f k_b^{-1} [A]_e$  (D)  $k_f k_b [A]^{-1}$

CE0077

28. The equilibrium  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$  shifts forward if :-

- (A) A catalyst is used.  
 (B) An adsorbent is used to remove  $\text{SO}_3$  as soon as it is formed.  
 (C) Small amounts of reactants are removed.  
 (D) None of these

CE0078

29. In manufacture of  $\text{NO}$ , the reaction  $\text{N}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{NO}_{(\text{g})}$ ,  $\Delta H$  +ve is favourable if :-

- (A) Pressure is increased (B) Pressure is decreased  
 (C) Temperature is increased (D) Temperature is decreased

CE0079

30. In which of the following reactions, increase in the pressure at constant temperature does not affect the moles at equilibrium :

- (A)  $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$  (B)  $\text{C}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g})$   
 (C)  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$  (D)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

CE0080

31. Change in volume of the system does not alter the number of moles in which of the following equilibrium

- (A)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$  (B)  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$   
 (C)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  (D)  $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$

CE0081

32. The conditions favourable for the reaction :



are :

- (A) low temperature, high pressure (B) any value of T and P  
 (C) low temperature and low pressure (D) high temperature and high pressure

CE0082

33. Densities of diamond and graphite are 3.5 and 2.3 gm/mL.



favourable conditions for formation of diamond are

- (A) high pressure and low temperature (B) low pressure and high temperature  
 (C) high pressure and high temperature (D) low pressure and low temperature

CE0083

34. The equilibrium  $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$  is attained at  $25^\circ\text{C}$  in a closed rigid container and an inert gas, helium is introduced. Which of the following statements is/are correct.
- (A) concentrations of  $\text{SO}_2$ ,  $\text{Cl}_2$  and  $\text{SO}_2\text{Cl}_2$  do not change  
(B) more chlorine is formed  
(C) concentration of  $\text{SO}_2$  is reduced  
(D) more  $\text{SO}_2\text{Cl}_2$  is formed

CE0084

35. The yield of product in the reaction



would be lower at :

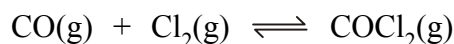
- (A) low temperature and low pressure      (B) high temperature & high pressure  
(C) low temperature and to high pressure      (D) high temperature & low pressure

CE0085

**EXERCISE # O-II**

*More than one may be correct*

1. Following two equilibrium is simultaneously established in a container



If some Ni(s) is introduced in the container forming Ni(CO)<sub>4</sub>(g) then at new equilibrium

- (A) PCl<sub>3</sub> concentration will increase      (B) PCl<sub>3</sub> concentration will decrease  
(C) Cl<sub>2</sub> concentration will remain same      (D) CO concentration will remain same

**CE0086**

2. For the reaction  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ , the forward reaction at constant temperature is favoured by

- (A) introducing an inert gas at constant volume  
(B) introducing chlorine gas at constant volume  
(C) introducing an inert gas at constant pressure  
(D) introducing PCl<sub>5</sub> at constant volume.

**CE0087**

3. When NaNO<sub>3</sub> is heated in a closed vessel, oxygen is liberated and NaNO<sub>2</sub> is left. At equilibrium

- (A) addition of NaNO<sub>2</sub> favours reverse reaction  
(B) addition of NaNO<sub>3</sub> favours forward reaction  
(C) increasing temperature favours forward reaction  
(D) increasing pressure favours reverse reaction

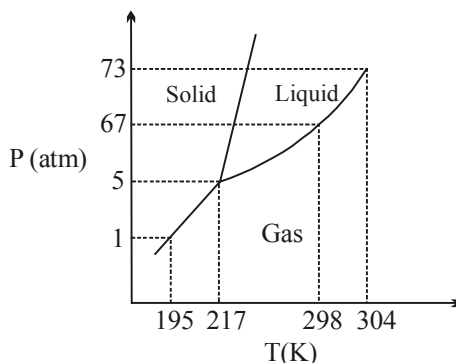
**CE0088**

4. For the gas phase reaction,  $\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$  ( $\Delta H = -32.7$  kcal), carried out in a closed vessel, the equilibrium moles of C<sub>2</sub>H<sub>4</sub> can be increased by

- (A) increasing the temperature      (B) decreasing the pressure  
(C) removing some H<sub>2</sub>      (D) adding some C<sub>2</sub>H<sub>6</sub>

**CE0089**

5. Phase diagram of  $\text{CO}_2$  is shown as following



Based on above find the correct statement(s)

- (A) 298K is the normal boiling point of liquid  $\text{CO}_2$   
 (B) At 1 atm & 190 K  $\text{CO}_2$  will exist as gas.  
 (C)  $\text{CO}_2(\text{s})$  will sublime above 195K under normal atmospheric pressure  
 (D) Melting point & boiling point of  $\text{CO}_2$  will increase on increasing pressure

CE0090

6. The equilibrium between, gaseous isomers A, B and C can be represented as

Reaction	Equilibrium constant
$\text{A (g)} \rightleftharpoons \text{B (g)}$	$K_1 = ?$
$\text{B (g)} \rightleftharpoons \text{C (g)}$	$K_2 = 0.4$
$\text{C (g)} \rightleftharpoons \text{A (g)}$	$K_3 = 0.6$

If one mole of A is taken in a closed vessel of volume 1 litre, then

- (A)  $[\text{A}] + [\text{B}] + [\text{C}] = 1 \text{ M}$  at any time of the reactions  
 (B) Concentration of C is 4.1 M at the attainment equilibrium in all the reactions  
 (C) The value of  $K_1$  is  $\frac{1}{0.24}$

(D) Isomer [A] is least stable as per thermodynamics.

CE0091

7. For the gas phase exothermic reaction,  $\text{A}_2 + \text{B}_2 \rightleftharpoons \text{C}_2$ , carried out in a closed vessel, the equilibrium moles of  $\text{A}_2$  can be increased by

- (A) increasing the temperature  
 (B) decreasing the pressure  
 (C) adding inert gas at constant pressure  
 (D) removing some  $\text{C}_2$

CE0092

8. Consider the equilibrium  $\text{HgO}(\text{s}) + 4\text{I}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HgI}_4^{2-}(\text{aq}) + 2\text{OH}^-(\text{aq})$ , which changes will decrease the equilibrium concentration of  $\text{HgI}_4^{2-}$

- (A) Addition of 0.1 M HI (aq)  
 (B) Addition of HgO (s)  
 (C) Addition of  $\text{H}_2\text{O}(\text{l})$   
 (D) Addition of KOH (aq)

CE0093

9. Decrease in the pressure for the following equilibria :  $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$  result in the :  
 (A) formation of more  $\text{H}_2\text{O}(\text{s})$  (B) formation of more  $\text{H}_2\text{O}(\text{l})$   
 (C) increase in melting point of  $\text{H}_2\text{O}(\text{s})$  (D) decrease in melting point of  $\text{H}_2\text{O}(\text{s})$

CE0094

**Assertion Reason**

10. **Statement -1** : Total number of moles in a closed system at new equilibrium is less than the old equilibrium if some amount of a substance is removed from a system  
 (consider a reaction  $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g})$ ) at equilibrium.

**Statement -2** : The number of moles of the substance which is removed, is partially compensated as the system reached to new equilibrium.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is false, statement-2 is true.  
 (D) Statement-1 is true, statement-2 is false.

CE0095

11. **Statement-1** : Ammonia at a pressure of 10 atm and  $\text{CO}_2$  at a pressure of 20 atm are introduced into an evacuated chamber. If  $K_p$  for the reaction  
 $\text{NH}_2\text{COONH}_4(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$  is  $2020 \text{ atm}^3$ , the total pressure after a long time is less than 30 atm.

**Statement-2** : Equilibrium can be attained from both directions.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CE0096

12. **Statement-1** : Catalyst does not alter the equilibrium constant

**Statement-2** : Because for the catalysed reaction and uncatalysed reaction  $\Delta H$  remain same an equilibrium constant depend on  $\Delta H$ .

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CE0097

13. **Statement-1** : Equilibrium constant may show higher or lower values with increase in temperature  
**Statement-2** : The change depend on heat of reaction.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CE0098

## Comprehension :

## Paragraph for Question Nos. 12 to 15

In a 7.0 L evacuated chamber, 0.50 mol  $H_2$  and 0.50 mol  $I_2$  react at  $427^\circ C$ .  
 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ . At the given temperature,  $K_C = 49$  for the reaction.

14. What is the value of  $K_p$  ?  
 (A) 7 (B) 49 (C) 24.5 (D) None
15. What is the total pressure (atm) in the chamber?  
 (A) 83.14 (B) 831.4 (C) 8.21 (D) None
16. How many moles of the iodine remain unreacted at equilibrium?  
 (A) 0.388 (B) 0.112 (C) 0.25 (D) 0.125
17. What is the partial pressure (atm) of HI in the equilibrium mixture?  
 (A) 6.385 (B) 12.77 (C) 40.768 (D) 646.58

CE0099

CE0099

CE0099

CE0099

## Paragraph for Question Nos. 16 to 18

Influence of pressure, temperature, concentration and addition of inert gas on a reversible chemical reaction in equilibrium can be explained by formulating the expression for equilibrium constant  $K_c$  or  $K_p$  for the equilibrium. On the other hand Le Chatelier principle can be theoretically used to explain the effect of P, T or concentration on the physical or chemical equilibrium both.

18. For the reaction :  $PCl_5 \rightleftharpoons PCl_3 + Cl_2$  increase of pressure shows :  
 (A) An increase in degree of dissociation and a decrease in  $K_c$   
 (B) A decrease in degree of dissociation and a decrease in  $K_c$   
 (C) An increase in degree of dissociation but  $K_c$  remains constant  
 (D) A decrease in degree of dissociation but  $K_c$  remains constant
19. For the reaction :  $2SO_2 + O_2 \rightleftharpoons 2SO_3$ ;  $\Delta H = -ve$ , An increase in temperature shows :  
 (A) More dissociation of  $SO_3$  and a decrease in  $K_c$   
 (B) Less dissociation of  $SO_3$  and an increase in  $K_c$   
 (C) More dissociation of  $SO_3$  and an increase in  $K_c$   
 (D) Less dissociation of  $SO_3$  and an decrease in  $K_c$

CE0100

CE0101



20. For the reaction :  $\underset{\text{Yellow}}{\text{Fe}^{3+}(\text{aq.})} + \text{SCN}^{-}(\text{aq.}) \rightleftharpoons \underset{\text{Red}}{[\text{Fe}(\text{NCS})]^{2+}(\text{aq.})}$  ; in equilibrium if little more aqueous solution of  $\text{FeCl}_3$  is added, than :
- (A) Forward reaction becomes more and red colours is deepened  
 (B) Backward reaction becomes more and red colour faintens  
 (C) Solution becomes colourless  
 (D) None of these

CE0102

Match the column :

- | 21. | Column I  | Column II  |
|-----|---|--|
| (A) | $K_p < K_C$   | (P) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$                                     |
| (B) | Introduction of inert gas at constant pressure will decrease the concentration of reactants | (Q) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$     |
| (C) | $K_p^\circ$ is dimensionless  | (R) $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$                     |
| (D) | Temperature increase will shift the reaction on product side.                               | (S) $\text{NH}_3(\text{g}) + \text{HI}(\text{g}) \rightleftharpoons \text{NH}_4\text{I}(\text{s})$ |

CE0103

- | 22. | Column-I<br>(Reactions)   | Column-II<br>(Favourable conditions)           |
|-----|---|--|
| (A) | Oxidation of nitrogen<br>$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) + 180.5 \text{ kJ} \rightleftharpoons 2\text{NO}(\text{g})$   | (p) Addition of inert gas at constant pressure |
| (B) | Dissociation of $\text{N}_2\text{O}_4(\text{g})$<br>$\text{N}_2\text{O}_4(\text{g}) + 57.2 \text{ kJ} \rightleftharpoons 2\text{NO}_2(\text{g})$                                    | (q) Decrease in pressure                       |
| (C) | Oxidation of $\text{NH}_3(\text{g})$<br>$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g}) + 905.6 \text{ kJ}$ | (r) Decrease in temperature                    |
| (D) | Formation of $\text{NO}_2(\text{g})$<br>$\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightleftharpoons \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) + 200 \text{ kJ}$               | (s) Increase in temperature                    |

CE0104

## Matching list type :

Answer Q.No. 23, 24 and 25 by appropriately matching the information given in the three columns of the following table.

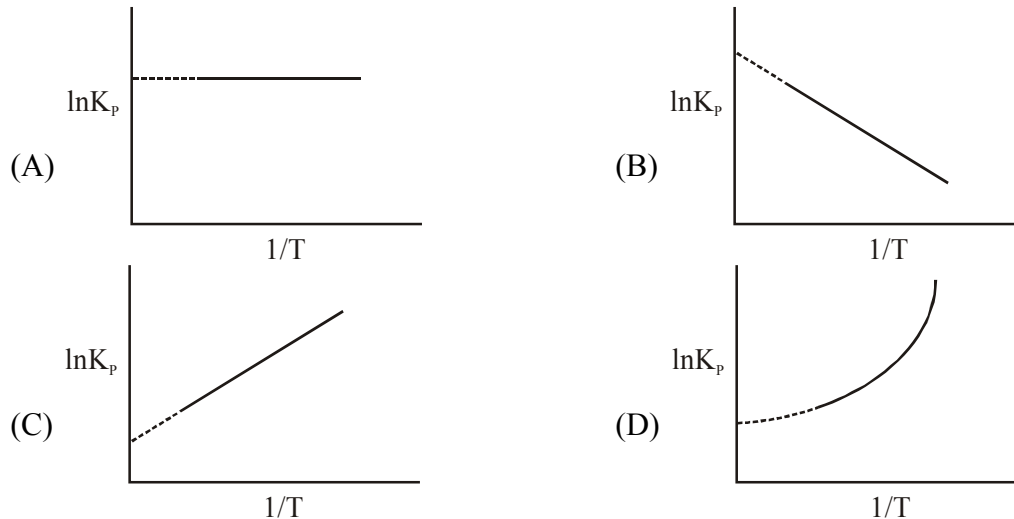
Column-I (Reaction)	Column-II (If $\alpha$ is negligible w.r.t. 1)	Column-III
(A) $2X(g) \rightleftharpoons Y(g) + Z(g), \Delta H = -ve$	(P) $\alpha = 2 \times \sqrt{K_p}$	(I) K increase with increase in temperature
(B) $X(g) \rightleftharpoons Y(g) + Z(g), \Delta H = +ve$	(Q) $\alpha = 3 \times \sqrt{K_p P}$	(II) K decrease with increase in temperature
(C) $3X(g) \rightleftharpoons Y(g) + Z(g), \Delta H = +ve$	(R) $\alpha = \left(\frac{2K_p}{P}\right)^{1/3}$	(III) Pressure has no effect
(D) $2X(g) \rightleftharpoons Y(g) + 2Z(g), \Delta H = +ve$	(S) $\alpha = \sqrt{K_p/P}$	(IV) Addition of inert gas at constant pressure shift equilibrium in forward direction

23. Which of the following option is correctly matched ?

- (A) A-Q-III                      (B) B-S-II                      (C) C-Q-II                      (D) D-R-IV

CE1015

24. Correct representation of reaction in option (A) is represented by graph



CE1016

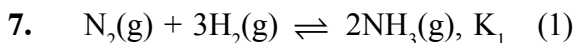
25. For the reaction of option (B) if degree of dissociation varies inversely as square root of pressure of the system. Suppose at constant temperature volume is increased 16 times of its initial volume the degree of dissociation ( $\alpha$ ) for this reaction will become :

- (A) 4 times                      (B) 2 times                      (C) 1/4 times                      (D) 1/2 times

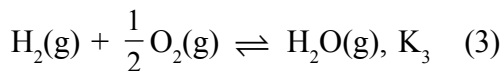
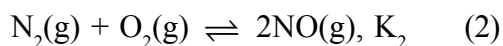
CE1017

## EXERCISE # J-MAIN

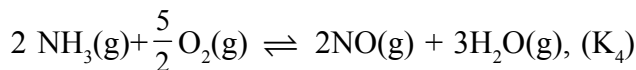
1. A vessel at 1000 K contains  $\text{CO}_2$  with a pressure of 0.5 atm. Some of the  $\text{CO}_2$  is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is :-  
[AIEEE-2011]  
(1) 0.3 atm                      (2) 0.18 atm                      (3) 1.8 atm                      (4) 3 atm  
CE0108
2. The equilibrium constant ( $K_C$ ) for the reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$  at temperature T is  $4 \times 10^{-4}$ . The value of  $K_C$  for the reaction.  $\text{NO}(\text{g}) \longrightarrow \frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$  at the same temperature is :-  
[AIEEE-2012]  
(1) 50.0                      (2) 0.02                      (3)  $2.5 \times 10^2$                       (4)  $4 \times 10^{-4}$   
CE0109
3. 8 mol of  $\text{AB}_3(\text{g})$  are introduced into a 1.0  $\text{dm}^3$  vessel. If it dissociates as  $2\text{AB}_3(\text{g}) \rightleftharpoons \text{A}_2(\text{g}) + 3\text{B}_2(\text{g})$ . At equilibrium, 2mol of  $\text{A}_2$  are found to be present. The equilibrium constant of this reaction is :-  
[JEE-MAINS(online)-12]  
(1) 36                      (2) 3                      (3) 27                      (4) 2  
CE0110
4. The value of  $K_p$  for the equilibrium reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  is 2. The percentage dissociation of  $\text{N}_2\text{O}_4(\text{g})$  at a pressure of 0.5 atm is  
[JEE-MAINS(online)-12]  
(1) 71                      (2) 50                      (3) 88                      (4) 25  
CE0111
5.  $K_1$ ,  $K_2$  and  $K_3$  are the equilibrium constants of the following reactions (I), (II) and (III), respectively  
(I)  $\text{N}_2 + 2\text{O}_2 \rightleftharpoons 2\text{NO}_2$  (II)  $2\text{NO}_2 \rightleftharpoons \text{N}_2 + 2\text{O}_2$  [JEE-MAINS(online)-12]  
(III)  $\text{NO}_2 \rightleftharpoons \frac{1}{2}\text{N}_2 + \text{O}_2$   
The correct relation from the following is :  
(1)  $K_1 = \sqrt{K_2} = K_3$                       (2)  $K_1 = \frac{1}{K_2} = \frac{1}{K_3}$   
(3)  $K_1 = \frac{1}{K_2} = K_3$                       (4)  $K_1 = \frac{1}{K_2} = \frac{1}{(K_3)^2}$   
CE0112
6. One mole of  $\text{O}_2(\text{g})$  and two moles of  $\text{SO}_2(\text{g})$  were heated in a closed vessel of one litre capacity at 1098 K. At equilibrium 1.6 moles of  $\text{SO}_3(\text{g})$  were found. The equilibrium constant  $K_C$  of the reaction would be :-  
[JEE-MAINS(online)-12]  
(1) 60                      (2) 80                      (3) 30                      (4) 40  
CE0113



[JEE-MAINS(online)-13]



The equation for the equilibrium constant of the reaction



in terms of  $K_1, K_2$  and  $K_3$  is :

(1)  $\frac{K_1 K_3^2}{K_2}$

(2)  $\frac{K_2 K_3^3}{K_1}$

(3)  $\frac{K_1 K_2}{K_3}$

(4)  $K_1 K_2 K_3$

CE0114

8. In reaction  $\text{A} + 2\text{B} \rightleftharpoons 2\text{C} + \text{D}$ , initial concentration of B was 1.5 times of  $[\text{A}]$ , but at equilibrium the concentrations of A and B became equal. The equilibrium constant for the reaction is :

[JEE-MAINS(online)-13]

(1) 4

(2) 6

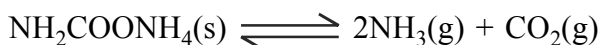
(3) 12

(4) 8

CE0115

9. For the decomposition of the compound, represented as

[JEE-MAINS(online)-14]



the  $K_p = 2.9 \times 10^{-5} \text{ atm}^3$ .

If the reaction is started with 1 mol of the compound, the total pressure at equilibrium would be

(1)  $38.8 \times 10^{-2} \text{ atm}$

(2)  $1.94 \times 10^{-2} \text{ atm}$

(3)  $5.82 \times 10^{-2} \text{ atm}$

(4)  $7.66 \times 10^{-2} \text{ atm}$

CE0116

10. For the reaction  $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$ , if  $K_p = K_C (\text{RT})^x$  where the symbols have usual meaning

then the value of x is : (assuming ideality)

[JEE-MAINS-14]

(1)  $\frac{1}{2}$

(2) 1

(3) -1

(4)  $-\frac{1}{2}$

CE0117

11. The equilibrium constants at 298 K for a reaction  $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$  is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in  $\text{mol L}^{-1}$ ) will be :

[JEE-MAINS-16]

(1) 1.182

(2) 0.182

(3) 0.818

(4) 1.818

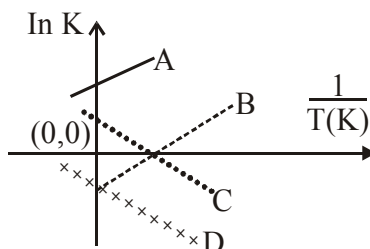
CE0118

12. The following reaction occurs in the Blast Furnace where iron ore is reduced to iron metal:  

$$\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightleftharpoons 2\text{Fe}(\text{l}) + 3\text{CO}_2(\text{g})$$
 [JEE-MAINS(online)-17]  
 Using the Le Chatelier's principle, predict which one of the following will **not** disturb the equilibrium?  
 (1) Removal of  $\text{CO}_2$  (2) Addition of  $\text{Fe}_2\text{O}_3$   
 (3) Addition of  $\text{CO}_2$  (4) Removal of  $\text{CO}$

CE0119

13. Which of the following lines correctly show the temperature dependence of equilibrium constant,  $K$ , for an exothermic reaction ? [JEE-MAINS(offline)-18]



- (1) B and C (2) C and D (3) A and D (4) A and B

CE0120

14. In which of the following reactions, an increase in the volume of the container will favour the formation of products ? [JEE-MAINS(online)-18]  
 (1)  $2\text{NO}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$   
 (2)  $3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$   
 (3)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$   
 (4)  $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$

CE0121

15. At a certain temperature in a 5 L vessel, 2 moles of carbon monoxide and 3 moles of chlorine were allowed to reach equilibrium according to the reaction, [JEE-MAINS(online)-18]  

$$\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$$

At equilibrium, if one mole of  $\text{CO}$  is present then equilibrium constant ( $K_c$ ) for the reaction is :-

- (1) 4 (2) 3 (3) 2 (4) 2.5 [JEE-MAINS(online)-18]

CE0122

16. At 320 K, a gas  $\text{A}_2$  is 20% dissociated to  $\text{A}(\text{g})$ . The standard free energy change at 320 K and 1 atm in  $\text{J mol}^{-1}$  is approximately : [JEE-MAINS(online)-18]  
 $(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}; \ln 2 = 0.693; \ln 3 = 1.098)$   
 (1) 4281 (2) 4763 (3) 2068 (4) 1844

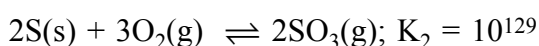
CE0123

17. The gas phase reaction  $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$  is an exothermic reaction. The decomposition of  $\text{N}_2\text{O}_4$ , in equilibrium mixture of  $\text{NO}_2(\text{g})$  and  $\text{N}_2\text{O}_4(\text{g})$ , can be increased by :-

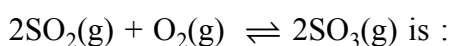
- (1) Addition of an inert gas at constant volume. [JEE-MAINS(online)-18]  
 (2) Increasing the pressure.  
 (3) Lowering the temperature.  
 (4) Addition of an inert gas at constant pressure.

CE0124

18. For the following reactions, equilibrium constants are given : [JEE-MAINS(online)-19]



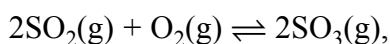
The equilibrium constant for the reaction,



- (1)  $10^{181}$                       (2)  $10^{154}$                       (3)  $10^{25}$                       (4)  $10^{77}$

CE0125

19. For the reaction, [JEE-MAINS(online)-19]



$$\Delta H = -57.2 \text{ kJ mol}^{-1} \text{ and}$$

$$K_c = 1.7 \times 10^{16}.$$

Which of the following statement is INCORRECT?

- (1) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required.  
 (2) The equilibrium will shift in forward direction as the pressure increase.  
 (3) The equilibrium constant decreases as the temperature increases.  
 (4) The addition of inert gas at constant volume will not affect the equilibrium constant.

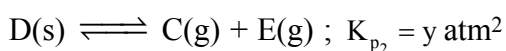
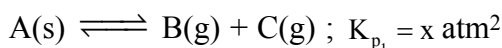
CE0126

20. In which one of the following equilibria,  $K_p \neq K_c$  ? [JEE-MAINS(online)-19]

- (1)  $\text{NO}_2(\text{g}) + \text{SO}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \text{SO}_3(\text{g})$       (2)  $2 \text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$   
 (3)  $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$                       (4)  $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$

CE0127

21. Two solids dissociate as follows [JEE-MAINS(online)-19]



The total pressure when both the solids dissociate simultaneously is :-

- (1)  $(x + y) \text{ atm}$                       (2)  $x^2 + y^2 \text{ atm}$                       (3)  $2(\sqrt{x + y}) \text{ atm}$                       (4)  $\sqrt{x + y} \text{ atm}$

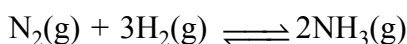
CE0128

22. In a chemical reaction,  $A + 2B \xrightleftharpoons{K} 2C + D$ , the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant(K) for the aforesaid chemical reaction is : [JEE-MAINS(online)-19]

(1) 16                                      (2) 4                                      (3) 1                                      (4)  $\frac{1}{4}$

CE0129

23. Consider the reaction,

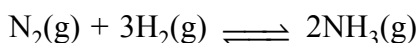
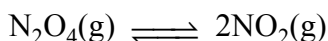
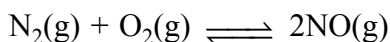


The equilibrium constant of the above reaction is  $K_p$ . If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that  $P_{NH_3} \ll P_{total}$  at equilibrium)

(1)  $\frac{3^{\frac{3}{2}} K_p^{\frac{1}{2}} P^2}{4}$                                       (2)  $\frac{3^{\frac{3}{2}} K_p^{\frac{1}{2}} P^2}{16}$                                       (3)  $\frac{K_p^{\frac{1}{2}} P^2}{16}$                                       (4)  $\frac{K_p^{\frac{1}{2}} P^2}{4}$

CE0130

24. The value of  $K_p/K_C$  for the following reactions at 300K are, respectively :  
(At 300K,  $RT = 24.62 \text{ dm}^3\text{atm mol}^{-1}$ )

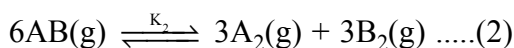
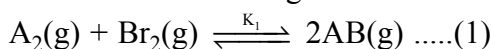


(1) 1,  $24.62 \text{ dm}^3\text{atm mol}^{-1}$ ,  $606.0 \text{ dm}^6\text{atm}^2\text{mol}^{-2}$   
 (2) 1,  $4.1 \times 10^{-2} \text{ dm}^{-3}\text{atm}^{-1} \text{ mol}^{-1}$ ,  $606.0 \text{ dm}^6 \text{ atm}^2 \text{ mol}^{-2}$   
 (3)  $606.0 \text{ dm}^6\text{atm}^2\text{mol}^{-2}$ ,  $1.65 \times 10^{-3} \text{ dm}^3\text{atm}^{-2} \text{ mol}^{-1}$   
 (4) 1,  $24.62 \text{ dm}^3\text{atm mol}^{-1}$ ,  $1.65 \times 10^{-3} \text{ dm}^{-6}\text{atm}^{-2} \text{ mol}^2$

CE0131

25. Consider the following reversible chemical reactions :

[JEE-MAINS(online)-19]



The relation between  $K_1$  and  $K_2$  is :

(1)  $K_2 = K_1^3$                                       (2)  $K_2 = K_1^{-3}$                                       (3)  $K_1 K_2 = 3$                                       (4)  $K_1 K_2 = \frac{1}{3}$

CE0132

26. 5.1g  $NH_4SH$  is introduced in 3.0 L evacuated flask at  $327^\circ\text{C}$ . 30% of the solid  $NH_4SH$  decomposed to  $NH_3$  and  $H_2S$  as gases. The  $K_p$  of the reaction at  $327^\circ\text{C}$  is ( $R = 0.082 \text{ L atm mol}^{-1}\text{K}^{-1}$ , Molar mass of S =  $32 \text{ g mol}^{-1}$ , molar mass of N =  $14 \text{ g mol}^{-1}$ ) [JEE-MAINS(online)-19]

(1)  $1 \times 10^{-4} \text{ atm}^2$                                       (2)  $4.9 \times 10^{-3} \text{ atm}^2$                                       (3)  $0.242 \text{ atm}^2$                                       (4)  $0.242 \times 10^{-4} \text{ atm}^2$

CE0133

**EXERCISE # J-ADVANCED**

1. The thermal dissociation equilibrium of  $\text{CaCO}_3(\text{s})$  is studied under different conditions.



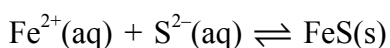
[JEE 2013]

For this equilibrium, the correct statement(s) is(are)

- (A)  $\Delta H$  is dependent on T  
(B) K is independent of the initial amount of  $\text{CaCO}_3$   
(C) K is dependent on the pressure of  $\text{CO}_2$  at a given T  
(D)  $\Delta H$  is independent of the catalyst, if any

CE0134

2. For the following reaction, the equilibrium constant  $K_c$  at 298 K is  $1.6 \times 10^{17}$ .



When equal volumes of 0.06 M  $\text{Fe}^{2+}(\text{aq})$  and 0.2 M  $\text{S}^{2-}(\text{aq})$  solutions are mixed, the equilibrium concentration of  $\text{Fe}^{2+}(\text{aq})$  is found to be  $Y \times 10^{-17}$  M. The value of Y is (upto two decimal places.)

[JEE 2019]

CE0135



## ANSWER KEY

## EXERCISE # S-I

1. (a) incomplete (b) almost complete

$$2. \quad (a) \quad K_p = \frac{(P_{SO_3})}{(P_{SO_2})(P_{O_2})^{\frac{1}{2}}}; \quad K_c = \frac{[SO_3]}{[SO_2][O_2]^{\frac{1}{2}}}$$

(b)  $K_c = [H_2O]$  [here  $H_2O(\ell)$  is a pure liquid so its concentration is 1.]

$$K_p = P_{H_2O}$$

= vapour pressure

= aqueous tension

(c)  $K_c = [NH_3]^2 [CO_2]$  ( $\because$  active mass of solid is 1)

$$K_p = (P_{NH_3})^2 P_{CO_2}$$

(d)  $K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$  [here  $H_2O$  is not in excess]

$K_p$  is not defined for liquid phase.

(e)  $K_c = \frac{[NH_4^+][OH^-]}{[NH_3]}$  [here  $H_2O(\ell)$  is in excess (solvent) so its concentration is 1]

(f)  $K_{PC} = \frac{P_{H_2} \times [Zn^{2+}]}{[H^+]^2}$  [ $\because$  active mass of solid is 1]

3. (a) Here,  $\Delta n_g = 1 + 1 - 1 = 1$

$$K_p = K_c (RT)^1 = K_c RT$$

(b) Here,  $\Delta n_g = 2 - (3+1) = -2$

$$K_p = K_c (RT)^{-2}$$

(c) Here,  $\Delta n_g = 2 - (1+1) = 0$

$$K_p = K_c (RT)^0 = K_c$$

(d) Here,  $\Delta n_g = 2 + 1 - 2 = 1$

$$K_p = K_c (RT)^1 = K_c RT$$

(e) Here,  $\Delta n_g = 2 - (2 + 1) = -1$

$$K_p = K_c (RT)^{-1} = K_c / RT$$

4.  $\therefore K_1 > K_2$

So the stability of  $XO < XO_2$ For reactants, stability increases when value of  $K$  decreases.

5.  $Q_c > K_c$  so the reaction will proceed in the reverse direction.

6. (a)  $Q_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$  [  $\therefore$  Water is not a solvent here]

(b)  $K_c = \frac{(0.171) \times (0.171)}{(1 - 0.171) \times (0.180 - 0.171)} = 3.92$

(c)  $Q_c = \frac{(0.214) \times (0.214)}{(0.786) \times (0.286)} = 0.204 \neq K_c$

 $\therefore$  Equilibrium has not been reached.

7.  $2 \times 10^9$

8. 0.9

9.  $K_c = 100$

10.  $K_p = 0.2463$

11.  $64 \times 10^{-32}$

12.  $K_c = 0.44$

13.  $K_p = 1.2 \text{ atm}$ .

14.  $[HI] = \frac{1}{3} M$

$[I_2] = [H_2] = \frac{1}{30} M$

15. (a) 0.1 (b) 0.4

16.  $[A] = 5 M, [B] = 5 M, [C] = 1 M, [D] = 25 M$

17. new equilibrium	$PCl_5$	$PCl_3$	$Cl_2$
Mole	4	4	2
Partial pressure	20 atm	20 atm	10 atm

18.  $\alpha = \sqrt{\frac{K_p}{4P + K_p}}$

19. (A)  $\alpha = \frac{4}{5} = 0.8$  (B)  $K_c = 16$

20.  $K_c = 0.001$

21.  $[NO] = 2M, [N_2] = [O_2] = 0.5M$

22.  $P_{ClF} = P_{F_2} = 0.1 \text{ atm}, P_{ClF_3} = 0.5 \text{ atm}$  23.  $K_p = 0.4, a \sim 0.1$

24. 50% 25.  $K_p = 0.01 \text{ atm}$

26.  $K_p = 2.5 \text{ atm}, P = 15 \text{ atm}$  27.  $K = 4$



**EXERCISE # O-II**

- |          |            |            |              |
|----------|------------|------------|--------------|
| 1. (B)   | 2. (C,D)   | 3. (C,D)   | 4. (A,B,C,D) |
| 5. (C,D) | 6. (A,C,D) | 7. (A,B,C) | 8. (C,D)     |
| 9. (A,C) | 10. (A)    | 11. (D)    | 12. (A)      |
| 13. (A)  | 14. (B)    | 15. (C)    | 16. (B)      |
| 17. (A)  | 18. (D)    | 19. (A)    | 20. (A)      |

Match the column :

21. (A) - P,R,S (B) - P,Q,R,S (C) - P, Q, R, S ; (D) - Q  
 22. A - (s), B - (p,q,s), C - (p,q,r), D - (r)  
 23. (D)                      24. (C)                      25. (A)

**EXERCISE # J-MAIN**

- |              |             |             |             |
|--------------|-------------|-------------|-------------|
| 1. Ans.(3)   | 2. Ans.(1)  | 3. Ans(3)   | 4. Ans(1)   |
| 5. Ans(4)    | 6. Ans(2)   | 7. Ans(2)   | 8. Ans(1)   |
| 9. Ans(3)    | 10. Ans.(4) | 11. Ans.(4) | 12. Ans.(2) |
| 13. Ans.(4)  | 14. Ans.(1) | 15. Ans.(4) | 16. Ans.(2) |
| 17. Ans.(4)  | 18. Ans.(3) | 19. Ans.(1) | 20. Ans.(4) |
| 21. Ans. (3) | 22. Ans.(2) | 23. Ans.(2) | 24. Ans.(4) |
| 25. Ans.(2)  | 26. Ans.(3) |             |             |

**EXERCISE # J-ADVANCED**

1. Ans.(A,B,D)  
 2. Ans.(8.92 or 8.93)

## RADIOACTIVITY

### 1. NUCLEAR CHEMISTRY

Nuclear chemistry deals with the phenomenon related with nucleus, like Radioactivity, Nuclear fission and fusion reactions, etc.

### 2. NUCLEAR STABILITY

The number of discovered elements till date is 118. All have some isotopes. The total number of isotopes is about 2000. Among these isotopes, the number of non-radioactive isotopes is even less than 300. Most of the isotopic forms have unstable nucleus due to very strong protonic repulsion. These unstable nuclei undergo spontaneous disintegration, causing radioactivity.

The stability of few nuclei against very strong protonic repulsion may be explained by the following theories :

#### 2.1 NUCLEAR FORCE THEORY :

Nuclear force is an imaginary force which holds the nucleons together.

- i. The exact nature of force is not known because it does not obey inverse square law.
- ii. It is a very short range force & it drops to 0 at  $10^{-14}$ m. The nuclear force becomes repulsive at very small distance ( $8 \times 10^{-16}$ m).
- iii. Nuclear force acts equally between all the nucleons.  $p-p = n-n = n-p$
- iv. In the stable nucleus, the nuclear force is stronger than protonic repulsion.
- v. On increasing atomic number, protonic repulsion increases. As the nuclear force can't hold the particles, nucleus becomes unstable.

#### 2.2 YUKAWA'S MESON THEORY :

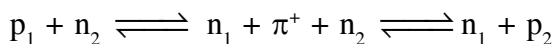
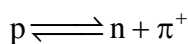
Yukawa suggested that inside the nucleus, interconversion between proton & neutron occur with the help of mesons by which nucleons hold each other.

p-meson or pions  $\pi^0 \quad \pi^+ \quad \pi^-$

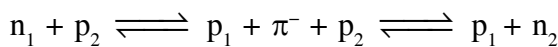
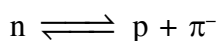
$\mu$ -meson or muons  $\mu^0 \quad \mu^+ \quad \mu^-$

mass of meson = (200 to 300)  $\times m_e$

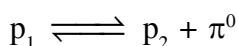
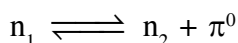
##### (i) Role of positive meson :



##### (ii) Role of negative meson :



##### (iii) Role of neutral meson :



### 2.3 MASS DEFECT AND BINDING ENERGY :

For all the isotopes (radioactive/non-radioactive), the theoretical mass (sum of masses of protons, neutrons and electrons) is greater than its isotopic (actual) mass. This difference in mass is called **mass defect** ( $\Delta m$ ). For example,

For  ${}^4_2\text{He}$ , isotopic mass = 4.0026 u

Now, Mass due to  $e^- = 2 \times 0.00054 = 0.00108\text{u}$

Mass due to p =  $2 \times 1.00727 = 2.01454\text{u}$

Mass due to n =  $2 \times 1.00867 = 2.01734\text{u}$

	4.03296u
Total	

The decrease in mass is due to its conversion into energy at the time of atom formation, by Einstein equation :

$$E = \Delta m \cdot c^2$$

As this energy is released in binding the particles together, it is called

**binding energy.**

If  $\Delta m = 1 \text{ a.m.u.}$ ,

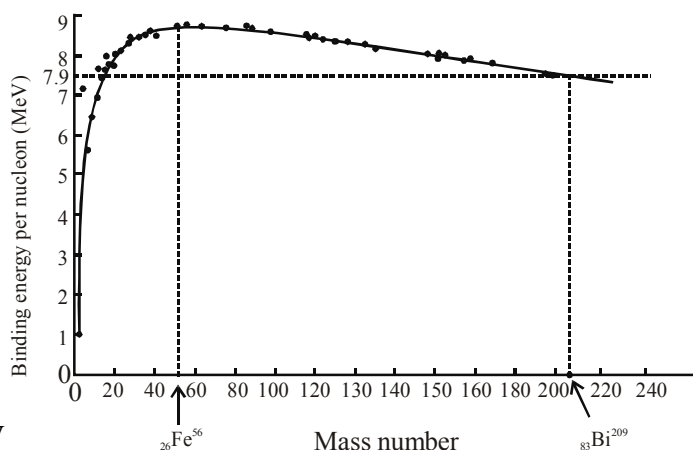
then B.E.,  $E \simeq 1.5 \times 10^{-10} \text{ J} \simeq 931.5 \text{ MeV}$

\* Binding energy per nucleon gives a quantitative measure

of nuclear stability.  $\text{B.E. per nucleon} = \frac{\text{B.E.}}{\text{No. of nucleons}}$

Greater the value of B.E. per nucleon, more is the stability of nucleus.

- (i) Nuclear binding energy is maximum for mass number 50 – 60.
- (ii) Fe, Co, Ni have very high binding energy per nucleon.
- (iii) A very heavy nucleus, say  $A = 240$ , has lower binding energy per nucleon compared to that of a nucleus with  $A = 120$ . Thus if a nucleus  $A = 240$  breaks into two  $A = 120$  nuclei, energy would be released in the process. This implies nucleons get more tightly bound. It has very important applications for energy production through fission.
- (iv) Consider two very light nuclei ( $A \leq 10$ ) joining to form a heavier nucleus. The binding energy per nucleon of the heavier nuclei is more than the binding energy per nucleon of the lighter nuclei, again energy would be released in such a process of fusion.
- (v) All the nuclei having BE/nucleon greater than 7.9 MeV are stable. The value 7.9 is not applicable for lighter nuclei because they may be stable even at lower value.



**Ex.1.** Calculate BE/nucleon for  ${}_{17}\text{Cl}^{35}$

$$m_e = 0.00054 \text{ u}, m_p = 1.00727 \text{ u}, m_n = 1.00867 \text{ u}$$

**Sol.**  $\Delta m = (17 \times 0.00054 + 17 \times 1.00727 + 18 \times 1.00867) - 35 = 0.28883 \text{ u}$

$$\text{B.E.} = 0.28883 \times 931.5 = 269.045 \text{ MeV}$$

$$\therefore \text{B.E. nucleon} = \frac{269.045}{35} = 7.687 \text{ MeV}$$

**Ex.2.** Calculate BE for an additional neutron in  ${}_{3}\text{Li}^6$  nucleus. Nuclear mass of  $\text{Li}^6 = 6.0025$ ,  $\text{Li}^7 = 7.0081$ ,  $m_n = 1.0087 \text{ u}$

**Sol.**  ${}_{3}\text{Li}^6 + {}_0\text{H}^1 \rightarrow {}_{3}\text{Li}^7$

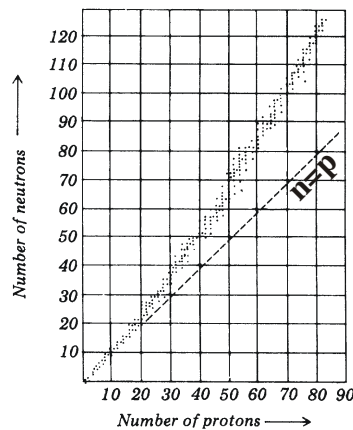
$$\Delta m = (6.0025 + 1.0087) - 7.0081 = 0.0031 \text{ u}$$

$$\therefore \text{Energy released} = 0.0031 \times 931.5 = 2.888 \text{ MeV}$$

**Ex.3.** A nucleus  $A^{240}$  (BE/nucleon = 7.3 MeV) dissociate into two identical nuclei  $B^{120}$ , (BE/nucleon = 8.2 MeV). Calculate the amount of energy absorbed or released.

**Sol.** Energy released =  $2 \times 120 \times 8.2 - 240 \times 7.3 = 216 \text{ MeV}$

#### 2.4. NEUTRON / PROTON RATIO AND STABILITY BELT :



- ◆ All the stable nuclei lie in a zone or belt of stability, as shown in the figure.
- ◆ None of the stable nucleus have  $\frac{n}{p}$  ratio less than 1 (except  ${}_{1}\text{H}^1$ ) and greater than 1.52 ( $\frac{n}{p}$  ratio of heaviest stable nucleus  ${}_{83}\text{Bi}^{209}$ ).
- ◆ In lighter nuclei ( $Z < 20$ ),  $\frac{n}{p}$  ratio of stable nuclei is very close to 1.

## 2.5 EVEN ODD THEORY :

The number of stable nuclides is maximum when both protons and neutrons are even numbers.

p	n	No. of stable nucleus	Examples
even	even	~ 165	${}^2_2\text{He}^4, {}^6_6\text{C}^{12}, {}^8_8\text{O}^{16}$ , etc
even	odd	~ 55	${}^4_4\text{Be}^9, {}^6_6\text{C}^{13}, {}^8_8\text{O}^{17}$ , etc
odd	even	~ 50	${}^3_3\text{Li}^7, {}^5_5\text{B}^{11}, {}^9_9\text{F}^{19}$ , etc
odd	odd	5	${}^1_1\text{H}^2, {}^3_3\text{Li}^6, {}^5_5\text{B}^{10}, {}^7_7\text{N}^{14}, {}^{73}_{73}\text{Ta}^{180}$

- ◆ Nearly 60% of stable nuclei have even number of protons and neutrons.

## 2.6 MAGIC NUMBERS :

Nuclei with 2, 8, 20, 28, 50, 82 or 126 protons or neutrons are exceptionally stable and have a larger number of stable isotopes than neighboring nuclei in the periodic table. These numbers are called magic numbers. They are supposed to represent completely filled nuclear shells or energy levels.

e.g.  ${}_{50}\text{Sn}$  having 10 stable isotopes while  ${}_{51}\text{Sb}$  has only two stable isotopes.

- ◆ Nuclei with magic number of protons as well as neutrons have notably high stabilities. [eg.  ${}^4_2\text{He}$ ,  ${}^{16}_8\text{O}$ ,  ${}^{40}_{20}\text{Ca}$  and  ${}^{208}_{82}\text{Pb}$  ].

## 3. RADIO ACTIVITY

The spontaneous emission of particles, electromagnetic radiation or both by unstable nuclei, is known as radioactivity. Only unstable nuclei exhibit this property.

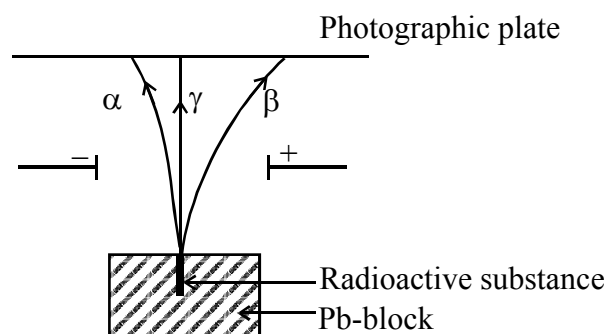
This phenomenon (radioactivity) was discovered by Henry Becquerel. On working with uranium salt, he observed that some radiations having the following properties come out from these salts:

- They blacken the photographic plates.
- They cause fluorescence on ZnS screen.
- They ionise the gas through which they pass.

He gave the name **becquerel rays** to these radiations.

Later on, **Madam Curie** discovered two elements Radium (Ra) and Polonium (Po). She found that these elements as well as their salts emit similar radiations. She generalised the name of Becquerel rays as **radioactive rays** and the phenomenon, as **radioactivity**.

## 4. NATURE OF RADIOACTIVE RAYS





4.1 PROPERTIES OF  $\alpha$ ,  $\beta$ -PARTICLES AND  $\gamma$ -RAYS :

	Properties	Alpha	Beta	Gamma
1.	Nature	Fast moving He nuclei	Fast moving electrons	Electromagnetic radiation of very high energy.
2.	Representation	${}_2\text{He}^4$ or $\alpha$	${}_{-1}\text{e}^0$ or ${}_{-1}\beta^0$ or $\beta^-$	$\gamma$ or ${}_0^0\gamma$
3.	Charge	2 unit (+ve)	1 unit (-ve)	no charge
4.	Velocity	10-20% of speed of light	33% to 90% of speed of light	Same as light waves
5.	Relative penetrating power	1 (0.01 mm of Al foil)	100 (0.1 cm Al foil)	10000 (8 cm lead or 25 cm steel)
6.	Travel distance in air (Range)	2 – 4 cm	200 – 300 cm	–
7.	Kinetic energy	high	low	–
8.	Effect on ZnS plate	Luminosity	Little effect	–
9.	Mass g/particle	$6.64 \times 10^{-27}$ kg	$9.109 \times 10^{-31}$ kg	–
10.	Relative ionising power	10000	100	1

4.2.  $\alpha$ -DECAY :

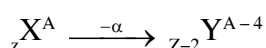
If any  $\alpha$ -emitter is taken in a closed vessel, after sufficient time, presence of He gas is observed in the vessel. It is experimental fact considering  $\alpha$ -particle as  $\text{He}^{2+}$  ion or He nucleus.

It is assumed that inside the nuclides, some p & n exists as a  $\alpha$ -particle due to the following facts :

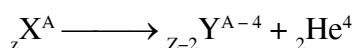
- (a) Initially all the lighter nuclides ( $Z \leq 19$ ) were transmuted by  $\alpha$ -particles except  ${}_2\text{He}^4$ ,  ${}_4\text{Be}^8$ ,  ${}_6\text{C}^{12}$ . These nuclides were supposed to have 1, 2 and 3  $\alpha$ -particles respectively.
- (b) Among the lighter nucleides, BE/nucleon for He is exceptionally high ( $\approx 7\text{MeV}$ ). Hence the combination of 2p & 2n as  $\alpha$ -particles is considered stable combination.
- (c) Among p, n, deuteron (d) &  $\alpha$ -decay, Q value is positive only for  $\alpha$ -decay (energy is released). Hence among these decay,  $\alpha$ -decay is only spontaneous decay.

(i) Effects of  $\alpha$ -decay :

- (a) The atomic number decreases by two units and mass number by 4 units per decay.



- (b) n/p ratio increases on  $\alpha$ -decay.
- (c) Isodiaphers are formed. Isodiaphers are the atoms of different elements having the same number of excess neutron over proton. [Same  $[N - P]$  difference.]

**(ii) Q-value for  $\alpha$ -emission :**

$$\Delta m = (\text{nucleidic mass } {}_Z X^A) - (\text{nucleidic mass } {}_{Z-2} Y^{A-4} + {}_2 \text{He}^4)$$

$$= \text{Atomic mass of } {}_Z X^A - \text{At mass of } ({}_{Z-2} Y^{A-4} + {}_2 \text{He}^4)$$

$$\text{Now, } Q = \Delta m C^2 = \Delta m \times 931.5 \text{ MeV.}$$

**(iii) KE of emitted  $\alpha$ -particle :**

$$Q \text{ value} = (\text{KE})_\alpha + (\text{KE})_Y \quad \begin{array}{c} X \\ \longleftarrow \bullet \longrightarrow \\ Y \qquad \qquad \alpha \end{array}$$

$$\& \quad (mV)_\alpha = (mV)_Y$$

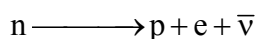
$$(\text{KE})_\alpha = \frac{m_Y}{m_Y + m_\alpha} \times Q = \frac{A-4}{A} Q$$

All the  $\alpha$ -particle emitted out from a particular radio-nucleide must have same KE, if the contribution of  $\gamma$ -photon is neglected.

**4.3  $\beta$ -DECAY :**

On  $\beta$ -decay, the atomic species get changed and hence  $\beta$  decay is always due to some nuclear change.

(i) A neutron breaks into proton, electron & anti-neutrino. As e and anti-neutrino can never exist in the nucleus, they come out.

**(ii) Effect of  $\beta$ -decay :**

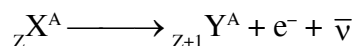
(a) The atomic number increases by one unit but the mass number remains unchanged.

(b) n/p ratio decreases.

(c) Isobars are formed. (Atom of different elements having same mass number)

(d) Isotopes are formed by the sequential decay of  $1\alpha$  &  $2\beta$  particles. (Atoms of same element having different mass numbers.)

(e) Normally a radio nucleide either undergoes  $\alpha$  or  $\beta$  decay. There are very few radio nucleides which undergo simultaneous  $\alpha$  &  $\beta$  decay.

**(iii) Q-value**

$$\Delta m = \text{nucleidic mass } [{}_Z X^A - ({}_{Z+1} Y^A + m_e + m_{\bar{\nu}})]$$

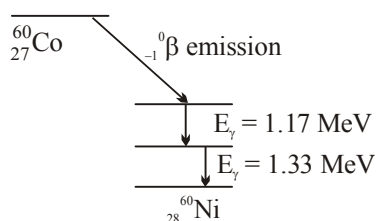
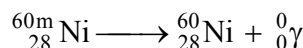
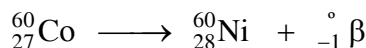
$$= \text{At mass } ({}_Z X^A - {}_{Z+1} Y^A)$$

$$Q = \Delta m c^2$$

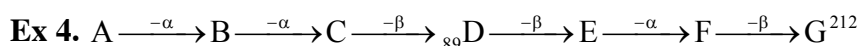
(iv) **K.E. of  $\beta$ -particle :** The Q value will be shared between emitted  $\beta$ -particles & antineutrino. Hence KE of  $\beta$ -particles may have any value from 0 to Q value. The  $\beta$ -particle emitted out from a particular radionucleide may have different KE.

4.4.  $\gamma$ -DECAY :

This is a secondary phenomenon. When an  $\alpha$  or  $\beta$  decay takes place, the daughter nucleus generally formed is in excited state & comes to ground state by a single or successive transitions by emitting electromagnetic radiations i.e.  $\gamma$  rays.



- i. The atomic number & mass number remain unchanged.
- ii. Nuclear isomers are formed. They have same nuclear composition but different energy.



(i) Identify isotopic pairs

**Sol.** (B, E) ; (C, F) ; (D, G)

(ii) What is the atomic & mass number of A

**Sol.** 92, 224

**Ex 5.** Which of the following may be the disintegration product of  ${}_{92}\text{U}^{238}$

- I. (a)  ${}_{90}\text{Th}^{234}$       (b)  ${}_{88}\text{Ra}^{232}$       (c)  ${}_{85}\text{Ra}^{235}$       (d)  ${}_{87}\text{Fr}^{227}$

(a)

- II. (a)  ${}_{88}\text{Ra}^{230}$       (b)  ${}_{89}\text{Ac}^{230}$       (c)  ${}_{87}\text{Fr}^{230}$       (d)  ${}_{87}\text{Fr}^{226}$

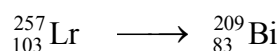
(e)  ${}_{86}\text{Rn}^{226}$

**Sol.** (a, b, d, e)

**Ex 6.** Russian and American scientist have artificially prepared elements with atomic number greater than 100. The number of alpha and beta particles produced when one atom of  ${}_{103}^{257}\text{Lr}$  decay after being produced by artificial means to its stable product is -

- (A) 4  $\alpha$  and 5  $\beta$       (B) 4  $\alpha$  and 12  $\beta$       (C) 12  $\alpha$  and 4  $\beta$       (D) 12  $\alpha$  and 5  $\beta$

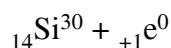
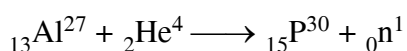
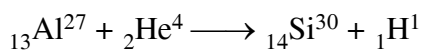
**Sol. 6. Ans. (C)**



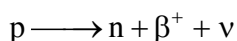
### 4.5 POSITRON DECAY :

Given by Irene Curie and F. Juliot.

When  $\text{Mg}^{24}$ ,  $\text{Al}^{27}$  or  $\text{B}^{10}$  were bombarded by  $\alpha$ -particle, emission of p, n &  $\beta^+$  (positron) occur. On stopping the bombardment, p & n emission stop but  $\beta^+$  emission continues obeying 1<sup>st</sup> order kinetics. The isotope responsible for such  $\beta^+$  emission is called artificial **radio isotope** and the phenomenon as artificial radioactivity.



In positron decay, a proton (inside the nucleus) breaks into neutron, positron and neutrino.

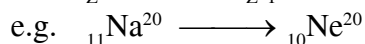
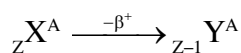


As  $\beta^+$  and  $\nu$  can never exist in the nucleus, they come out, resulting positron decay.

**Note:** A free neutron may break into proton (mass decreases) but a free proton can never break into neutron (mass increases). Inside the nucleus, both conversions are possible because of involvement of nucleus.

#### (i) Effect of $\beta^+$ -decay :

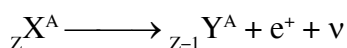
- (a) The atomic number decreases by one unit but the mass number remain unchanged.



- (b) Isobars are formed.

- (c) n/p ratio increase.

#### (ii) Q-value :

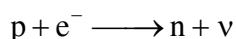


$$\begin{aligned} \Delta m &= (\text{nucleidic mass of } {}_Z\text{X}^A) - (\text{nucleidic mass of } {}_{Z-1}\text{Y}^A + \text{mass of } \beta^+ + \text{mass of } \nu) \\ &= \text{At mass } ({}_Z\text{X}^A - {}_{Z-1}\text{Y}^A) - 2m_e \end{aligned}$$

- (iii) **K.E. of  $\beta^+$  :** The KE of emitted  $e^+$  may have any value from 0 to Q-value.

### 4.6. K-CAPTURE OR ELECTRON CAPTURE :

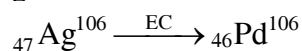
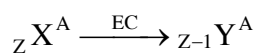
In electron capture, nucleus captures an electron of K-shell. Proton converts into neutron inside the nucleus.



As neutrino can not exist in the nucleus, it comes out.

#### (i) Effects of electron capture :

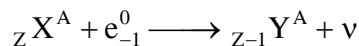
- (a) Atomic number decreases by one unit but mass number remains unchanged.



- (b)  $\frac{n}{p}$  ratio increases

- (c) Isobar is formed.
- (d) As one electron from K-shell is captured by nucleus, electron from higher shell de-excite to K-shell, emitting X-rays.

(ii) **Q-value :**



$$\Delta m = (\text{nuclear mass of } {}_Z X^A + \text{mass of electron}) - (\text{nuclear mass of } {}_{Z-1} Y^A + \text{mass of neutrino})$$

$$= \text{Atomic mass of } {}_Z X^A - \text{Atomic mass of } {}_{Z-1} Y^A$$

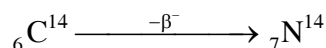
$$\text{and Q-value} = \Delta m \cdot C^2$$

(iii) **K.E. of emitted neutrino** = Q-value

**5. PREDICTION OF KIND OF RADIOACTIVE DECAY:**

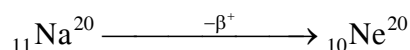
- (i)  $\frac{n}{p}$  ratio increases in  $\alpha$ -decay,  $\beta^+$ -decay and electron capture but  $\frac{n}{p}$  ratio decreases in  $\beta^-$ -decay.

If the  $\frac{n}{p}$  ratio of any radioisotope is greater than that of non-radioactive (stable) isotope of the same element, the possible mode of decay is  $\beta^-$ -decay. For example,  ${}_6 C^{12}$  is non-radioactive and  ${}_6 C^{14}$  is  $\beta^-$  emitter.



$$\frac{n}{p} = \frac{8}{6} > \frac{6}{6} \text{ of } {}_6 C^{12} \quad \frac{n}{p} = \frac{7}{7}$$

If the  $\frac{n}{p}$  ratio is smaller, the possible mode of decay may be  $\alpha$ -decay or  $\beta^+$ -decay or electron capture. For example,  ${}_{11} Na^{23}$  is non-radioactive and  ${}_{11} Na^{20}$  is  $\beta^+$ -emitter.



$$\frac{n}{p} = \frac{9}{11} < \frac{12}{11} \text{ of } {}_{11} Na^{23} \quad \frac{n}{p} = \frac{10}{10}$$

- (ii) Normally,  $\alpha$ -decay occurs only in heavier nucleus
- (iii) If (atomic mass of  ${}_Z X^A$  - Atomic mass of  ${}_{Z-1} Y^A$ ) is less than mass of two electrons,  $\beta^+$ -decay is not possible (Q-value will become negative)

**Ex.7.** Predict the possible mode of radioactive decay by (i)  ${}_1 H^3$  (ii)  ${}_8 O^{18}$  (iii)  ${}_2 He^3$  (iv)  ${}_2 He^6$

**Sol.** (i)  $\left(\frac{n}{p}\right)$  of  ${}_1 H^3 = \frac{2}{1} > \left(\frac{n}{p}\right)$  of  ${}_1 H^1$  or  ${}_1 H^2$

hence,  ${}_1 H^3$  is  $\beta^-$ -emitter.

$$(ii) \left(\frac{n}{p}\right) \text{ of } {}_8\text{O}^{18} = \frac{10}{8} > \left(\frac{n}{p}\right) \text{ of } {}_8\text{O}^{16}$$

hence,  ${}_8\text{O}^{18}$  is  $\beta^-$  - emitter

$$(iii) \left(\frac{n}{p}\right) \text{ of } {}_2\text{He}^3 < \left(\frac{n}{p}\right) \text{ of } {}_2\text{He}^4$$

hence,  ${}_2\text{He}^3$  may be  $\beta^+$  - emitter

$$(iv) \left(\frac{n}{p}\right) \text{ of } {}_2\text{He}^6 > \left(\frac{n}{p}\right) \text{ of } {}_2\text{He}^4$$

hence,  ${}_2\text{He}^6$  is  $\beta^-$  -emitter

**Ex.8.** The isotope  ${}_{71}\text{Lu}^{173}$  is neutron deficient for stability. The isotopic masses of  ${}_{71}\text{Lu}^{173}$  and stable isotope  ${}_{70}\text{Yb}^{173}$  are 172.9390 and 172.9383 amu, respectively. Predict whether  ${}_{71}\text{Lu}^{173}$  decays by  $\beta^+$  - emission or electron capture or both.

**Sol.**  $\Delta m = 172.9390 - 172.9383 = 0.0007 \text{ amu} < 2 \times \text{mass of electron}$

Hence,  ${}_{71}\text{Lu}^{173}$  can not undergo  $\beta^+$ -decay. The decay mode must be electron capture.

## 6. RADIOACTIVE DISINTEGRATION SERIES

Many radioactive nucleus ( $Z > 82$ ) are obtained as a member of decay series.

The series of nuclei is known as radioactive disintegration series.

Series	Parent Nucleus	Last Nucleus	No. of $\alpha$ -particles	No. of $\beta$ -particles
4n or Thorium series	${}_{90}\text{Th}^{232}$	${}_{82}\text{Pb}^{208}$	6	4
(4n+1) or Neptunium series	${}_{94}\text{Pu}^{241}$	${}_{83}\text{Bi}^{209}$	8	5
4n+2 or Uranium series	${}_{92}\text{U}^{238}$	${}_{82}\text{Pb}^{206}$	8	6
4n + 3 or Actinium series	${}_{92}\text{U}^{235}$	${}_{82}\text{Pb}^{207}$	7	4

4n, 4n + 2 and 4n + 3 series are natural while (4n + 1) is artificial.



## 7. RATE LAW

## • Rutherford and Soddy's law :

At an instant, rate of decay or disintegration of active nuclei is directly proportional to the number of active nuclei at that instant.

$-\frac{dN}{dt}$  = rate of decay or activity (A) at time t and N = active nuclei at time t

$$-\frac{dN}{dt} \propto N \text{ or } -\frac{dN}{dt} = \lambda N \quad \dots(i)$$

Here  $\lambda$  is the decay constant or disintegration constant, which is characteristic of that radioisotope, independent from any chemical or physical condition.

**Integral rate law :**  $N = N_0 e^{-\lambda t}$

## 7.1 UNITS OF RATE OF DECAY OR ACTIVITY :

1 Becquerel (1 Bq) = 1 dps (SI unit)

1 Curie (Ci) =  $3.70 \times 10^{10}$  dps

1 Rutherford (1 Rd) =  $10^6$  dps

• **Specific activity :** Activity of 1 gm sample of radioactive substance. Its unit is (dps per gram)

Specific activity of radium (226) is 1 Ci/gm.

• **Geiger – Muller counter** is used for detecting and counting the  $\alpha$  and  $\beta$ -particles.7.2 HALF LIFE ( $T_{1/2}$ ) :

It is the time in which half of the active nuclei decay

$$T_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

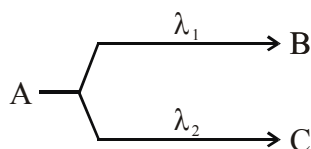
After 'n' half lives, the activity as well as the number of active nuclei reduced to  $\frac{1}{2^n}$  times of initial value.

7.3 MEAN OR AVERAGE LIFE ( $T_{av}$ ) :

It is the average age of all active nuclei i.e.

$$T_{av} = \frac{\text{sum of times of existance of all nuclei in a sample}}{\text{initial number of active nuclei in that sample}} = \frac{1}{\lambda}$$

## 7.4 PARALLEL DECAY:





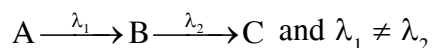
(a) The overall decay constant of A,  $\lambda = \lambda_1 + \lambda_2$

(b) 
$$\frac{N_B}{N_C} = \frac{\lambda_1}{\lambda_2}$$

(c)  $\lambda_1 =$  fractional yield of B  $\times \lambda$

(d)  $\lambda_2 =$  fractional yield of C  $\times \lambda$

### 7.5 SEQUENTIAL DECAY :



(a) At any time, t:

$$N_A = N_A^0 \cdot e^{-\lambda \cdot t}$$

$$N_B = \frac{\lambda_1 \cdot N_A^0}{\lambda_2 - \lambda_1} \cdot (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

$$N_C = N_A^0 - (N_A + N_B)$$

(b) Time for maximum nuclei fo B,

$$T_{\max} = \frac{1}{\lambda_2 - \lambda_1} \cdot \ln \frac{\lambda_2}{\lambda_1}$$

(c) Maximum nuclei of B,

$$N_{B_{\max}} = N_A^0 \cdot \left( \frac{\lambda_2}{\lambda_1} \right)^{\frac{-\lambda_2}{\lambda_2 - \lambda_1}}$$

(d) For steady state of B (radioactive equilibrium  $\lambda_1 \cdot N_A = \lambda_2 \cdot N_B$ )

**Ex.9** A free neutron is unstable against  $\beta$ -decay with a half life of about 600 seconds.—

(i) Write the expression of this decay process.

(ii) If there are 600 free neutrons initially, calculate the time by which 450 of them have decayed.

Also determine the initial decay rate of the sample.

**Sol.** (i)  $n \rightarrow p + e^- + \bar{\nu}$

(ii) The number of undecayed neutron would be 150 by using  $N = N_0 e^{-\lambda t}$

$$150 = 600 e^{-\lambda t} \Rightarrow t = 2T_{1/2} = 1200 \text{ sec}$$

$$\text{Decay rate (initial) } R = \lambda N_0 = \frac{0.693}{600} \times 600 = 0.693 \text{ dps}$$

**Ex.10.** Obtain the amount of polonium necessary to provide a radioactivity source of 5.0 mili curie strength. The half life of polonium is 138 days.

Given : 1 curie =  $3.7 \times 10^{10}$  disintegration/sec., Avogadro number =  $6.02 \times 10^{26}$  per k-mole

**Sol.** Given :  $r = 5 \times 10^{-3} \times 3.7 \times 10^{10}$  disint./sec. &  $t_{1/2} = 138 \times 24 \times 3600$  sec and  $r = \lambda N$

$$= \frac{0.693}{t_{1/2}} N$$

$$\Rightarrow N = \frac{138 \times 24 \times 3600 \times 5 \times 3.7 \times 10^7}{0.693} = 3.18 \times 10^{15} \text{ atoms}$$

$$\therefore \text{Amount of } {}_{84}\text{Po}^{210} \text{ in grams required} = \frac{210 \times 3.18 \times 10^{15}}{6.02 \times 10^{23}} = 1.11 \times 10^{-6}$$

**Ex.11.** Calculate the radioactive disintegration constant if  $3.7 \times 10^{10}$  alpha particles are emitted by 1 gram of radium per second. Avogadro's number is  $6.03 \times 10^{23}$  and the mass number of radium is 226.

**Sol.** Activity =  $N\lambda = \left( \frac{N_A}{M_w} \times m \right) \lambda$

$$\Rightarrow 3.7 \times 10^{10} = \left( \frac{6.03 \times 10^{23}}{226} \times 1 \right) \lambda$$

$$\lambda = \frac{3.7 \times 10^{10} \times 226}{6.03 \times 10^{23}} = 1.38 \times 10^{-11} \text{ per second}$$

**Ex.12.** The half lives of X and Y are 3 minutes and 27 minutes respectively. At some instant activity of both are same, then the ratio of active nuclei of X and Y at that instant is ?

**Sol.**  $A_1 = \lambda_1 N_1$  and  $A_2 = \lambda_2 N_2$

$$A_1 = A_2 \Rightarrow \frac{0.693}{T_1} N_1 = \frac{0.693}{T_2} N_2$$

$$\Rightarrow \frac{N_1}{T_1} = \frac{N_2}{T_2} \Rightarrow \frac{N_1}{N_2} = \frac{3}{27} = \frac{1}{9}$$

$$\Rightarrow N_1 : N_2 = 1 : 9$$

**Ex.13.** Decay constant of two radioactive samples is  $\lambda$  and  $3\lambda$  respectively. At  $t = 0$ , they have equal number of active nuclei. Calculate when will be the ratio of active nuclei becomes  $e : 1$ .

**Sol.** Number of active nuclei of two radioactive sample is

$$N_1 = N_{01} e^{-\lambda t} \text{ and } N_2 = N_{02} e^{-3\lambda t}$$

$$\therefore \frac{N_1}{N_2} = \frac{e}{1} = \frac{N_{01} e^{-\lambda t}}{N_{02} e^{-3\lambda t}} = e^{2\lambda t} \quad [ \because N_{01} = N_{02} ]$$

$$\therefore 1 = 2\lambda t \Rightarrow t = \frac{1}{2\lambda}$$

**Ex.14.** The fraction of a radioactive sample which remains active after time  $t$  is  $\frac{9}{16}$ . What fraction remains active after  $\frac{t}{2}$  time ?

**Sol.** Active fraction  $= \frac{N}{N_0} = e^{-\lambda t}$  At time  $t$ ,  $\frac{9}{16} = e^{-\lambda t}$

At time  $t/2$  active fraction  $= x = e^{-\lambda t/2} = (e^{-\lambda t})^{\frac{1}{2}}$

$$\text{So } x = \left(\frac{9}{16}\right)^{\frac{1}{2}} = \frac{3}{4}$$

**Ex.15.** Two radioactive nuclides A and B have half life 150 min and 15 mins respectively. A fresh sample contains nuclides of B to be 32 times that of A. How much time should elapse so that number of nuclides of A becomes twice that of B ?

**Sol.** (100 sec)

$N_0$  = initial nuclides of A

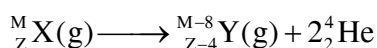
$$\text{After } t \text{ mins, } N_0 e^{-\left(\frac{\ln 2}{150}\right)t} = 2 \left[ 32 N_0 e^{-\left(\frac{\ln 2}{15}\right)t} \right] \Rightarrow t = 100 \text{ sec.}$$

**Ex.16.**  ${}^M_Z X(g) \longrightarrow {}^{M-8}_{Z-4} Y(g) + \alpha - \text{particles}$

The radioactive disintegration follows first order kinetics starting with one mole of X in a 12-litre closed flask at 27°C. Find the total pressure (in atm) after two half lives.

$$[R = 0.08 \text{ L atm mol}^{-1} \text{ K}^{-1}]$$

**Ans. 5**



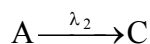
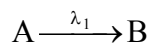
$$t = 0 \quad 1 \text{ mol} \quad 0 \quad 0$$

$$t = 2t_{1/2} \quad 0.25 \text{ mol} \quad 0.75 \text{ mol} \quad 1.5 \text{ mol}$$

$$\begin{aligned} \text{total gaseous moles} &= 0.25 + 0.75 + 1.5 \\ &= 2.5 \text{ mol} \end{aligned}$$

$$p = \frac{nRT}{V} = \frac{2.5 \times 0.08 \times 300}{12} = 5 \text{ atm}$$

**Ex.17.** In the parallel radioactive decay,



the time when number of radioactive nuclei of A, B & C becomes equal is

$$[\text{Given } \lambda_1 = \ln 3 \text{ hr}^{-1}, \lambda_2 = \ln 3 \text{ hr}^{-1}]$$

(1) 0.5 min (2) 30 min (3) 60 min (4) 90 min

**Ex.17. Ans.(2)**

**Sol.**  $C_A = C_{A_0} - C_B - C_C$

$$x = C_{A_0} - x - x$$

$$\text{or } 3x = C_{A_0} \Rightarrow x = \frac{C_{A_0}}{3}$$

$$\therefore C_A = C_{A_0} e^{-(\lambda_1 + \lambda_2)t}$$

$$\text{or } \frac{C_{A_0}}{3} = C_{A_0} e^{-(\lambda_1 + \lambda_2)t}$$

$$\text{or } 3 = e^{(\lambda_1 + \lambda_2)t}$$

$$\text{or } t = \frac{\ln 3}{2 \ln 2} = \frac{1}{2} \text{ hr} = 30 \text{ min}$$

**8. APPLICATION OF RADIOACTIVITY AND RADIO ISOTOPES****8.1 IN MEDICINE :**

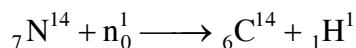
- (i) Testing of blood circulation –  $\text{Cr}^{57}$
- (ii) Brain tumour detecting –  $\text{Hg}^{203}$
- (iii) Thyroid testing (cancer) –  $\text{I}^{131}$
- (iv) Cancer cure –  $\text{Co}^{60}$
- (v) Blood cancer cure –  $\text{Au}^{189}, \text{Na}^{24}, \text{P}^{32}$

**8.2 IN AGRICULTURE :**

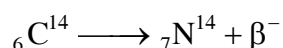
- (i) For protecting potato from earthworm –  $\text{Co}^{60}$
- (ii) Fertilizers –  $\text{P}^{32}$

**8.3 IN ARCHAEOLOGY :****8.3.1 Carbon dating (age of fossils) :**

Radiocarbon ( ${}^6\text{C}^{14}$ ) dating of historical wooden derived objects is based on the knowledge that the cosmic ray intensity (responsible for  $\text{C}^{14}$  production) has been practically constant for thousands of years.  $\text{C}^{14}$  is formed in the upper atmosphere by the action of cosmic radiation of  $\text{N}^{14}$ .



The  $\text{C}^{14}$  so produced is eventually converted into  $\text{CO}_2$ , which in turn is incorporated into plants and trees by the process of photosynthesis and then finds way into animals, which eat plants. Because of the natural plant-animal cycle, an equilibrium is set up and all living matter contains the same proportion of  $\text{C}^{14}$  as it occurs in the atmosphere. Once the plant or animal dies, the uptake of the  $\text{CO}_2$  by it ceases and the level of  $\text{C}^{14}$  in the dead begins to fall due to  $\beta^-$  decay.



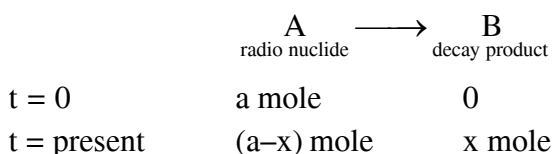
A comparison of the  $\beta^-$ -activity of the dead matter with that of the carbon still in circulation enables measurement of the period of isolation of the material from the living cycle (age of fossil).

**Ex.18.** The beta activity of 1 g of carbon made from green wood is 15.3 counts per minute. If the activity of 1 g of carbon derived from the wood of an Egyptian mummy case is 9.4 counts per minute under the same conditions, how old is the wood of the mummy case?  $t_{1/2}$  of  $C^{14} = 5770$  yrs.

**Sol.** 
$$t = \frac{t_{1/2}}{\log 2} \cdot \log \frac{r_0}{r} = \frac{5770}{\log 2} \cdot \log \frac{15.3}{9.4} \approx 3920 \text{ yrs.}$$

**8.3.2 Rock dating (Age of minerals, rocks, earth, etc) :**

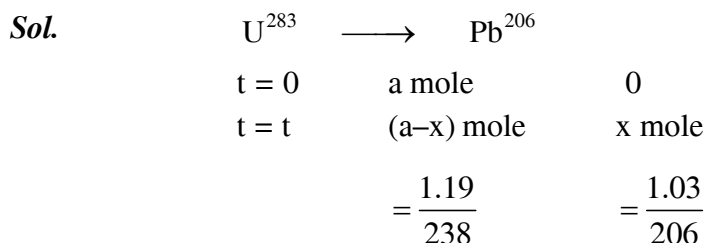
The age of the rocks and minerals may be determined by analysing the sample for a radionuclide (say  $U^{238}$ ) and its decay product ( $Pb^{206}$ ). Assuming that no decay product was present initially and all the intermediate products ( if any) have achieved steady state, we can determine the age.



$\therefore$  age of rock,  $t = \frac{1}{\lambda}, \ln \frac{a}{a-x}$

In the determination of age of earth, moon, etc, it is assumed that the rock was present from the time of evolution of earth, moon, etc.

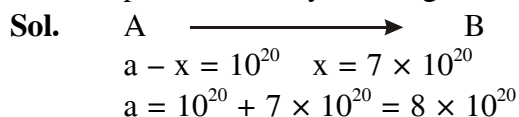
**Ex.19.** A rock was found to contain  $U^{238}$  and  $Pb^{206}$  in 1.19: 1.03 mass ratio. What is the age of rock?  $t_{1/2}$  of  $U^{238} = 4.5 \times 10^9$  yrs.



$\therefore x = 5 \times 10^{-3}$  and  $a = 10 \times 10^{-3}$

Now,  $t = \frac{t_{1/2}}{\log 2} \cdot \log \frac{a}{a-x} = 4.5 \times 10^9$  yrs

**Ex.20.** To determine age of a stone it was analysed and  $10^{20}$  nuclei of A &  $7 \times 10^{20}$  nuclei of B were obtained. If nuclei B are assumed to be obtained only due to radioactive decay of A and no B was present initially. Find age of stone in days. [Half life of A = 1000 days]

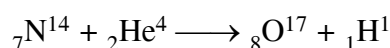


$$\frac{a}{a-x} = \frac{8}{1}$$

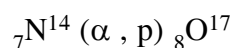
$$t = 3 \times t_{1/2} = 3 \times 1000 = 3000 \text{ days}$$

## 9. NUCLEAR REACTIONS

The reactions in which nuclei of atoms interact with other nuclei or elementary particles such as  $\alpha$ -particle, proton, neutron, deuteron, etc, resulting in the formation of new nuclei with or without liberation of one or more elementary particles, are called nuclear reactions. The particles causing nuclear reactions are also called projectiles. In all the nuclear reactions, the sum of number of protons and neutrons and the total charge are conserved. Nuclear reactions may be expressed as similar as chemical reactions, like



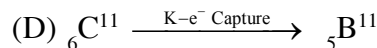
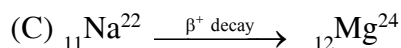
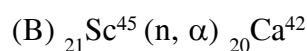
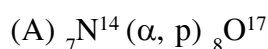
Here, the nucleus of nitrogen atom is converted in to the nucleus of oxygen atom by  $\alpha$ -particle and proton is also produced as a by-product. These reactions may be expressed by short hand notation, in which the projectile and the liberating particle are expressed by their symbols, in a small bracket in between the parent and the product nucleus. For example, the above reaction may also be expressed as :



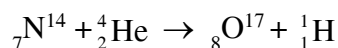
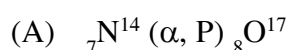
### 9.1 SOME DIFFERENCES BETWEEN NUCLEAR AND CHEMICAL REACTIONS :

No.	Chemical reaction	Nuclear reaction
1.	No new element is formed	New element is formed
2.	Valence electrons of atoms participates	Only the nucleus of atoms participates
3.	Balanced by the conservation of atoms	Balanced by the conservation of nuclear charge and mass number (total number of neutrons and protons)
4.	Mass conservation is obeyed	Disobey mass conservation
5.	May be exothermic or endothermic, liberating or absorbing relatively small amount of energy	May be exothermic or endothermic, liberating or absorbing relatively very high amount of energy
6.	May be reversible	Irreversible
7.	May obey kinetics of any order	Obeys only first order kinetics
8.	Rate depends on external factors like temperature and the catalytic conditions	Rate is independent of any external condition

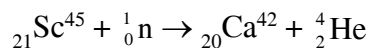
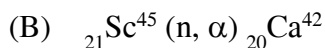
**Ex.21.** Select the incorrect nuclear reaction -



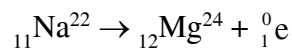
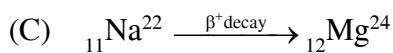
**Ans (B, C)**



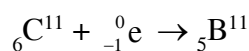
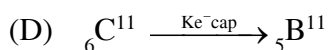
(A) is correct



(B) is incorrect



(C) is incorrect

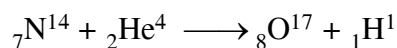


(D) is correct

hence Ans is (B) & (C)

## 9.2 ARTIFICIAL TRANSMUTATION :

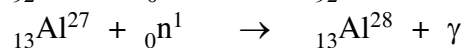
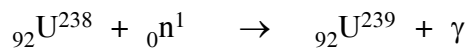
It is the method of conversion of atom of one element in to the atom of other element with the help of some particles like alpha particle, proton, deuteron, neutron, etc (called projectiles). The first such transmutation was performed by Rutherford. When  $\text{N}^{14}$  atoms were bombarded by very fast moving  $\alpha$ -particles, the nitrogen atom has changed in to oxygen atom and proton is produced simultaneously



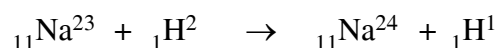
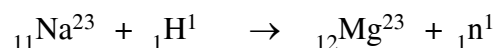
Later on, Rutherford and Chadwick showed that most of the nuclei may be transmuted by the suitable projectile. After the discovery of cyclotron, a particle accelerating machine, such transmutations became easier.

## 9.3 TYPES OF NUCLEAR REACTIONS :

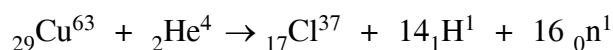
### (A) Projectile Capture Reactions :



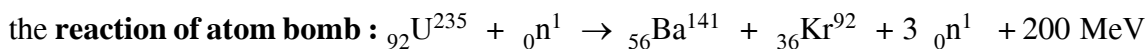
### (B) Particle - particle reactions :



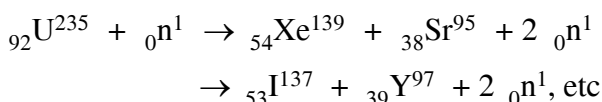
### (C) Spallation reactions : High speed projectiles with 400MeV bombarded on high nucleus giving smaller nucleus.



(D) **Fission reactions** : It is the nuclear reaction in which a heavy nucleus is broken down by a slow or thermal neutron (energy about 0.04 eV) into two relatively smaller nuclei with the emission of two or more neutrons and large amount of energy. For example,



It is also found that the products of nuclear fission reactions are not unique. Some more products are formed. The most probable mass numbers of the two nuclides formed are around 95 and 140 and an average of 2.5 neutrons is emitted out per fission.



The destructive action of atom bomb is due to the following reasons:

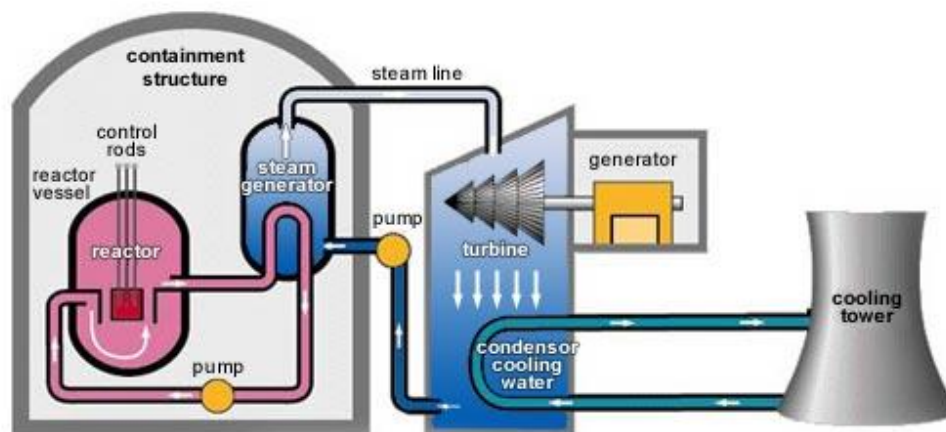
- (i) As some neutrons are produced in each fission, they may collide efficiently with the other  $\text{U}^{235}$  nuclei to produce more neutrons and thus the reaction occurs in chain like fashion. It results the emission of a large amount of energy in very small time.
- (ii) Each product of fission is radioactive and hence increases the intensity of radiation in that region, causing the problems due to radiations.

(E) **Fusion reactions**: It is the nuclear reaction in which two or more light nuclei fused together to form heavier nuclei, with the evolution of tremendous amount of energy. In such reactions, relatively more stable nucleus having higher binding energy per nucleon is formed. Such reaction is difficult to occur because when the nuclei of different atoms come closer, they repel each other strongly. This is why, very high temperature of the order  $10^6\text{K}$  is needed for the occurrence of such reactions. However, the overall reaction is highly exothermic due to large mass defect. Some examples of nuclear fusion reactions are :



## 10. NUCLEAR REACTOR

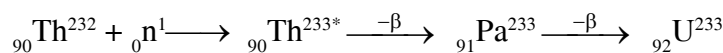
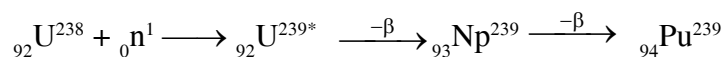
A nuclear reactor is the furnace, place where nuclear fission reaction is performed to get energy. The essentials of a nuclear reactor are:





(A) **Fuel** : Nuclear fuels are of two types:

- (i) **Fissile materials** : These are the nuclides which directly results chain reaction on bombardment with slow neutrons. Such nuclides are  $U^{235}$ ,  $Pu^{239}$ ,  $U^{233}$ , etc.
- (ii) **Fertile material** : These are the nuclides which are non-fissile, but they may be converted in to a fissile material by the action of neutrons. Such nuclides are  $U^{238}$  and  $Th^{232}$ .



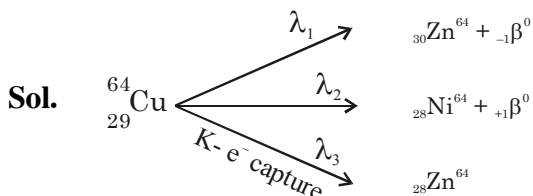
Such conversions are performed in a special type of nuclear reactor called **Breeder Reactor**.

- (B) **Moderator**: It is used to slow down the fast neutrons without absorbing them. Example: water, graphite, helium,  $D_2O$  etc.
- (C) **Control rods**: These are the rods of material which can absorb neutrons and hence control the fission reaction. Example: Cadmium, boron, etc.
- (D) **Coolant** : These are the material which transforms the energy produced in the fission reaction in to heat energy. Example: Liquid alloy of sodium and potassium, heavy water, polyphenyls, etc

## PREVIOUS MISCELLANEOUS QUESTION

Q.1  $^{64}\text{Cu}$  (half-life = 12.8 hr) decays by  $\beta^-$  emission (38%),  $\beta^+$  emission (19%) and electron capture (43%). Write the decay product and calculate partial half-lives for each of the decay processes. [JEE 2002]

Ans.  $^{64}_{30}\text{Zn}$ ,  $^{64}_{28}\text{Ni}$ ,  $(t_{1/2})_1 = 33.68$  hr,  $(t_{1/2})_2 = 67.36$  hr,  $(t_{1/2})_3 = 29.76$  hr



$$\frac{\lambda_1}{\lambda_1 + \lambda_2 + \lambda_3} \times 100 = 38 \quad \text{.....(i)}$$

$$\frac{\lambda_2}{\lambda_1 + \lambda_2 + \lambda_3} \times 100 = 18 \quad \text{.....(ii)}$$

$$\frac{\ln 2}{\lambda_1 + \lambda_2 + \lambda_3} = 12.8 \quad \text{.....(iii)}$$

On solving equations :

$$\lambda_1 = 0.38 (t_{1/2})_I = 33.68 \text{ hr} ; (t_{1/2})_{II} = 67.36 ; (t_{1/2})_{III} = 29.7 \text{ hr}$$

Q.2 A radioactive sample emits  $n$   $\beta$ -particles in 2 sec. In next 2 sec it emits  $0.75n$   $\beta$ -particles, what is the mean life of the sample? [JEE 2003]

Ans.  $1.75n = N_0(1 - e^{-4\lambda})$ , 6.95 sec,  $\frac{2}{\ln\left(\frac{4}{3}\right)}$

Sol.  $n = N_0[1 - e^{-2\lambda}] \quad \text{.....(i)}$

$1.75n = N_0[1 - e^{-4\lambda}] \quad \text{.....(ii)}$

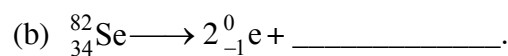
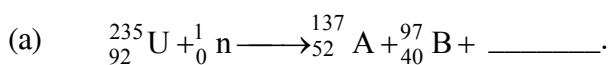
$\Rightarrow 1.75 = 1 + e^{-2\lambda}$

$$\frac{3}{4} = e^{-2\lambda}$$

$$\lambda = \frac{1}{2} \ln\left(\frac{4}{3}\right)$$

Q.3 Fill in the blanks

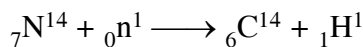
[JEE 2005]



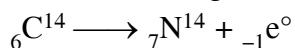
Ans. (a)  $2 {}^1_0\text{n}$ , (b)  $^{82}_{36}\text{Kr}$

**Question No. 4 to 6 (3 questions)**

Carbon 14 is used to determine the age of organic material. The procedure is based on the formation of  $^{14}\text{C}$  by neutron capture in the upper atmosphere.



$^{14}\text{C}$  is absorbed by living organisms during photosynthesis. The  $^{14}\text{C}$  content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of  $^{14}\text{C}$  in the dead being falls due to the decay which  $\text{C}^{14}$  undergoes.



The half life period of  $^{14}\text{C}$  is 5770 years. The decay constant ( $\lambda$ ) can be calculated by using the

following formula  $\lambda = \frac{0.693}{t_{1/2}}$

The comparison of the  $\beta^-$  activity of the dead matter with that of carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 years. The proportion of  $^{14}\text{C}$  to  $^{12}\text{C}$  in living matter is 1 :  $10^{12}$

[JEE 2006]

Q.4 Which of the following option is correct ?

- (A) In living organisms, circulation of  $^{14}\text{C}$  from atmosphere is high so the carbon content is constant in organism
- (B) Carbon dating can be used to find out the age of earth crust and rocks
- (C) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbon content remains constant in living organism
- (D) Carbon dating cannot be used to determine concentration of  $^{14}\text{C}$  in dead beings.

Ans. (C)

Q.5 What should be the age of fossil for meaningful determination of its age?

- (A) 6 years
- (B) 6000 years
- (C) 60000 years
- (D) it can be used to calculate any age

Ans. (B)

Q.6 A nuclear explosion has taken place leading to increase in concentration of  $\text{C}^{14}$  in nearby areas.  $\text{C}^{14}$  concentration is  $C_1$  in nearby areas and  $C_2$  in areas far away. If the age of the fossil is determined to be  $t_1$  and  $t_2$  at the places respectively, then

(A) The age of the fossil will increase at the place where explosion has taken place and

$$t_1 - t_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

(B) The age of the fossil will decrease at the place where explosion has taken place and

$$t_1 - t_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

(C) The age of fossil will be determined to be the same

$$(D) \frac{t_1}{t_2} = \frac{C_1}{C_2}$$

Ans. (A)

**Sol.** Age in nearby areas :

$$\lambda t_1 = \ln \frac{C_1}{C_t} \dots\dots(i)$$

age in for away area

$$\lambda t_2 = \ln \frac{C_2}{C_t} \dots\dots(ii)$$

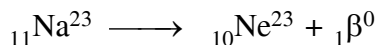
as  $C_1 > C_2$  so age of fossil increase is nearby areas by value.

$$(t_1 - t_2) = \frac{1}{\lambda} \ln \left( \frac{C_1}{C_2} \right)$$

Q.7 A positron is emitted from  ${}_{11}^{23}\text{Na}$ . The ratio of the atomic mass and atomic number of the resulting nuclide is [JEE 2006]

- (A) 22/10 (B) 22/11 (C) 23/10 (D) 23/12

**Ans.** (C)



$$\frac{n}{p} = \frac{23}{10}$$

Q.8 **STATEMENT-1** : The plot of atomic number (y-axis) versus number of neutrons (x-axis) for stable nuclei shows a curvature towards x-axis from the line of  $45^\circ$  slope as the atomic number is increased.

**and**

**STATEMENT-2** : Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides. [JEE 2008]

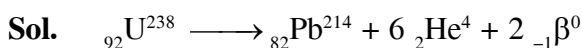
- (A) STATEMENT-1 is True, STATEMENT-2 is True ; STATEMENT-2 is a correct explanation for STATEMENT-1  
 (B) STATEMENT-1 is True, STATEMENT-2 is True ; STATEMENT-2 is NOT a correct explanation for STATEMENT-1  
 (C) STATEMENT-1 is True, STATEMENT-2 is False  
 (D) STATEMENT-1 is False, STATEMENT-2 is True

**Ans.** (A)

Q.9 The total number of  $\alpha$  and  $\beta$  particles emitted in the nuclear reaction  ${}_{92}^{238}\text{U} \rightarrow {}_{82}^{214}\text{Pb}$  is.

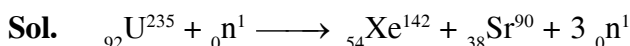
[JEE 2009]

**Ans.** (8)



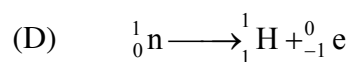
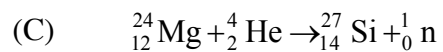
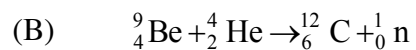
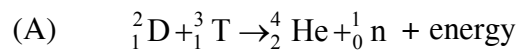
Q.10 The number of neutrons emitted when  ${}_{92}^{235}\text{U}$  undergoes controlled nuclear fission to  ${}_{54}^{142}\text{Xe}$  and  ${}_{38}^{90}\text{Sr}$  is - [JEE 2010]

**Ans.** (4)



Q.11 Match the Column-I with Column-II

Column-I



Column-II

(P)  $\beta$ -emission

(Q) Artificial transmutation

(R) Discovery of neutrons

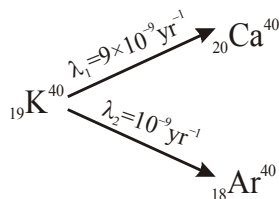
(S) Hydrogen bomb

Ans. (A) - S ; (B) - Q, R; (C) - Q ; (D) - P

## EXERCISE (S-1)

- Q.1 Of the three isobars  ${}_{48}^{114}\text{Cd}$ ,  ${}_{49}^{114}\text{In}$  and  ${}_{50}^{114}\text{Sn}$ , which is likely to be radioactive? Explain your choice. **RA0001**
- Q.2 Classify each of the following nuclides as "beta ( ${}_{-1}^0\beta$ ) emitter", or "positron ( ${}_{+1}^0\beta$ ) emitter":  
 ${}_{20}^{49}\text{Ca}$ ,  ${}_{80}^{195}\text{Hg}$ ,  ${}_{5}^8\text{B}$ ,  ${}_{67}^{150}\text{Ho}$ ,  ${}_{13}^{30}\text{Al}$ ,  ${}_{36}^{94}\text{Kr}$ . Note:  ${}_{36}^{84}\text{Kr}$ ,  ${}_{80}^{200}\text{Hg}$  and  ${}_{67}^{165}\text{Ho}$  are stable  
**RA0002**
- Q.3. (a) Calculate number of  $\alpha$  and  $\beta$ -particles emitted when  ${}_{92}\text{U}^{238}$  changes into radioactive  ${}_{82}\text{Pb}^{206}$ .  
 (b)  ${}_{92}\text{U}^{235}$  disintegrates and emits 4 $\beta$ - and 7 $\alpha$ -particles to form a stable element. Find the atomic number and mass number of the stable product. Also identify the element. **RA0003**
- Q.4 A radioactive isotope disintegrates and emits 6  $\beta$  and 7  $\alpha$  particles to form a stable product. Find the difference between atomic number of parent radioactive isotope and the stable product. **RA0004**
- Q.5 Find the  $\alpha$ -activity of 1 gm  ${}^{200}\text{Ra}$ . ( $\lambda = 4.8 \times 10^{-7} \text{min}^{-1}$ ) in dpm. ( $N_A = 6 \times 10^{23}$ ) **RA0005**
- Q.6 The half life of the nuclide  $\text{Rn}^{220}$  is 54.5 sec. Find mass (in kg) of radon is equivalent to 1 millicurie. **RA0006**
- Q.7 At any given time a piece of radioactive material ( $t_{1/2} = 30$  days) contains  $10^{12}$  atoms. Calculate the activity of the sample in dps. **RA0007**
- Q.8 The activity of the radioactive sample drops to 1/64 of its original value in 2 hr. Find the decay constant ( $\lambda$ ). **RA0008**
- Q.9 A radioactive substance decays 20% in 10 min. If at start there are  $5 \times 10^{20}$  atoms present, find time after which the number of atoms will be reduced to  $10^{18}$ . ( $\log 2 = 0.3$ ) **RA0009**
- Q.10 The half life period of  ${}_{53}\text{I}^{125}$  is 60 days. What % of radioactivity would be present after 240 days. **RA0010**
- Q.11 The activity of a radioactive sample decreases to 1/3 of the original activity ( $A_0$ ) in a period of 9 years. After 9 years more, its activity is  $A_0/x$ . Find the value of x. **RA0011**
- Q.12 5 moles of a radio-active isotope  ${}^A_Z\text{X}(s)$  were taken in a 24.6 litre vessel at 600K and the following decay started :  ${}^A_Z\text{X}(s) \longrightarrow {}^{A-8}_{Z-4}\text{Y}(s)$   
 If pressure developed after 16 hours was 15 atm, calculate half life of sample 'X' in hours.  
 Use :  $R = 0.082 \text{ L-atm/mol-K}$ . **RA0012**
- Q.13 Calculate the age of a vegetarian beverage whose tritium content is only 15% of the level in living plants. Given  $t_{1/2}$  for  ${}^3_1\text{H} = 12.3$  years. ( $\log 2 = 0.3$ ,  $\log 3 = 0.48$ ) **RA0013**
- Q.14 The volume of the blood in a patient is estimated by recording the activity of  $\text{Na}^{24}$  administered into the patient's blood. Find the volume (in  $\ell$ ) of the blood if the activity after 25 hrs is 8 dpm  $\text{m}\ell^{-1}$ . Given the initial activity of  $\text{Na}^{24}$  sample is  $2 \times 10^3 \text{ Bq}$  when administered & the  $t_{1/2}$  for  $\text{Na}^{24} = 15$  hrs. (use  $32^{1/3} \approx 3$ ) **RA0014**

- Q.15 A sample of  $U^{238}$  (half life =  $4.5 \times 10^9$  yr) ore is found to contain 23.8 g of  $U^{238}$  and 20.6 g of  $Pb^{206}$ . Calculate the age of the ore. **RA0015**
- Q.16 An isotopes of Potassium  $^{40}_{19}K$  has a half life of  $1.4 \times 10^9$  year and decays to Argon  $^{40}_{18}Ar$  which is stable.
- (i) Write down the nuclear reaction representing this decay.
- (ii) A sample of rock taken from the moon contains both potassium and argon in the ratio 1/3. Find age of rock. **RA0016**
- Q.17  $K^{40}$  decays into  $Ca^{40}$  &  $Ar^{40}$  simultaneously as follows



Ratio of atoms of 'Ar' to 'K' in a rock sample is 3 :10. Calculate age of rock sample assuming that source of 'Ar' is radioactive decay of ' $K^{40}$ ' only and no 'Ar' was present at the time of formation of rock.

**If your answer is  $(\ln x) \times 10^8$  years, then the value of 'x' is.** **RA0017**

- Q.18 Complete the following nuclear equations:
- (a)  ${}^1_7N + {}^4_2He \rightarrow {}^{17}_8O + \dots$  (b)  ${}^9_4Be + {}^4_2He \rightarrow {}^{12}_6C + \dots$
- (c)  ${}^9_4Be (p, \alpha) \dots$  x(d)  ${}^{30}_{15}P \rightarrow {}^{30}_{14}Si + \dots$
- (e)  ${}^3_1H \rightarrow {}^3_2He + \dots$  (f)  ${}^{43}_{20}Ca(\alpha, \dots) \rightarrow {}^{46}_{21}Sc$  **RA0018**
- (g)  ${}^{23}_{11}Na + {}^4_2He \rightarrow {}^{26}_{12}Mg + \dots$  (h)  ${}^{64}_{29}Cu \rightarrow \beta^+ + \dots$
- (i)  ${}^{106}_{47}Ag \rightarrow {}^{106}_{48}Cd + \dots$  (j)  ${}^{10}_5B + {}^4_2He \rightarrow {}^{13}_7N + \dots$  **RA0018**
- Q.19 Consider the following reaction ;  ${}^2H_1 + {}^2H_1 \rightarrow {}^4He_2 + Q$  : Mass of the deuterium atom = 2.0141 u ; Mass of the helium atom = 4.0024 u. Find approximate value of 'Q' (in MeV) **RA0020**
- Q.20 Calculate the energy released in MeV in the following nuclear reaction:
- $${}^2_1H + {}^2_1H \rightarrow {}^3_2He + {}^1_0n$$
- Assume that the masses of  ${}^2_1H$ ,  ${}^3_2He$  and neutron (n) respectively are 2.020, 3.016 and 1.008 in amu. **RA0021**

## EXERCISE (S-2)

- Q.1 In the nuclear reaction  $X^{200} \longrightarrow A^{110} + B^{90}$ . If the binding energy per nucleon for X, A and B is 7.4 MeV, 8.2 MeV and 8.2 MeV respectively, Find the energy released. **RA0022**
- Q.2 The binding energies per nucleon for  ${}_1\text{H}^2$  and  ${}_2\text{He}^4$  are 1.1 MeV and 7.0 MeV respectively. Find the energy released when two deuterons fuse to form a helium nucleus. **RA0023**
- Q.3 When  ${}_c^a\text{X}$  changes to  ${}_d^b\text{Y}$ . Find number of  $\alpha$  and  $\beta$  particle. **RA0024**
- Q.4 At a given instant there are 25 % undecayed radioactive nuclei in a sample. After 10 sec, the number of undecayed nuclei remains 12.5 % . Calculate :
- (i) mean – life of the nuclei and
- (ii) The time in which the number of undecayed nuclear will further reduce to 6.25 % of the reduced number. **RA0025**
- Q.5 One of the hazards of nuclear explosion is the generation of  $\text{Sr}^{90}$  and its subsequent incorporation in bones. This nuclide has a half life of 40 year. Suppose one microgram was absorbed by a new-born child, how much  $\text{Sr}^{90}$  will remain in his bones after 20 years? **RA0026**
- Q.6 During the decay of 928 gm  ${}_{90}\text{Th}^{232}$  to  ${}_{82}\text{Pb}^{208}$ , total  $9.3 \times 10^{24}$   $\beta$ -particle are emitted upto 't' time. Then calculate t/T.
- $[\lambda \text{ of "Th"} = \frac{\ln 2}{T}; N_A = 6 \times 10^{23}]$ . **RA0027**
- Q.7 The  $\beta$  count given by carbon obtained from an ancient fossil was 12 counts per second, while the  $\beta$ -count given by carbon sample from freshly cut tree was found to be 15 count per second. What is the age of fossil in years. Given : ( $t_{1/2}$  of  $\text{C}^{14} = 5770$  yrs,  $\ln 5 = 1.6$ ,  $\ln 2 = 0.7$ ) **RA0028**
- Q.8 The nuclidic ratio  ${}^3_1\text{H}$  to  ${}^1_1\text{H}$  in a sample of water is  $8.0 \times 10^{-18} : 1$  Tritium undergoes decay with a half-life period of 12 years. How many tritium atoms would 10.0 g of such a sample contain 36 years after the original sample is collected. **RA0029**
- Q.9  $\text{Ac}^{227}$  has a half life of 22 year w.r.t radioactive decay. The decay follows two parallel paths, one leading the  $\text{Th}^{227}$  and the other leading to  $\text{Fr}^{223}$ . the percentage yields of these two daughters nucleides are 2% and 98% respectively. What is the rate constant in  $\text{yr}^{-1}$ , for each of the separate paths? **RA0030**
- Q.10. Consider the following process of decay,
- ${}_{92}\text{U}^{234} \rightarrow {}_{90}\text{Th}^{230} + {}_2\text{He}^4; \quad t_{1/2} = 250000 \text{ yr}$
- ${}_{90}\text{Th}^{230} \rightarrow {}_{88}\text{Ra}^{226} + {}_2\text{He}^4; \quad t_{1/2} = 80000 \text{ yr}$
- ${}_{88}\text{Ra}^{226} \rightarrow {}_{86}\text{Rn}^{222} + {}_2\text{He}^4; \quad t_{1/2} = 1600 \text{ yr}$
- After the above process has occurred for a long time, a state is reached where for every two thorium atoms formed from  ${}_{92}\text{U}^{234}$ , one decomposes to form  ${}_{88}\text{Ra}^{226}$  and for every two  ${}_{88}\text{Ra}^{226}$  formed, one decomposes. Calculate the ratio of number of atoms of  ${}_{90}\text{Th}^{230}$  to  ${}_{88}\text{Ra}^{226}$  at this state. **RA0031**



EXERCISE (O-1)

- Q.1  ${}^{14}_6\text{C}$  decays by emission of  
 (A)  $\beta^-$  (B)  $\beta^+$  (C) n (D)  $\alpha$  **RA0032**
- Q.2 When  ${}^{30}_{15}\text{P}$  emits a positron, the daughter nuclide formed is  
 (A)  ${}^{15}_{15}\text{P}^{29}$  (B)  ${}^{30}_{16}\text{Si}^{30}$  (C)  ${}^{30}_{14}\text{Si}^{30}$  (D)  ${}^{30}_{16}\text{P}^{30}$  **RA0033**
- Q.3  ${}^{27}_{13}\text{Al}$  is a stable isotope.  ${}^{29}_{13}\text{Al}$  is expected to disintegrated by  
 (A)  $\alpha$  emission (B)  ${}^0_{-1}\beta$  emission (C) Positron emission (D) Proton emission **RA0034**
- Q.4 Loss of a  $\beta$  – particle is equivalent to  
 (A) Increase of one proton only  
 (B) Decrease of one neutron only  
 (C) Increase of one proton and decrease of one neutron  
 (D) None of these. **RA0035**
- Q.5 Which of the following nuclear reactions will generate an isotope?  
 (A) neutron emission (B) positron emission  
 (C)  $\alpha$ -emission (D)  $\beta$ -emission **RA0036**
- Q.6 The  $\text{S}^{35}$  is neutron-rich, therefore, it is likely to undergo radioactive decay by  
 (A) electron capture (B) beta emission (C) positron emission (D) alpha emission **RA0037**
- Q.7 The number of  $\alpha$  and  $\beta$ -particles emitted, when the following nuclear transformation takes place are \_\_\_\_\_ and \_\_\_\_\_ respectively.  

$${}^{238}_{92}\text{X} \longrightarrow {}^{206}_{82}\text{Y}$$
  
 (A) 6, 2 (B) 5, 6 (C) 8, 4 (D) 8, 6 **RA0038**
- Q.8  ${}^{88}_{35}\text{X}$  an unstable isotope, decays in two successive steps to produce stable isotope  ${}^{84}_{32}\text{Z}$  as  

$${}^{88}_{35}\text{X} \xrightarrow{\text{I}} \text{Y} \xrightarrow{\text{II}} {}^{84}_{32}\text{Z}$$
  
 The correct statement is (possible emission are  $\alpha$ ,  $\beta$ , positron, neutron, and K-capture)  
 (A) I may involve a  $\beta$ -emission. (B) II may involve a neutron emission  
 (C) Y and Z may be isodiaphers (D) X and Z may be isodiaphers **RA0039**
- Q.9 Which of the following can not be natural decay product (only  $\alpha$ ,  $\beta$  &  $\gamma$  decay) of  ${}^{232}_{90}\text{Th}$   
 (A)  ${}^{228}_{89}\text{Ac}$  (B)  ${}^{220}_{86}\text{Rn}$  (C)  ${}^{226}_{88}\text{Ra}$  (D)  ${}^{216}_{84}\text{Po}$  **RA0040**
- Q.10 The half-life of a radioactive isotope is three hours. If the initial mass of the isotope were 256 g, the mass of it remaining undecayed after 18 hours would be  
 (A) 16.0 g (B) 4.0 g (C) 8.0 g (D) 12.0 g **RA0041**
- Q.11 The half-life of a radioisotope is four hours. If the initial rate of the isotope was 200 dpm, the rate after 24 hours is  
 (A) 6.25 dpm (B) 2.084 dpm (C) 3.125 dpm (D) 4.167 dpm **RA0042**

- Q.12 The half life of  $Tc^{99}$  is 6.0 hr. The delivery of a sample of  $Tc^{99}$  from the reactor to the nuclear medicine lab of a certain hospital takes 3.0 hr. What is the minimum amount of  $Tc^{99}$  that must be shipped in order for the lab to receive 10.0 mg? ( $\sqrt{2} = 1.41$ )  
 (A) 20.0 mg (B) 15.0 mg (C) 14.1 mg (D) 12.5 mg **RA0043**
- Q.13 Two radioactive nuclides A and B have half lives of 50 min and 10 min respectively. A fresh sample contains the nuclides of B to be eight time that of A. How much time should elapse so that the number of nuclides of A becomes double of B  
 (A) 30 min. (B) 40 min. (C) 50 min. (D) 100 min. **RA0044**
- Q.14 A radioactive sample had an initial activity of 56 dpm (disintegration per min). After 69.3 min it was found to have an activity of 28 dpm. Find the number of atoms in a sample having an activity of 10 dpm.  
 (A) 693 (B) 1000 (C) 100 (D) 10,000 **RA0045**
- Q.15. The radioactivity of a sample is  $R_1$  at a time  $T_1$  and  $R_2$  at a time  $T_2$ . If the half life of the specimen is  $T$ , the number of atoms that have disintegrated in the time  $(T_2 - T_1)$  is equal to  
 (A)  $(R_1 T_1 - R_2 T_2)$  (B)  $(R_1 - R_2)$  (C)  $(R_1 - R_2) / T$  (D)  $(R_1 - R_2) T / 0.693$  **RA0046**
- Q.16 The analysis of a mineral of uranium reveals that ratio of mole of  $^{206}Pb$  and  $^{238}U$  in sample is 0.2. If effective decay constant of process  $^{238}U \longrightarrow ^{206}Pb$  is  $\lambda$  then age of rock is  
 (A)  $\frac{1}{\lambda} \ln \left( \frac{5}{4} \right)$  (B)  $\frac{1}{\lambda} \ln \left( \frac{5}{1} \right)$  (C)  $\frac{1}{\lambda} \ln \left( \frac{4}{1} \right)$  (D)  $\frac{1}{\lambda} \ln \left( \frac{6}{5} \right)$  **RA0047**
- Q.17 Wooden article and freshly cut tree show activity of 7.6 and 15.2  $\text{min}^{-1} \text{gm}^{-1}$  of carbon ( $t_{1/2} = 5760$  years) respectively. The age of article in years, is  
 (A) 5760 (B)  $5760 \times \left( \frac{15.2}{7.6} \right)$  (C)  $5760 \times \left( \frac{7.6}{15.2} \right)$  (D)  $5760 \times (15.2 - 7.6)$  **RA0048**
- Q.18 Symbol is needed to complete the nuclear equation  $^{63}_{29}\text{Cu}(p, \dots) ^{62}_{29}\text{Cu}$   
 (A)  $^1_1\text{H}^2$  (B)  $^1_0\text{n}^1$  (C)  $^4_2\text{He}^4$  (D)  $^0_{-1}\text{n}^0$  **RA0049**
- Q.19 Consider the following nuclear reactions:  
 $^{238}_{92}\text{M} \rightarrow ^X_Y\text{N} + 2\ ^4_2\text{He}$ ;  
 $^X_Y\text{N} \rightarrow ^A_B\text{L} + 2\beta^+$   
 The number of neutrons in the element L is  
 (A) 142 (B) 144 (C) 140 (D) 146 **RA0050**
- Q.20 The number of neutrons accompanying the formation of  $^{139}_{54}\text{X}$  and  $^{94}_{38}\text{Sr}$  from the absorption of slow neutron by  $^{235}_{92}\text{U}$  followed by nuclear fission is  
 (A) 0 (B) 2 (C) 1 (D) 3 **RA0051**

## EXERCISE (O-2)

- Q.1 Helium nuclei combine to form an oxygen nucleus. The energy released per nucleon of oxygen nucleus is if  $m_0 = 15.834$  amu and  $m_{\text{He}} = 4.0026$  amu  
 (A) 10.27 MeV (B) 0 MeV (C) 5.24 MeV (D) 164.3 MeV **RA0052**
- Q.2 A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial activity is ten times the permissible value, after how many minimum days will it be safe to enter the room?  
 (A) 1000 days (B) 300 days (C) 10 days (D) 100 days **RA0053**
- Q.3 The radioactive sources A and B of half lives of  $t$  hr and  $2t$  hr respectively, initially contain the same number of radioactive atoms. At the end of  $t$  hours, their rates of disintegration are in the ratio :  
 (A)  $2\sqrt{2} : 1$  (B)  $1 : 8$  (C)  $\sqrt{2} : 1$  (D)  $1 : \sqrt{2}$  **RA0054**
- Q.4 The average (mean) life at a radio nuclide which decays by parallel path is  
 $A \xrightarrow{\lambda_1} B; \quad \lambda_1 = 1.8 \times 10^{-2} \text{ sec}^{-1}$   
 $A \xrightarrow{\lambda_2} C; \quad \lambda_2 = 2 \times 10^{-3} \text{ sec}^{-1}$   
 (A) 52.63 sec (B) 500 sec (C) 50 sec (D) None **RA0055**
- Q.5 A sample of  $^{14}\text{CO}_2$  was to be mixed with ordinary  $\text{CO}_2$  for a biological tracer experiment. In order that  $10 \text{ cm}^3$  of diluted gas at STP should have  $10^4$  dis/min, what activity (in  $\mu\text{Ci}$ ) of radioactive carbon is needed to prepare 60 L of diluted gas at STP. [ $1 \text{ Ci} = 3.7 \times 10^{10} \text{ dps}$ ]  
 (A) 270  $\mu\text{Ci}$  (B) 27  $\mu\text{Ci}$  (C) 2.7  $\mu\text{Ci}$  (D) 2700  $\mu\text{Ci}$  **RA0056**

**Multiple correct :**

- Q.6 Select **correct** statement(s):  
 (A) The emission of gamma radiation involves transition between energy levels within the nucleus.  
 (B)  $^4_2\text{He}$  is formed due to emission of beta particle from tritium  $^3_1\text{H}$ .  
 (C) When positron ( $^0_{+1}\text{e}$ ) is emitted,  $\frac{n}{p}$  ratio increases.  
 (D) Decay constant of radioactive substance is independent of temperature. **RA0057**
- Q.7 Select the correct statements  
 (A) A radioactive element decays by emitting one  $\alpha$  and two  $\beta$ -particles. The daughter element formed is an isotope of the parent element.  
 (B) The daughter product formed by the emission of  $\alpha$ -particle has mass number less by 4 units than the parent nuclide.  
 (C)  $^{27}_{13}\text{Al}$  is a stable isotope hence  $^{29}_{13}\text{Al}$  is expected to disintegrate by  $\beta$ -emission.  
 (D) Emission of a  $\beta$ -particle by a radioactive nuclide results in decrease in  $n/p$  ratio. **RA0058**

- Q.8 Select the correct statements  
 (A) The decay constant of the end product of a radioactive series is zero  
 (B) Positron has same mass as that of an electron.  
 (C)  ${}^{14}_9\text{N}$  and  ${}^{16}_8\text{O}$  are isotones.  
 (D) The S.I. unit of activity is Curie (Ci). RA0059
- Q.9 Select the correct statements  
 (A) Half-life period of a radioactive substance can be changed by using some suitable catalyst.  
 (B) The nuclides with same difference of number of neutrons and number of protons are called isodiaphers  
 (C) Half life for certain radioactive element is 15 min. Four nuclei of that element are observed at a certain instant of time. After fifteen minutes, it can be definitely said that two nuclei will be left undecayed.  
 (D)  $5\alpha$  and  $4\beta^-$  are emitted during the radioactive decay chain starting from  ${}^{226}_{88}\text{Ra}$  and ending at  ${}^{206}_{82}\text{Pb}$  RA0060
- Q.10 Select the correct statement(s) -  
 (A)  ${}_{15}\text{P}^{29}$  may emit positron to increase n / p ratio  
 (B) During  $\beta^-$  emission, neutron changes into proton in nucleus  
 (C) Energy liberated during nuclear fission or fusion is mainly due to mass defect  
 (D) Binding energy per nucleon increases continuously with mass number RA0061

**Assertion & Reason**

- Q.11. **Statement-1** :  ${}^{238}\text{UF}_6$  and  ${}^{238}\text{U}$  both have same specific activity.  
**Statement-2** :  ${}^{238}\text{U}$  has same half life whether in free state or bonded state.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true. RA0062
- Q.12. **Statement-1** : An element may belong to more than one disintegration series.  
**Statement-2** : Mass number of an element decides the disintegration series to which it belongs.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true. RA0063

☐ **COMPREHENSION :**

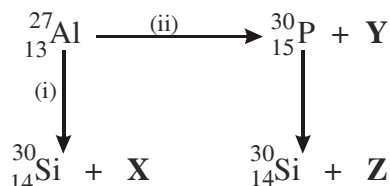
**Paragraph for Q.13 to 14**

Mass defect in the nuclear reactions may be expressed in terms of the atomic masses of the parent and daughter nuclides in place of their nuclear masses.

- Q.13 The mass defect of nuclear reaction:  ${}_4\text{Be}^{10} \rightarrow {}_5\text{B}^{10} + e^-$  is
- (A)  $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{B}^{10}$
- (B)  $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{B}^{10} - \text{mass of one electron}$
- (C)  $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{B}^{10} + \text{mass of one electron}$
- (D)  $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{B}^{10} - \text{mass of two electrons}$  **RA0064**
- Q.14 The mass defect of the nuclear reaction:  ${}_5\text{B}^8 \rightarrow {}_4\text{Be}^8 + e^+$  is
- (A)  $\Delta m = \text{At. mass of } {}_5\text{B}^8 - \text{At. mass of } {}_4\text{Be}^8$
- (B)  $\Delta m = \text{At. mass of } {}_5\text{B}^8 - \text{At. mass of } {}_4\text{Be}^8 - \text{mass of one electron}$
- (C)  $\Delta m = \text{At. mass of } {}_5\text{B}^8 - \text{At. mass of } {}_4\text{Be}^8 + \text{mass of one electron}$
- (D)  $\Delta m = \text{At. mass of } {}_5\text{B}^8 - \text{At. mass of } {}_4\text{Be}^8 - \text{mass of two electrons}$  **RA0065**
- Q.15
- | <b>Column-I</b>   | <b>Column-II</b>       |               |
|---|------------------------|---------------|
| (A) $n \longrightarrow p + \dots\dots$  | (P) Positron emission  |               |
| (B) $p \longrightarrow n + \dots\dots$  | (Q) $\beta$ -emission  |               |
| (C) K-electron capture  | (R) X-ray emission     |               |
| (D) $4[{}_1^1\text{H}] \longrightarrow \dots\dots + 2\beta^+ + \text{energy}$ | (S) $\alpha$ -emission | <b>RA0066</b> |

## EXERCISE : J-ADVANCED

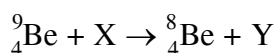
- Q.1 Bombardment of aluminium by  $\alpha$ -particle leads to its artificial disintegration in two ways, (i) and (ii) as shown. Products **X**, **Y** and **Z** respectively are : [JEE 2011]



- (A) proton, neutron, positron (B) neutron, positron, proton  
 (C) proton, positron, neutron (D) positron, proton, neutron RA0067
- Q.2 The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element **X** as shown below. To which group, element **X** belongs in the periodic table ? [JEE 2012]



- Q.3 In the nuclear transmutation [JEE 2013]



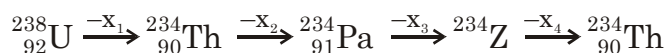
(X, Y) is(are)

- (A) ( $\gamma$ , n) (B) (p, D) (C) (n, D) (D) ( $\gamma$ , D) RA0069
- Q.4 A closed vessel with rigid walls contains 1 mol of  ${}^{238}_{92}\text{U}$  and 1 mol of air at 298 K. Considering complete decay of  ${}^{238}_{92}\text{U}$  to  ${}^{206}_{82}\text{Pb}$ , the ratio of the final pressure to the initial pressure of the system at 298 K is - [JEE 2015]

RA0070

- Q.5 A plot of the number of neutrons (N) against the number of protons (P) of stable nuclei exhibits upwards deviation from linearity for atomic number,  $Z > 20$ . For an unstable nucleus having N/P ratio less than 1, the possible mode(s) of decay is(are) - [JEE 2016]

- (A)  $\beta^-$  decay ( $\beta$  emission) (B) orbital or K-electron capture  
 (C) Neutron emission (D)  $\beta^+$  decay (positron emission) RA0071
- Q.6 In the decay sequence : [JEE 2019]



$x_1$ ,  $x_2$ ,  $x_3$  and  $x_4$  are particles/ radiation emitted by the respective isotopes. The correct option(s) is/are-

- (1) Z is an isotope of uranium  
 (2)  $x_2$  is  $\beta^-$   
 (3)  $x_1$  will deflect towards negatively charged plate  
 (4)  $x_3$  is  $\gamma$ -ray RA0072

## ANSWER KEY

## EXERCISE (S-1)

- Q.1 Ans.  ${}_{49}^{114}\text{In}$ , odd number of nucleons
- Q.2 Ans. beta emitter :  ${}^{49}\text{Ca}$ ,  ${}^{30}\text{Al}$ ,  ${}^{94}\text{Kr}$ , positron emitter :  ${}^{195}\text{Hg}$ ,  ${}^8\text{B}$ ,  ${}^{150}\text{Ho}$
- Q.3. Ans. (a) No. of  $\alpha$ -particles = 8, No. of  $\beta$ -particles = 6 ; (b)  ${}_{82}\text{Pb}^{207}$
- Q.4 Ans. (8) Q.5 Ans.  $1.44 \times 10^{15}$  dpm.
- Q.6 Ans.  $1.06 \times 10^{-15}$  Q.7 Ans.  $2.67 \times 10^5$  dps
- Q.8 Ans.  $\lambda = 2.079 \text{ hr}^{-1}$  Q.9 Ans. 4.5 hr
- Q.10 Ans. 6.25 % Q.11 Ans. 9
- Q.12 Ans. (8) Q.13 Ans. 33.62 years
- Q.14 Ans.(5) Q.15 Ans.  $4.5 \times 10^9$  year
- Q.16 Ans. (i)  ${}_{19}^{40}\text{K} \longrightarrow {}_{18}^{40}\text{Ar} + {}_{+1}^0\beta^0 + \nu$  (ii)  $2.8 \times 10^9$  years
- Q.17 Ans (4)
- Q.18 (a)  ${}^1_1\text{H}$ , (b)  ${}^1_0\text{n}$ , (c)  ${}^6_3\text{Li}$ , (d)  ${}^0_{+1}\text{e}$ , (e)  ${}^0_{-1}\text{e}$ , (f) p (proton)  
 (g)  ${}^1_1\text{H}^1$  (h)  ${}_{28}^{64}\text{Ni}$  (i)  ${}^0_{-1}\text{e}$  (j)  ${}^0_0\text{n}^1$
- Q.19 Ans. 24
- Q.20 Ans.  $\Delta E = 14.904 \text{ MeV}$

## EXERCISE (S-2)

- Q.1 Ans. 160 MeV. Q.2 Ans. 23.6 MeV
- Q.3 Ans.  $\alpha = \frac{a-b}{4}$  ;  $\beta = d + \frac{(a-b)}{2} - c$  Q.4 Ans. (i)  $t_{\text{means}} = 14.43 \text{ s}$  (ii) 40 seconds
- Q.5 Ans.  $7.07 \times 10^{-7} \text{ gm}$  Q.6 Ans. (5)
- Q.7 Ans. 1648.6 Q.8 Ans.  $6.67 \times 10^5$
- Q.9 Ans. ( $6.30 \times 10^{-4} \text{ yr}^{-1}$ ,  $3.087 \times 10^{-2} \text{ yr}^{-1}$ ) Q.10. Ans. 100

**EXERCISE (O-1)**

Q.1	Ans.(A)	Q.2	Ans.(C)	Q.3	Ans.(B)	Q.4	Ans.(C)
Q.5	Ans.(A)	Q.6	Ans.(B)	Q.7	Ans.(D)	Q.8.	Ans.(C)
Q.9	Ans.(C)	Q.10	Ans.(B)	Q.11	Ans.(C)	Q.12	Ans.(C)
Q.13	Ans.(C)	Q.14	Ans.(B)	Q.15.	Ans.(D)	Q.16	Ans.(D)
Q.17	Ans.(A)	Q.18	Ans.(A)	Q.19	Ans.(B)	Q.20	Ans.(D)

**EXERCISE (O-2)**

Q.1	Ans.(A)	Q.2	Ans.(D)	Q.3	Ans.(C)	Q.4	Ans.(C)
Q.5	Ans.(B)	Q.6	Ans.(A,C,D)	Q.7	Ans.(A,B,C,D)	Q.8	Ans.(A,B)
Q.9	Ans.(B,D).	Q.10.	Ans (A,B,C)	Q.11.	Ans.(D)	Q.12.	Ans.(A)
Q.13	Ans.(A)	Q.14	Ans.(D)				
Q.15	Ans. (A) - Q; (B) - P; (C) - R; (D) - S						

**EXERCISE : J-ADVANCED**

Q.1	Ans. (A)	Q.2	Ans. (8)
Q.3	Ans. (A,B)	Q.4	Ans. (9)
Q.5	Ans.(B, D)	Q.6	Ans.(1,2,3)



## CHEMICAL KINETICS

### 1. INTRODUCTION

Chemical kinetics deals with the rates of chemical processes. Any chemical process may be broken down into a sequence of one or more single-step processes known either as elementary processes, elementary reactions, or elementary steps. Elementary reactions usually involve either a single reactive collision between two molecules, which we refer to as a bimolecular step, or dissociation/isomerisation of a single reactant molecule, which we refer to as a unimolecular step. Very rarely, under conditions of extremely high pressure, a termolecular step may occur, which involves simultaneous collision of three reactant molecules. An important point to recognise is that, many reactions that are written as a single reaction equation, in actual fact, consist of a series of elementary steps. This will become extremely important as we learn more about the theory of chemical reaction rates.

As a general rule, elementary processes involve a transition between two atomic or molecular states separated by a potential barrier. The potential barrier constitutes the activation energy of the process, and determines the rate at which it occurs. When the barrier is low, the thermal energy of the reactants will generally be high enough to surmount the barrier and move over to products, and the reaction will be fast. However, when the barrier is high, only a few reactants will have sufficient energy, and the reaction will be much slower. The presence of a potential barrier to reaction is also the source of the temperature dependence of reaction rates.

The huge variety of chemical species, types of reaction, and the accompanying potential energy surfaces involved means that the time scale over which chemical reactions occur covers many orders of magnitude, from very slow reactions, such as iron rusting, to extremely fast reactions, such as the electron transfer processes involved in many biological systems or the combustion reactions occurring in flames.

A study into the kinetics of a chemical reaction is usually carried out with one or both of two main goals in mind :

- (i) Analysis of the sequence of elementary steps giving rise to the overall reaction. i.e. the reaction mechanism.
- (ii) Determination of the absolute rate of the reaction and/or its individual elementary steps.

### 2. CLASSIFICATION OF REACTION

- (i) There are certain reactions which are too slow. **Ex.** Rusting of Iron, weathering of rocks.
- (ii) Instantaneous reactions i.e. too fast. **Ex.** Detonation of explosives, acid-base neutralization, precipitation of  $\text{AgCl}$  by  $\text{NaCl}$  and  $\text{AgNO}_3$ .
- (iii) Neither too fast nor too slow. **Ex.** Combination of  $\text{H}_2$  and  $\text{Cl}_2$  in presence of light, hydrolysis of ethyl acetate catalysed by acid, decomposition of Azomethane.

### 3. Types of Rates of chemical reaction :

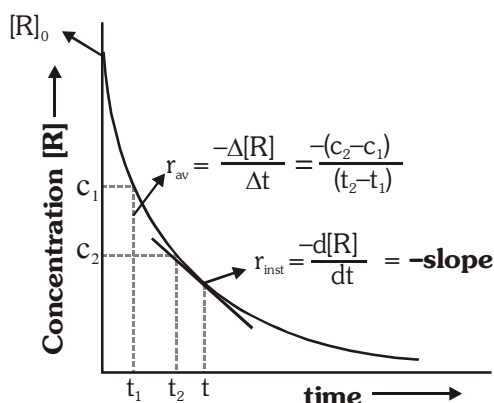
For a reaction  $R \longrightarrow P$ ,

- **Average rate** =  $\frac{\text{Total change in concentration}}{\text{Total time taken}} = \frac{|\Delta c|}{\Delta t} = -\frac{\Delta[\text{Reactant}]}{\Delta t} = \frac{\Delta[\text{Product}]}{\Delta t}$
- **Instantaneous rate** : Rate of reaction at a particular instant.

$$R_{\text{instantaneous}} = \lim_{\Delta t \rightarrow 0} \left[ \frac{|\Delta c|}{\Delta t} \right] = \left| \frac{dc}{dt} \right| = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

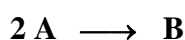
Instantaneous rate can be determined from slope of a tangent at time  $t$  on curve drawn for concentration versus time.

#### 3.1 Initial Rate : Instantaneous rate at ' $t = 0$ ' is called initial rate [Slope of tangent at $t = 0$ ].



#### ❖ Reaction rates and stoichiometry :

We have seen that for stoichiometrically simple reactions of the type  $A \rightarrow B$ , the rate can be either expressed in terms of the decrease in reactant concentration with time,  $-\Delta[A]/\Delta t$  or the increase in product concentration with time,  $\Delta[B]/\Delta t$ . For more complex reactions, we must be careful in writing the rate expressions. Consider for example, the reaction,



Two moles of A disappear for each mole of B that forms – that is, the rate of disappearance of A is twice as fast as the rate of appearance of B. We write the overall rate of reaction as either

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

In general, for the reaction,  $aA + bB \longrightarrow cC + dD$

the rate is given by

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

**Ex. :** For the reaction in terms :  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$

Rate of reaction in terms of  $\text{N}_2 = -\frac{d[\text{N}_2]}{dt}$  = rate of disappearance of  $\text{N}_2$

Rate of reaction in terms of  $\text{H}_2 = -\frac{d[\text{H}_2]}{dt}$  = rate of disappearance of  $\text{H}_2$

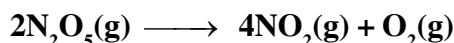
Rate of reaction in terms of  $\text{NH}_3 = \frac{d[\text{NH}_3]}{dt}$  = rate of appearance of  $\text{NH}_3$

These rates are not all equal. Therefore, by convention, the rate of a reaction is defined as

$$\bullet \quad \text{Rate of reaction} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

**Note:** The value of rate of reaction is dependent on the stoichiometric coefficients used in the reaction while the rate of increase or decrease in amount of any species will be fixed value under given conditions.

**Ex.1** The following reaction was studied in a closed vessel



It was found that the concentration of  $\text{NO}_2$  increases by  $2.0 \times 10^{-2} \text{ mol L}^{-1}$  in five seconds. Calculate.

- (i) The rate of reaction  
(ii) The rate of decrease of concentration of  $\text{N}_2\text{O}_5$

**Sol.** (i) Rate of reaction =  $\frac{1}{4} \frac{d[\text{NO}_2]}{dt}$

$$\text{But } \frac{d[\text{NO}_2]}{dt} = \frac{2.0 \times 10^{-2} \text{ mol L}^{-1}}{5\text{s}} = 4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{Rate of reaction } \frac{1}{4} \times 4 \times 10^{-3} = 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

- (ii) Rate of decrease of conc. of  $\text{N}_2\text{O}_5$

$$= -\frac{d[\text{N}_2\text{O}_5]}{dt} = -\frac{1}{2} \times \text{Rate of formation of } \text{NO}_2 = +\frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

$$= +\frac{1}{2} \times 4 \times 10^{-3} = 2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

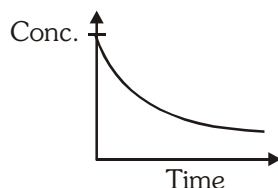
### 3.3 FACTORS AFFECTING RATE OF CHEMICAL REACTION

- |  |   |
|--|---|
| (i) Concentration                      | (ii) Temperature                        |
| (iii) Nature of reactants and products | (iv) Catalyst                           |
| (v) pH of the solution                 | (vi) Dielectric constant of the medium. |
| (vii) Radiations / light               | (viii) Pressure                         |
| (ix) Electrical and magnetic field.    |   |

The first four factors generally affect rate of almost all reactions while other factors are specific to some reactions only.

**(i) Effect of concentration :**

For most of the reactions, rate depends on concentration of reactants. So rate of reaction decreases with passage of time, since concentration of reactants decreases.

**(ii) Effect of temperature :** Generally rate of reaction increases on increasing temperature.**(iii) Effect of nature of reactants and products :**

**(a) Physical state of reactants :** Gaseous state > Liquid state > Solid state  
(Decreasing order of rate of reaction)

Because collisions in gaseous systems are more effective than condensed systems (solid & liquid).

**(b) Physical size of reactants :** In heterogeneous reactions, as we decrease the particle size, rate of reaction increases since surface area increases.

**(c) Chemical nature of reactants :**

- If more bonds are to be broken, the rate of reaction will be slow.
- Similarly if bond strength in reactants is more, rate of reaction will be slow.

**(iv) Effect of Catalyst :**

- Presence of catalyst or positive catalyst lowers down the activation energy hence increases the rate of reaction.
- Presence of inhibitor or negative catalyst increases activation energy hence decreases the rate of reaction.

**(v) Effect of pH of solution : Ex.**  $[\text{Fe}(\text{CN})_6]^{4-} \xrightarrow{(\text{Ti}^{3+})} [\text{Fe}(\text{CN})_6]^{3-}$ 

This reaction takes place with appreciable rate in acidic medium, but does not take place in basic medium.

**(vi) Effect of dielectric constant of the medium :** More is the dielectric constant of the medium greater will be the rate of ionic reactions.**(vii) Effect of radiations / light :** Radiations are useful for photochemical reactions.**(viii) Effect of pressure :** Pressure is important factor for gaseous reactions.**(ix) Effect of electrical & magnetic field :** Electric and magnetic fields are rate determining factors if a reaction involves polar species.**4. RATE LAW (DEPENDENCE OF RATE ON CONCENTRATION OF REACTANTS) :**

The representation of rate of reaction in terms of the concentration of the reactants is called the rate law. It can only be established by experiments.

Generally rate law expressions are not simple and these may differ for the same reaction on conditions under which the reaction is being carried out. But for large number of reactions starting with pure reactants we can obtain simple rate laws. For these reactions :

$$\text{Rate} \propto (\text{conc.})^{\text{order}}$$

$$\text{Rate} = K (\text{conc.})^{\text{order}} \quad \text{This is the differential rate equation or rate expression.}$$

Where  $K$  = Rate constant = specific reaction rate = rate of reaction when concentration is unity

$$\text{unit of } K = (\text{conc})^{1-\text{order}} \text{ time}^{-1}$$

**Note:** Value of  $K$  is a constant for a given reaction, depending only on temperature and catalyst use.

#### 4.1 Order of reaction :

Let there be a reaction,  $m_1A + m_2B \longrightarrow \text{products}$ .

Now, if on the basis of experiment, we find that

$$R \propto [A]^p [B]^q$$

where  $p$  may or may not be equal to  $m_1$  and similarly  $q$  may or may not be equal to  $m_2$ .

$p$  is order of reaction with respect to reactant  $A$  and  $q$  is order of reaction with respect to reactant  $B$  and  $(p + q)$  is **overall order of the reaction**.

**Note:** Order of a reaction can be 'zero', any whole number, fractional number or even be negative with respect to a particular reactant.

#### ❖ Examples showing different values of order of reactions :

Reaction	Rate law	Order
(i) $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$	$R = K [\text{N}_2\text{O}_5]^1$	1
(ii) $5\text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\ell) + 3\text{H}_2\text{O}(\ell)$	$R = K [\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$	$1 + 1 + 2 = 4$
(iii) $\text{H}_2(\text{Para}) \rightarrow \text{H}_2(\text{ortho})$	$R = K [\text{H}_2(\text{Para})]^{3/2}$	3/2
(iv) $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$	$R = K [\text{NO}_2]^2 [\text{CO}]^0$	$2 + 0 = 2$
(v) $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$	$R = K [\text{O}_3]^2 [\text{O}_2]^{-1}$	$2 - 1 = 1$
(vi) $\text{H}_2 + \text{Cl}_2 \xrightarrow{h\nu} 2\text{HCl}$	$R = K [\text{H}_2]^0 [\text{Cl}_2]^0$	$0 + 0 = 0$

The reaction (ii) does not take place in one single step. It is almost impossible for all the 12 molecules of the reactants to be in a state of encounter simultaneously. Such a reaction is called **Complex reaction** and takes place in a sequence of a number of **Elementary reactions**. For an elementary reaction, the sum of stoichiometric coefficients of reactants = order of the reaction. But for complex reactions, order is to be experimentally calculated.

#### 4.2 Molecularity of reaction :

The number of molecules that react in an elementary step is the molecularity of the elementary reaction. Molecularity is defined only for the elementary reactions and not for complex reactions. No elementary reactions involving more than three molecules are known, because of very low probability of simultaneous collision of more than three molecules.

The rate law for the elementary reaction



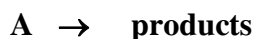
where  $a + b = 1, 2$  or  $3$

For an elementary reaction, the orders in the rate law equal the coefficients of the reactants. It must be noted that the order is defined for complex as well as elementary reactions and is always experimentally calculated from the mechanism of the reaction, usually by the slowest step of the mechanism known as rate determining step (RDS) of the reaction.

Comparison between molecularity and order of reaction			
Molecularity of Reaction		Order of Reaction	
1	It is defined as the no. of molecules of reactant taking part in a chemical reaction. $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ , molecularity = 1	1	It is defined as the sum of the power of concentration terms that appear in rate law. $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ . Rate = $k[\text{NH}_4\text{NO}_2]$ , order = 1
2	It is always a whole number. It can neither be zero nor fractional.	2	It may be zero, fractional or integer.
3	It is derived from RDS in the mechanism of reaction	3	It is derived from rate expression.
4	It is theoretical value.	4	It is experimental value.
5	Reactions with molecularity > 3 are rare.	5	Reactions with order of reaction > 4 are also rare.
6	Molecularity is independent of pressure and temperature.	6	Order of reaction may depend upon pressure and temperature.

## 5. INTEGRATED RATE LAW :

For a single reactant reaction where the chemical equation has the form



and the rate law is assumed to be of the form

$$\text{Rate} = -d[\text{A}]/dt = k[\text{A}]^m$$

Where  $m$  is the order of the reaction with respect to substance A. Three important cases can be treated :  $m = 0$ ,  $m = 1$ , and  $m = 2$ . These are called *zeroth order*, *first order*, and *second order*, respectively.

### 5.1 Zero - order reaction :

For a reaction where the chemical equation has the form



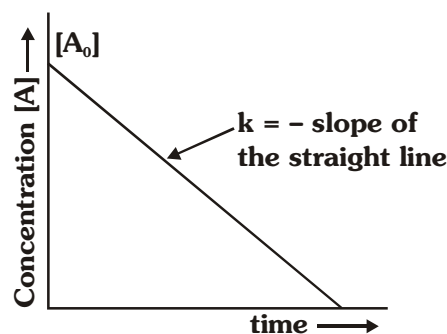
and the rate law is assumed to be of the form

$$\text{Rate} = -d[\text{A}]/dt = k[\text{A}]^0$$

$$-\int_{C_0}^{C_t} d[\text{A}] = k \int_0^t dt$$

$$k = \frac{C_0 - C_t}{t}$$

$$\text{or } kt = C_0 - C_t \quad \text{or} \quad C_t = C_0 - kt$$



- Unit of K is same as that of Rate = mol lit<sup>-1</sup> sec<sup>-1</sup>.
- Time for completion =  $\frac{C_0}{k}$
- $t_{1/2}$  (half life period)

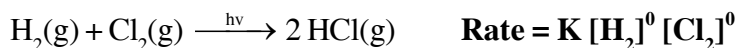
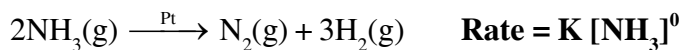
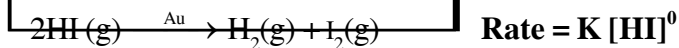
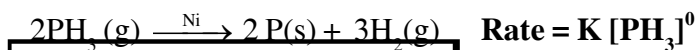
$$\text{At } t_{1/2}, C_t = \frac{C_0}{2},$$

$$\text{So } kt_{1/2} = \frac{C_0}{2} \quad \Rightarrow \quad t_{1/2} = \frac{C_0}{2k}$$

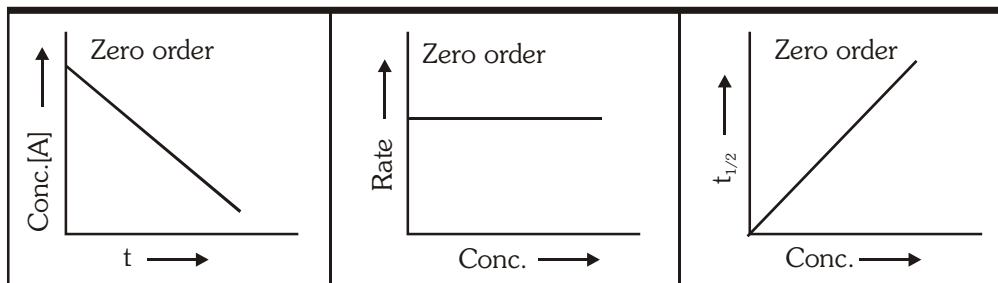
$$\therefore t_{1/2} \propto C_0$$

❖ **Examples of Zero order reactions :**

Generally decomposition of gases on metal surfaces at high concentrations follow zero order kinetics as rate depends on surface area of catalyst.



❖ **Graphs :**



**Ex.2** For the zero order reaction :  $\text{A} \rightarrow \text{P}$ ,  $K = 10^{-2}$  (mol/litre) sec<sup>-1</sup> If initial concentration of A is 0.3M, then find concentration of A left at 10 sec.

- (A) 0 M                      (B) 0.2 M                      (C) 0.1 M                      (D) 0.15 M

**Sol.** (B)

$$[\text{A}]_t = [\text{A}]_0 - Kt = 0.3 - 10^{-2} \times 10 = 0.2 \text{ M}$$

**5.2 First order reaction :**

Consider a first order reaction with single reactant.



$$t = 0 \quad a \quad 0$$

$$t = t \quad a-x$$

$$\text{Rate} = -d[\text{A}]/dt = k [\text{A}]^1$$

$$\therefore \frac{dx}{dt} = k(a-x)^1 \quad \text{or} \quad \frac{dx}{a-x} = kdt.$$

• **On solving**  $k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{C_0}{C_t}$

$$K = \frac{2.303}{t} \log \frac{C_0}{C_t} \quad \boxed{\text{Wilhemmy formula : } C_t = C_0 e^{-kt}} \quad \boxed{\text{Interval formula : } k = \frac{2.303}{(t_2 - t_1)} \log \frac{C_1}{C_2}}$$

• Unit of  $k = \text{sec}^{-1}, \text{min}^{-1}, \text{etc.}$

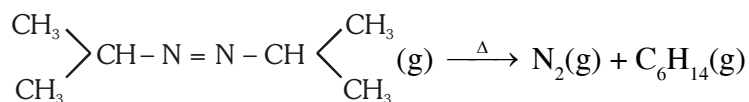
• **Half-life time ( $t_{1/2}$ ) :**

$$k = \frac{2.303}{t_{1/2}} \log \frac{2C_0}{C_0} \Rightarrow t_{1/2} = \frac{2.303 \log 2}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

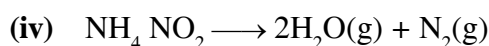
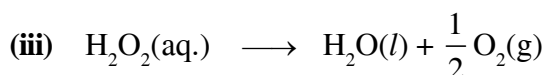
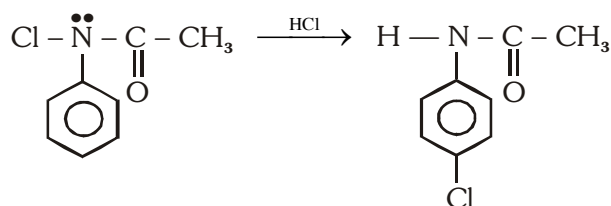
∴ Half-life period for a first order reaction is a constant quantity at given temperature.

• **Examples of first order reactions :**

(i) Decomposition of azoisopropane

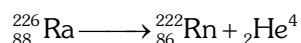


(ii) Conversion of N-chloro acetanilide into p-chloroacetanilide

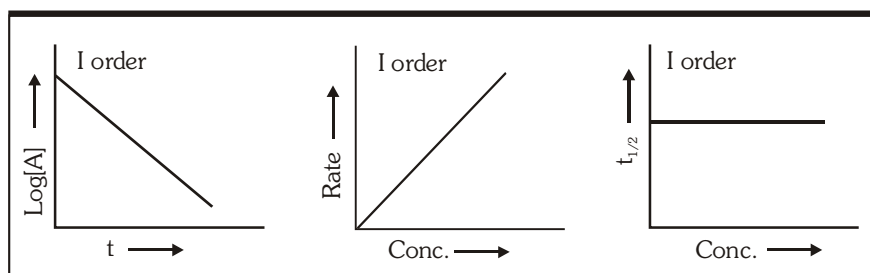


(v) Radioactive decay

All radioactive decays always follow first order kinetics.



• **Graphs :**





**Ex.3** Calculate  $\frac{t_{0.75}}{t_{0.50}}$  for a first order reaction :

**Sol.**  $k = \frac{2.303}{t_{3/4}} \log \frac{C_0}{\frac{1}{4}C_0} = \frac{2.303}{t_{1/2}} \log \frac{C_0}{\frac{C_0}{2}} \Rightarrow \frac{t_{3/4}}{t_{1/2}} = \frac{\log 4}{\log 2} = \frac{2 \log 2}{\log 2} = 2$

**Ex.4** 90% of a first order reaction was completed in 10 hours. When will 99.9% of the reaction complete ?

**Sol.**  $K = \frac{2.303}{t} \log \frac{a}{a-x}$

$a = 100, x = 90, t = 10$

So  $K = \frac{2.303}{10} \log \frac{100}{10}$

$K = 2.303 \times 10^{-1} \text{ hour}^{-1}$

Now for 99.9% completion -

$a = 100$  and  $x = 99.9$

$t = \frac{2.303}{K} \log \frac{100}{0.1} = \frac{2.303}{2.303 \times 10^{-1}} \times 3 = 30 \text{ hours}$

**Ex.5** A first order reaction is 90% complete after 40 min. Calculate the half life of reaction.

**Sol.**  $a = 100, x = 90$

$K_1 = \frac{2.303}{t} \log \frac{a}{a-x}$

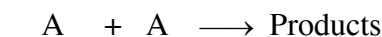
$= \frac{2.303}{40} \log \frac{100}{10}$

$= \frac{2.303}{40} = 5.757 \times 10^{-2} \text{ min}^{-1}$

$t_{1/2} = \frac{0.693}{K_1} = \frac{0.693}{5.757 \times 10^{-2}} = 12.03 \text{ min.}$

### 5.3.1 Second order reaction :

#### • Case : 1



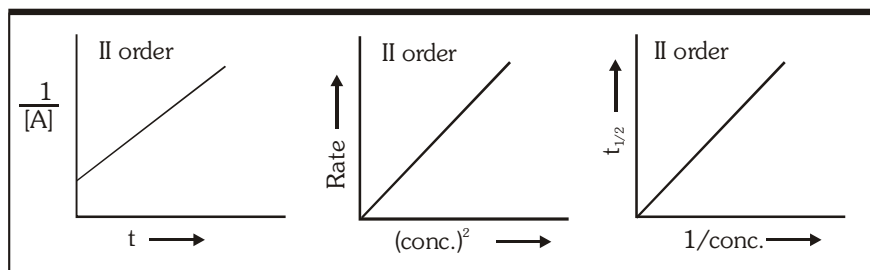
$\begin{matrix} a & a \\ (a-x) & (a-x) \end{matrix}$

$\therefore \frac{dx}{dt} = k(a-x)^2$

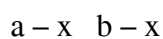
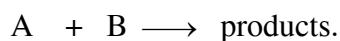
$\Rightarrow \frac{1}{(a-x)} - \frac{1}{a} = kt \quad \text{or} \quad \frac{1}{C_t} - \frac{1}{C_0} = kt$

- Unit of  $k = \text{Lmol}^{-1} \text{sec}^{-1}$
- Half life,  $t_{1/2} = \frac{1}{k.C_0}$

- **Graphs :**



### 5.3.2 Case : 2



Rate law

$$\frac{dx}{dt} = k(a-x)(b-x)$$

$$\int_0^x \frac{dx}{(a-x)(b-x)} = \int_0^t k dt$$

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad (\text{no need to remember})$$

where  $a \neq b$

**Ex.6** For a second order reaction in which both the reactants have equal initial concentration, the time taken for 60% completion of reaction is 3000 second. What will be the time taken for 20% of the reaction?

**Sol.**  $k_2 = \frac{1}{t} \frac{x}{a(a-x)}$

Let  $a = 1$ ,

$$k_2 = \frac{1}{t} \frac{x}{1-x}$$

$$= \frac{1}{3000} \left( \frac{0.6}{1-0.6} \right)$$

$$= \frac{1}{3000} \times \frac{0.6}{0.4} = \frac{1}{2000}$$

So time for the 20% completion :

$$t = \frac{1}{k_2} \frac{x}{a(a-x)}$$

$$= 2000 \times \frac{0.20}{0.80} = 500 \text{ sec.}$$

**5.4 Pseudo order reaction :**

For,  $A + B \longrightarrow \text{Products}$

$t=0$      $a$                      $b$

$t=t$      $a-x$                      $b-x$

$$\text{Rate} = K [A]^n [B]^m$$

If  $[B] = \text{constant} \Rightarrow [b-x] \approx \text{constant}$

$$\text{Rate} = K' [A]^n$$

when  $K' = K[B]^m$

• **Case 1 :**

If concentration of B is much greater than A, then  $[B] = \text{Constant} \Rightarrow [b-x] \approx \text{Constant}$ .

• **Case 2 :**

If B is a catalyst, then  $[B] = \text{Constant} \Rightarrow [b-x] \approx \text{Constant}$ .

• **Case 3 :**

If B is a solvent, then  $[B] = \text{Constant} \Rightarrow [b-x] \approx \text{Constant}$ .

**5.4.1 PSEUDO FIRST ORDER REACTIONS :**

A second order (or of higher order) reactions can be converted into a first order reaction if the other reactant is taken in large excess. Such first order reactions are known as **pseudo first order reactions**.

$\therefore$  For  $A + B \longrightarrow \text{Products}$     **[Rate] = K [A]<sup>1</sup> [B]<sup>1</sup>**

$$K = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad (\text{from 5.3.2})$$

Now if 'B' is taken in large excess  $b \gg a$ .

$$\therefore K = \frac{2.303}{-bt} \log \frac{(a-x)}{a} \Rightarrow K = \frac{2.303}{bt} \log \frac{a}{a-x}$$

$$\Rightarrow K \cdot b = \frac{2.303}{t} \log \frac{a}{a-x} \Rightarrow K' = \frac{2.303}{t} \log \frac{a}{a-x}$$

$K'$  is pseudo first order rate constant.

$K'$  will have units of first order.

$K$  will have units of second order.

❖ **Table :** Characteristics of Zero, First, Second and  $n^{\text{th}}$  order reactions of the type  $A \longrightarrow \text{Products}$

	Zero order	First order	Second order	$n^{\text{th}}$ order
Differential Rate law	$-\frac{d[A]}{dt} = k[A]^0$	$-\frac{d[A]}{dt} = k[A]$	$-\frac{d[A]}{dt} = k[A]^2$	$-\frac{d[A]}{dt} = k[A]^n$
Integrated Rate law	$[A]_t = [A]_0 - kt$	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} = (n-1)kt$
Linear graph	$[A]_t$ v/s $t$	$\ln [A]$ v/s $t$	$\frac{1}{[A]}$ v/s $t$	$\frac{1}{[A]_t^{n-1}}$ v/s $t$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$ (depends on $[A]_0$ )	$t_{1/2} = \frac{0.693}{k}$ (independent of $[A]_0$ )	$t_{1/2} = \frac{1}{k[A]_0}$ (depends on $[A]_0$ )	$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$

## 6 Methods to determine order of a reaction :

### 6.1 Initial rate method :

By comparison of different initial rates of a reaction by varying the concentration of one of the reactants while others are kept constant.

$$r = k [A]^a [B]^b [C]^c \quad \text{if } [B] = \text{constant and } [C] = \text{constant}$$

then for two different initial concentrations of A we have

$$r_{01} = k [A_0]_1^a \quad r_{02} = k [A_0]_2^a \quad \Rightarrow \quad \frac{r_{01}}{r_{02}} = \left( \frac{[A_0]_1}{[A_0]_2} \right)^a$$

or in log form we have 
$$a = \frac{\log (r_{01}/r_{02})}{\log ([A_0]_1/[A_0]_2)}$$

### 6.2 Integrated rate law method :

It is method of hit and trial. By checking if the kinetic data (experimental data) best fits into a particular integrated rate law, we determine the order. It can also be done graphically.

**Ex.7** The rate of decomposition of  $N_2O_5$  in  $CCl_4$  solution has been studied at 318 K and the following results have been obtained :

t/min	0	135	342	683	1693
c/M	2.08	1.91	1.67	1.35	0.57

Find the order of the reaction and calculate its rate constant. What is the half-life period?

**Sol.** It can be shown that these data will not satisfy the integrated rate law of zero order. We now try integrated first order equation i.e.,  $k = \frac{\ln(c_0/c)}{t}$ .

t / min	c / M	$k = \frac{\ln(c_0/c)}{t} \text{ min}^{-1}$
0	2.08	$6.32 \times 10^{-4}$
135	1.91	$6.30 \times 10^{-4}$
339	1.68	$6.32 \times 10^{-4}$
683	1.35	$6.32 \times 10^{-4}$
1680	0.72	$6.31 \times 10^{-4}$

It can be seen that the value of  $k$  is almost constant for all the experimental results and hence it is first order reaction with  $k = 6.31 \times 10^{-4} \text{ min}^{-1}$ .

$$t_{1/2} = \frac{0.693}{6.31 \times 10^{-4} \text{ min}^{-1}} = 1.094 \times 10^3 \text{ min}^{-1}$$

### 6.3 Method of half lives :

The half lives of each order is unique so by comparing half lives we can determine order for  $n^{\text{th}}$

order reaction  $t_{1/2} \propto \frac{1}{[A_0]^{n-1}}$  (Remember)

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{[A_0]_2^{n-1}}{[A_0]_1^{n-1}} \quad (\text{Remember})$$

**Ex.8** In a decomposition reaction, the reaction was found to be 50% complete in 210 seconds when the initial pressure of the mixture was 200 mm. In a second experiment the time of half reaction was 140 seconds when the initial pressure was 300 mm. Calculate the total order of the reaction.

**Sol.** For a  $n^{\text{th}}$  order reaction  $t_{1/2} \propto \frac{1}{c_0^{n-1}}$

$$\frac{210}{140} = \left(\frac{300}{200}\right)^{n-1} \Rightarrow n = 2$$

### 6.4 Ostwald's isolation method :

This method is useful for reactions which involve a large number of reactants. In this method, the concentration of all the reactants are taken in large excess except that of one, so if

$$\text{Rate} = k [A]^a [B]^b [C]^c = k_0 [A]^a$$

Then value of 'a' can be calculated by previous methods and similarly 'b' and 'c' can also be calculated.

**6.5 Initial rate method :**

For reaction :  $A + B \longrightarrow \text{Products}$

Initial rate,  $r_0 = K \cdot [A_0]^n [B_0]^m$

Now, order with respect to A may be determined by comparing the initial rate of reaction at different initial concentration of A but fixed initial concentration of B.

**Ex.9 Consider the following data for the reaction :**

$A + B \longrightarrow \text{Products}$

Run	Initial concentration	Initial concentration	Initial rate (mol s <sup>-1</sup> )
1	0.10 M	1.0 M	$2.1 \times 10^{-3}$
2.	0.20 M	1.0 M	$8.4 \times 10^{-3}$
3.	0.20 M	2.0 M	$8.4 \times 10^{-3}$

**Determine the order of reaction with respect to A and with respect B and the over all order of reaction.**

**Sol.** The rate law may be expressed as :

$$\text{Rate} = k [A]^p [B]^q$$

Comparing experiments 2 and 3

$$(\text{Rate})_2 = k[0.2]^p [1.0]^q = 8.4 \times 10^{-3} \quad (1)$$

$$(\text{Rate})_3 = k[0.2]^p [2.0]^q = 8.4 \times 10^{-3} \quad (2)$$

Dividing equation (2) by (1)

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{k[0.2]^p [2.0]^q}{k[0.2]^p [1.0]^q} = \frac{8.4 \times 10^{-3}}{8.4 \times 10^{-3}}$$

$$[2]^q = [1]^0$$

$$\text{or } q = 0$$

Comparing experiments 1 and 2,

$$(\text{Rate})_2 = k[0.20]^p [1.0]^q = 8.4 \times 10^{-3} \quad (3)$$

$$(\text{Rate})_1 = k[0.10]^p [1.0]^q = 2.1 \times 10^{-3} \quad (4)$$

Dividing equation (3) by (4)

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k[0.20]^p [1.0]^q}{k[0.10]^p [1.0]^q} = \frac{8.4 \times 10^{-3}}{2.1 \times 10^{-3}} = 4$$

$$[2]^p = [1]^2 \quad \text{or} \quad p = 2$$

so order with respect to A = 2

order with respect to B = 0

overall order = 2

## 7. APPLICATION OF FIRST ORDER REACTION

(Methods to monitor the progress of the reaction)

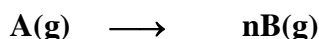
## 7.1 Case : 1

**First order gaseous reaction :**

Progress of gaseous reactions can be monitored by measuring total pressure at a fixed volume & temperature. This method can be applied for those reactions also in which a gas is produced because of decomposition of a solid or liquid. We can get an idea about the concentration of reacting species at a particular time by measuring pressure.

The pressure data can be given in terms of

- (i) Partial pressure of the reactant
- (ii) Total pressure of the reaction system
- (iii) Pressure at only some points of time.

**Ex.10 Find the expression for K in terms of  $P_0$ ,  $P_t$  and n. For the reaction****Sol.**  $A(g) \longrightarrow nB(g)$ 

$$P_0$$

$$P_A = (P_0 - x) \quad nx$$

$$\therefore P_t (\text{Total pressure at time 't'}) = P_0 - x + nx = P_0 + (n - 1)x$$

$$\therefore x = \frac{P_t - P_0}{n - 1}$$

$$\therefore P_A = P_0 - \frac{P_t - P_0}{n - 1} = \frac{P_0 n - P_t}{n - 1}$$

$$\therefore a \propto p_0 \quad \& \quad (a - x) \propto P_A = \frac{nP_0 - P_t}{n - 1}$$

$$\therefore k = \frac{2.303}{t} \log \frac{P_0(n - 1)}{(nP_0 - P_t)}$$

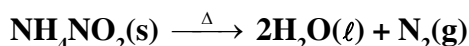
Final total pressure after infinite time =  $P_f = nP_0$

Do not remember the formula but derive it for each question.

## 7.2 Case : 2

**Volume measurement :**

- (i) By measuring the volume of product formed we can monitor the progress of reactions.

**Ex.11 Study of a reaction whose progress is monitored by measuring the volume of an escaping gas.****Sol.** Let,  $V_t$  be the volume of  $N_2$  collected at time 't'

$V_{\infty}$  = be the volume of  $N_2$  collected at the end of the reaction.

$$a \propto V_{\infty} \quad \text{and} \quad x \propto V_t$$

$$(a - x) \propto V_{\infty} - V_t$$

$$\therefore k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$$

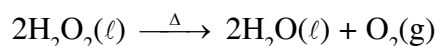
- (ii) **By titration method :** By measuring the volume of titrating agent we can monitor amount of reactant remaining or amount of product formed at any time. It is the **titre value**. Here the milliequivalent or millimoles are calculated using valence factors.

**Ex.12** From the following data show that the decomposition of hydrogen peroxide in aqueous solution is a first - order reaction. What is the value of the rate constant?

<b>Time in minutes</b>	0	10	20	30	40
<b>Volume V in mL</b>	25.0	20.0	15.7	12.5	9.6

Where V is the volume in mL of standard  $KMnO_4$  solution required to react with a definite volume of hydrogen peroxide solution.

**Sol.** The equation for a first order reaction is,



the volume of  $KMnO_4$  used, evidently corresponds to the undecomposed hydrogen peroxide.

Hence the volume of  $KMnO_4$  used, at zero time corresponds to the initial concentration a and the volume used after time t, corresponds to (a - x) at that time. Inserting these values in the above equation, we get

$$\text{When } t = 10 \text{ min. } k_1 = \frac{2.303}{10} \log \frac{25}{20.0} = 0.022318 \text{ min}^{-1} = 0.000372 \text{ s}^{-1}$$

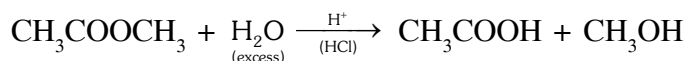
$$\text{When } t = 20 \text{ min. } k_1 = \frac{2.303}{20} \log \frac{25}{15.7} = 0.023265 \text{ min}^{-1} = 0.000387 \text{ s}^{-1}$$

$$\text{When } t = 30 \text{ min. } k_1 = \frac{2.303}{30} \log \frac{25}{12.5} = 0.02311 \text{ min}^{-1} = 0.000385 \text{ s}^{-1}$$

$$\text{When } t = 40 \text{ min. } k_1 = \frac{2.303}{40} \log \frac{25}{9.6} = 0.023932 \text{ min}^{-1} = 0.0003983 \text{ s}^{-1}$$

The constancy of k, shows that the decomposition of  $H_2O_2$  in aqueous solution is a **first order** reaction. The average value of the rate constant is  $0.0003879 \text{ s}^{-1}$ .



**Ex.13 Study of acid hydrolysis of an ester.**

The progress of this reaction is monitored or determined by titrating the fixed volume of reaction mixture at different time intervals against a standard solution of NaOH using phenolphthalein as indicator. Find out rate constant of the reaction in terms of volume of NaOH consumed at  $t = 0, V_0$ , at  $t = \infty, V_\infty$  & at time  $t, V_t$ .

**Sol.** Let,  $V_0$  = Volume of NaOH used at  $t = 0$  [this is exclusively for HCl.]

$V_t$  = Volume of NaOH used at 't'

$V_\infty$  = Volume of NaOH used at  $t = \infty$

$$a \propto (V_\infty - V_0)$$

$$(a - x) \propto (V_\infty - V_t)$$

$$x \propto (V_t - V_0)$$

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

**7.3 Case : 3****Optical rotation measurement :**

**It is used for optically active sample.** It is applicable if there is at least one optically active species involved in chemical reaction.

- The optically active species may be present in reactant or product.

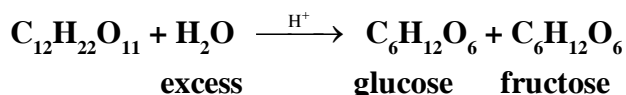
It is found that  $(r_\infty - r_0) \propto a$  ( $a$  = concentration,  $x$  = amount consumed)

$$(r_\infty - r_t) \propto (a - x)$$

Where are  $r_0, r_t, r_\infty$  are angle of optical rotation at time  $t = 0, t = t$  and  $t = \infty$ .

$$k = \frac{2.303}{t} \log \frac{r_\infty - r_0}{r_\infty - r_t} \quad (\text{Remember})$$

**Ex.14 Study of hydrolysis of sucrose, progress of this reaction is monitored with the help of polarimeter because a solution of sucrose is dextrorotatory and on hydrolysis, the mixture of glucose and fructose obtained becomes laevorotatory. That's why this reaction is also known as inversion of cane sugar.**



Let the readings in the polarimeter be

$t = 0, \theta_0$ ;  $t = 't', \theta_t$  and at  $t = \infty, \theta_\infty$

Then calculate rate constant 'k' in terms of these readings.

**Sol.** The principle of the experiment is that change in the rotation is directly proportional to the amount of sugar hydrolysed.

$$\therefore a \propto (\theta_0 - \theta_\infty) \quad ; \quad (a - x) \propto (\theta_t - \theta_\infty) ; x \propto (\theta_0 - \theta_t)$$

$$k = \frac{2.303}{t} \log \left( \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty} \right)$$

#### 7.4 Case : 4

##### First order growth reaction :

For bacteria multiplication or virus growth use following concept

Consider a growth reaction,

**Time** **Population (or colony)**

0 a

t (a + x)

$$\frac{dx}{dt} = k(a + x) \quad \text{or} \quad \frac{dx}{(a + x)} = k dt$$

On integration

$$\log_e (a + x) = kt + C \quad \text{at} \quad t = 0 ; x = 0 \Rightarrow C = \log_e a$$

$$kt = -\log_e \frac{a}{(a + x)} = -\frac{2.303}{t} \log_{10} \left( \frac{a}{(a + x)} \right)$$

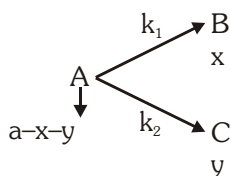
$$\boxed{k = \frac{2.303}{t} \log_{10} \left( \frac{a + x}{a} \right)}$$

❖ **Generation time :**

$$\text{At } t = \text{generation time, } x = a \quad \therefore \quad t = \frac{0.693}{K}$$

## 8. SOME SPECIAL CASES :

### 8.1 FIRST ORDER PARALLEL OR COMPETING OR SIMULTANEOUS REACTIONS



$$\text{At } t = 0 \quad [A] = a \quad [B] = [C] = 0$$

(i) **Differential rate law :**

$$\frac{d[B]}{dt} = k_1 [A] ; \quad \frac{d[C]}{dt} = k_2 [A]$$

$$\text{and, } \frac{-d[A]}{dt} = \frac{d[B]}{dt} + \frac{d[C]}{dt} \Rightarrow \frac{-d[A]}{dt} = (k_1 + k_2) [A] = k_{\text{eff}} [A]$$

$$k_{\text{eff}} = k_1 + k_2 = \text{overall rate constant for the disappearance of 'A'}$$

(ii) **Integral rate law :**

$$[A]_t = a e^{-k_{\text{eff}} t} = a e^{-(k_1 + k_2)t}$$

$$\frac{d[B]}{dt} = k_1 [A] \Rightarrow \frac{d[B]}{dt} = k_1 a e^{-(k_1 + k_2)t}$$

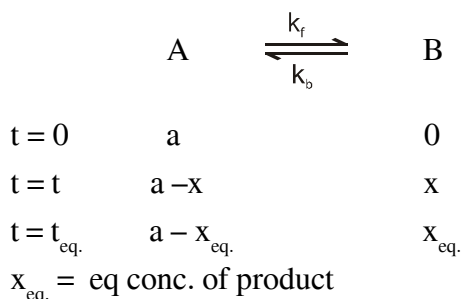
$$[B] = \left( \frac{k_1 a}{k_1 + k_2} \right) (1 - e^{-(k_1 + k_2)t})$$

$$\text{Similarly, } [C] = \left[ \frac{k_2 a}{k_1 + k_2} \right] (1 - e^{-(k_1 + k_2)t})$$

**(iii) Composition of product :**

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$

**8.2 FIRST ORDER REVERSIBLE REACTION**



(i)  $\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0$  ( $\because$  At equilibrium, conc. will not changed)

(ii)  $\frac{d[A]}{dt} = -k_f[A] + k_b[B] \Rightarrow \frac{d[B]}{dt} = -k_b[B] + k_f[A]$

$$\frac{d(a-x)}{dt} = -k_f(a-x) + k_b x$$

$$-\frac{dx}{dt} = -k_f a + (k_f + k_b)x$$

At eq<sup>m</sup>,  $\frac{dx}{dt} = 0 = k_f a + (k_f + k_b)x_{eq}$

$$k_f a = (k_f + k_b)x_{eq}$$

$$-\frac{dx}{dt} = -(k_f + k_b)x_{eq} + (k_f + k_b)x$$

$$\frac{dx}{dt} = (k_f + k_b)(x_{eq} - x)$$

$$\int_0^x \frac{dx}{(x_{eq} - x)} = (k_f + k_b) \int_0^t dt$$

$$k_f + k_b = \frac{1}{t} \ln \left( \frac{x_{eq.}}{x_{eq.} - x} \right) \text{ (No need to remember this equation)}$$

## 8.3 FIRST ORDER SEQUENTIAL REACTION



All first order reactions

$$t = 0 \quad a \quad 0 \quad 0$$

$$t = t \quad a - x \quad y \quad z$$

For 'A'

$$\frac{-d[A]}{dt} = r_1 = k_1 [A]$$

$$\frac{-d[A]}{[A]} = k_1 dt$$

$$[A]_t = [A]_0 e^{-k_1 t}$$

$$a - x = a e^{-k_1 t}$$

$$x = a(1 - e^{-k_1 t})$$

Calculate time at which concentration of B will be maximum.

$$\frac{dy}{dt} = 0$$

$$-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0$$

$$e^{-k_2 t} = \frac{k_1}{k_2} e^{-k_1 t}$$

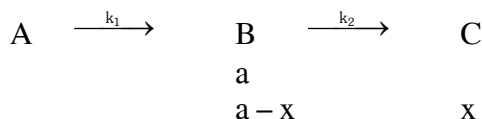
$$e^{k_1 t} = \frac{k_1}{k_2} e^{k_2 t} \Rightarrow k_1 t = \ln \frac{k_1}{k_2} + k_2 t$$

$$t_{\max.} = \frac{1}{(k_1 - k_2)} \ln \frac{k_1}{k_2}$$

$$[B]_{\max} = a \times \left[ \frac{k_2}{k_1} \right]^{\frac{k_2}{k_1 - k_2}} = [A_0] \left[ \frac{k_2}{k_1} \right]^{\frac{k_2}{k_1 - k_2}}$$

## 8.3.1 Case -I

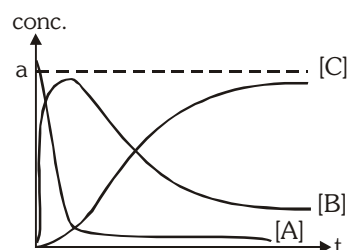
$$k_1 \gg k_2$$



$$[A] = a e^{-k_1 t}$$

$$[B] = a e^{-k_2 t}$$

$$[C] = a(1 - e^{-k_2 t})$$



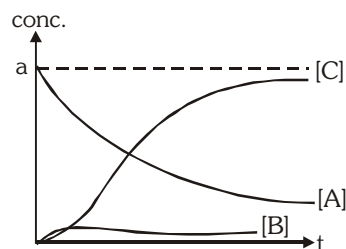
## 8.3.2 Case -II

$$k_2 \gg k_1$$

$$[B]_t \rightarrow 0$$

$$[A] = ae^{-k_1 t}$$

$$[C] = a(1 - e^{-k_1 t})$$



**Note :** Both Case (I) and Case (II) show that rate of overall reaction depends on rate of slowest step (RDS.)

## 9. EFFECT OF TEMPERATURE ON RATE OF REACTION :

In early days the effect of temperature on reaction rate was expressed in terms of *temperature coefficient* ( $\mu$ ) which was defined as the ratio of rate of reaction at two different temperature differing by  $10^\circ\text{C}$  (usually these temperatures were taken as  $25^\circ\text{C}$  and  $35^\circ\text{C}$ )

$$\text{T.C., } \mu = \frac{K_{T+10}}{K_T} \approx 2 \text{ to } 3 \quad (\text{for most of the reactions})$$

**Note :** Rate of reaction increases on increasing temperature (Generally ; T.C > 1)

**Ex.15** For a reaction T.C. = 2, Calculate  $\frac{k_{40^\circ\text{C}}}{k_{25^\circ\text{C}}}$  for this reaction. Assuming T.C remains constant.

**Sol.** 
$$\frac{k_2}{k_1} = (\text{T.C.})^{\frac{\Delta t}{10}} = (2)^{\frac{15}{10}} = (2)^{\frac{3}{2}} = \sqrt{8}$$

But the method of temperature coefficient was not exact to explain the effect of temperature on reaction rate. For that a new theory was evolved.

## 9.1 Collision theory of reaction rate :

It was developed by *Max Trautz* and *William Lewis*. It gives insight in to the energetics and mechanistic aspects of reactions.

It is based upon kinetic theory of gases.

*According to this theory :*

- (i) A chemical reaction takes place due to the collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency ( $Z$ ).
- (ii) Every collision does not bring a chemical change. The collision that actually produce the products are effective collision. For a collision to be effective the following two barriers are to be cleared.

❖ **Energy barrier :** The minimum amount of absolute energy which the colliding molecules must possess as to make the chemical reaction to occur is known as **threshold energy**.

- Reactant molecules having energy equal or greater than the threshold are called *active molecules* and those having energy less than the threshold are called *passive molecules*.

- At a given temperature there exists a dynamic equilibrium between active and passive molecules. The process of transformation from passive to active molecules being endothermic, increase of temperature increases the number of active molecules and hence the reaction.

**Passive molecules  $\rightleftharpoons$  Active molecules,  $\Delta H = +ve$**

- “The minimum amount of excess energy required by reactant molecules to participate in a reaction is called **activation energy ( $E_a$ )**”.

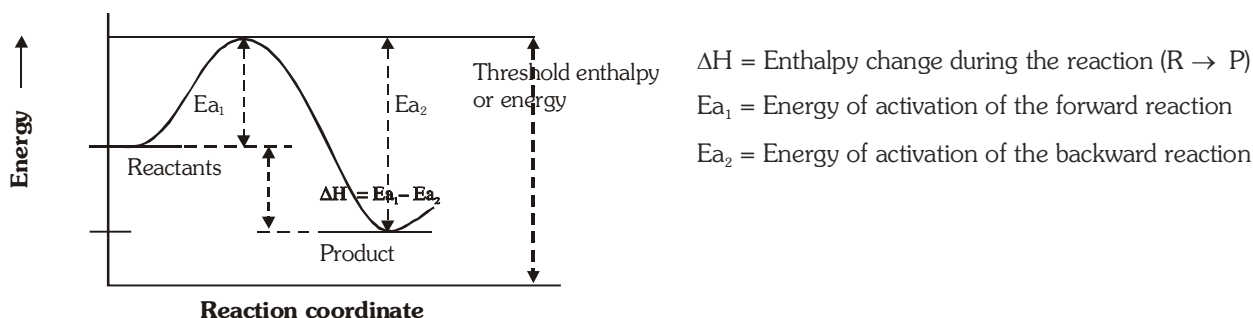
### CONCEPT OF ENERGY OF ACTIVATION ( $E_a$ ) :

- The average extra amount of energy which the reactant molecules (having energy less than the threshold) must acquire so that their mutual collision may lead to the breaking of bond(s) and hence the energy is known as energy of activation of the reaction. It is denoted by the symbol  $E_a$ . Thus,

**$E_a = \text{Threshold energy} - \text{Actual average energy of reactants}$**

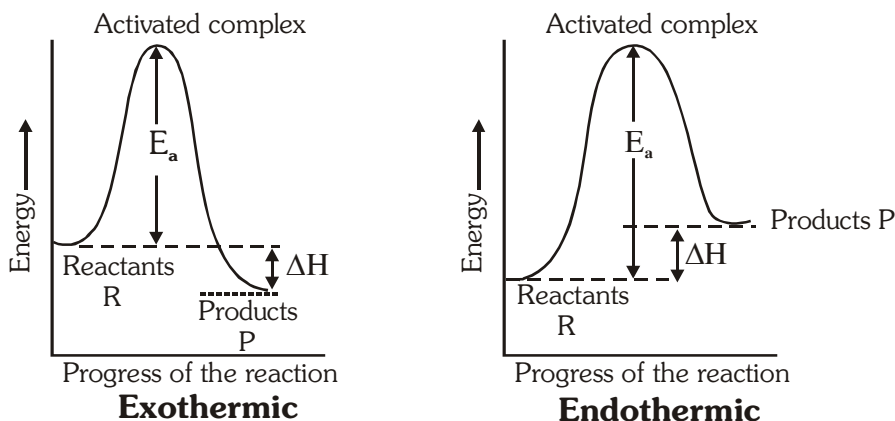
**$E_a$  is expressed in  $\text{kcal mole}^{-1}$  or  $\text{kJ mole}^{-1}$ .**

- The essence of Collision Theory of reaction rate is that there exists an energy barrier in the reaction path between reactant(s) and product(s) and for reaction to occur, the reactant molecules must climb over the top of the barrier which they do by collision. The existence of energy barrier and concept of  $E_a$  can be understood from the following diagram.



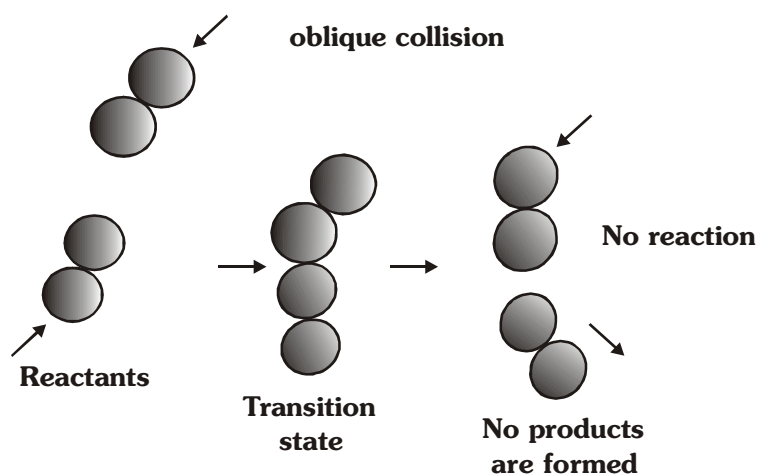
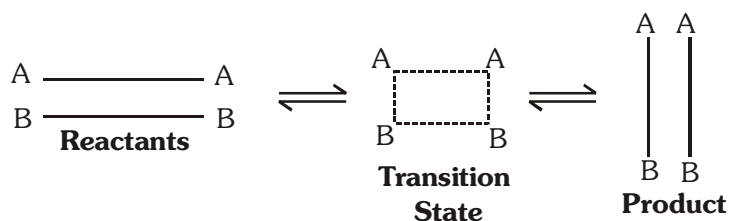
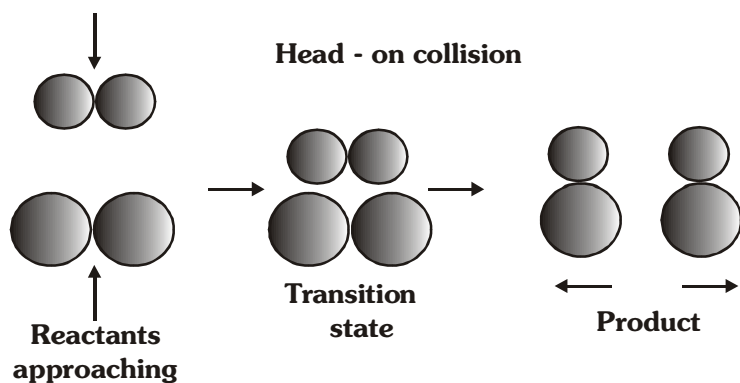
From the figure above it can be concluded that the minimum activation energy of any exothermic reaction will be zero while minimum activation energy for any endothermic reaction will be equal to  $\Delta H$ .

Greater the height of energy barrier, greater will be the energy of activation and more slower will be the reaction at a given temperature.



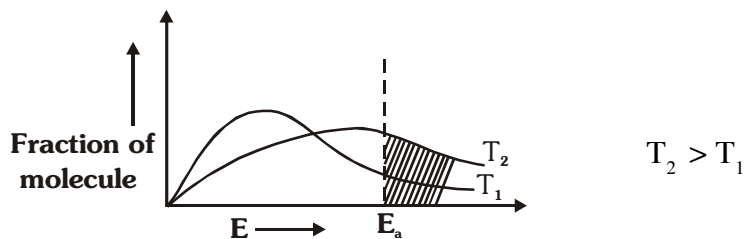
- ❖ **Orientation barrier :** Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper direction to make collision effective. Following diagrams can explain importance of suitable direction for collision.

Consider reaction :  $A_2 + B_2 \rightarrow 2AB$



- (iii) **Rate of any chemical reaction** = Collision frequency  $\times$  fraction of the total number of effective collision.
- = Collision frequency  $\times$  fraction of the total number of collision in which K.E. of the colliding molecules equals to  $E_a$  or exceeds over it  $\times$  fraction of collision in proper orientation.

From Maxwellian distribution, it is found that fraction of molecules having excess energy greater than threshold energy lead to the formation of product.



$e^{-E_a/RT} \rightarrow$  Represents fraction of molecules having K.E. greater than or equal to  $E_a$ .

$$\text{Rate} \propto e^{-E_a/RT}$$

Dependence of rate on temperature is due to dependence of  $k$  on temperature.

$$k \propto e^{-E_a/RT}$$

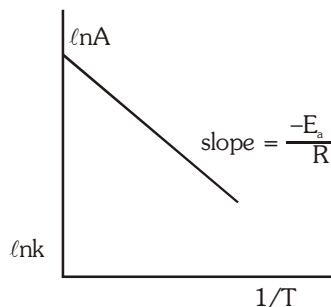
$$k = Ae^{-E_a/RT}$$

### [Arrhenius equation]

'A' is **pre-exponential** factor or **frequency factor** representing collisions taking place with proper orientation. A and  $E_a$  are assumed to be independent of temperature.

$$\ln k = \ln A - \frac{E_a}{RT}$$

As  $T \rightarrow \infty$ ,  $k \rightarrow A$



At temperature  $T_1$ , Rate constant =  $k_1$

At temperature  $T_2$ , Rate constant =  $k_2$

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \& \quad \ln k_2 = \ln A - \frac{E_a}{RT_2} \Rightarrow \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

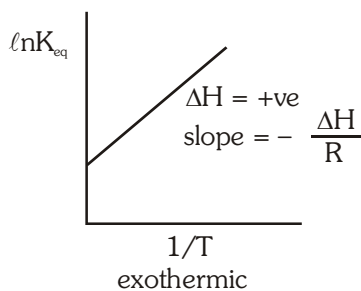
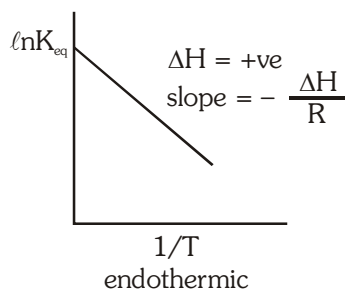
## 9.2 REVERSIBLE REACTIONS

$$k_f = A_f e^{-E_{af}/RT}$$

$$k_b = A_b e^{-E_{ab}/RT}$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f}{A_b} \frac{e^{-E_{af}/RT}}{e^{-E_{ab}/RT}} = \left( \frac{A_f}{A_b} \right) e^{-(E_{af}-E_{ab})/RT}$$

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \ln \left( \frac{A_f}{A_b} \right)$$





**Ex.16** For a reaction, temperature coefficient = 2, then calculate the activation energy (in kJ) of the reaction.

**Sol.** Given : Temperature coefficient =  $\frac{K_2}{K_1} = 2$

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$T_2 = 35 + 273 = 308 \text{ K}$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \left( \frac{10}{298 \times 308} \right)$$

$$E_a = 52.31 \text{ kJ mol}^{-1}$$

**Ex.17** For first order gaseous reaction, log k when plotted against  $\frac{1}{T}$ , it give a straight the with a slope of -8000. Calculate the activation energy of the reaction.

**Sol.** For an arrhenius equation  $k = Ae^{-E_a/RT}$

$$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

when curve is plotted between log k and  $\frac{1}{T}$ . A straight line is obtained and a slope of this curve

$$= -\frac{E_a}{2.303R}$$

$$\text{Then, } \frac{E_a}{2.303R} = 8000$$

$$\text{or } E_a = 8000 \times 2.303 \times 2 = 36848 \text{ calories}$$

**Ex.18** The slope of the plot of log k vs  $\frac{1}{T}$  for a certain reaction was found to be  $-5.4 \times 10^3$ . Calculate the energy of activation of the reaction. If the rate constant of the reaction is  $1.155 \times 10^{-2} \text{ sec}^{-1}$  at 373 K, what is its frequency factor ?

**Sol.** (a) Slope =  $\frac{-E}{2.303 R} = -5.4 \times 10^3$

$$E_a = 5.4 \times 10^3 \times 2.303 \times 1.987 \\ = 24.624 \text{ cal mol}^{-1}$$

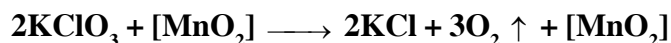
(b)  $K = Ae^{-E/RT}$ ;  $\log 1.155 \times 10^{-2} = \log A - \frac{24.624}{2.303 \times 1.987 \times 373}$

$$\text{or } A = 1.764 \times 10^3 \text{ sec}^{-1}$$

## 10. CATALYST AND CATALYSIS :

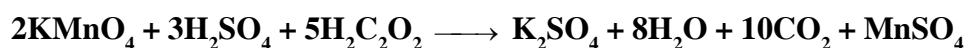
A catalyst is a substance, which increases the rate of a reaction without itself being consumed at the end of the reaction, and the phenomenon is called *catalysis*.

Thermal decomposition of  $\text{KClO}_3$  is found to be accelerated by the presence of  $\text{MnO}_2$ . Here  $\text{MnO}_2$  acts as a catalyst.



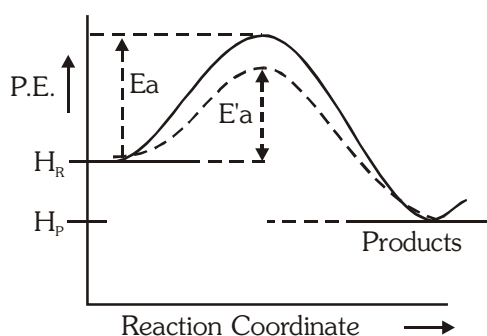
- $\text{MnO}_2$  can be received in the same composition and mass at the end of the reaction.
- The word catalyst should not be used when the added substance reduces the rate of reaction. The substance is then called **inhibitor**.
- Catalyst are generally foreign substances but sometimes one of the product may act as a catalyst and such catalyst is called "*auto catalyst*" and the phenomena is called *auto catalysis*.

In the permanganate titration of oxalic acid initially there is slow discharge of the colour of permanganate solution but afterwards the discharge of the colour become faster. This is due to the formation of  $\text{MnSO}_4$  during the reaction which acts as a catalyst for the same reaction. Thus,  $\text{MnSO}_4$  is an "*auto catalyst*" for this reaction. This is an example of auto catalyst.



### 10.1 General characteristics of catalyst :

- A catalyst does not initiate the reaction normally. It simply fastens it.
- Only a small amount of catalyst can catalyse the reaction.
- A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence  $\Delta G^\circ$ . It simply lowers the time needed to attain equilibrium. This means if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst, the reaction will still go to 75% of completion on the attainment of equilibrium but the time needed for this will be less than 20 minutes.

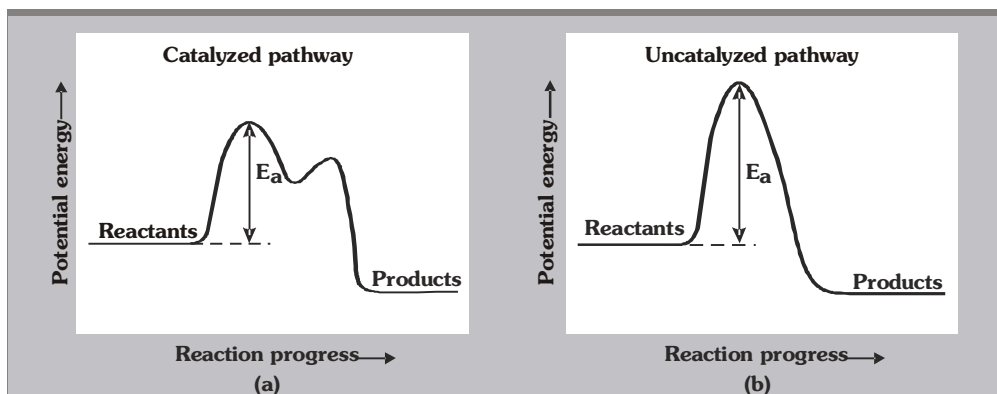


A catalyst drives the reaction through a low energy path and hence  $E_a$  is less. That is, the function of the catalyst is to lower down the activation energy.

$E_a$  = Energy of activation in absence of catalyst.

$E'_a$  = Overall Energy of activation in presence of catalyst.

$E_a - E'_a$  = Lowering of activation energy by catalyst.



## 10.2 Comparison of rates of reaction in presence and absence of catalyst :

If  $k$  and  $k_{\text{cat}}$  be the rate constant of a reaction at a given temperature  $T$ ,  $E_a$  and  $E'_a$  are the activation energies of the reaction in absence and presence of catalyst, respectively, the

$$\frac{k_{\text{cat}}}{k} = \frac{Ae^{-E'_a/RT}}{Ae^{-E_a/RT}} = Ae^{(E_a - E'_a)/RT}$$

Since  $E_a - E'_a$  is positive so  $k_{\text{cat}} > k$ . the ratio  $\frac{k_{\text{cat}}}{k}$  gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature.

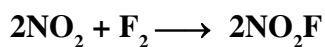
The rate of reaction in the presence of catalyst at any temperature  $T_1$  may be made equal to the rate of reaction in absence of catalyst but for this sake we will have to raise the temperature. Let this temperature

$$\text{be } T_2 = e^{-E'_a/RT_1} = e^{-E_a/RT_2} \quad \text{or} \quad \frac{E'_a}{T_1} = \frac{E_a}{T_2}$$

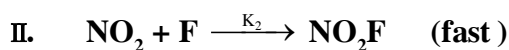
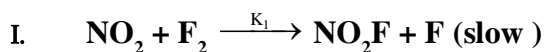
## 11 CALCULATION OF RATE LAW / ORDER

### 11.1 When first step is rate determining step.

#### Ex.19 Calculate order and rate law of reaction -



with help of mechanism

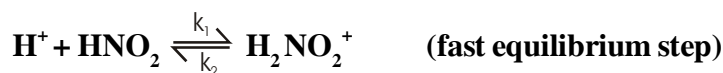


Sol. According to RDS

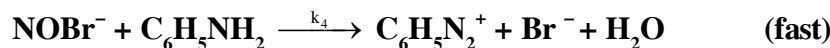
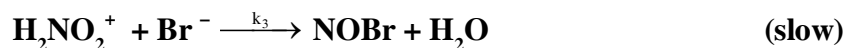
$$\text{Rate} = k_1 [\text{NO}_2] [\text{F}_2]$$

## 11.2 Equilibrium approach :

Ex.20 For the reaction,  $\text{H}^+ + \text{HNO}_2 + \text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{Br}^-} \text{C}_6\text{H}_5\text{N}_2^+ + 2\text{H}_2\text{O}$ , the mechanism is,



intermediate



Derive the rate law expression for the reaction

Sol.  $r = k_3 [\text{Br}^-] [\text{H}_2\text{NO}_2^+]$

$$K_{\text{eq}} = \frac{k_1}{k_2} = \frac{[\text{H}_2\text{NO}_2^+]}{[\text{H}^+][\text{HNO}_2]}$$

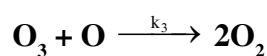
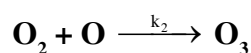
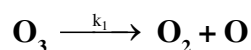
$$[\text{H}_2\text{NO}_2^+] = \left[ \frac{k_1}{k_2} \right] [\text{H}^+] [\text{HNO}_2]$$

$$r = \frac{k_1 k_3}{k_2} [\text{H}^+] [\text{HNO}_2] [\text{Br}^-].$$

**Note :** Rate law can have reactant product or catalyst concentration terms but not any intermediate terms.

## 11.3 CASE-III : STEADY STATE APPROXIMATION :

Ex.21 For the reaction,  $2\text{O}_3 \rightarrow 3\text{O}_2$ , the mechanism is



Derive the rate law expression for the reaction

Sol.  $\text{rate} = \frac{-1}{2} \frac{d[\text{O}_3]}{dt} = \frac{1}{3} \frac{d[\text{O}_2]}{dt}$

$$\frac{d[\text{O}_3]}{dt} = -k_1 [\text{O}_3] + k_2 [\text{O}_2][\text{O}] - k_3 [\text{O}_3][\text{O}]$$

$$\frac{d[\text{O}_2]}{dt} = k_1 [\text{O}_3] - k_2 [\text{O}_2][\text{O}] + k_3 [\text{O}_3][\text{O}]$$

At steady state  $\frac{d[\text{O}]}{dt} = 0$

$$\frac{d[\text{O}]}{dt} = k_1 [\text{O}_3] - k_2 [\text{O}_2][\text{O}] - k_3 [\text{O}_3][\text{O}] = 0$$

$$[O] = \frac{k_1[O_3]}{k_2[O_2] + k_3[O_3]}$$

$$\begin{aligned} \frac{d[O_3]}{dt} &= -k_1[O_3] + \frac{\{k_2[O_2] + k_3[O_3]\}}{k_2[O_2] + k_3[O_3]} - \frac{k_1 k_3[O_3]^2}{k_2[O_2] + k_3[O_3]} \\ &= -k_1[O_3] + \frac{k_1 k_2[O_2][O_3] - k_1 k_3[O_3]^2}{k_2[O_2] + k_3[O_3]} \\ &= \frac{k_1 k_2[O_2][O_3] - k_1 k_3[O_3]^2 + k_1 k_2[O_2][O_3] - k_1 k_3[O_3]^2}{k_2[O_2] + k_3[O_3]} \\ &= \frac{-2k_1 k_3[O_3]^2}{k_2[O_2] + k_3[O_3]} \end{aligned}$$

$$\left[ \frac{-1}{2} \frac{d[O_3]}{dt} \right] = \frac{k_1 k_3 [O_3]^2}{k_2[O_2] + k_3[O_3]}$$

$$\text{Rate} = -\frac{1}{2} \frac{d}{dt} [O_3]$$

$$\text{So, Rate (r)} = \frac{k_1 k_3 [O_3]^2}{k_2[O_2] + k_3[O_3]}$$

if 3<sup>rd</sup> step is RDS then  $k_1 \gg k_3$   
 $k_2 \gg k_3$

$$\text{Rate (r)} = \frac{k_1 k_3}{k_2} [O_3]^2 [O_2]^{-1} \text{ (ie. first order)}$$

### MISSLENIIOUS PREVIOUS YEARS QUESTION

1. Which of the following statement(s) is (are) correct [JEE 1999]

- (A) A plot of  $\log K_p$  versus  $1/T$  is linear  
 (B) A plot of  $\log [X]$  versus time is linear for a first order reaction,  $X \longrightarrow P$   
 (C) A plot of  $\log P$  versus  $1/T$  is linear at constant volume.  
 (D) A plot of  $P$  versus  $1/V$  is linear at constant temperature.

**Ans. (A,B,D)**

2. The rate constant for an isomerisation reaction  $A \rightarrow B$  is  $4.5 \times 10^{-3} \text{ min}^{-1}$ . If the initial concentration of A is 1 M. Calculate the rate of the reaction after 1 h. [JEE 1999]

**Ans.  $3.435 \times 10^{-3} \text{ M/min}$**

**Sol.**  $r = k[A]$

$$r = K[A]_0 e^{-kt}$$

$$r = (4.5 \times 10^{-3}) e^{-4.5 \times 10^{-3} \times 60} \text{ M/min.}$$

3. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by  $20 \text{ kJmol}^{-1}$ . [JEE 2000]

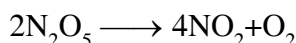
**Ans.  $100 \text{ kJmol}^{-1}$**

**Sol.**  $\ln \left( \frac{r_2}{r_1} \right) = -\frac{1}{R} \left( \frac{E_{a_2}}{T_2} - \frac{E_{a_1}}{T_1} \right)$

$$\ln (1) = -\frac{1}{R} \left( \frac{E_{a_1} - 20}{40} - \frac{E_{a_1}}{500} \right)$$

$$E_{a_1} = 100$$

4. The rate constant for the reaction [JEE SCR 2000]



is  $3.0 \times 10^{-5} \text{ sec}^{-1}$ . if the rate is  $2.4 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$ , then the concentration of  $\text{N}_2\text{O}_5$  (in  $\text{mol litre}^{-1}$ ) is

- (A) 1.4                      (B) 1.2                      (C) 0.004                      (D) 0.8

**Ans. (D)**

**Sol.**  $r = k[\text{N}_2\text{O}_5]^2$

$$2.4 \times 10^{-5} = 3 \times 10^{-5} [\text{N}_2\text{O}_5]^2$$

5. If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process:  $\text{AB} + h\nu \longrightarrow \text{AB}$ , the rate of formation of AB is directly proportional to [JEE SCR 2001]

- (A) C                      (B) I                      (C)  $I^2$                       (D) CI

**Ans. (B)**

**Sol.** For phot chemical reaction

$$r \propto I$$

6. The rate of a first order reaction is  $0.04 \text{ mole litre}^{-1} \text{ s}^{-1}$  at 10 minutes and  $0.03 \text{ mol litre}^{-1} \text{ s}^{-1}$  at 20 minutes after initiation. Find the half life of the reaction. [JEE 2001]

**Ans.**  $t_{1/2} = 24.14 \text{ min}$

**Sol.**  $\left(\frac{\ln 2}{t_{1/2}}\right) (20 - 10) = \ln \left(\frac{0.04}{0.03}\right)$

7. Consider the chemical reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ . The rate of this reaction can be expressed in term of time derivative of concentration of  $\text{N}_2(\text{g})$ ,  $\text{H}_2(\text{g})$  or  $\text{NH}_3(\text{g})$ . Identify the correct relationship amongst the rate expressions. [JEE SCR 2002]

(A)  $\text{Rate} = -d[\text{N}_2]/dt = -1/3 d[\text{H}_2]/dt = 1/2 d[\text{NH}_3]/dt$

(B)  $\text{Rate} = -d[\text{N}_2]/dt = -3 d[\text{H}_2]/dt = 2d[\text{NH}_3]/dt$

(C)  $\text{Rate} = d[\text{N}_2]/dt = 1/3 d[\text{H}_2]/dt = 1/2 d[\text{NH}_3]/dt$

(D)  $\text{Rate} = -d[\text{N}_2]/dt = -d[\text{H}_2]/dt = d[\text{NH}_3]/dt$

**Ans.** (A)

**Sol.**  $\frac{-d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$

8. In a first order reaction the concentration of reactant decreases from  $800 \text{ mol/dm}^3$  to  $50 \text{ mol/dm}^3$  in  $2 \times 10^4 \text{ sec}$ . The rate constant of reaction in  $\text{sec}^{-1}$  is [JEE SCR 2003]

(A)  $2 \times 10^4$

(B)  $3.45 \times 10^{-5}$

(C)  $1.3486 \times 10^{-4}$

(D)  $2 \times 10^{-4}$

**Ans.** (C)

**Sol.**  $K(2 \times 10^4) = \ln \left(\frac{800}{50}\right)$

9. The reaction,  $\text{X} \longrightarrow \text{Product}$  follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. Then the rate of reaction when concentration of X is 0.01 M

(A)  $1.73 \times 10^{-4} \text{ M min}^{-1}$

(B)  $3.47 \times 10^{-5} \text{ M min}^{-1}$

(C)  $3.47 \times 10^{-4} \text{ M min}^{-1}$

(D)  $1.73 \times 10^{-5} \text{ M min}^{-1}$

[JEE SCR 2004]

**Ans.** (C)

**Sol.**  $K(40) = \ln \left(\frac{0.1}{0.025}\right)$

$$K = \frac{\ln 2}{20}$$

$$r = K[X]$$

$$= \frac{\ln 2}{20} \times 0.1$$

10.	$2X(g) \longrightarrow 3Y(g) + 2Z(g)$		
<b>Time (in Min)</b>	0	100	200
<b>Partial pressure of X</b>	800	400	200
	<b>(in mm of Hg)</b>		

Assuming ideal gas condition. Calculate

- (a) Order of reaction  
 (b) Rate constant ( $K_x$ )  
 (c) Time taken for 75% completion of reaction  
 (d) Total pressure when  $P_x = 700$  mm.

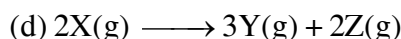
[JEE 2005]

**Ans.** (a) 1, (b)  $6.93 \times 10^{-3} \text{ min}^{-1}$ , (c) 200, (d) 950 mm

**Sol.** (a) As half life is constant so it will be of first order.

$$(b) K_x(100) = \ln \left( \frac{800}{400} \right)$$

$$(c) t = 75\% = 2t_{50\%} = 2 \left( \frac{\ln 2}{K_x} \right)$$



$$800 - x \quad \frac{3x}{2} \quad x$$

Here  $x = 100$

$$\text{So } P_T = 800 + \frac{3x}{2} = 950$$

11. Which of the following statement is incorrect about order of reaction?

[JEE 2005]

- (A) Order of reaction is determined experimentally  
 (B) It is the sum of power of concentration terms in the rate law expression  
 (C) It does not necessarily depend on stoichiometric coefficients  
 (D) Order of the reaction can not have fractional value.

**Ans.** (D)

12. Consider a reaction  $aG + bH \rightarrow \text{Products}$ . When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is :

[JEE 2006]

- (A) 0 (B) 1 (C) 2 (D) 3

12. **Ans.**(D)

$$\text{Sol. } \frac{r_2}{r_1} \left( \frac{[G]_2}{[G]_1} \right)^\alpha \left( \frac{[H]_2}{[H]_1} \right)^\beta$$

$$8 = 2^\alpha \cdot 2^\beta \quad \dots\dots(1)$$

$$2 = 2^\alpha \quad \dots\dots(2)$$

$$\alpha = 1, \beta = 2$$



13. Under the same reaction conditions, initial concentration of  $1.386 \text{ mol dm}^{-3}$  of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio

$\left(\frac{k_1}{k_0}\right)$  of the rate constants for first order ( $k_1$ ) and zero order ( $k_0$ ) of the reactions is [JEE 2008]

- (A)  $0.5 \text{ mol}^{-1} \text{ dm}^3$  (B)  $1.0 \text{ mol dm}^{-3}$  (C)  $1.5 \text{ mol dm}^{-3}$  (D)  $2.0 \text{ mol}^{-1} \text{ dm}^3$

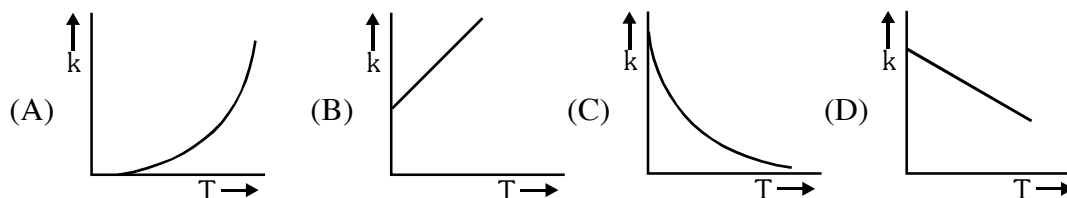
Ans. (A)

Sol.  $K_1 = \frac{\ln 2}{40}$

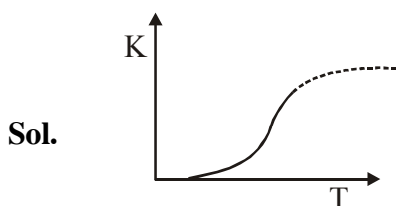
$$K_0 = \frac{1.386}{2 \times 20}$$

$$\frac{K_1}{K_0} = 0.5$$

14. Plots showing the variation of the rate constant ( $k$ ) with temperature ( $T$ ) are given below. The plot that follows Arrhenius equation is – [JEE 2010]



Ans. (A)



15. The concentration of R in the reaction  $R \rightarrow P$  was measured as a function of time and the following data is obtained :

[R] (molar)	1.0	0.75	0.40	0.10
t(min.)	0.0	0.05	0.12	0.18

The order of the reaction is.

[JEE 2010]

Ans. Zero

Sol. By hit and trial method the reaction is zero order.

$$K_1 = \frac{[A]_0 - [A]_1}{t_1}$$

$$K_1 = \frac{1 - 0.75}{0.05} = 5$$

$$K_2 = \frac{[A]_0 - [A]_2}{t_2}$$

$$K_2 = \frac{1 - 0.4}{0.12} = 5$$

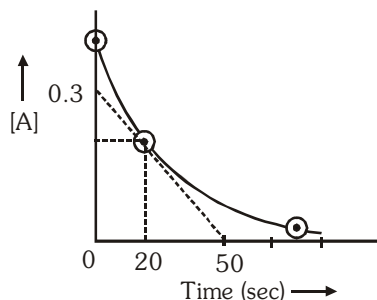
As  $K_1 \approx K_2$  so reaction will be zero order reaction.

## EXERCISE # S-1

## RATE OF REACTION

1. Ammonia and oxygen reacts at higher temperatures as  

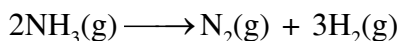
$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$$
 In an experiment, the concentration of NO increases by  $1.08 \times 10^{-2}$  mol litre<sup>-1</sup> in 3 seconds. Calculate.  
 (i) rate of reaction  
 (ii) rate of disappearance of ammonia  
 (iii) rate of formation of water **CK0001**
2. The reaction  $2\text{A} + \text{B} + \text{C} \rightarrow \text{D} + \text{E}$  is found to be first order in A, second order in B and zero order in C.  
 (i) Give the rate law for the reaction in the form of differential equation.  
 (ii) What is the effect in rate of increasing concentrations of A, B, and C two times? **CK0002**
3. At 27°C, it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of disappearance reaction in M sec<sup>-1</sup> and in terms of atm min<sup>-1</sup>. [Use : R = 0.08 atm-L/K-mole] **CK0003**
4. For the elementary reaction  $2\text{A} + \text{B}_2 \longrightarrow 2\text{AB}$ . Calculate how much the rate of reaction will change if the volume of the vessel is suddenly reduced to one third of its original volume? **CK0004**
5. For the reaction  $3\text{BrO}^- \rightarrow \text{BrO}_3^- + 2\text{Br}^-$  in an alkaline aqueous solution, the value of the second order (in BrO<sup>-</sup>) rate constant at 80°C in the rate law for  $-\frac{d[\text{BrO}^-]}{dt}$  was found to be 0.057 L mol<sup>-1</sup> s<sup>-1</sup>. What is the rate constant when the rate law is written for :  
 (a)  $\frac{d[\text{BrO}_3^-]}{dt}$ , (b)  $\frac{d[\text{Br}^-]}{dt}$ ? **CK0005**
6.  $x\text{A} + y\text{B} \rightarrow z\text{C}$ . If  $-\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = 1.5 \frac{d[\text{C}]}{dt}$ , then (x + y + z) is. (x, y & z are the lowest integral value.) **CK0006**
7. For the reaction :  $3\text{A}(\text{g}) \rightarrow 2\text{B}(\text{g})$ , the rate of formation of 'B' at 298 K, is represented as  
 $\ln\left(\frac{d[\text{B}]}{dt}\right) = -0.04 + 2 \times \ln[\text{A}]$ . The order of reaction is- **CK0007**
8. A certain reaction  $\text{A} \rightarrow \text{B}$  follows the given concentration (Molarity) – time graph. Calculate the rate for this reaction at 20 second.

**CK0008**

9. The reaction  $A(g) + 2B(g) \longrightarrow C(g) + D(g)$  is an elementary process. In an experiment, the initial partial pressure of A & B are  $P_A = 0.6$  and  $P_B = 0.8$  atm. Calculate the ratio of rate of reaction relative to initial rate when  $P_C$  becomes 0.2 atm. **CK0009**

### ZERO ORDER REACTIONS

10. In the reaction  $(A \longrightarrow B)$  rate constant is  $1.2 \times 10^{-2} \text{ M s}^{-1}$ . What is concentration of B after 10 and 20 min., if we start with 10 M of A. **CK0010**
11. From the following data for the zero order reaction :  $A \longrightarrow$  products. Calculate the value of k.
- | Time (min.) | [A]    |
|-------------|--------|
| 0.0         | 0.10 M |
| 1.0         | 0.09 M |
| 2.0         | 0.08 M |
- CK0011**
12. A drop of solution (volume 0.10 ml) contains  $6 \times 10^{-6}$  mole of  $H^+$ . If the rate constant of disappearance of  $H^+$  is  $1 \times 10^7 \text{ mole litre}^{-1} \text{ sec}^{-1}$ , how long would it take for  $H^+$  in drop to disappear? **CK0012**
13. A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero for both A & B.) **CK0013**
14. For a zero order chemical reaction,



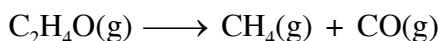
rate of reaction = 0.1 atm/sec. Initially only  $NH_3$  is present & its pressure = 3 atm. Calculate total pressure at  $t = 10$  sec. **CK0014**

### FIRST ORDER REACTIONS

15. A first order reaction is 75% completed in 72 min. How long time will it take for  
(i) 50% completion (ii) 87.5% completion **CK0015**
16. A first order reaction is 20% complete in 10 min. Calculate (i) the specific rate constant, (ii) the time taken for the reactions to go to 75% completion. [ $\ln 10 = 2.3$ ,  $\ln 2 = 0.7$ ] **CK0016**
17. Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place is ten times that required for half of the reaction. **CK0017**
18. A drug is known to be ineffective after it has decomposed 75%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 250 units/ml. Assuming that decomposition is of I order, what will be the expiry time of the drug? **CK0018**
19. A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment, 2.0 % of the virus was found to be inactivated per minute. Evaluate k for inactivation process. [ $\ln 10 = 2.3$ ,  $\ln 98 = 4.58$ ] **CK0019**
20. The reaction  $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$  is a first order gas reaction with  $k = \left(\frac{35}{9}\right) \times 10^{-4} \text{ sec}^{-1}$  at  $320^\circ\text{C}$ . What % of  $SO_2Cl_2$  is decomposed on heating this gas for 90 min. ( $\ln 2 = 0.7$ ) **CK0020**

21. The decomposition of a compound A in solution follow first order kinetics. If 10% w/v solution of A is 10% decomposed in 10 minutes at 10°C, then 20% w/v solution of A is ..... % decomposed in 20 minutes at 10°C. **CK0021**

22. Calculate the half-life of the first-order reaction



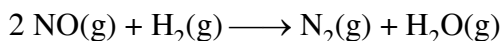
if the initial pressure of  $\text{C}_2\text{H}_4\text{O}(\text{g})$  is 80 mm of Hg and the total pressure at the end of 20 minutes is 120 mm of Hg **CK0022**

### SECOND ORDER REACTIONS

23. In the II order reaction :  $2\text{A} \rightarrow \text{A}_2$ . The rate of formation of  $\text{A}_2$  is  $10^{-5} \text{ M sec}^{-1}$  at 0.01M concentration of A. Calculate the rate constant in the rate of disappearance of 'A'. **CK0023**
24. If  $t_{1/2}$  of a second order reaction is 1.0 hr. After what time, the amount of reactant will be 25% of the initial amount? **CK0024**
25. Reaction :  $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ , follows the rate law :  $r = (2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}) [\text{A}] [\text{B}]$ . The reaction is started with 1.0 mole each of 'A' and 'B', in constant volume of 5 litre. In what time, the moles of 'A' become 0.25 ? **CK0025**

### DETERMINATION OF ORDER OF REACTION & RATE LAW

26. At 800° C, the rate of reaction



changes with the concentration of  $\text{NO}(\text{g})$  and  $\text{H}_2(\text{g})$  as-

Exp.no.	[NO] in M	[H <sub>2</sub> ] in M	$-\frac{1}{2} \frac{d[\text{NO}]}{dt}$ in M sec <sup>-1</sup>
(i)	$1.5 \times 10^{-3}$	$4 \times 10^{-3}$	$4.50 \times 10^{-9}$
(ii)	$1.5 \times 10^{-3}$	$2 \times 10^{-3}$	$2.25 \times 10^{-9}$
(iii)	$3.0 \times 10^{-3}$	$2 \times 10^{-3}$	$9.00 \times 10^{-9}$

- (a) What is the order of reaction?  
 (b) What is the rate equation for the reaction?  
 (c) What is the rate of reaction when  $[\text{H}_2] = 1.5 \times 10^{-3} \text{ M}$  and  $[\text{NO}] = 1.0 \times 10^{-3} \text{ M}$ ? **CK0026**
27. The catalytic decomposition of  $\text{N}_2\text{O}(\text{g})$  by gold at 900°C and at an initial pressure of 200 mm is 50% complete in 53 minutes and 73% complete in 100 minutes.
- (i) What is the order of the reaction?  
 (ii) Calculate the velocity constant.  
 (iii) How much of percentage  $\text{N}_2\text{O}(\text{g})$  will decompose in 100 min. at the same temperature but at initial pressure of 600 mm of Hg ? **CK0027**

28. The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different time and the results are given below

t (sec)	0	100	200	300
Pr. (Pascal)	$4 \times 10^3$	$3.5 \times 10^3$	$3 \times 10^3$	$2.5 \times 10^3$

Determine the order of reaction and its rate constant. **CK0028**

29. The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction? **CK0029**

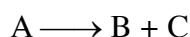
30. For a chemical reaction  $\text{A} + \text{B} \rightarrow \text{products}$ , the order is one with respect to each A and B. The sum of x and y from the following data is.

Rate (mol l <sup>-1</sup> s <sup>-1</sup> )	[A](mol l <sup>-1</sup> )	[B](mol l <sup>-1</sup> )
0.10	0.20	0.05
0.40	x	0.05
0.80	0.40	y

**CK0030**

## CALCULATION OF RATE CONSTANT USING DIFFERENT PARAMETERS

31. For the 1st order reaction



<b>Time</b>	t	$\infty$
<b>Total pressure of (A + B + C)</b>	$P_2$	$P_3$

Find k in term of  $P_2$ ,  $P_3$  and t

CK0031

32. For the 1st order reaction
- $S \longrightarrow G + F$

<b>Time</b>	t	$\infty$
<b>Rotation of (G + F)</b>	$r_t$	$r_\infty$

Find k in term of  $r_t$ ,  $r_\infty$  and t

CK0032

33. The thermal decomposition of dimethyl ether was measured by finding the increase in pressure at 500°C in the reaction



<b>Time (sec.)</b>	200	400	$\infty$
<b>Pressure increase (mm Hg)</b>	540	594	600

The initial pressure of ether was 300 mm Hg. Determine the rate constant of reaction.

CK0033

34. From the following data, show that decomposition of
- $\text{H}_2\text{O}_2$
- in aqueous solution is first order.

<b>Time (in minutes)</b>	0	10	20
<b>Volume (in c.c. of <math>\text{KMnO}_4</math>)</b>	22.8	11.4	5.7

CK0034

35. The following data were obtained in experiment of inversion of cane sugar.

<b>Time (minutes)</b>	0	60	120	180	$\infty$
<b>Angle of rotation (degree)</b>	+15	+7	+3	+1	-1

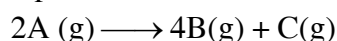
Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?

CK0035

36. The decomposition of
- $\text{N}_2\text{O}_5$
- according to the equation
- $2 \text{N}_2\text{O}_5(\text{g}) \longrightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
- is a first order reaction. After 60 min. from start of decomposition in a closed rigid vessel, the total pressure developed is found to be 350 mm Hg. On complete decomposition, the total pressure is 500 mm Hg. Calculate the rate constant for disappearance of
- $\text{N}_2\text{O}_5$
- (
- $k_{\text{N}_2\text{O}_5}$
- ) for the reaction.

CK0036

37. The reaction given below, rate constant for disappearance of A is
- $8 \times 10^{-3} \text{ sec}^{-1}$
- . Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm and also find the total pressure after 100 sec. [
- $\ln 7 = 1.9$
- ,
- $\ln 10 = 2.3$
- ].

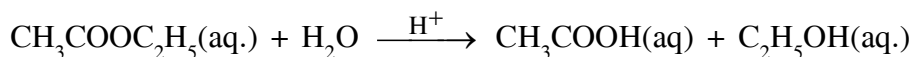


CK0037

38. The reaction
- $\text{A}(\text{aq}) \longrightarrow \text{B}(\text{aq}) + \text{C}(\text{aq})$
- is monitored by measuring optical rotation of reaction mixture at different time interval. The species A, B and C are optically active with specific rotations
- $20^\circ$
- ,
- $30^\circ$
- and
- $-40^\circ$
- per mole respectively. Starting with pure A, if the value of optical rotation was found to be
- $2.5^\circ$
- after 6.93 minutes and optical rotation was
- $-5^\circ$
- after infinite time. Find the rate constant for first order conversion of A into B and C.

CK0038

39. For the hydrolysis of ethyl acetate in presence of  $H^+$  as catalyst.



the experimentally observed rate law is

$$\text{rate} = k [\text{ester}] [H_2O] [H^+]. \quad \text{CK0039}$$

If the value of rate constant is  $1.386 \times 10^{-3} M^{-2} \text{min}^{-1}$  and concentration of  $[H^+]$  ion is 1.8 M, how many seconds will it take for concentration of ester to become half of initial value ?

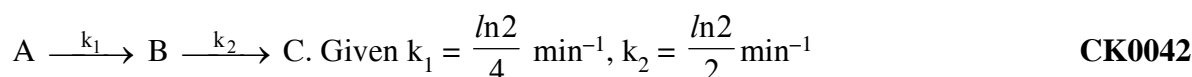
40. If 0.01 % of a substance undergoing decomposition is consumed in 1 milli seconds when the concentration is 0.02M and in 0.25 milli seconds when the concentration is 0.04M. The order of reaction is. CK0040

### PARALLEL , SEQUENTIAL REACTIONS AND REVERSIBLE

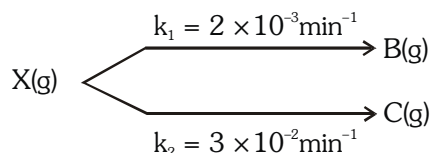
41.  $A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$ ,  $k_1 = x \text{ hr}^{-1}$ ;  $k_1 : k_2 = 1 : 10$ . Calculate  $\frac{[C]}{[A]}$  after one hour from the start of the reaction.

Assuming only A was present in the beginning. CK0041

42. How much time would be required for the B to reach maximum concentration for the reaction



43. A gaseous reactant X decompose to produce gaseous product B & C in a parallel reaction, both by first order, as follows :

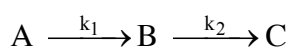


If the decomposition is carried out in a sealed flask, partial pressure of B after very long time was found to be 100 mm Hg. Determine the time when pressure of X(g) was 100 mm Hg.

$[\ln 2 = 0.693]$  CK0043

44. The reaction A proceeds in parallel channels  $A \begin{cases} \rightarrow B \\ \rightarrow C \end{cases}$ . Suppose the half life values for the two branches are 60 minutes and 90 minutes, what is the overall half-life value? CK0044

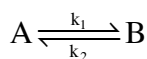
45. For the given sequential reaction



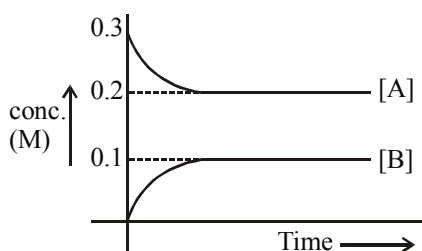
Initial concentration of A is 20M. Calculate the approximate concentration of C after 10 min,

if  $k_1 = 2 \times 10^8 \text{ min}^{-1}$  &  $k_2 = 0.0693 \text{ min}^{-1}$  CK0045

46. Consider a reversible reaction :



Which is a first order in both the direction ( $k_1 = \frac{1.38}{3} \times 10^{-2} \text{ min}^{-1}$ ). The variation in concentration is plotted with time as shown below.



Calculate the time (in minute) at which 25% of A would be exhausted. [ $\ln 2 = 0.69$ ] **CK0046**

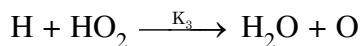
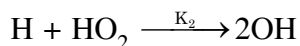
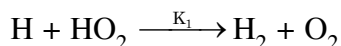
47. 3 mole mixture of two different substances A & B (mole fraction of A = 2/3) undergoes parallel first order reaction to form product 'C' as follow at 300 K.



The time at which there will be 2 mole of 'C' is

**CK0047**

48. For the series of competitive reactions :



It has been found that  $K_1 : K_2 : K_3 = 0.60 : 0.30 : 0.10$ . The molar ratio of the product,  $H_2$ ,  $O_2$ ,  $OH$ ,  $H_2O$  and  $O$ , at time  $t$ , is -

**CK0048**

49. In the parallel reactions :  $A \xrightarrow{K_1 = \ln 3 \text{ min}^{-1}} B$  and  $A \xrightarrow{K_2 = \ln 3 \text{ min}^{-1}} C$ , the time when the concentration of A, B and C becomes equal is -

**CK0049**

50. For the sequential reactions :

$A \xrightarrow{K_1 = 0.02 \text{ min}^{-1}} B \xrightarrow{K_2 = 0.02 \text{ min}^{-1}} C$ , the initial concentration of 'A' was 0.2M and initially 'B' and 'C' were absent. The time at which the concentration of 'B' becomes maximum and the maximum concentration of 'B' are respectively.

**CK0050**

### TEMPERATURE DEPENDENCE OF RATE

51. In gaseous reactions important for understanding the upper atmosphere,  $H_2O$  and  $O$  react bimolecularly to form two  $OH$  radicals.  $\Delta H$  for this reaction is 72 kJ at 500 K and  $E_a = 77 \text{ kJ mol}^{-1}$ , then calculate  $E_a$  for the bimolecular recombination of  $2OH$  radicals to form  $H_2O$  &  $O$  at 500 K **CK0051**

52. The specific rate constant for a reaction increases by a factor of 4, if the temperature is changed from  $27^\circ\text{C}$  to  $47^\circ\text{C}$ . Find the activation energy (in kcal) for the reaction (Use  $\ln 2 = 0.7$ )

**CK0052**

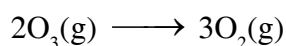
53. Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate activation energy for the saponification of ethyl acetate. Let initial temperature is 298K. [Use :  $\ln(1.75) = 0.56$ ] **CK0053**
54. The energy of activation for a reaction is at 27°C 10 kJ/mol. The presence of catalyst lowers the energy of activation by 75%. Find the factor by which rate of reaction increases at 27°C due to catalyst. (Take  $R = 25/3 \text{ J/mol-k}$ ) **CK0054**
55. At 380°C, the half-life period for the first order decomposition of  $\text{H}_2\text{O}_2$  is 360 min. The energy of activation of the reaction is 200 kJ mol<sup>-1</sup>. Calculate the time required for 75% decomposition at 450°C. Use :  $\left[ \frac{1}{653} - \frac{1}{723} \right] = 1.5 \times 10^{-4}$ ,  $e^{3.6} = 36$ ,  $R = \frac{25}{3} \text{ J/k-mol}$  **CK0055**
56. The rate constant for decomposition of  $\text{COCl}_2(\text{g})$  according to following reaction  $\text{COCl}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$ ;  $\Delta H = 19 \text{ kcal/mol}$ , is expressed as  $\ln k = 15 - \frac{5000}{T}$ . Calculate activation energy for given reaction (in Kcal/mol.) **CK0056**
57. At 300 K, 50% of molecule collide with energy greater than or equal to  $E_a$ . At what temperature, 25% molecule will have energy greater than or equal to  $E_a$ . **CK0057**
58. For a zero order reaction at 200K reaction complete in 5 minutes while at 300K, same reaction completes in 2.5 minutes. What will be the activation energy in calorie. ( $R = 2 \text{ Cal/mol-k}$ ;  $\ln 2 = 0.7$ ) **CK0058**
59. For a first order reaction :  $A \rightarrow P$ , the temperature (T) dependent rate constant (k) was found to follow the equation  $\log_{10} k = -(2000) \frac{1}{T} + 6$ . Then activation energy equation of reaction will be ( $\ln x = 2.3 \times \log x$ ) **CK0059**
60. A reaction takes place in three steps. The rate constants are  $k_1, k_2, k_3$ . The overall rate constant  $k = \frac{k_1 \sqrt{k_3}}{k_2}$ . If energy of activation is 40, 30 and 20 kJ respectively, the overall energy of activation is : **CK0060**

### MECHANISM OF REACTION

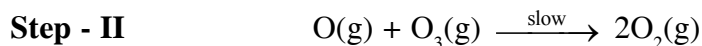
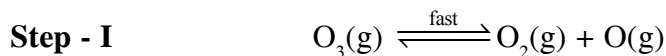
61. The reaction  $2\text{NO} + \text{Br}_2 \longrightarrow 2\text{NOBr}$ , is supposed to follow the following mechanism  
 (i)  $\text{NO} + \text{Br}_2 \xrightleftharpoons{\text{fast}} \text{NOBr}_2$   
 (ii)  $\text{NOBr}_2 + \text{NO} \xrightarrow{\text{slow}} 2\text{NOBr}$   
 Suggest the rate law expression. **CK0061**
62. For the reaction  $2\text{H}_2 + 2\text{NO} \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$ , the following mechanism has been suggested :  
 $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$  equilibrium constant =  $K_1$  (fast)  
 $\text{N}_2\text{O}_2 + \text{H}_2 \xrightarrow{k_2} \text{N}_2\text{O} + \text{H}_2\text{O}$  (slow)  
 $\text{N}_2\text{O} + \text{H}_2 \xrightarrow{k_3} \text{N}_2 + \text{H}_2\text{O}$  (fast)  
 Establish the rate law for given reaction. **CK0062**



63. For the reaction :



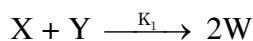
**Mechanism :**



Overall order of reaction based on mechanism is

**CK0063**

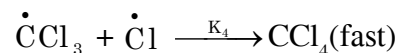
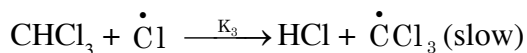
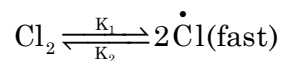
64. A complex reaction :  $2\text{X} + \text{Y} \rightarrow \text{Z}$ , takes place in two steps :



If  $\text{K}_1 \ll \text{K}_2$ , order of reaction will be -

**CK0064**

65. The suggested mechanism for the reaction :  $\text{CHCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{g}) + \text{HCl}(\text{g})$ , is -

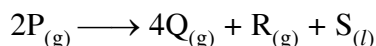


The experimental rate law consistent with the mechanism.

**CK0065**

## EXERCISE # S-2

1. The decomposition of a compound P, at temperature T according to the equation



is the first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 minutes, if volume of liquid S is supposed to be negligible. Also calculate the time fraction  $t_{7/8}$ .

**Given :** Vapour pressure of S (l) at temperature T = 32.5 mm Hg.

$$[\ln = 1.169] = 0.156, \ln 2 = 0.7, e^{0.39} = 1.5]$$

CK0066

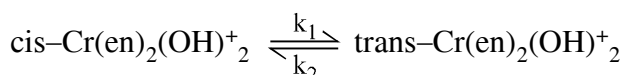
2. For the reaction :  $A + B \longrightarrow \text{Product}$ , rate law is :  $\text{rate} = k [A]^2 [B]$ , where  $k = 5 \times 10^{-5} (\text{mol/L})^{-2} \text{min}^{-1}$ . Determine the **time (in minutes)** in which concentration of 'A' becomes half of its initial concentration, if initial concentration of A and B are 0.2 M and  $2 \times 10^3$  M respectively.

CK0067

3. An optically active compound A upon acid catalysed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was  $5^\circ$  while after completion of the reaction it was  $-20^\circ$ . If optical rotation per mole of A, B & C are  $60^\circ$ ,  $40^\circ$  &  $-80^\circ$ . Calculate half life of the reaction.

CK0068

4. The reaction



is first order in both directions. At  $25^\circ\text{C}$ , the equilibrium constant is 0.1 and the rate constant  $k_1$  is  $2 \times 10^{-4} \text{s}^{-1}$ . In an experiment starting with the pure *cis* form, how long would it take for half the equilibrium amount of the *trans* isomer to be formed ?  $[\ln 2 = 0.693]$

CK0069

5. For the two parallel first order reactions  $A \xrightarrow{k_1} B$  and  $A \xrightarrow{k_2} C$ , show that the activation energy  $E'$  for the disappearance of A is given in terms of activation energies  $E_1$  and  $E_2$  for the two

$$\text{paths by } E' = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

CK0070

6. At room temperature ( $27^\circ\text{C}$ ), orange juice gets spoilt in about 64 hours. In a refrigerator at  $7^\circ\text{C}$ , juice can be stored three times as long before it gets spoilt. Estimate

(a) the activation energy of the reaction that causes the spoiling of juice.

(b) How long should it take for juice to get spoilt at  $47^\circ\text{C}$ ?

$$[e^{0.9625} = 2.5, \ln 3 = 1.1, R = 2 \text{ cal/mol-K}]$$

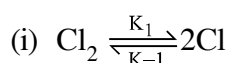
CK0071

7. Two reactions (i)  $A \rightarrow \text{products}$  (ii)  $B \rightarrow \text{products}$ , follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310K. The half life for this reaction at 310K is 30 minutes. At 310K temperature and same concentration of reactant in both reaction B, decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300K.

CK0072

8. The reaction of formation of phosgene from CO and  $\text{Cl}_2$  is  $\text{CO} + \text{Cl}_2 \longrightarrow \text{COCl}_2$

The proposed mechanism is



(fast equilibrium)

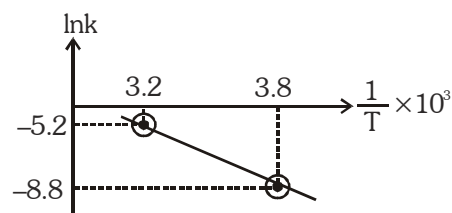


Show that the above mechanism leads to the following rate law  $\frac{d[\text{COCl}_2]}{dt} = K[\text{CO}][\text{Cl}_2]^{3/2}$ ,

where  $K = k_3 \cdot \frac{k_2}{k_{-2}} \left( \frac{k_1}{k_{-1}} \right)^{1/2}$ .

CK0073

9. For any elementary reaction, following observation is made :



If the above reaction is carried out in the presence of catalyst at 300K, the reaction proceeds with same rate as without catalyst at 400K. By what amount (in kcal) catalyst has decreased  $E_a$ .

CK0074

10. Milk is pasteurised if it is heated at 67°C for 4 hours. If  $\frac{E_a}{2.303}$  for the process is 23.8 kcal / mol then minimum how much seconds will be required for the the process at 77°C ? [R = 2cal /K-mol]

CK0075

11. When  $\text{CrI}_3$  reacts with  $\text{H}_2\text{O}_2$  in presence of  $\text{NaOH}$  forming  $\text{Na}_2\text{CrO}_4$ ,  $\text{NaIO}_4$  &  $\text{H}_2\text{O}$  then find how many times will be rate of disappearance of  $\text{NaOH}$  compared to  $\text{CrI}_3$ .

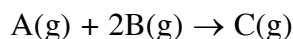
CK0076

12. Conversion of A into B and C follows first order kinetics. A, B and C all are optically active, initially A is present in 500 ml solution and 100 minutes after the start of reaction, the resulting solution becomes optically inactive. If angle of rotation of A is +50 degree per molar, B is -20 degree per molar and C is +10 degree per molar, then find the time for completion of  $\left(\frac{875}{9}\right)\%$  of the chemical reaction in minutes.



CK0077

13. A gas phase reaction is,



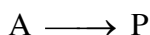
The reaction was carried out with stoichiometric proportions of A and B and the following data is obtained

Half life (min)	10	160
Initial pressure of A(atm)	40 atm	10 atm

What is overall order of reaction

CK0078

14. For the reaction ,



If ratio of  $t_{7/8} : t_{1/4}$  is 7 : 2 what is order of reaction.

$t_{7/8}$  = time in which 7/8 part of reactant is reacted

$t_{1/4}$  = time in which 1/4 part of reactant is reacted

CK0079

15. A certain reactant  $A^{n+}$  is getting converted to  $A^{(n+4)+}$  in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with  $A^{n+}$  and  $A^{(n+4)+}$ . In this process, it converts  $A^{n+}$  to  $A^{(n-2)+}$  and  $A^{(n+4)+}$  to  $A^{(n-1)+}$ .

**Time** 0 10 min

**Volume of reagent consumed** 30 ml 45 ml

Calculate the rate constant (in  $\text{min}^{-1}$ ) of the conversion of  $A^{n+}$  to  $A^{(n+4)+}$  assuming it to be first order reaction.

[n-factor of reagent remain same when it reacts with  $A^{n+}$  &  $A^{(n+4)+}$ ]

[Given:  $\ln 3/2 = 0.4$ ]

CK0080

16. Consider two 1<sup>st</sup> order reactions at 25°C with same initial concentrations of 1M

I.  $A \xrightarrow{t_{1/2} = 40 \text{ min}}$  product (temperature coefficient = 2)

II.  $B \xrightarrow{t_{1/2} = 30 \text{ min}}$  product (temperature coefficient = 3)

If both reactions are carried out at 35°C. Find ratio of concentrations of A & B after one hour.

CK0081

17. Consider two reactions at 27°C

(I).  $A \longrightarrow B$  ; ( First order kinetics)

(II).  $X \longrightarrow Y$  ; ( Zero order kinetics)

If both A & X each having initial concentration 0.1M & same half life period. Then find simplest ratio of rate constants for I & II reactions. [ $\ln 2 = 0.7$ ]

CK0082

18. The rate of first-order reaction is  $0.04 \text{ mol litre}^{-1}\text{s}^{-1}$  at 10 minutes and  $0.03 \text{ mol litre}^{-1}\text{s}^{-1}$  at 22 minutes after initiation. The half life of the reaction (in seconds) is ( $\ln 2 = 0.7$ ,  $\ln 3 = 1.1$ ).

CK0083

19. In order to determine the order of reaction :  $A(g) \rightarrow 2B(g)$ , vapour density of the system is determined at different stages of reaction, at constant temperature. The reaction is started with pure A(g). From the following data, the order of reaction is -

**Time (min)** 0 10 20

**Vapour density** 42 35 30

CK0084

20. In the reaction :  $A \rightarrow P$ , the rate is doubled when the concentration of 'A' is quadrupled. If 50% of the reaction occurs in  $8\sqrt{2}$  hr , how long (in hours) would it take for the completion of next 50% reaction.

CK0085

EXERCISE # 0-1

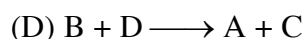
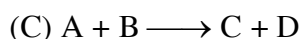
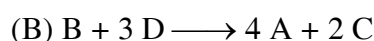
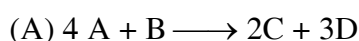
SINGLE CORRECT

RATE OF REACTION

1. The rate of a reaction is expressed in different ways as follows :

$$+\frac{1}{2} \frac{d[C]}{dt} = -\frac{1}{3} \frac{d[D]}{dt} = +\frac{1}{4} \frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is:



CK0086

2. For the reaction  $2A + 3B \rightarrow 4C$

the rate of reaction may be represented as :-

(A)  $r = -2 \frac{d(A)}{dt} = -3 \frac{d(B)}{dt} = 4 \frac{d(C)}{dt}$

(B)  $r = -2 \frac{d(A)}{dt} = -4 \frac{d(B)}{dt} = 3 \frac{d(C)}{dt}$

(C)  $r = -\frac{1}{2} \frac{d(A)}{dt} = \frac{1}{3} \frac{d(B)}{dt} = \frac{1}{4} \frac{d(C)}{dt}$

(D)  $r = -\frac{1}{2} \frac{d(A)}{dt} = -\frac{1}{3} \frac{d(B)}{dt} = \frac{1}{4} \frac{d(C)}{dt}$

CK0087

3. In a reaction  $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ , the rate of appearance of  $NH_3$  is  $2.5 \times 10^{-4} \text{ molL}^{-1} \text{ sec}^{-1}$ . The rate of reaction & rate of disappearance of  $H_2$  will be (In  $\text{molL}^{-1} \text{ sec}^{-1}$ )

(A)  $3.75 \times 10^{-4}, 1.25 \times 10^{-4}$

(B)  $1.25 \times 10^{-4}, 2.5 \times 10^{-4}$

(C)  $1.25 \times 10^{-4}, 3.75 \times 10^{-4}$

(D)  $5.0 \times 10^{-4}, 3.75 \times 10^{-4}$

CK0088

4. For the reaction  $4A + B \rightarrow 2C + 2D$ , the incorrect statement is :-

(A) The rate of disappearance of B is one fourth the rate of disappearance of A

(B) The rate of appearance of C is half the rate of disappearance of B

(C) The rate of formation of D is half the rate of consumption of A

(D) The rates of formation of C and D are equal

CK0089

5. Which of the following rate law has an overall order of 0.5 for reaction involving substances x, y and z ?

(A) Rate =  $k [C_x] [C_y] [C_z]$

(B) Rate =  $k [C_x]^{0.5} [C_y]^{0.5} [C_z]^{0.5}$

(C) Rate =  $k [C_x]^{1.5} [C_y]^{-1} [C_z]^0$

(D) Rate =  $k [C_x] [C_z]^0 / [C_y]^2$

CK0090

6. For a reaction  $A + B \rightarrow \text{products}$ , the rate of the reaction was doubled when the concentration of A was doubled, the rate was again doubled when the conc. of A & B were doubled. The order of the reaction with respect to A & B are:-

(A) 1, 1

(B) 2, 0

(C) 1, 0

(D) 0, 1

CK0091

7. If the rate of the reaction is equal to the rate constant, the order of the reaction is:-  
 (A) 0 (B) 1 (C) 2 (D) 3 **CK0092**
8. If the first order reaction involves gaseous reactants and gaseous products the units of its rate may be –  
 (A) atm. (B) atm - sec. (C) atm – sec<sup>-1</sup> (D) atm<sup>2</sup> sec<sup>2</sup>  
**CK0093**
9. If concentration of reactants is increased by 'x', then the rate constant (k) becomes –  
 (A)  $\ln \frac{k}{x}$  (B)  $\frac{k}{x}$  (C) k + x (D) k **CK0094**
10. The rate constant of n<sup>th</sup> order reaction has units  
 (A) litre<sup>1-n</sup> mol<sup>1-n</sup> sec<sup>-1</sup> (B) mol<sup>1-n</sup> litre<sup>1-n</sup> sec<sup>-1</sup>  
 (C) mol<sup>1-n</sup> litre<sup>n-1</sup> sec<sup>-1</sup> (D) None **CK0095**
11. A reaction is found to have the rate constant x sec<sup>-1</sup>. By what factor the rate is increased if initial conc. of A is tripled ?  
 (A) 3 (B) 9 (C) x (D) Remains same  
**CK0096**
12. Consider following two reactions  
 A  $\longrightarrow$  Product ;  $-\frac{d[A]}{dt} = k_1 [A]^0$   
 B  $\longrightarrow$  Product ;  $-\frac{d[B]}{dt} = k_2 [B]$   
 k<sub>1</sub> and k<sub>2</sub> are expressed in terms of molarity (mol L<sup>-1</sup>) and time (sec) as  
 (A) sec<sup>-1</sup>, M sec<sup>-1</sup> (B) M sec<sup>-1</sup>, M sec<sup>-1</sup>  
 (C) sec<sup>-1</sup>, M<sup>-1</sup> sec<sup>-1</sup> (D) M sec<sup>-1</sup>, sec<sup>-1</sup> **CK0097**
13. A(g)  $\longrightarrow$  B(g) + 3C(g)  
 In a closed container at a given temperature, pressure increases from 100 mm Hg to 160 mm Hg in 10 sec. for reaction.  
 Then the average rate of reaction in first 10 sec. will be -  
 (A) 2 mm/sec. (B) 4 mm/sec. (C) 6 mm/sec. (D) 3 mm/sec.  
**CK0098**

### ZERO ORDER REACTION

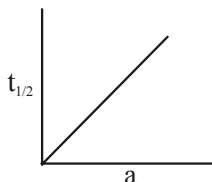
14. H<sub>2</sub> gas is adsorbed on the metal surface like tungsten. This follows ..... order reaction -  
 (A) Third (B) Second (C) Zero (D) First **CK0099**

15. The rate constant of a zero order reaction is  $0.2 \text{ mol dm}^{-3}\text{h}^{-1}$ . If the concentration of the reactant after 30 minutes is  $0.05 \text{ mol dm}^{-3}$ . Then its initial concentration would be :

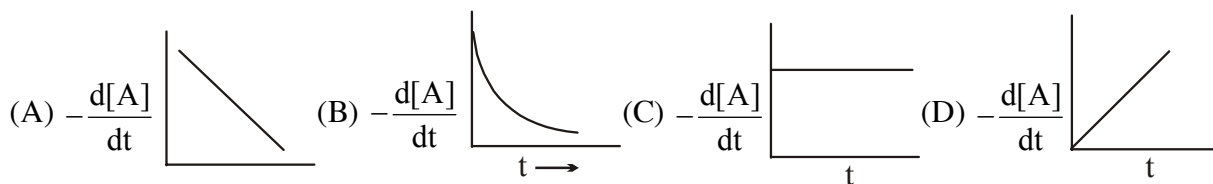
- (A)  $0.15 \text{ mol dm}^{-3}$  (B)  $1.05 \text{ mol dm}^{-3}$   
 (C)  $0.25 \text{ mol dm}^{-3}$  (D)  $4.00 \text{ mol dm}^{-3}$

CK0100

16. Consider the reaction  $A \longrightarrow B$ , graph between half life ( $t_{1/2}$ ) and initial concentration (a) of the reactant is

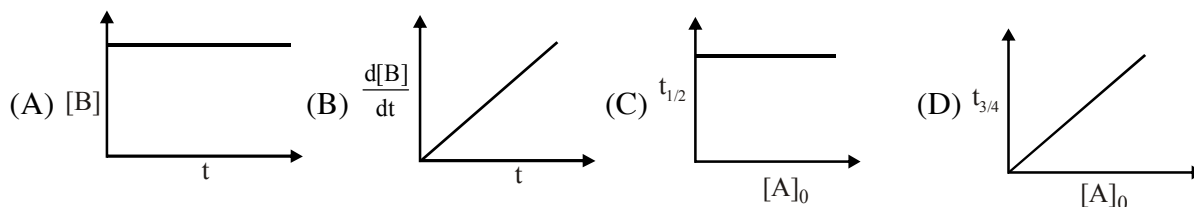


Hence graph between  $-\frac{d[A]}{dt}$  and time will be



CK0101

17. Which graph represents zero order reaction  $[A(g) \rightarrow B(g)]$  :



CK0102

18. K for a zero order reaction is  $2 \times 10^{-2} \text{ molL}^{-1} \text{ sec}^{-1}$ . If the concentration of the reactant after 25 sec is 0.5 M, then concentration after 50 sec. must have been.

- (A) 0.5 M (B) 0.25 M (C) 0.125 M (D) 0.0 M

CK0103

**FIRST ORDER REACTION**

19. The rate constant of a first order reaction is  $4 \times 10^{-3} \text{ sec}^{-1}$ . At a reactant concentration of 0.02 M, the rate of reaction would be –

- (A)  $8 \times 10^{-5} \text{ M sec}^{-1}$  (B)  $4 \times 10^{-3} \text{ M sec}^{-1}$   
 (C)  $2 \times 10^{-1} \text{ M sec}^{-1}$  (D)  $4 \times 10^{-1} \text{ M sec}^{-1}$

CK0104

20. In a first order reaction the concentration of the reactant is decreased from 1.0 M to 0.25 M in 20 min. The rate constant of the reaction would be –

- (A)  $10 \text{ min}^{-1}$  (B)  $6.931 \text{ min}^{-1}$  (C)  $0.6931 \text{ min}^{-1}$  (D)  $0.06931 \text{ min}^{-1}$

CK0105

21. A first order reaction has a half life period of 69.3 sec. At 0.10 mol lit<sup>-1</sup> reactant concentration rate will be –

(A) 10<sup>-4</sup> M sec<sup>-1</sup>      (B) 10<sup>-3</sup> M sec<sup>-1</sup>      (C) 10<sup>-1</sup> M sec<sup>-1</sup>      (D) 6.93 × 10<sup>-1</sup> Msec<sup>-1</sup>

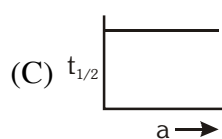
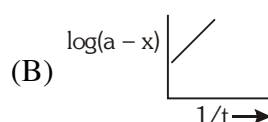
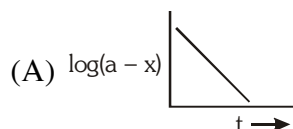
CK0106

22. What fraction of a reactant (in first order reaction) is left after 40 minute if t<sub>1/2</sub> is 20 minute

(A) 1/4      (B) 1/2      (C) 1/8      (D) 1/6

CK0107

23. Which of the following curve represents a 1<sup>st</sup> order reaction :-



(D) 1 & 3 both

CK0108

24. After how many seconds will the conc. of the reactant in a first order reaction be halved, if the rate constant is 1.155 × 10<sup>-3</sup> sec<sup>-1</sup> :-

(A) 600      (B) 100      (C) 60      (D) 10

CK0109

25. Correct statement about first order reaction is:-

(A) t<sub>completion</sub> = finite      (B) t<sub>1/2</sub> ∝ 1/a

(C) Unit of k is mole lit<sup>-1</sup> sec<sup>-1</sup>      (D) t<sub>1/2</sub> × k = const.

CK0110

26. For a given reaction of first order, it takes 20 minute for the concentration to drop from 1 M to 0.6 M. The time required for the concentration to drop from 0.6 M to 0.36 M will be :

(A) More than 20 min      (B) Less than 20 min

(C) Equal to 20 min      (D) Infinity

CK0111

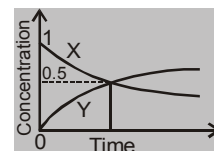
27. The accompanying figure depicts the change in concentration of species X and Y for the reaction X → Y as a function of time. The point of intersection of the two curves represents.

(A) t<sub>1/2</sub>

(B) t<sub>3/4</sub>

(C) t<sub>2/3</sub>

(D) Data insufficient to predict



CK0112

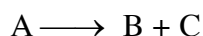
28. A reaction is of first order. After 100 minutes, 75 g of the reactant A are decomposed when 100g are taken initially. Calculate the time required when 150g of the reactant A are decomposed, the initial weight taken is 200g.

(A) 100 minutes      (B) 200 minutes      (C) 150 minutes      (D) 175 minutes

CK0113



29. Consider the reaction :



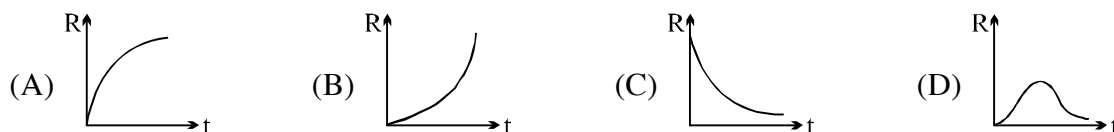
Initial concentration of A is 1 M. 20 minutes time is required for completion of 80 % reaction.

If  $\frac{d[B]}{dt} = k[A]$ , then half life ( $t_{1/2}$ ) is (Use :  $\ln 5 = 1.6$ ,  $\ln 2 = 0.7$ )

- (A) 55.44 min.      (B) 50 min      (C) 8.75 min      (D) 12.5 min

CK0114

30. If decomposition reaction  $A(g) \longrightarrow B(g)$  follows first order kinetics, then the graph of rate of formation (R) of B against time t will be

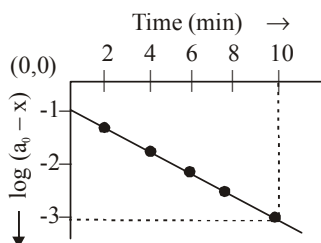


CK0115

31. For the first order decomposition of  $SO_2Cl_2(g)$ ,



a graph of  $\log(a_0 - x)$  vs t is shown in figure. What is the rate constant ( $sec^{-1}$ )?



- (A) 0.2      (B)  $4.6 \times 10^{-1}$       (C)  $7.7 \times 10^{-3}$       (D)  $1.15 \times 10^{-2}$

CK0116

32. The rate constant for a second order reaction is  $8 \times 10^{-5} M^{-1} min^{-1}$ . How long will it take a 1M solution to be reduced to 0.5 M ?

- (A)  $8.665 \times 10^3 min$       (B)  $8 \times 10^{-3} min$       (C)  $1.25 \times 10^4 min$       (D)  $4 \times 10^{-5} min$

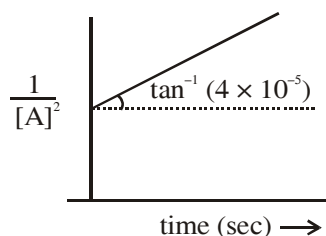
CK0117

33. The rate law of the reaction :  $A + 2B \rightarrow \text{product}(P)$  is given by  $\frac{d[P]}{dt} = K[A]^2 [B]$ . If A is taken in large excess, the order of the reaction will be –

- (A) Zero      (B) 1      (C) 2      (D) 3      CK0118

## CALCULATION OF ORDER OF REACTION

34. Time required to complete a half fraction of a reaction varies inversely to the concentration of reactant then the order of reaction is –  
 (A) Zero (B) 1 (C) 2 (D) 3 **CK0119**
35. The reaction  $L \rightarrow M$  is started with 10 g of L. After 30 and 90 minute, 5 g and 1.25 g of L are left respectively. The order of reaction is –  
 (A) 0 (B) 2 (C) 1 (D) 3 **CK0120**
36. From different sets of data of  $t_{1/2}$  at different initial concentrations say 'a' for a given reaction,  $[t_{1/2} \propto a]$  is found. The order of reaction is :-  
 (A) 0 (B) 1 (C) 2 (D) 3 **CK0121**
37. At certain temperature, the half life period for the thermal decomposition of a gaseous substance depends on the initial partial pressure of the substance as follows
- |                     |     |     |
|---------------------|-----|-----|
| P(mmHg)             | 500 | 250 |
| $t_{1/2}$ (in min.) | 235 | 950 |
- Find the order of reaction [Given  $\log(23.5) = 1.37$ ;  $\log(95) = 1.97$ ;  $\log 2 = 0.30$ ]  
 (A) 1 (B) 2 (C) 2.5 (D) 3 **CK0122**
38. For a reaction  $A \longrightarrow \text{Product}$

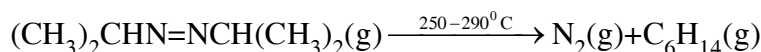


What is the value of k for the given reaction-

- (A)  $4 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$  (B)  $\frac{4}{3} \times 10^{-5} \text{ M}^{-2}\text{s}^{-1}$  (C)  $2 \times 10^{-5} \text{ M}^{-2}\text{s}^{-1}$  (D)  $\frac{2}{3} \times 10^{-5} \text{ M}^{-2}\text{s}^{-1}$

**CK0123**

39. Azo isopropane decomposes according to the equation :-



It is found to be a first order reaction. If initial pressure is  $P_o$  and pressure of the mixture at time  $t$  is ( $P_t$ ) then rate constant  $K$  would be :-

- (A)  $k = \frac{2.303}{t} \log \frac{P_o}{2P_o - P_t}$  (B)  $k = \frac{2.303}{t} \log \frac{P_o - P_t}{P_o}$   
 (C)  $k = \frac{2.303}{t} \log \frac{P_o}{P_o - P_t}$  (D)  $k = \frac{2.303}{t} \log \frac{2P_o}{2P_o - P_t}$

**CK0124**

40. For a 1<sup>st</sup> order homogeneous gaseous reaction



if the pressure after time  $t$  was  $P_t$  and after long time was  $P_\infty$ , then rate constant ( $k$ ) in terms of  $P_t$  &  $P_\infty$  and  $t$  is -

$$(A) k = \frac{2.303}{t} \log \left( \frac{P_\infty}{P_\infty - P_t} \right)$$

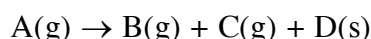
$$(B) k = \frac{2.303}{t} \log \left( \frac{2P_\infty}{P_\infty - P_t} \right)$$

$$(C) k = \frac{2.303}{t} \log \left( \frac{2P_\infty}{3(P_\infty - P_t)} \right)$$

(D) None of these

CK0125

41. The first order reaction



taking place at constant pressure and temperature condition. Initially volume of the container containing only A was found to be  $V_0$  and after time ' $t$ ' it was  $V_t$ . Rate constant for the reaction is.

$$(A) \frac{1}{t} \ln \frac{V_0}{2V_0 - V_t}$$

$$(B) \frac{1}{t} \ln \frac{V_0}{V_0 - V_t}$$

$$(C) \frac{1}{t} \ln \frac{2V_0}{2V_0 - V_t}$$

$$(D) \frac{1}{t} \ln \frac{2V_0}{V_0 + V_t}$$

CK0126

42. For the inversion of cane sugar ( $C_{12}H_{22}O_{11}$ ) obeying I order following data were obtained

Time (min.)	0	10	$\infty$
Angle of rotation of solution (degree)	+20	-2.5	-10

What will be rate constant in  $\text{min}^{-1}$  ( $\ln 2 = 0.7$ )

(A) 0.7

(B) 0.14

(C) 0.21

(D) 0.07

CK0127

### COLLISION THEORY AND ARRHENIUS EQUATION

43. The rate constant for the forward reaction  $A(g) \rightleftharpoons 2B(g)$  is  $1.5 \times 10^{-3} \text{ s}^{-1}$  at 100 K. If  $10^{-5}$  moles of A and 100 moles of B are present in a 10 litre vessel at equilibrium then rate constant for the backward reaction at this temperature is

$$(A) 1.50 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$(B) 1.5 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$$

$$(C) 1.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$$

$$(D) 1.5 \times 10^{-11} \text{ L mol}^{-1} \text{ s}^{-1}$$

CK0128

44. According to collision theory of reaction -

(A) Every collision between reactant leads to chemical reaction

(B) Rate of reaction is proportional to velocity of molecules

(C) All reactions which occur in gaseous phase are zero order reaction

(D) Rate of reaction is directly proportional to collision frequency.

CK0129

45. Activation energy of a reaction is –  
 (A) The energy released during the reaction  
 (B) The energy evolved when activated complex is formed  
 (C) Minimum amount of energy needed to overcome the potential barrier of reaction  
 (D) The energy needed to form one mole of the product **CK0130**
46. The minimum energy for molecules to enter into chemical reaction is called  
 (A) Kinetic energy (B) Potential energy  
 (C) Threshold energy (D) Activation energy **CK0131**
47. For producing the effective collisions, the colliding molecules must possess:-  
 (A) A certain minimum amount of energy  
 (B) Energy equal to or greater than threshold energy  
 (C) Proper orientation  
 (D) Threshold energy as well as proper orientation of collision **CK0132**
48. A large increase in the rate of a reaction for a rise in temperature is due to –  
 (A) Increase in the number of collisions (B) Increase in the number of activated molecules  
 (C) Lowering of activation energy (D) Shortening of the mean free path  
**CK0133**
49. Slope of which plot can give the value of activation energy  
 (A)  $k$  versus  $T$  (B)  $\frac{1}{k}$  versus  $T$  (C)  $\log k$  versus  $1/T$  (D)  $C$  versus  $T$   
**CK0134**
50. Given that  $K$  is the rate constant for any order reaction at temperature  $T$ , then the value of  $\lim_{T \rightarrow \infty} \log k$  \_\_\_\_\_.  
 (A)  $\frac{A}{2.303}$  (B)  $A$  (C)  $2.303 A$  (D)  $\log A$  **CK0135**
51. For a certain gaseous reaction a  $10^\circ \text{C}$  rise of temperature from  $25^\circ \text{C}$  to  $35^\circ \text{C}$  doubles the rate of reaction. What is the value of activation energy :-  
 (A)  $\frac{10}{2.303R \times 298 \times 308}$  (B)  $\frac{2.303 \times 10}{298 \times 308R}$   
 (C)  $\frac{0.693R \times 10}{290 \times 308}$  (D)  $\frac{0.693R \times 298 \times 308}{10}$  **CK0136**
52. From the following data, the activation energy (cal/mol) for the reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ , is about
- | $T$ (in $\text{k}$ ) | $1/T$ , (in, $\text{k}^{-1}$ ) | $\log_{10} k$ |
|----------------------|--------------------------------|---------------|
| 769                  | $1.3 \times 10^{-3}$           | 2.9           |
| 667                  | $1.5 \times 10^{-3}$           | 1.1           |
- (A)  $4 \times 10^4$  (B)  $2 \times 10^4$  (C)  $8 \times 10^4$  (D)  $3 \times 10^4$  **CK0137**

53. The rate constant, the activation energy and the Arrhenius parameter (A) of a chemical reaction at 25°C are  $3.0 \times 10^{-4} \text{ s}^{-1}$ ,  $104.4 \text{ kJ mol}^{-1}$  and  $6.0 \times 10^{14} \text{ s}^{-1}$  respectively. The value of the rate constant at  $T \rightarrow \infty$  is

- (A)  $2.0 \times 10^{18} \text{ s}^{-1}$       (B)  $6.0 \times 10^{14} \text{ s}^{-1}$       (C) infinity      (D)  $3.6 \times 10^{30} \text{ s}^{-1}$

CK0138

54. A first order reaction is 50% completed in 20 minutes at 27°C and in 5 min at 47°C. The energy of activation of the reaction is

- (A) 100 kJ/mol      (B) 55.14 kJ/mol      (C) 11.97 kJ/mol      (D) 6.65 kJ/mol

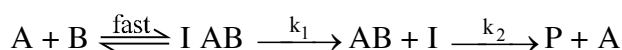
CK0139

55. For the first order reaction  $A \longrightarrow B + C$ , carried out at 27 °C if  $3.8 \times 10^{-16} \%$  of the reactant molecules can overcome energy barrier, the  $E_a$  (activation energy) of the reaction is [log 3.8 = 0.58,  $2.303 \times 8.314 \times 17.42 = 333.33$ ]

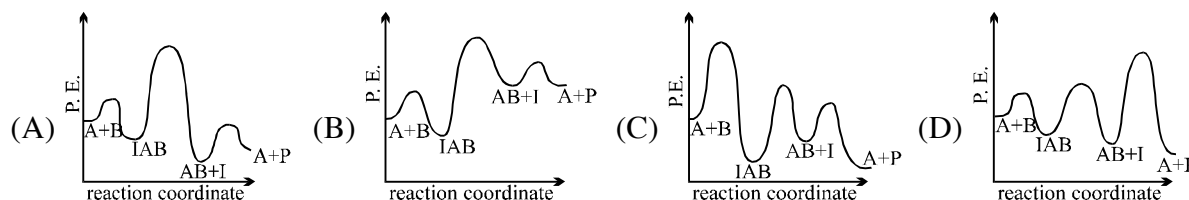
- (A) 12 kJ/mole      (B) 831.4 kJ/mole      (C) 100 kJ/mole      (D) 111.11 J/mole

CK0140

56. The following mechanism has been proposed for the exothermic catalyzed complex reaction.

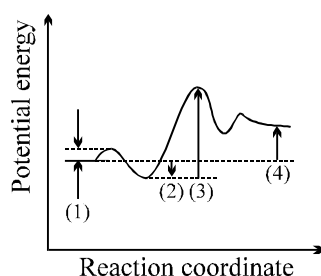
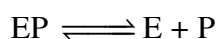
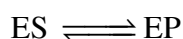
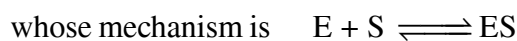
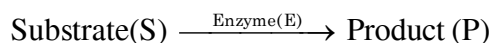


If  $k_1$  is much smaller than  $k_2$ . The most suitable qualitative plot of potential energy (P.E.) versus reaction coordinate for the above reaction.



CK0141

57. Choose the correct set of identifications for the reaction .



(1)	(2)	(3)	(4)
(A) $\Delta E$ for $E + S \rightarrow ES$	$E_a$ for $ES \rightarrow EP$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$	$E_a$ for $EP \rightarrow E + P$
(B) $E_a$ for $E + S \rightarrow ES$	$\Delta E$ for $E + S \rightarrow ES$	$E_a$ for $ES \rightarrow EP$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$
(C) $E_a$ for $ES \rightarrow EP$	$E_a$ for $EP \rightarrow E + P$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$	$\Delta E$ for $EP \rightarrow E + P$
(D) $E_a$ for $E + S \rightarrow ES$	$E_a$ for $ES \rightarrow EP$	$E_a$ for $EP \rightarrow E + P$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$
(E) $\Delta E$ for $E + S \rightarrow ES$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$	$\Delta E$ for $EP \rightarrow E + P$	$E_a$ for $EP \rightarrow E + P$

CK0142

### RATE LAW OF MECHANISM OF REACTION

58. Following mechanism has been proposed for a reaction :  $2A + B \rightarrow D + E$

**Step - I :**  $A + B \rightarrow C + D$  (slow)

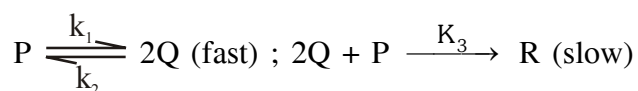
**Step - II :**  $A + C \rightarrow E$  (fast)

The rate law expression for the reaction is –

- (A)  $r = k[A]^2 [B]$       (B)  $r = k[A] [B]$       (C)  $r = k[A]^2$       (D)  $r = k[A][C]$

CK0143

59. The reaction mechanism for the reaction  $P \rightarrow R$  is as follows :



the rate law for the main reaction ( $P \rightarrow R$ ) is :

- (A)  $k_1[P] [Q]$       (B)  $k_1 k_2 [P]$       (C)  $\frac{k_1 k_3 [P]^2}{k_2}$       (D)  $k_1 k_2 [a]$

CK0144

60. The energies of activation for forward and reverse reactions for  $A_2 + B_2 \rightleftharpoons 2AB$  are  $180 \text{ kJ mol}^{-1}$  and  $200 \text{ kJ mol}^{-1}$  respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by  $100 \text{ kJ mol}^{-1}$ . The enthalpy change of the reaction ( $A_2 + B_2 \rightarrow 2AB$ ) in the presence of catalyst will be (in  $\text{kJ mol}^{-1}$ ) -

- (A) 300      (B) 120      (C) 280      (D) -20

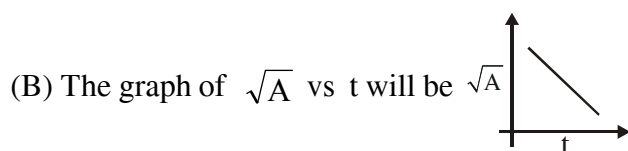
CK0145

## EXERCISE (O-2)

## MORE THAN ONE MAY BE CORRECT

1. For the reaction  $A \rightarrow B$ , the rate law expression is  $-\frac{d[A]}{dt} = k[A]^{1/2}$ . If initial concentration of  $[A]$  is  $[A]_0$ , then

(A) The integrated rate expression is  $k = \frac{2}{t}(A_0^{1/2} - A^{1/2})$

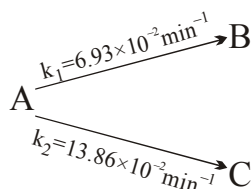


(C) The half life period,  $t_{1/2} = \frac{K}{2[A]_0^{1/2}}$

(D) The time taken for 75% completion of reaction  $t_{3/4} = \frac{\sqrt{[A]_0}}{k}$

CK0146

2. Consider the reaction,



A, B and C all are optically active compound. If optical rotation per unit concentration of A, B and C are  $60^\circ$ ,  $-72^\circ$ ,  $42^\circ$  and initial concentration of A is 2 M then select correct statement(s).

- (A) Solution will be optically active and dextrorotatory after very long time  
 (B) Solution will be optically active and levorotatory after very long time  
 (C) Half life of reaction is 15 min  
 (D) After 75% conversion of A into B and C angle of rotation of solution will be  $36^\circ$ .

CK0147

3. Select **incorrect** statement(s):

- (A) Unit of pre-exponential factor (A) for second order reaction is  $\text{mol L}^{-1} \text{ s}^{-1}$ .  
 (B) A zero order reaction must be a complex reaction.  
 (C) Molecularity is defined only for RDS in a complex reaction.  
 (D) Rate constant (k) remain unaffected on changing temperature.

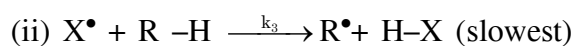
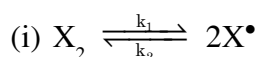
CK0148

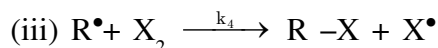
4. Which of the following is/are **correct** statement?

- (A) Stoichiometry of a reaction tells about the order of the elementary reactions.  
 (B) For a zero order reaction, rate and the rate constant are identical.  
 (C) A zero order reaction is controlled by factors other than concentration of reactants.  
 (D) A zero order reaction is always elementary reaction.

CK0149

5. For the gas phase reaction :  $R-H + X_2 \rightarrow R-X + HX$ , following mechanism has been proposed





Based on this, select the correct option (s)

(A) Effective rate constant for the formation of RX is  $k_3 k_4 \sqrt{\frac{k_1}{k_2}}$

(B)  $\frac{d[RX]}{dt} \propto [X_2]$

(C) Overall order of the reaction is 3/2

(D)  $\frac{d[RX]}{dt} \propto [RH]^1$

CK0150

6. For a first order reaction :  $A(g) \rightarrow 2B(g)$

Time(in second)	0	20	40	$\infty$
Total pressure of system (in mm.of Hg)	64	112	124	128

(A) Half life of reaction is 10 sec

(B) Value of rate constant for reaction is  $6.93 \times 10^{-3} \text{sec}^{-1}$

(C) Total pressure at  $t = 50$  sec will be 126 mm of Hg

(D) Reaction must be a complex reaction

CK0151

7. Which of the following is **INCORRECT** for first order reaction ?

(A) On introducing catalyst, both rate constant and rate of reaction increases.

(B) On increasing temperature both rate constant & rate of reaction increases.

(C) On decreasing volume both rate constant & rate of gaseous reaction increases.

(D) On increasing concentration of gaseous reactant at constant volume & constant temperature both total pressure and rate of the reaction increases.

CK0152

8.  $2X(g) + Y(g) + 3Z(g) \rightarrow \text{Products}$ . The rate equation of above reaction is given by :

$$\text{Rate} = K [X]^1 [Y]^0 [Z]^2$$

Choose the correct statements

(A) If  $[z] \gg [x]$  and 75% of X undergoes reaction in 20 sec, then 50% of X will react in 10 sec.

(B) Rate of reaction decreases by reducing the concentration of Y to half of the original value

(C) The half life of Z increases by increasing its concentration if  $[x] \gg [z]$

(D) On increasing the concentration of X, Y & Z double, rate of reaction becomes 8 times

CK0153

9. Select the correct statement -

(A) In a mixture of  $KMnO_4$  &  $H_2C_2O_4$ ,  $KMnO_4$  decolorises faster at higher temperature than lower temperature

(B) A catalyst participate in a chemical reaction by forming temporary bonds with the reactant resulting in an intermediate complex

(C) In collision theory only activation energy determine the criteria for effective collision

(D) Collision theory assumes molecules to be soft spheres & consider their structural aspects.

CK0154



10. For the reaction  $A + 3B \rightarrow C$ , select the correct statement (s)-

(A)  $\frac{d[C]}{dt} = -\frac{d[A]}{dt}$

(B)  $\frac{3d[C]}{dt} = -\frac{d[B]}{dt}$

(C) Rate law must be  $r = k [A][B]^3$

(D) Units for rate of reaction are independent of order of reaction

CK0155

11. Choose the incorrect statement(s) -

(A) Activation energy of reaction always decreases on decreasing temperature

(B) Order of reaction may change with change in temperature

(C) When slowest step is the first step in a mechanism, then the rate law of overall reaction is the same as the rate law for this step

(D) Rate of photochemical reaction is directly proportional to intensity of absorbed photons.

CK0156

12. The forward rate constant of a reaction increases by 7% when its temperature is raised from 300K to 301K while its equilibrium constant increases by 3%. Which of the following is/are correct -

(A) Activation energy of forward reaction  $(E_a)_F$  is  $= 300 \times 301 \times R \times \ln(1.03)$

(B) Standard heat of reaction  $(\Delta H^\circ)$  is  $= 300 \times 301 \times R \times \ln(1.07)$

(C) Activation energy of backward reaction  $(E_a)_B$  is  $= 300 \times 301 \times R \times \ln\left(\frac{1.07}{1.03}\right)$

(D) Activation energy of backward reaction  $(E_a)_B$  is  $= 300 \times 301 \times R \times \ln\left(\frac{1.03}{1.07}\right)$

CK0157

13. Which statement(s) is/are false ?

(A) Every reaction has defined overall order

(B) All rate constant have same dimension.

(C) Every chemical species that appears in the rate law of reaction must be reactant or product in that reaction.

(D) Rate constant is never negative.

CK0158

**ASSERTION & REASONING TYPE QUESTIONS**

14. **Statement-1** : A fractional order reaction must be a complex reaction.

**Statement-2** : Fractional order of RDS equals to overall order of a complex reaction.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

CK0159

15. **Statement-1** : The time of completion of reactions of type  $A \rightarrow \text{product}$  (order  $< 1$ ) may be determined.  
**Statement-2** : Reactions with order  $\geq 1$  are either too slow or too fast and hence the time of completion can not be determined.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true. **CK0160**
16. **Statement-1** : In a reversible endothermic reaction, ( $E_{\text{act}}$ ) of forward reaction is higher than that of backward reaction  
**Statement-2** : The threshold energy of forward reaction is more than that of backward reaction  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true. **CK0161**
17. **Statement-1** : A catalyst provides an alternative path to the reaction in which conversion of reactants into products takes place quickly  
**Statement-2** : The catalyst forms an activated complex of lower potential energy, with the reactants by which more number of molecules are able to cross the barrier per unit of time.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true. **CK0162**

### COMPREHENSION

#### Paragraph for Question Nos. 18 & 19

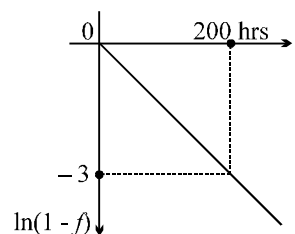
When metal surface is exposed to air it gets oxidised by first order kinetics if  $(1-f)$  is fraction of unoxidised. metal surface thickness and  $T$  is total thickness after very long time then it's rate can be represented as.

$$\text{Rate law : } \frac{df}{dt} = k(1-f), \text{ where } f = x/T,$$

$x$  = thickness of oxide film at time 't'

&  $T$  = thickness of oxide film at  $t = \infty$

A graph of  $\ln(1-f)$  vs  $t$  is shown in the adjacent figure.



18. The time taken for thickness to grow 50% of 'T' is  
 (A) 23.1 hrs (B) 46.2 hrs (C) 100 hrs (D) 92.4 hrs **CK0163**
19. The exponential variation of 'f' with t(hrs) is given by  
 (A)  $1 - e^{-3t/200}$  (B)  $e^{-3t/200} - 1$  (C)  $e^{-3t/200}$  (D)  $e^{3t/200}$  **CK0163**

Paragraph for Question Nos. 20 & 21

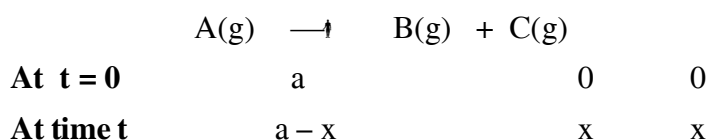
For a hypothetical elementary reaction :  $A \begin{matrix} \xrightarrow{k_1} 2B \\ \xrightarrow{k_2} 2C \end{matrix}$  where  $\frac{k_1}{k_2} = \frac{1}{2}$

Initially only 2 moles of A are present.

20. The total number of moles of A, B & C at the end of 50% reaction is -  
 (A) 2 (B) 3 (C) 4 (D) 5 **CK0164**
21. Number of moles of B at the end of 50% reaction, is -  
 (A) 2 (B) 1.333 (C) 0.667 (D) 0.333 **CK0164**

Paragraph for Question Nos. 22 & 23

A reaction is said to be first order if its rate is proportional to the concentration of reactant. Let us consider a reaction



The rate of reaction is given by the expression  $\frac{dx}{dt} = k(a - x)$  and integrated rate equation for a given reaction is represented as  $k = \frac{1}{t} \ln \left( \frac{a}{a - x} \right)$  where a = initial concentration and (a - x) = concentration of A after time t.

22. Thermal decomposition of compound X is a first order reaction. If 75% of X is decomposed in 100 min. How long will it take for 90% of the compound to decompose?  
**Given : log 2 = 0.30**  
 (A) 190 min (B) 176.66 min (C) 166.66 min (D) 156.66 min **CK0165**
23. Consider a reaction  $A(g) \longrightarrow 3B(g) + 2C(g)$  with rate constant  $1.386 \times 10^{-2} \text{ min}^{-1}$ . Starting with 2 moles of A in 12.5 litre a closed vessel initially, if reaction is allowed to take place at constant pressure & at 298K then find the concentration of B after 100 min.  
 (A) 0.04 M (B) 0.36 M (C) 0.09 M (D) None of these **CK0166**

Paragraph for Question Nos. 24 & 25

For the given sequential reaction



the concentration of A, B & C at any time 't' is given by

$$[A]_t = [A]_0 e^{-k_1 t} ;$$

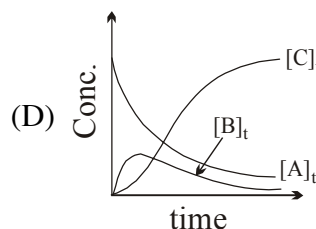
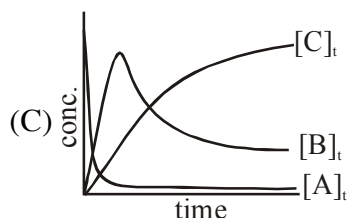
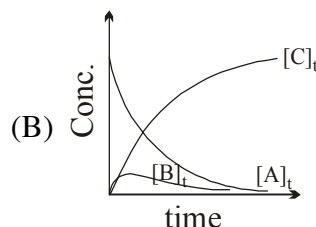
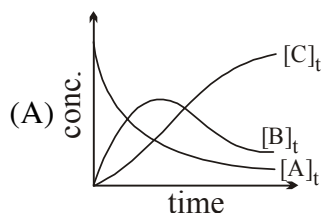
$$[B]_t = \frac{k_1 [A]_0}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}]$$

$$[C]_t = [A]_0 - ([A]_t + [B]_t)$$

24. The time at which concentration of B is maximum is

- (A)  $\frac{k_1}{k_2 - k_1}$       (B)  $\frac{1}{k_2 - k_1} \ln \frac{k_1}{k_2}$       (C)  $\frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$       (D)  $\frac{k_2}{k_2 - k_1}$       **CK0167**

25. Select the correct graph if  $k_1 = 1000 \text{ s}^{-1}$  and  $k_2 = 20 \text{ s}^{-1}$ .



**CK0168**

### MATCH THE COLUMN

26. For the reaction of type  $A(g) \longrightarrow 2B(g)$

**Column-I** contains four entries and **column-II** contains four entries. Entry of column-I are to be matched with **ONLY ONE ENTRY** of column-II

#### Column I

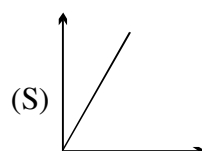
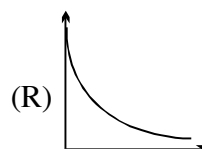
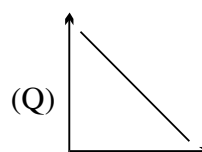
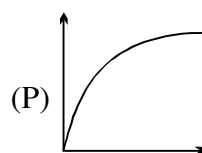
(A)  $\frac{d[B]}{dt}$  vs  $-\frac{d[A]}{dt}$  for first order

(B)  $[A]$  vs  $t$  for first order

(C)  $[B]$  vs  $t$  for first order

(D)  $[A]$  vs  $t$  for zero order

#### Column II



**CK0169**

27. Match the column :

Column-I

- (A) Inversion of cane sugar in excess water.
- (B) saponification reaction with 1M NaOH
- (C) decomposition of HI on gold
- (D) radioactive decay

Column-II

- (P) not 100% complete
- (Q) pseudo-first order
- (R) zero order
- (S) second order

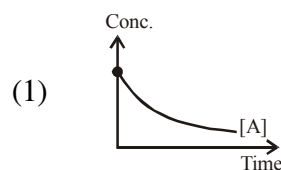
CK0170

28. For the reaction  $A + B \rightarrow \text{product}$ , Given :  $[A]_0 = [B]_0$

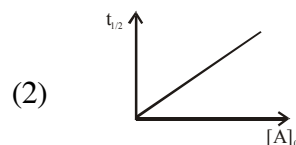
List-I (Observed Rate Law) is -

List-II (Graph)

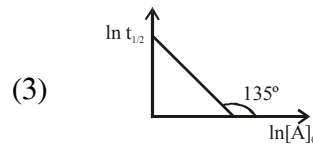
(P)  $r = k[A]$



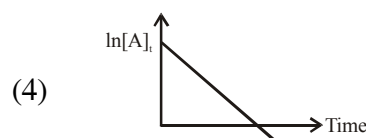
(Q)  $r = k[A]^{1/2}[B]^{1/2}$



(R)  $r = k[A][B]$



(S)  $r = k[A]^0[B]^0$



Code:

	P	Q	R	S
(A)	4	1	3	2
(B)	2	3	1	4
(C)	1	2	3	4
(D)	4	3	2	1

CK0170

Match the Columns for Reaction  $A \rightarrow P$

Column - I	Column - II	Column - III
(I) First Order	(i) Reaction complete in finite time	(P) Rate depends on concentration
(II) Second Order	(ii) Reaction complete in infinite time	(Q) After equal interval of time concentration of reactant left are in G.P.
(III) Third Order	(iii) Half life is independent of concentration of reactant	(R) After equal interval of time concentration of reactant left are in A.P.
(IV) Zero Order	(iv) Half life decreases when concentration of reactant increases	(S) Half life depends on temperature

29. Select only incorrect option

(A) (II), (ii), (P)

(B) (IV), (iii), (R)

(C) (III), (ii), (P)

(D) (I), (ii), (Q)

**CK0171**

30. Select only incorrect option

(A) (IV), (i), (S)

(B) (III), (iv), (P)

(C) (I), (iv), (Q)

(D) (II), (iv), (S)

**CK0171**

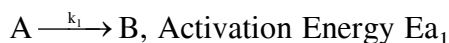
EXERCISE # J-MAIN

1. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about :- [AIEEE-2011]

(1) 32 times                      (2) 64 times                      (3) 10 times                      (4) 24 times

CK0172

2. A reactant (1) forms two products : [AIEEE-2011]



If  $E_{a2} = 2 E_{a1}$ , then  $k_1$  and  $k_2$  are related as :-

(1)  $k_1 = 2k_2 e^{E_{a2}/RT}$                       (2)  $k_1 = k_2 e^{E_{a1}/RT}$                       (3)  $k_2 = k_1 e^{E_{a2}/RT}$                       (4)  $k_1 = [A] k_2 e^{E_{a1}/RT}$

CK0173

3. For the non-stoichiometric reaction  $2A + B \rightarrow C + D$ , the following kinetic data were obtained in three separate experiments, all at 298 K. [J-MAIN 2014]

Initial Concentration (A)	Initial Concentration (B)	Initial rate of formation of C (mol L <sup>-1</sup> S <sup>-1</sup> )
0.1M	0.1M	$1.2 \times 10^{-3}$
0.1M	0.2M	$1.2 \times 10^{-3}$
0.2M	0.1M	$2.4 \times 10^{-3}$

(1)  $\frac{dc}{dt} = k[A][B]^2$                       (2)  $\frac{dc}{dt} = k[A]$                       (3)  $\frac{dc}{dt} = k[A][B]$                       (4)  $\frac{dc}{dt} = k[A]^2 [B]$

CK0174

4. Higher order (>3) reactions are rare due to :- [JEE-MAIN-(Offline)2015]

(1) shifting of equilibrium towards reactants due to elastic collision  
 (2) loss of active species on collision  
 (3) low probability of simultaneous collision of all the reacting species  
 (4) increase in entropy and activation energy as more molecules are involved.

CK0175

5. The reaction :  $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ , follows first order kinetics. The pressure of a vessel containing only  $N_2O_5$  was found to increase from 50 mm Hg to 87.5 mm Hg in 30 min. The pressure exerted by the gases after 60 min. will be (Assume temperature remains constant)

(A) 106.25 mm Hg                      (B) 116.25 mm Hg [JEE-MAIN-(Online)2015]  
 (3) 125 mm Hg                      (4) 150 mm Hg

CK0176

6. For the equilibrium,  $A(g) \rightleftharpoons B(g)$ ,  $\Delta H$  is  $-40$  kJ/mol. If the ratio of the activation energies of the forward ( $E_f$ ) and reverse ( $E_b$ ) reactions is  $\frac{2}{3}$  then :- [JEE-MAIN-(Online)2015]

(1)  $E_f = 60 \text{ kJ/mol}$ ;  $E_b = 100 \text{ kJ/mol}$

(2)  $E_f = 30 \text{ kJ/mol}$ ;  $E_b = 70 \text{ kJ/mol}$

(3)  $E_f = 80 \text{ kJ/mol}$ ;  $E_b = 120 \text{ kJ/mol}$

(4)  $E_f = 70 \text{ kJ/mol}$ ;  $E_b = 30 \text{ kJ/mol}$

CK0177

7. Decomposition of  $\text{H}_2\text{O}_2$  follows a first order reaction. In fifty minutes the concentration of  $\text{H}_2\text{O}_2$  decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of  $\text{H}_2\text{O}_2$  reaches 0.05 M, the rate of formation of  $\text{O}_2$  will be :-

[JEE-MAIN-(Offline)2016]

(1)  $1.34 \times 10^{-2} \text{ mol min}^{-1}$

(2)  $6.93 \times 10^{-2} \text{ mol min}^{-1}$

(3)  $6.93 \times 10^{-4} \text{ mol min}^{-1}$

(4)  $2.66 \text{ L min}^{-1}$  at STP

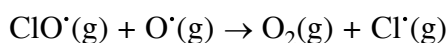
CK0178

8. The reaction of ozone with oxygen atoms in the presence of chlorine atoms can occur by a two step process shown below :

[JEE-MAIN-(Online)2016]



$$k_i = 5.2 \times 10^9 \text{ L mol}^{-1}\text{s}^{-1}$$



$$k_{ii} = 2.6 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1} \quad \text{.....(ii)}$$

The closest rate constant for the overall reaction  $\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{O}_2(\text{g})$  is :

(1)  $3.1 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}$

(2)  $2.6 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}$

(3)  $5.2 \times 10^9 \text{ L mol}^{-1}\text{s}^{-1}$

(4)  $1.4 \times 10^{20} \text{ L mol}^{-1}\text{s}^{-1}$

CK0179

9. Two reactions  $R_1$  and  $R_2$  have identical pre-exponential factors. Activation energy of  $R_1$  exceeds that of  $R_2$  by  $10 \text{ kJ mol}^{-1}$ . If  $k_1$  and  $k_2$  are rate constants for reactions  $R_1$  and  $R_2$  respectively at 300 K, then  $\ln(k_2/k_1)$  is equal to :

[JEE-MAINS-2017]

(R =  $8.314 \text{ J mol}^{-1}\text{K}^{-1}$ )

(1) 8

(2) 12

(3) 6

(4) 4

CK0180

10. The rate of a reaction quadruples when the temperature changes from 300 to 310 K. The activation energy of this reaction is (Assume activation energy and pre-exponential factor are independent of temperature ;  $\ln 2 = 0.693$ ,  $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$ ) :

[MAINS-2017(online)]

(1)  $107.2 \text{ kJ mol}^{-1}\text{K}^{-1}$  (2)  $53.6 \text{ kJ mol}^{-1}\text{K}^{-1}$  (3)  $214.4 \text{ kJ mol}^{-1}\text{K}^{-1}$  (4)  $26.8 \text{ kJ mol}^{-1}\text{K}^{-1}$

CK0181

11. The rate of a reaction A doubles on increasing the temperature from 300 to 310 K. By how much, the temperature of reaction B should be increased from 300 K so that rate doubles if activation energy of the reaction B is twice to that of reaction A :

[MAINS-2017(online)]

(1) 2.45 K

(2) 4.92 K

(3) 9.84 K

(4) 19.67 K

CK0182

12. At  $518^\circ \text{C}$ , the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was  $1.00 \text{ Torr s}^{-1}$  when 5% had reacted and  $0.5 \text{ Torr s}^{-1}$  when 33% had reacted. The order of the reaction is :

[JEE-MAINS-2018]

(1) 3

(2) 1

(3) 0

(4) 2

CK0183

13. For a first order reaction,  $\text{A} \rightarrow \text{P}$ ,  $t_{1/2}$  (half life) is 10 days. The time required for  $\frac{1}{4}$  conversion of A (in days) is :-

[MAINS-2018(online)]



(ln 2 = 0.693, ln 3 = 1.1)

- (1) 5 (2) 4.1 (3) 3.2 (4) 2.5 **CK0184**
14.  $N_2O_5$  decomposes to  $NO_2$  and  $O_2$  and follows first order kinetics. After 50 minutes, the pressure inside the vessel increases from 50 mmHg to 87.5 mmHg. The pressure of the gaseous mixture after 100 minute at constant temperature will be: **[MAINS-2018(online)]**
- (1) 116.25 mmHg (2) 175.0 mmHg (3) 106.25 mmHg (4) 136.25 mmHg **CK0185**
15. The following results were obtained during kinetic studies of the reaction : **[MAINS-2019(online)]**  
 $2A + B \rightarrow \text{Products}$

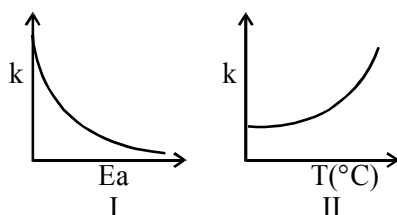
Experiment	[A] (in mol L <sup>-1</sup> )	[B] (in mol L <sup>-1</sup> )	Initial Rate of reaction (in mol L <sup>-1</sup> min <sup>-1</sup> )
(I)	0.10	0.20	$6.93 \times 10^{-3}$
(II)	0.10	0.25	$6.93 \times 10^{-3}$
(III)	0.20	0.30	$1.386 \times 10^{-2}$

The time (in minutes) required to consume half of A is :

- (1) 10 (2) 5 (3) 100 (4) 1 **CK0186**
16. For the reaction,  $2A + B \rightarrow \text{products}$ , when the concentrations of A and B both were doubled, the rate of the reaction increased from  $0.3 \text{ mol L}^{-1}\text{s}^{-1}$  to  $2.4 \text{ mol L}^{-1}\text{s}^{-1}$ . When the concentration of A alone is doubled, the rate increased from  $0.3 \text{ mol L}^{-1}\text{s}^{-1}$  to  $0.6 \text{ mol L}^{-1}\text{s}^{-1}$  **[MAINS-2019(online)]**
- Which one of the following statements is correct ?
- (1) Order of the reaction with respect to B is 2  
 (2) Order of the reaction with respect to A is 2  
 (3) Total order of the reaction is 4  
 (4) Order of the reaction with respect to B is 1 **CK0187**
17. For an elementary chemical reaction, **[MAINS-2019(online)]**

$A_2 \xrightleftharpoons[k_{-1}]{k_1} 2A$ , the expression for  $\frac{d[A]}{dt}$  is :

- (1)  $2k_1[A_2] - k_{-1}[A]^2$  (2)  $k_1[A_2] - k_{-1}[A]^2$   
 (3)  $2k_1[A_2] - 2k_{-1}[A]^2$  (4)  $k_1[A_2] + k_{-1}[A]^2$  **CK0188**
18. Consider the given plots for a reaction obeying Arrhenius equation ( $0^\circ\text{C} < T < 300^\circ\text{C}$ ) : (k and  $E_a$  are rate constant and activation energy, respectively) **[MAINS-2019(online)]**



Choose the correct option :

(1) Both I and II are wrong (2) I is wrong but II is right

(3) Both I and II are correct (4) I is right but II is wrong

CK0189

19. The reaction  $2X \rightarrow B$  is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be :-

(1) 18.0 h (2) 7.2 h (3) 9.0 h (4) 12.0 h

CK0190

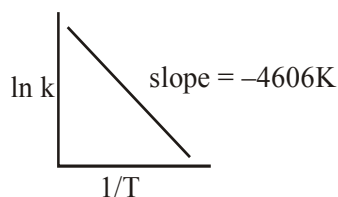
20. If a reaction follows the Arrhenius equation, the plot  $\ln k$  vs  $\frac{1}{RT}$  gives straight line with a gradient

(-y) unit. The energy required to activate the reactant is : [MAINS-2019(online)]

(1) y unit (2) -y unit (3) yR unit (4) y/R unit

CK0191

21. For a reaction, consider the plot of  $\ln k$  versus  $1/T$  given in the figure. If the rate constant of this reaction at 400 K is  $10^{-5} \text{ s}^{-1}$ , then the rate constant at 500 K is : [MAINS-2019(online)]



(1)  $2 \times 10^{-4} \text{ s}^{-1}$  (2)  $10^{-4} \text{ s}^{-1}$  (3)  $10^{-6} \text{ s}^{-1}$  (4)  $4 \times 10^{-4} \text{ s}^{-1}$

$\Rightarrow K_2 = 10^{-4} \text{ s}^{-1}$

CK0192

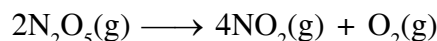
22. Decomposition of X exhibits a rate constant of  $0.05 \mu\text{g}/\text{year}$ . How many years are required for the decomposition of  $5 \mu\text{g}$  of X into  $2.5 \mu\text{g}$  ? [MAINS-2019(online)]

(1) 50 (2) 25 (3) 20 (4) 40

CK0193

## EXERCISE # J-ADVANCED

1. For the first order reaction [JEE 2011]



- (A) the concentration of the reactant decreases exponentially with time  
 (B) the half-life of the reaction decreases with increasing temperature.  
 (C) the half-life of the reaction depends on the initial concentration of the reactant.  
 (D) the reaction proceeds to 99.6% completion in eight half-life duration. CK0194

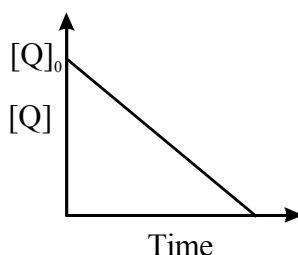
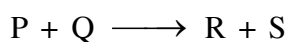
2. An organic compound undergoes first-order decomposition. The time taken for its decomposition to  $1/8$  and  $1/10$  of its initial concentration are  $t_{1/8}$  and  $t_{1/10}$  respectively. What is the value of  $\frac{[t_{1/8}]}{t_{1/10}} \times 10$  ?

(take  $\log_{10} 2 = 0.3$ )

[JEE 2012]

CK0195

3. In the reaction : [JEE 2013]



the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is -

- (A) 2 (B) 3 (C) 0 (D) 1 CK0196

4. For the elementary reaction  $\text{M} \rightarrow \text{N}$ , the rate of disappearance of  $\text{M}$  increases by a factor of 8 upon doubling the concentration of  $\text{M}$ . The order of the reaction with respect to  $\text{M}$  is

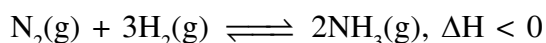
- (A) 4 (B) 3 (C) 2 (D) 1 [JEE 2014]

CK0197

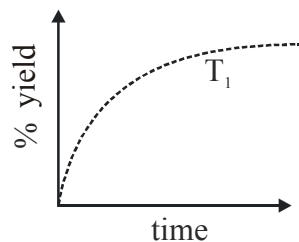
5. In dilute aqueous  $\text{H}_2\text{SO}_4$ , the complex diaquodioxalatoferate(II) is oxidized by  $\text{MnO}_4^-$ . For this reaction, the ratio of the rate of change of  $[\text{H}^+]$  to the rate of change of  $[\text{MnO}_4^-]$  is. [JEE 2015]

CK0198

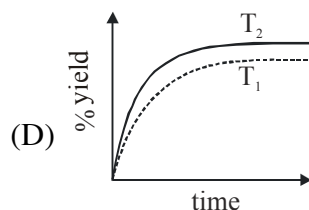
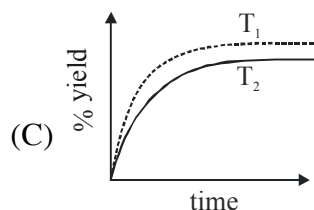
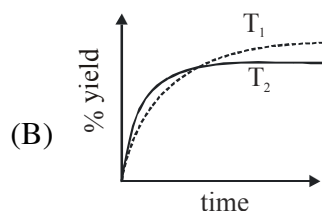
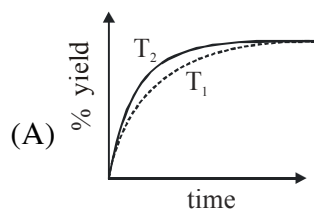
6. The % yield of ammonia as a function of time in the reaction [JEE 2015]



at  $(P, T_1)$  is given below -



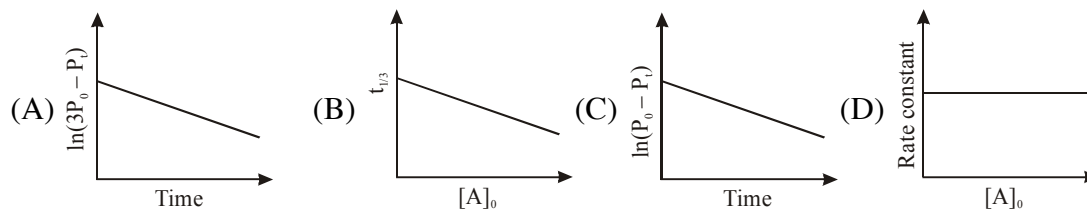
If this reaction is conducted at  $(P, T_2)$ , with  $T_2 > T_1$ , the % yield of ammonia as a function of time is represented by -



CK0199

7. According to the Arrhenius equation, [JEE 2016]
- (A) A high activation energy usually implies a fast reaction
- (B) Rate constant increase with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy
- (C) Higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant
- (D) The pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy. CK0200
8. In a bimolecular reaction, the steric factor  $P$  was experimentally determined to be 4.5. The correct option(s) among the following is(are) : [JEE 2017]
- (A) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally
- (B) The activation energy of the reaction is unaffected by the value of the steric factor
- (C) Since  $P = 4.5$ , the reaction will not proceed unless an effective catalyst is used.
- (D) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation. CK0201
9. For a first order reaction  $A(g) \rightarrow 2B(g) + C(g)$  at constant volume and 300 K, the total pressure at the beginning ( $t = 0$ ) and at time  $t$  are  $P_0$  and  $P_t$ , respectively. Initially, only A is present with concentration  $[A]_0$ , and  $t_{1/3}$  is the time required for the partial pressure of A to reach  $1/3^{\text{rd}}$  of its initial value. The correct option(s) is (are) :- [JEE 2018]

(Assume that all these gases behave as ideal gases)



CK0202

10. Consider the kinetic data given in the following table for the reaction  $A + B + C \rightarrow \text{Product}$ .

Experiment No.	[A] (mol dm <sup>-3</sup> )	[B] (mol dm <sup>-3</sup> )	[C] (mol dm <sup>-3</sup> )	Rate of reaction (mol dm <sup>-3</sup> s <sup>-1</sup> )
1	0.2	0.1	0.1	$6.0 \times 10^{-5}$
2	0.2	0.2	0.1	$6.0 \times 10^{-5}$
3	0.2	0.1	0.2	$1.2 \times 10^{-4}$
4	0.3	0.1	0.1	$9.0 \times 10^{-5}$

The rate of the reaction for  $[A] = 0.15 \text{ mol dm}^{-3}$ ,  $[B] = 0.25 \text{ mol dm}^{-3}$  and  $[C] = 0.15 \text{ mol dm}^{-3}$  is found to be  $Y \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ . The value of  $Y$  is \_\_\_\_\_ [JEE 2019]

CK0203

11. The decomposition reaction  $2\text{N}_2\text{O}_5(\text{g}) \xrightarrow{\Delta} 2\text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g})$  is started in a closed cylinder under isothermal isochoric condition at an initial pressure of 1 atm. After  $Y \times 10^3 \text{ s}$ , the pressure inside the cylinder is found to be 1.45 atm. If the rate constant of the reaction is  $5 \times 10^{-4} \text{ s}^{-1}$ , assuming ideal gas behavior, the value of  $Y$  is \_\_\_\_ [JEE 2019]

CK0204



- |  |  |
|--|--|
| 46. Ans. 100 min.  | 47. Ans.(4 hour)                                       |
| 48. Ans. (6 : 6 : 6 : 1 : 1)                               | 49. Ans. 30 sec.                                       |
| 50. Ans. 50 min, $\left(\frac{0.2}{e}\right)M$             |  |
| 51. Ans.5 kJ mol <sup>-1</sup>                             | 52. Ans. 13.44 kcal/mole                               |
| 53. Ans. 10.28 k cal mol <sup>-1</sup>                     | 54. Ans (e <sup>3</sup> )                              |
| 55. Ans.20 minutes   | 56. Ans (10)   |
| 57. Ans. (150 K)   |  |
| 58. Ans. (840)   | 59. Ans. (38.3 kJ mol <sup>-1</sup> )                  |
| 60. Ans.(20)   | 61. Ans. $r = K' [NO]^2[Br_2]$                         |
| 62. Ans. $r = K [NO]^2 [H_2]$ , where $K = k_2 \times K_1$ | 63. Ans.(1)  |
| 64. Ans.(2)  | 65. Ans.(rate = $K_3 K_1 / K_2 [CHCl_3][Cl_2]^{1/2}$ ) |

**EXERCISE # S-II**

- |   |                                       |
|---|---------------------------------------|
| 1. Ans.383.2 mm Hg , 403.8 min.           | 2. Ans. (50)                          |
| 3. Ans. 20 min                            | 4. Ans. 315 sec.                      |
| 6. Ans. (a) 9.24 kcal/mole, (b) 25.6 hour | 7. Ans. $k = 0.0327 \text{ min}^{-1}$ |
| 9. Ans. (3)                               |                                       |
| 10. Ans.(1440 sec)                        | 11. Ans.(5)                           |
| 12. Ans. (200 min)                        | 13. Ans. (3)                          |
| 14. Ans. (0)                              | 15. Ans.(0.04)                        |
| 16. Ans (8)                               | 17. Ans.(14)                          |
| 18. Ans.(1680)                            | 19. Ans.(0)                           |
| 20. Ans.(8)                               |                                       |

**EXERCISE # O-1**

- |             |             |              |             |
|-------------|-------------|--------------|-------------|
| 1. Ans.(B)  | 2. Ans.(D)  | 3. Ans.(C)   | 4. Ans.(B)  |
| 5. Ans.(C)  | 6. Ans.(C)  | 7. Ans.(A)   | 8. Ans.(C)  |
| 9. Ans.(D)  | 10. Ans.(C) | 11. Ans.(A)  | 12. Ans(D)  |
| 13. Ans(A)  | 14. Ans.(C) | 15. Ans.(A)  | 16. Ans.(C) |
| 17. Ans.(D) | 18. Ans.(D) | 19. Ans.(A)  | 20. Ans.(D) |
| 21. Ans.(B) | 22. Ans.(A) | 23. Ans.(D)  | 24. Ans.(A) |
| 25. Ans.(D) | 26. Ans.(C) | 27. Ans.(A)  | 28. Ans.(A) |
| 29. Ans.(C) | 30. Ans.(C) | 31. Ans.(C)  | 32. Ans.(C) |
| 33. Ans.(B) | 34. Ans.(C) | 35. Ans.(C)  | 36. Ans.(A) |
| 37. Ans.(D) | 38. Ans (C) | 39. Ans.(A)  | 40. Ans.(C) |
| 41. Ans.(A) | 42. Ans (B) | 43. Ans.(D)  | 44. Ans.(D) |
| 45. Ans.(C) | 46. Ans.(C) | 47. Ans.(D)  | 48. Ans.(B) |
| 49. Ans.(C) | 50. Ans.(D) | 51. Ans.(D)  | 52. Ans.(A) |
| 53. Ans.(B) | 54. Ans.(B) | 55. Ans.(C)  | 56. Ans.(A) |
| 57. Ans.(B) | 58. Ans.(B) | 59. Ans. (C) | 60. Ans.(D) |

**EXERCISE # O-2**

- |  |                 |                 |                 |
|--|-----------------|-----------------|-----------------|
| 1. Ans.(A,B,D)   | 2. Ans.(A,D)    | 3. Ans.(A,C, D) | 4. Ans.(A,B,C)  |
| 5. Ans.(C,D)   | 6. Ans.(A,C)    | 7. Ans. (C)     | 8. Ans.(A,D)    |
| 9. Ans.(A, B)  | 10. Ans.(A,B,D) | 11. Ans. (A)    | 12. Ans.(C)     |
| 13. Ans. (A ,B, C)   | 14. Ans.(C)     | 15. Ans.(C)     | 16. Ans.Ans.(C) |
| 17. Ans.(A)  | 18. Ans.(B)     | 19. Ans. (A)    | 20. Ans.(B)     |
| 21. Ans.(C)  | 22. Ans.(C)     | 23. Ans.(C)     | 24. Ans.(C)     |
| 25. Ans.(C)  |                 |                 |                 |
| 26. Ans. A $\rightarrow$ S ; B $\rightarrow$ R ; C $\rightarrow$ P : D $\rightarrow$ Q     |                 |                 |                 |
| 27. Ans. A $\rightarrow$ P,Q ; B $\rightarrow$ S,P ; C $\rightarrow$ R ; D $\rightarrow$ P |                 |                 |                 |
| 28. Ans.(A)  | 29. Ans.(B)     | 30. Ans.(C)     |                 |

**EXERCISE # J-MAIN**

- |              |                              |              |              |
|--------------|------------------------------|--------------|--------------|
| 1. Ans.(1)   | 2. Ans.(2)                   | 3. Ans.(2)   | 4. Ans.(3)   |
| 5. Ans.(1)   | 6. Ans.(3)                   | 7. Ans.(3)   | 8. Ans.(3)   |
| 9. Ans. (4)  | 10. Ans. (1)                 | 11. Ans. (2) | 12. Ans.(4)  |
| 13. Ans. (2) | 14. Ans.(3)                  | 15. Ans. (2) | 16. Ans. (1) |
| 17. Ans.(3)  | 18. Ans.(4) (NTA Answer (3)) |              |              |
| 19. Ans.(1)  | 20. Ans.(1)                  | 21. Ans.(2)  | 22. Ans.(1)  |

**EXERCISE # J-ADVANCED**

- |                |                |                 |               |
|----------------|----------------|-----------------|---------------|
| 1. Ans.(A,B,D) | 2. Ans.(9)     | 3. Ans.(D)      | 4. Ans.(B)    |
| 5. Ans.(8)     | 6. Ans.(B)     | 7. Ans. (B,C,D) | 8. Ans. (B,D) |
| 9. Ans.(A,D)   | 10. Ans.(6.75) | 11. Ans.(2.30)  |               |



## THERMOCHEMISTRY

### 1. INTRODUCTION

Thermochemistry deals with the energy changes involved in chemical reaction.

### 2. TYPES OF REACTIONS

#### (i) Exothermic reactions :

These are the chemical reactions involving release of heat.

Examples :- Neutralisation reactions, combustion reactions, slaking of lime, etc.

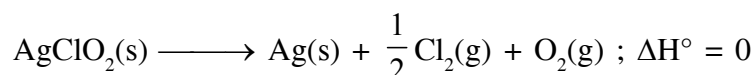
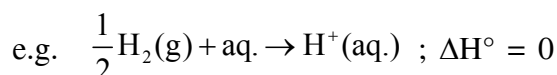
#### (ii) Endothermic reactions :

These are the chemical reactions involving absorption of heat.

Examples :- Decomposition reactions, elimination reaction, etc.

#### (iii) Thermo neutral reactions :

These are chemical reaction in which heat is neither absorbed nor released.



The reason behind release or absorption of heat in the reaction may be defined as difference in internal energy, bond energy, enthalpy, etc.

For exothermic reaction :

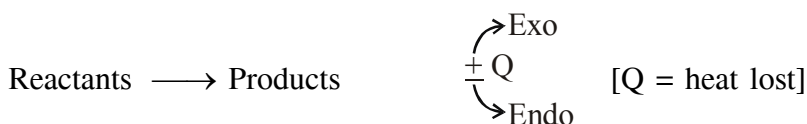
$$(i) \quad \sum U_{\text{Reactant}} > \sum U_{\text{Product}}$$

$$(ii) \quad \sum H_{\text{Reactant}} > \sum H_{\text{Product}}$$

$$(iii) \quad \sum (\text{BE})_{\text{Reactant}} < \sum (\text{BE})_{\text{Product}}$$

### 3. REPRESENTATION OF HEAT INVOLVED IN REACTIONS

#### (i) Old convention :

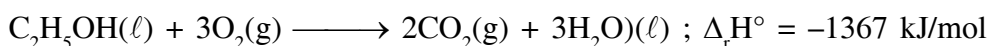


#### (ii) Modern convention :



#### 4. THERMO CHEMICAL EQUATION

It represents a balanced chemical reaction in which the physical state along with allotropic form of all the reaction components as well as heat involved in reaction, are given.

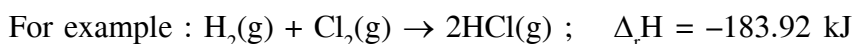


The above equation describes the combustion of liquid ethanol at constant temperature and pressure. The negative sign of enthalpy change indicates that this is an exothermic reaction.

The coefficients in a balanced thermochemical equation refer to the number of moles (never molecules) of reactants and products in the reaction. Per mole of  $\Delta_r H^\circ$  defines the mole of reaction. For above reaction per mole means per mole of  $\text{C}_2\text{H}_5\text{OH}(\ell)$ , per 3 moles of  $\text{O}_2(\text{g})$ , per 2 moles of  $\text{CO}_2(\text{g})$  and per 3 moles of  $\text{H}_2\text{O}(\ell)$ .

#### 5. ENTHALPY CHANGE OF REACTION OR REACTION ENTHALPY ( $\Delta_r H$ )

Enthalpy of reaction is defined as the quantity of heat evolved or absorbed when molar quantities of substances react completely in amounts represented by chemical equation, all components being maintained at same pressure and same temperature conditions.



Thus, when one mole of gaseous hydrogen reacts completely with one mole of gaseous chlorine, 183.92 kJ of heat is evolved.

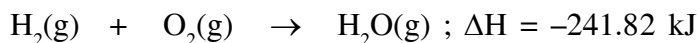
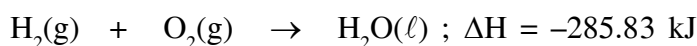
$$\Delta_r H = \sum H_{\text{products}} - \sum H_{\text{reactants}} = [2 \times H_m(\text{HCl}, \text{g})] - [1 \times H_m(\text{H}_2, \text{g}) + 1 \times H_m(\text{Cl}_2, \text{g})]$$

where  $H_m$  = molar enthalpy

##### 5.1 FACTORS AFFECTING HEAT OR ENTHALPY OF REACTION :

The enthalpy change of reaction ( $\Delta H$ ) depends upon the following factors :

- (i) **Physical state of the reactants and the products :** The  $\Delta H$  of a reaction depends upon the physical states of reactants and products. For example, when hydrogen and oxygen gases combine to give liquid water, the heat of reaction is different than when they combine to form gaseous water at the same temperature and pressure.



- (ii) **Quantities of reaction components :** The amount of heat evolved or absorbed depends upon the amount of components involved in the reaction. For example, the heat of combustion of 2 moles of carbon is double than heat of combustion of 1 mole of carbon.

- (iii) **Allotropic forms :** The amount of heat evolved or absorbed for different forms of the same substance are different. For example,



- (iv) **Temperature** : The heat of reaction depends upon the temperature of reactants and products.



The dependence of reaction enthalpy on temperature is given by Kirchoff's equation :

$$\Delta_r H_2 - \Delta_r H_1 = \int_{T_1}^{T_2} \Delta_r (C_p) \cdot dT$$

$$\text{and } \Delta_r U_2 - \Delta_r U_1 = \int_{T_1}^{T_2} \Delta_r (C_v) \cdot dT$$

However,  $\Delta_r H$  and  $\Delta_r U$  do not change significantly on changing the temperature.

- (v) **Measurement at constant pressure or volume** : The heat of reaction depends upon the conditions of measurement of heat at constant pressure or volume, as,

$$\Delta_r H = \Delta_r U + \Delta_r (PV)$$

$\Delta H$  may be equal, greater than or less than  $\Delta_r U$ .

For reaction involving gaseous components,

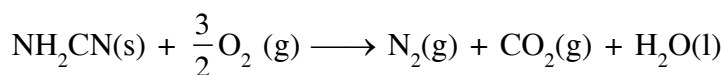
$$\Delta_r H = \Delta_r U + \Delta_r n_g \cdot RT$$

- (vi) **Pressure** : Enthalpy of any component may depend on pressure and  $\Delta_r H$  may change on changing the pressure. As, the enthalpy of an ideal gas is independent from the change in pressure, for the reactions involving ideal gases,  $\Delta_r H$  is pressure independent.

### EXERCISE-I

- Consider the reaction :  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$  carried out at constant temperature and pressure, if  $\Delta H$  and  $\Delta U$  are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ? [AIIEEE-2005]
  - $\Delta H = \Delta U$
  - $\Delta H = 0$
  - $\Delta H > \Delta U$
  - $\Delta H < \Delta U$
- For which reaction will  $\Delta H = \Delta U$  ?
  - $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{HBr}(\text{g})$
  - $\text{C}(\text{s}) + 2 \text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{CO}_2(\text{g})$
  - $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
  - $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g})$
- For which of the following change  $\Delta H \neq \Delta U$  ?
  - $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$
  - $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \longrightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
  - $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$
  - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
- A mixture of 2 moles of carbon monoxide and one mole of oxygen in a closed vessel is ignited to get carbon dioxide. If  $\Delta H$  is the enthalpy change and  $\Delta U$  is the change in internal energy, then :-
  - $\Delta H > \Delta U$
  - $\Delta H < \Delta U$
  - $\Delta H = \Delta U$
  - Not definite

5. For the reaction :  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ ,  $\Delta H$  is -  
 (A)  $\Delta U + 2RT$             (B)  $\Delta U - 2RT$             (C)  $\Delta U + RT$             (D)  $\Delta U - RT$
6. When the following reaction was carried out in a bomb calorimeter,  $\Delta U$  is found to be  $-742.7 \text{ kJ/mol}$  of  $\text{NH}_2\text{CN}(\text{s})$  at  $300 \text{ K}$ .



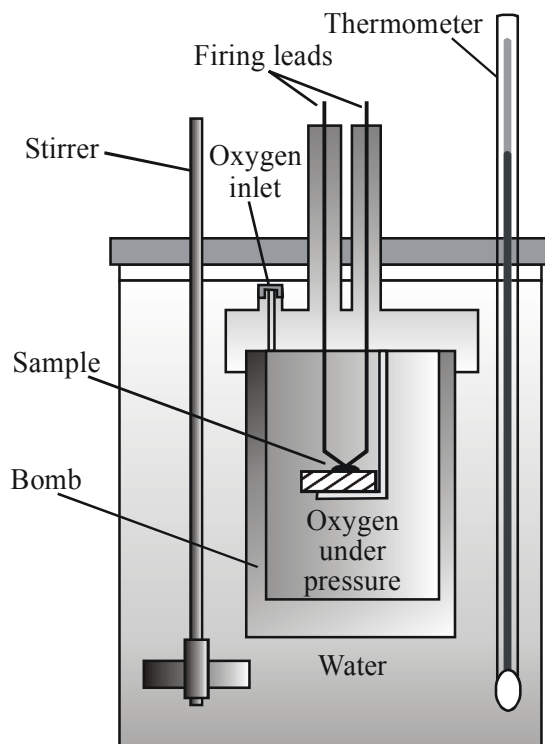
Calculate  $\Delta H_{300\text{K}}$  for the reaction. ( $R = 8 \text{ J/mole-K}$ ).

7. For the reaction :  $2\text{A}(\text{g}) + 3\text{B}(\text{g}) \longrightarrow 4\text{C}(\text{g}) + \text{D}(\text{l})$ ;  $\Delta H = -20 \text{ KJ/mole}$   
 Find the heat exchanged when  $0.4$  mole of  $\text{A}$  reacts with excess of  $\text{B}$  in a closed rigid container. The temperature is constant at  $300 \text{ K}$ . [ $R=8.3 \text{ J/K mole}$ ]

## 5.2 MEASUREMENT OF $\Delta U$ AND $\Delta H$ : CALORIMETRY :

We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made under two different conditions:

- (i) at constant volume,  $q_v$
  - (ii) at constant pressure,  $q_p$
- (a)  **$\Delta U$  measurements :** For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter (Figure). Here, a steel vessel (the bomb) is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is

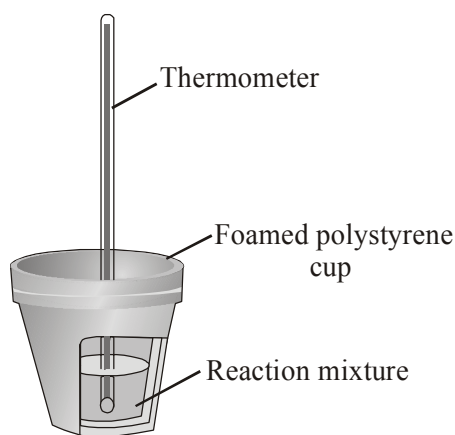


**Figure :** Bomb calorimeter

done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as  $\Delta V = 0$ . Temperature change of the calorimeter produced by the completed reaction is then converted to  $q_v$ , by using the known heat capacity of the calorimeter with the help of equation 6.11.

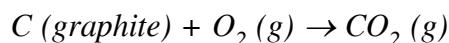
- (b)  **$\Delta H$  measurements :** Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in figure. We know that  $\Delta H = q_p$  (at constant p) and, therefore, heat absorbed or evolved,  $q_p$  at constant pressure is also called the heat of reaction or enthalpy of reaction,  $\Delta_r H$ .

In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore,  $q_p$  will be negative and  $\Delta_r H$  will also be negative. Similarly in an endothermic reaction, heat is absorbed,  $q_p$  is positive and  $\Delta_r H$  will be positive.



**Figure :** Calorimeter for measuring heat changes at constant pressure  
(atmospheric pressure)

**Ex.1.** 1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation



During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

**Sol. :** Suppose  $q$  is the quantity of heat from the reaction mixture and  $C_V$  is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter.

$$q = C_V \Delta T$$

Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.

$$q = -C_V \times \Delta T = -20.7 \text{ kJ/K} \times (299 - 298)\text{K} = -20.7 \text{ kJ}$$

(Here, negative sign indicates the exothermic nature of the reaction)

Thus,  $\Delta U$  for the combustion of the 1g of graphite = -20.7 kJ

For combustion of 1 mol of graphite,

$$\Delta H = \Delta U = \frac{12.0 \text{ g mol}^{-1} \times (-20.7 \text{ kJ})}{1 \text{ g}} = -2.48 \times 10^2 \text{ kJ.mol}^{-1}, \quad \text{Since } \Delta n_g = 0$$

## EXERCISE-II

- One gm sample of  $NH_4NO_3$  (s) is decomposed in a bomb calorimeter (constant volume). The temperature of the calorimeter system falls by 6K. If the heat capacity of system is 1.25 kJ/K, what is the molar enthalpy of decomposition of  $NH_4NO_3$ (s) at 300 K. [ $R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$ ].  
 $NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$ .
- 0.16 g of methane was subjected to combustion at 27°C in a bomb Calorimeter . The temperature of Calorimeter system (including water) was found to rise by 0.5°C . Calculate the heat of combustion of methane at
  - constant volume
  - constant pressure .
 The thermal capacity of Calorimeter system is 17.7 kJ K<sup>-1</sup> . ( $R = 8.313 \text{ mol}^{-1} \text{ K}^{-1}$ )
- If 1.22 gm of benzoic acid gives off 31.723 J of energy when burned in bomb calorimeter in the presence of excess oxygen at an initial temperature of 24.6°C. Calculate,  $W$  and  $\Delta U$  for the given amount of benzoic acid in the calorimeter, assuming ideal gas behaviour.

## 6. STANDARD ENTHALPY OF REACTION, $\Delta H^\ominus$

Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. **The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.**

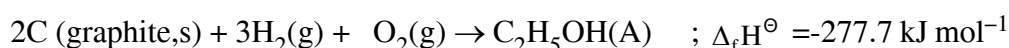
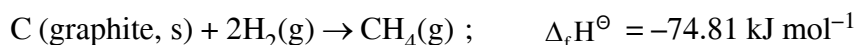
**The standard state of a substance at a specified temperature is its pure form at 1 bar.** For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pure iron at 1 bar. Usually data are taken at 298 K.

Standard conditions are denoted by adding the superscript  $\ominus$  to the symbol  $\Delta H$ , e.g.,  $\Delta H^\ominus$

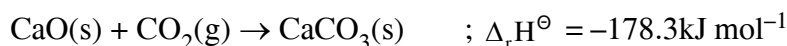
## 7. SOME DIFFERENT KINDS OF $\Delta_r H^\ominus$ :

### 7.1 STANDARD ENTHALPY OF FORMATION, $\Delta_f H^\ominus$ :

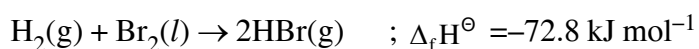
The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. The reference state of an element is its most stable state of aggregation at 25° C and 1 bar pressure. For example, the reference state of dihydrogen is  $H_2$  gas and those of dioxygen, carbon and sulphur are  $O_2$  gas,  $C_{\text{graphite}}$  and  $S_{\text{rhombic}}$  respectively. Some reactions with standard molar enthalpies of formation are given below.



It is important to understand that a standard molar enthalpy of formation,  $\Delta_f H^\ominus$ , is just a special case of  $\Delta_r H^\ominus$ , where one mole of a compound is formed from its constituent elements, as in the above three equations, where 1 mol of each, water, methane and ethanol is formed. In contrast, the enthalpy change for an exothermic reaction:



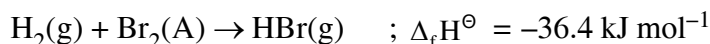
is not an enthalpy of formation of calcium carbonate, since calcium carbonate has been formed from other compounds, and not from its constituent elements. Also, for the reaction given below, enthalpy change is not standard enthalpy of formation,  $\Delta_f H^\ominus$  for  $HBr(g)$ .



Here two moles, instead of one mole of the product is formed from the elements, i.e.,

$$\Delta_r H^\ominus = 2\Delta_f H^\ominus$$

Therefore, by dividing all coefficients in the balanced equation by 2, expression for enthalpy of formation of HBr (g) is written as



- (i)  $\Delta_f \text{H}^\ominus = 0$  for all the elements in their reference state.
- (ii) **Standard enthalpy of reaction from standard enthalpy of formation :** The knowledge of standard enthalpy of formation of various substances can be used to calculate the standard enthalpy of reactions under standard conditions. The standard enthalpy of any reaction ( $\Delta \text{H}^\ominus$ ) is equal to the difference between the  $\Delta_f \text{H}^\ominus$  of all the products and the reactants.

$\Delta \text{H}^\ominus =$  Sum of the standard enthalpy of formation of products - Sum of the standard enthalpy of formation of reactants.

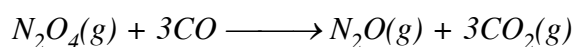
$$\text{i.e., } \Delta_r \text{H}^\ominus = \sum \Delta_f \text{H}^\ominus_{(\text{products})} - \sum \Delta_f \text{H}^\ominus_{(\text{reactants})}$$

For a reaction,  $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

$$\Delta_r \text{H}^\ominus = \sum \Delta_f \text{H}^\ominus_{(\text{products})} - \sum \Delta_f \text{H}^\ominus_{(\text{reactants})}$$

$$= [c\Delta_f \text{H}^\ominus (\text{C}) + d\Delta_f \text{H}^\ominus (\text{D})] - [a\Delta_f \text{H}^\ominus (\text{A}) + b\Delta_f \text{H}^\ominus (\text{B})]$$

**Ex.2.** Standard enthalpies of formation of  $\text{CO}(\text{g})$ ,  $\text{CO}_2(\text{g})$ ,  $\text{N}_2\text{O}(\text{g})$  and  $\text{N}_2\text{O}_4(\text{g})$  are  $-110$ ,  $-393$ ,  $-81$  and  $10 \text{ kJ/mole}$ , respectively. Find the  $\Delta_r \text{H}^\ominus$  for the reaction :



**Sol. :**  $\Delta_r \text{H}^\ominus = \sum \Delta_f \text{H}^\ominus_{(\text{products})} - \sum \Delta_f \text{H}^\ominus_{(\text{reactants})}$

$$= [\Delta_f \text{H}^\ominus_{\text{N}_2\text{O}(\text{g})} + 3 \times \Delta_f \text{H}^\ominus_{\text{CO}_2(\text{g})}] - [\Delta_f \text{H}^\ominus_{\text{N}_2\text{O}_4(\text{g})} + 3 \times \Delta_f \text{H}^\ominus_{\text{CO}(\text{g})}]$$

$$= [81 + 3 \times (-393)] - [10 + 3 \times (-110)] = -778 \text{ kJ/mol.}$$

## 7.2 STANDARD ENTHALPY OF COMBUSTION, $\Delta_c \text{H}^\ominus$ :

Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature.

For example, the standard enthalpy of combustion of methane at 298.15 K is  $-890.36 \text{ kJ mol}^{-1}$ . This implies the following reaction :

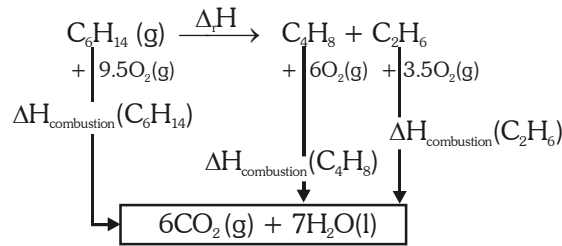


The standard enthalpy of combustion of methane at 298.15 K may be written as

$$\Delta_c \text{H}^\ominus(\text{CH}_4, \text{g}, 298.15 \text{ K}) = -890.36 \text{ kJ mol}^{-1}$$

**7.2.1 Application of enthalpy of combustion :** Consider a reaction of decomposition of  $\text{C}_6\text{H}_{14}$  into  $\text{C}_4\text{H}_8$  and  $\text{C}_2\text{H}_6$ . The following diagram show how enthalpy of combustions can be used to estimate enthalpy of reaction.



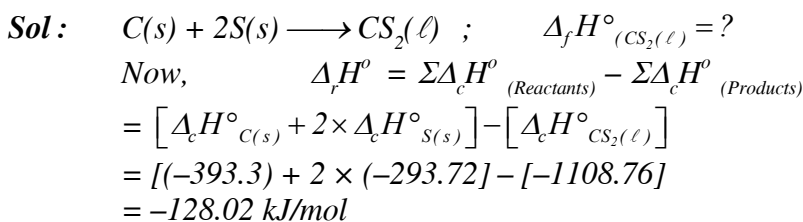


From the inspection of the above diagram, it is clear that

$$\Delta H_{\text{reaction}} = \Delta H_{\text{combustion}}(\text{C}_6\text{H}_{14}) - \Delta H_{\text{combustion}}(\text{C}_4\text{H}_8) - \Delta H_{\text{combustion}}(\text{C}_2\text{H}_6)$$

Hence  $\Delta_r H = \Sigma \Delta_c H(\text{Reactants}) - \Sigma \Delta_c H(\text{Products})$

**Ex.3.** Calculate the standard enthalpy of formation of carbon disulphide ( $\ell$ ). Given that the standard enthalpies of combustion of carbon ( $s$ ) sulphur ( $s$ ) and carbon disulphide ( $\ell$ ) are 393.3,  $-293.72$  and  $-1108.76 \text{ kJ mol}^{-1}$  respectively.



### EXERCISE-III

- On the basis of the following thermochemical data :  
 $\text{H}_2\text{O}(\ell) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) ; \Delta H = 57.32 \text{ kJ}$   
 $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\ell) ; \Delta H = -286.20 \text{ kJ}$   
 The value of enthalpy of formation of  $\text{OH}^-$  ion at  $25^\circ\text{C}$  is :- [AIIEE-2009]  
 (A)  $+228.88 \text{ kJ}$  (B)  $-343.52 \text{ kJ}$  (C)  $-22.88 \text{ kJ}$  (D)  $-228.88 \text{ kJ}$
- The enthalpies of combustion of carbon and carbon monoxide are  $-393.5$  and  $-283 \text{ kJ mol}^{-1}$  respectively. The enthalpy of formation of carbon monoxide per mole :- [AIIEE-2004]  
 (A)  $110.5 \text{ kJ}$  (B)  $676.5 \text{ kJ}$  (C)  $-676.5 \text{ kJ}$  (D)  $-110.5 \text{ kJ}$
- For which species  $\Delta H_{\text{formation}} \neq 0$   
 (A)  $\text{H}^+_{(\text{aq})}$  (B)  $\text{Br}_{2(\text{g})}$  (C)  $\text{I}_{2(\text{s})}$  (D)  $\text{C}_{(\text{graphite})}$
- Which of the following equations represents a reaction that provides the enthalpy of formation of  $\text{CH}_3\text{Cl}(\text{g})$  ?  
 (A)  $\text{C}(\text{s}) + \text{HCl}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g})$  (B)  $\text{C}(\text{s}) + 3/2 \text{H}_2(\text{g}) + 1/2 \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g})$   
 (C)  $\text{C}(\text{s}) + 3 \text{H}(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g})$  (D)  $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$
- Use the given standard enthalpies of formation to determine the enthalpy of reaction of the following reaction:  
 $\text{TiCl}_4(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \rightarrow \text{TiO}_2(\text{g}) + 4 \text{HCl}(\text{g})$   
 $\Delta H_f^\circ \text{TiCl}_4(\text{g}) = -763.2 \text{ kJ/mole}$   $\Delta H_f^\circ \text{TiO}_2(\text{g}) = -944.7 \text{ kJ/mole}$   
 $\Delta H_f^\circ \text{H}_2\text{O}(\text{g}) = -241.8 \text{ kJ/mole}$   $\Delta H_f^\circ \text{HCl}(\text{g}) = -92.3 \text{ kJ/mole}$   
 (A)  $-278.1 \text{ kJ}$  (B)  $+369.2 \text{ kJ}$  (C)  $+67.1 \text{ kJ}$  (D)  $-67.1 \text{ kJ}$
- Using the following information calculate the enthalpy of formation of  $\text{CH}_4$ .  
 $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) ; \Delta H^\circ = -890.4 \text{ kJ}$   
 $\Delta H_f^\circ \text{CO}_2(\text{g}) = -393.5 \text{ kJ/mole}$   $\Delta H_f^\circ \text{H}_2\text{O}(\text{l}) = -285.9 \text{ kJ/mole}$   
 (A)  $-98.6 \text{ kJ/mole}$  (B)  $-65.5 \text{ kJ/mole}$  (C)  $-74.9 \text{ kJ/mole}$  (D)  $-43.5 \text{ kJ/mole}$

- Q.17 The heats of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $-394 \text{ kJ/mole}$  and  $-285.8 \text{ kJ/mole}$  respectively. Using the data for the following combustion reaction, calculate the heat of formation of  $\text{C}_2\text{H}_2(\text{g})$ .  
 $2 \text{C}_2\text{H}_2(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 4 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) ; \Delta H^\circ = -2601 \text{ kJ}$   
 (A)  $-238.6 \text{ kJ/mole}$  (B)  $253.2 \text{ kJ/mole}$  (C)  $238.7 \text{ kJ/mole}$  (D)  $226.7 \text{ kJ/mole}$
- Q.18 The heats of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $-394 \text{ kJ/mole}$  and  $-285.8 \text{ kJ/mole}$  respectively &  $\Delta H^\circ_{\text{Combustion}} [\text{C}_3\text{H}_8(\text{g})] = -2221.6 \text{ kJ}$ . Then the heat of formation of  $\text{C}_3\text{H}_8(\text{g})$  is -  
 (A)  $212.2 \text{ kJ/mole}$  (B)  $-143.3 \text{ kJ/mole}$  (C)  $185.4 \text{ kJ/mole}$  (D)  $-103.6 \text{ kJ/mole}$
- Q.19 The standard enthalpy of formation of ammonia gas is -  
 Given :  $\text{N}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g}) ; \Delta H_r^\circ = -40 \text{ kJ/mol}$   
 $\Delta H_f^\circ[\text{N}_2\text{H}_4(\text{g})] = -120 \text{ kJ/mol}$   
 (A)  $-60 \text{ kJ/mol}$  (B)  $-180 \text{ kJ/mol}$  (C)  $40 \text{ kJ/mol}$  (D)  $-80 \text{ kJ/mol}$
- Q.20 Calculate standard enthalpy of formation of carbon-di-sulphide (*l*). Given the standard enthalpy of combustion of carbon (s), sulphur (s) & carbon-di-sulphide (*l*) are :  $-393$ ,  $-293$  and  $-1108 \text{ kJ mol}^{-1}$  respectively.
- Q.21 The enthalpy change for the reaction  $\text{C}_3\text{H}_8(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g}) + \text{CH}_4(\text{g})$  at  $25^\circ \text{C}$  is  $-55.7 \text{ kJ/mol}$ . Calculate the enthalpy of combustion of  $\text{C}_2\text{H}_6(\text{g})$ . The enthalpy of combustion of  $\text{H}_2$ ,  $\text{C}_3\text{H}_8$  &  $\text{CH}_4$  are  $-285.8$ ,  $-2220$  &  $-890.0 \text{ kJ/mol}$  respectively.

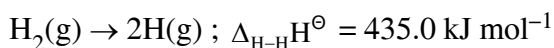
### 7.3 BOND ENTHALPY, $\Delta_{\text{bond}} H^\circ$ :

Chemical reactions involve the breaking and making of chemical bonds. Energy is required to break a bond and energy is released when a bond is formed. It is possible to relate heat of reaction to changes in energy associated with breaking and making of chemical bonds. With reference to the enthalpy changes associated with chemical bonds, two different terms are used in thermodynamics.

- (i) Bond dissociation enthalpy
- (ii) Mean bond enthalpy

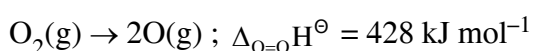
Let us discuss these terms with reference to diatomic and polyatomic molecules.

**Diatomic Molecules:** Consider the following process in which the bonds in one mole of dihydrogen gas ( $\text{H}_2$ ) are broken:



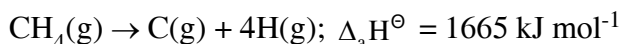
The enthalpy change involved in this process is the bond dissociation enthalpy of H-H bond. The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.

Note that it is the same as the enthalpy of atomization of dihydrogen. This is true for all diatomic molecules. For example:

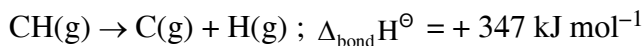
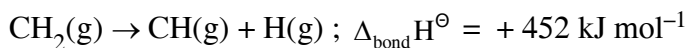
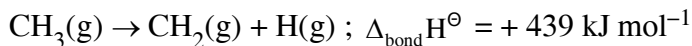
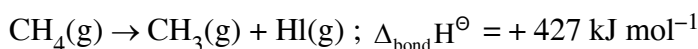


In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule.

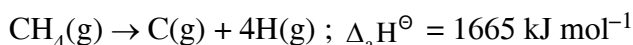
**Polyatomic Molecules:** Let us now consider a polyatomic molecule like methane,  $\text{CH}_4$ . The overall thermochemical equation for its atomization reaction is given below:



In methane, all the four C–H bonds are identical in bond length and energy. However, the energies required to break the individual C–H bonds in each successive step differ :



Therefore,



In such cases we use **mean bond enthalpy of C–H bond**.

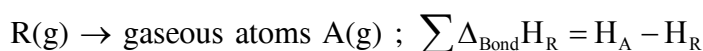
For example in  $\text{CH}_4$ ,  $\Delta_{\text{C-H}} \text{H}^\ominus$  is calculated as:

$$\Delta_{\text{C-H}} \text{H}^\ominus = \frac{1}{4} (\Delta_a \text{H}^\ominus) = \frac{1}{4} (1665 \text{ kJ mol}^{-1}) = 416 \text{ kJ mol}^{-1}$$

We find that mean C–H bond enthalpy in methane is 416 kJ/mol. It has been found that mean C–H bond enthalpies differ slightly from compound to compound, as in  $\text{CH}_3\text{CH}_2\text{Cl}$ ,  $\text{CH}_3\text{NO}_2$ , etc, but it does not differ in a great deal. Using Hess's law, bond enthalpies can be calculated.

- (i) Mean bond enthalpy may be used to calculate  $\Delta_r \text{H}$  of gaseous reaction :

Reactants (R, g)  $\longrightarrow$  Products (P, g), as



$$\boxed{\Delta_r \text{H} = \sum \Delta_{\text{bond}} \text{H}_{\text{Reactants}} - \sum \Delta_{\text{bond}} \text{H}_{\text{Products}}}$$

- (ii) If physical state of any component is different than gaseous, then it should be converted into gaseous atom.
- (iii)  $\Delta \text{H}$  calculated from bond enthalpy give  $\Delta_r \text{H}_{\text{theo}}$  because mean enthalpies are used in place of bond dissociation enthalpies. Normally it remain very close to experimental  $\Delta_r \text{H}$  but if any reaction component is more or less stable by any effect like resonance, hyperconjugation, strain, etc, the value differs largely. The difference is called energy or enthalpy of the kind responsible for the difference like resonance energy, strain energy, etc. It is given by

$$\Delta_r \text{H}_{\text{exp}} - \Delta_r \text{H}_{\text{theo}} = \Delta \text{H}_{\text{effect}}$$

**Ex.4.** If  $E_{\text{C-C}}$  is  $344 \text{ kJ mol}^{-1}$  and  $E_{\text{C-H}}$  is  $415 \text{ kJ mol}^{-1}$ , calculate the enthalpy of formation of propane. The enthalpies of atomization of carbon(s) and hydrogen (g) are  $716 \text{ kJ mole}^{-1}$  and  $433 \text{ kJ mole}^{-1}$  respectively.

**Sol. :** The enthalpy of formation is the sum of the atomization and bond energies. For propane, the enthalpies of atomization are



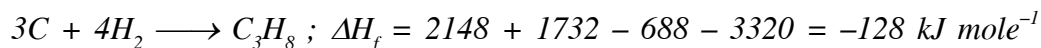


The bond enthalpies are

$$2E_{C-C} = 2 \times -344 = -688 \text{ kJ}$$

$$8E_{C-H} = 8 \times -415 = -3320 \text{ kJ}$$

Adding

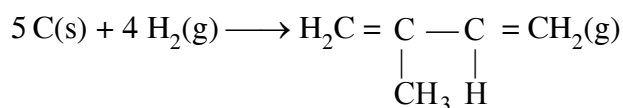


### EXERISE-IV

- 21 The enthalpy change for the following reaction is 513 kJ. Calculate the average Cl – F bond energy.



- (A) 1542 kJ/mole (B) 88 kJ/mole (C) 171 kJ/mole (D) 514 kJ/mole
- 22 Using bond enthalpy data, calculate enthalpy of formation of gaseous isoprene .



Given : C — H = 98.8 kcal/mol ; H — H = 104 kcal/mol ;

C — C = 83 kcal/mol ; C = C = 147 kcal/mol &

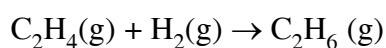
C(s) → C(g) = 171 kcal/mol.

- 30 For the reaction :  $N_2H_4(g) \rightarrow N_2H_2(g) + H_2(g) ; \Delta_r H^\circ = 109 \text{ kJ/mol}$

Calculate the bond enthalpy of N = N.

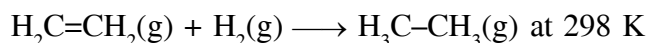
Given : B.E. (N – N) = 163 kJ/mol, B.E. (N–H) = 391 kJ/mol, B.E. (H–H) = 436 kJ/mol

- 24 Using the bond enthalpy data given below, calculate the enthalpy change for the reaction.



Bond	C–C	C = C	C–H	H–H
Bond Enthalpy	336 kJ/mol	606 kJ/mol	410 kJ/mol	431 kJ/mol

25. If at 298 K the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol<sup>-1</sup>, the value of enthalpy change for the reaction : [AIIEE-2003]



will be :-

- (A) +125 kJ (B) –125 kJ (C) +250 kJ (D) –250 kJ

26. The standard enthalpy of formation of NH<sub>3</sub> is –46.0 kJ mol<sup>-1</sup>. If the enthalpy of formation of H<sub>2</sub> from its atoms is –436 kJ mol<sup>-1</sup> and that of N<sub>2</sub> is –712 kJ mol<sup>-1</sup>, the average bond enthalpy of N–H bond in NH<sub>3</sub> is :- [AIIEE-2010]

- (A) –1102 kJ mol<sup>-1</sup> (B) –964 kJ mol<sup>-1</sup> (C) + 352 kJ mol<sup>-1</sup> (D) +1056 kJ mol<sup>-1</sup>

27. If the bond dissociation energies of XY, X<sub>2</sub> and Y<sub>2</sub> (all gaseous diatomic molecules) are in the ratio of 1 : 1 : 0.5 and Δ<sub>r</sub>H for the formation of XY is –200 kJ mol<sup>-1</sup>. The bond dissociation energy of X<sub>2</sub> will be [AIIEE-2005]

- (A) 200 kJ mol<sup>-1</sup> (B) 100 kJ mol<sup>-1</sup> (C) 800 kJ mol<sup>-1</sup> (D) 300 kJ mol<sup>-1</sup>

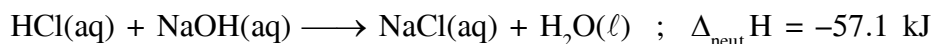
28. The enthalpy of atomization of  $\text{PH}_3(\text{g})$  is  $954 \text{ kJ mol}^{-1}$  and that of  $\text{P}_2\text{H}_4(\text{g})$  is  $1485 \text{ kJ mol}^{-1}$ . What is the bond enthalpy of the P–P bond?
29. The enthalpy changes for the following processes are listed below : [AIEEE-2006]  
 $\text{Cl}_2(\text{g}) = 2\text{Cl}(\text{g}), \quad 242.3 \text{ kJ mol}^{-1}$   
 $\text{I}_2(\text{g}) = 2\text{I}(\text{g}), \quad 151.0 \text{ kJ mol}^{-1}$   
 $\text{ICl}(\text{g}) = \text{I}(\text{g}) + \text{Cl}(\text{g}), \quad 211.3 \text{ kJ mol}^{-1}$   
 $\text{I}_2(\text{s}) = \text{I}_2(\text{g}), \quad 62.76 \text{ kJ mol}^{-1}$   
 Given that the standard states for iodine and chlorine are  $\text{I}_2(\text{s})$  and  $\text{Cl}_2(\text{g})$ , the standard enthalpy of formation for  $\text{ICl}(\text{g})$  is :-  
 (A)  $-16.8 \text{ kJ mol}^{-1}$     (B)  $+16.8 \text{ kJ mol}^{-1}$     (C)  $+244.8 \text{ kJ mol}^{-1}$     (D)  $-14.6 \text{ kJ mol}^{-1}$
30. The standard enthalpy of formation ( $\Delta_f H^\circ$ ) at 298K for methane,  $\text{CH}_4(\text{g})$ , is  $-74.8 \text{ kJ mol}^{-1}$ . The additional information required to determine the average energy for C–H bond formation would be:- [AIEEE-2006]  
 (A) Latent heat of vapourization of methane  
 (B) The first four ionization energies of carbon and electron gain enthalpy of hydrogen  
 (C) The dissociation energy of hydrogen molecule  $\text{H}_2$   
 (D) The dissociation energy of  $\text{H}_2$  and enthalpy of sublimation of carbon
31.  $\text{XeF}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2\text{HF}(\text{g}) + \text{Xe}(\text{g}); \quad \Delta H^\circ = -430 \text{ kJ}$   
 using the following bond energies :  $\text{H}-\text{H} = 435 \text{ kJ/mol}, \text{H}-\text{F} = 565 \text{ kJ/mol}$   
 Calculate the average bond energy of Xe-F in  $\text{XeF}_2$ .
32. Using the given data calculate enthalpy of formation of acetone (g). [All values in  $\text{kJ mol}^{-1}$ ]  
 Bond enthalpy of :  
 $\text{C}-\text{H} = 415$  ;  $\text{C}-\text{C} = 350$  ;  $(\text{C}=\text{O}) = 730$   
 $(\text{O}=\text{O}) = 495.0$  ;  $\text{H}-\text{H} = 435$  ;  $\Delta_{\text{sub}} H$  of C = 720

#### 7.4 ENTHALPY OF NEUTRALISATION, $\Delta_{\text{neut}} H^\circ$ :

The reaction in which an acid and a base react to give a salt and water is called neutralization reaction. Neutralization reactions are exothermic in nature. The enthalpy change when one gram equivalent of an acid and one gram equivalent of a base neutralise each other completely in dilute aqueous solution, is called enthalpy of neutralization.

For examples :

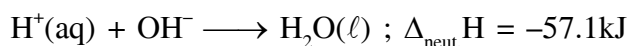
(i) Neutralization of HCl with NaOH



(ii) Neutralization of  $\text{CH}_3\text{COOH}$  with NaOH

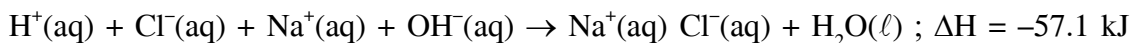


It is important to note that the term gram equivalent is used in the definition of heat of neutralization. This is because neutralization involves 1 mole of  $\text{H}^+$  ions and 1 mole of  $\text{OH}^-$  ions to form 1 mole of water and 57.1 kJ of heat is liberated.

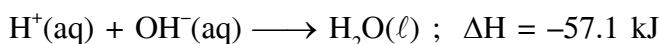


Now, one gram equivalent of various acids on complete dissociation liberates one mole of  $\text{H}^+$  ions. But one mole of the acid may produce more than one mole of  $\text{H}^+$  ions in solution depending upon its basicity; for example 1 mol of  $\text{H}_2\text{SO}_4$  gives 2 mol of  $\text{H}^+$  ions and 1 mol of  $\text{H}_3\text{PO}_4$  gives 3 mol of  $\text{H}^+$  ions on complete dissociation. But 1 gram equivalent of both ( $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ ) produces only 1 mol of  $\text{H}^+$  ions. Thus, it is more appropriate to use the term gram equivalent in the definition of enthalpy of neutralization.

The average enthalpy of neutralization of any strong acid by a strong base is found to be  $-57.1$  kJ/eq. This is because strong acids and strong bases are completely ionized in aqueous solutions. The aqueous solution of one gram equivalent of all strong acids contain the same number of  $H^+$  ions. Similarly, aqueous solution of one gram equivalent of all strong bases also contain same number of  $OH^-$ . The neutralization reactions between strong acids and strong bases in aqueous solutions involve simply the combination of  $H^+$  ions (from an acid) and  $OH^-$  ions (from a base) to form unionized water molecules. For example, the reaction between hydrochloric acid and sodium hydroxide. The neutralization can be represented as :



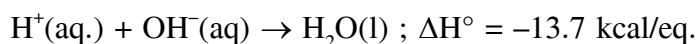
Cancelling common ions :



(i)  $\Delta_{\text{neut}} H$  for any strong acid by any strong base is almost constant.

$$\Delta_{\text{neut}} \Delta(H^+/OH^-) = -57.1 \text{ kJ/mole}^{-1} = -13.7 \text{ kcal mol}^{-1}$$

It is due to the only enthalpy change occurring in such process which is



(ii) If any of the acid or base is weak, the numerical value of  $\Delta_{\text{neut}} H$  decreases from 13.7 kcal by enthalpy of ionization for the weak component. **The weak component is assumed completely unionised in solution.**

**Ex5.** The acids HA, HB & HC are neutralised separately by NaOH. If  $\Delta_{\text{neut}} H$  are  $-12.1$ ,  $-3.9$  &  $-7.2$  kcal/eq. Arrange the acids in the increasing order of their acidic strength.

**Sol:**  $A > C > B$

**Ex.6.**  $\Delta_{\text{neut}} H$  of  $H_2C_2O_4$  by NaOH is  $-8.7$  kcal/mol,  $\Delta_{\text{ion}} H$  of oxalic acid is

**Sol :**  $-27.4 + H_{\text{ion}} = -8.7$

$$\therefore \Delta_{\text{ion}} H = +18.7 \text{ kcal/mol}$$

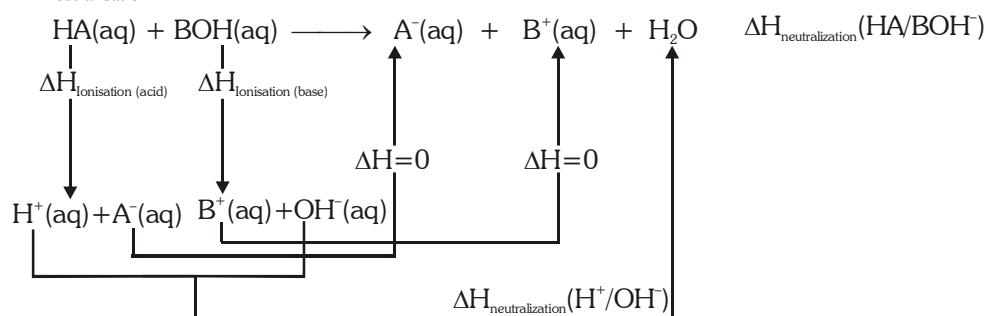
### 7.4.1 The enthalpy of neutralization of weak acid and weak base :

Consider the neutralisation of weak acid HA with weak base BOH.

Where,  $\Delta H_{\text{ionisation}}(HA)$  = Enthalpy of ionization of acid HA = Enthalpy to ionize 1 mole of weak acid in aq. soln.

$\Delta H_{\text{ionisation}}(BOH)$  = Enthalpy of ionization of base BOH

$\Delta H_{\text{neutralisation}}(H^+/OH^-)$  = Enthalpy change for the reaction of  $H^+$  and  $OH^-$  to form water.



Thus for weak acid :

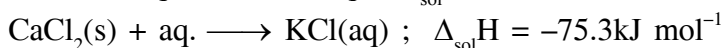
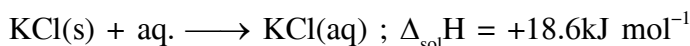
$$\Delta H_{\text{neut}}(BOH/HA) = \Delta H_{\text{ion.}}(HA) + \Delta H_{\text{ion.}}(BOH) + \Delta H_{\text{neut}}(H^+/OH^-)$$

## EXERCISE-V

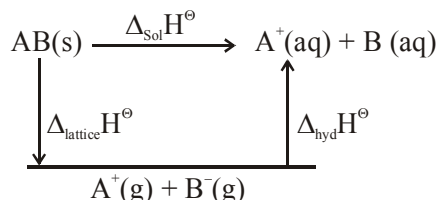
- 33 Calculate the enthalpy of ionisation of weak acid  $H_2A$  ( $H_2A \rightarrow 2H^+ + A^{2-}$ ) in Kcal/ mol, if enthalpies of neutralisation of HCl and  $H_2A$  by a strong base are  $-14$  Kcal/eq and  $-11$  Kcal/eq respectively.
- 34 Enthalpy of neutralization of  $H_3PO_3$  acid is  $-106.68$  kJ/mol using NaOH. If enthalpy of neutralization of HCl by NaOH is  $-55.84$  kJ/mol. Calculate  $\Delta H_{\text{ionization}}$  of  $H_3PO_3$  into its ions  
 (A) 50.84 kJ/mol      (B) 5 kJ/mol      (C) 2.5 kJ/mol      (D) 60.84 kJ/mol

7.5 ENTHALPY OF SOLUTION,  $\Delta_{\text{sol}}H^\ominus$  :

When a solute is dissolved in a solvent, a solution is formed. During dissolution of a solute in any solvent, a certain amount of heat is either absorbed or evolved. The change in enthalpy when one mole of a solute is dissolved in a specified quantity of a solvent at a given temperature is called enthalpy of solution. To avoid the amount of solvent, enthalpy of solution is usually defined for an infinite dilute solution. Thus, enthalpy of solution at infinite dilution is the enthalpy change when one mole of a substance is dissolved in such a large quantity of solvent so that further dilution does not give any further enthalpy change.



When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s)



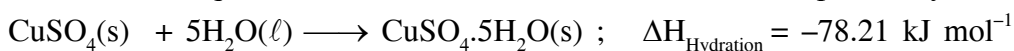
The enthalpy of solution of AB(s),  $\Delta_{\text{sol}}H^\ominus$ , in water is, therefore, determined by the selective values of the lattice enthalpy,  $\Delta_{\text{lattice}}H^\ominus$  and enthalpy of hydration of ions,  $\Delta_{\text{hyd}}H^\ominus$  as

$$\Delta_{\text{sol}}H^\ominus = \Delta_{\text{lattice}}H^\ominus + \Delta_{\text{hyd}}H^\ominus$$

For most of the ionic compounds,  $\Delta_{\text{sol}}H^\ominus$  is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature.

7.6 ENTHALPY OF HYDRATION,  $\Delta_{\text{Hyd}}H^\ominus$  :

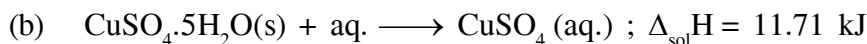
This is defined as the enthalpy change (evolved or absorbed) when one mole of the anhydrous salt combines with the required number of moles of water to form the specific hydrated salt.



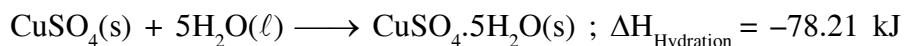
Hydration is generally exothermic change.

If enthalpy of solution of the hydrated and anhydrous salt is known, then heat of hydration can be calculated.

**For example :**



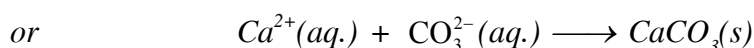
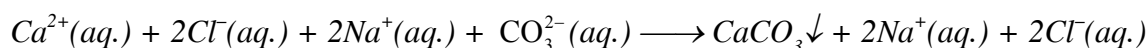
Thus, (a – b) gives



**Ex.7.** Calculate the enthalpy change when infinitely dilute solutions of  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  mixed.  $\Delta\text{H}_f^0$  for  $\text{Ca}^{2+}(\text{aq.})$ ,  $\text{CO}_3^{2-}(\text{aq.})$  and  $\text{CaCO}_3(\text{s})$  are  $-129.80$ ,  $-161.65$ ,  $-288.5 \text{ kcal mole}^{-1}$  respectively.

**Sol :** On mixing  $\text{CaCl}_2(\text{aq.})$  and  $\text{Na}_2\text{CO}_3$   
 $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3\downarrow + 2\text{NaCl}$

Solutions are very dilute and thus 100% dissociation occurs.



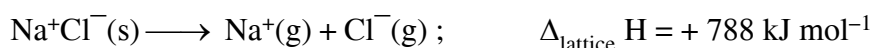
$$\therefore \Delta\text{H} = \sum \text{H}_{\text{products}}^0 - \sum \text{H}_{\text{reactants}}^0$$

or  $\Delta\text{H} = \text{H}_{\text{fCaCO}_3}^0 - [\text{H}_{\text{fCa}^{2+}}^0 + \text{H}_{\text{fCO}_3^{2-}}^0]$

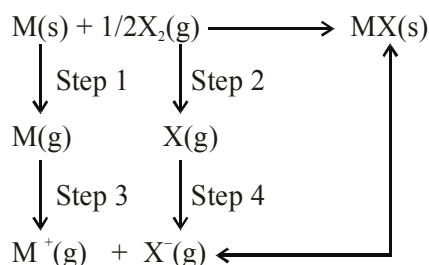
$$\therefore \Delta\text{H}^{\circ} \text{ of a compound} = \Delta\text{H}^{\circ} \text{ formation} = -288.5 - (-129.8 - 161.65) = 2.95 \text{ kcal}$$

## 7.7 LATTICE ENTHALPY ( $\Delta_{\text{lattice}}\text{H}$ ) :

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state under conditions of constant temperature and pressure.



**7.7.1 Determination of lattice energy (Born-Haber cycle) :** Since, it is impossible to find the lattice enthalpies by direct experiment, it is generally calculated by indirect method known as **Born-Haber cycle**.



**Born-Haber cycle**

The change in enthalpy that occurs when 1 mole of a solid crystalline substance is formed from its gaseous ions.



- Step 1 :** Conversion of metal to gaseous atoms.  
 $M(s) \longrightarrow M(g), \Delta H_1 = \text{sublimation energy}$
- Step 2 :** Dissociation of  $X_2$  molecules to X atoms  
 $X_2(g) \longrightarrow 2X(g), \Delta H_2 = \text{Dissociation energy}$
- Step 3 :** Conversion of gaseous metal atom to metal ions by losing electron  
 $M(g) \longrightarrow M^+(g) + e^-, \Delta H_3 = \text{Ionization enthalpy}$
- Step 4 :** X(g) atoms gain an electron to form  $M^-$  ions  
 $X(g) + e^- \longrightarrow X^-(g), \Delta H_4 = \text{Electron gain enthalpy}$
- Step 5 :**  $M^+(g)$  and  $X^-(g)$  get together and form the crystal lattice  
 $M^+(g) + X^-(g) \longrightarrow MX(s), \Delta H_5 = \text{Lattice enthalpy}$
- Applying Hess's law we get

$$\Delta H_1 + \frac{1}{2}\Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 = \Delta H_f(MX)$$

On putting the various known values, we can calculate the lattice energy.

**Ex.8.** Calculate the proton affinity of  $NH_3(g)$  from the following data (in kJ/mole)

$$\Delta H_{\text{dissociation}}^0 : H_2(g) = 218$$

$$\Delta H_{\text{formation}}^0 : NH_3(g) = -46$$

$$\text{Lattice energy of } NH_4Cl = -683$$

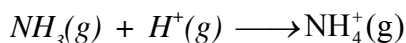
$$\text{Ionisation energy of } H = 1310$$

$$\text{Electron affinity of } Cl = 348$$

$$\text{Bond dissociation energy } Cl_2(g) = 124$$

$$\Delta H_{\text{formation}}^0 : NH_4Cl(s) = -314$$

**Sol:** We have to calculate  $\Delta H$  for the following equation



$$\text{Given : } H_2(g) \longrightarrow 2H(g) \quad : \quad \Delta H_1 = 218 \text{ kJ/mole}$$

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) \quad : \quad \Delta H_2 = -46 \text{ kJ/mole}$$

$$NH_4Cl(s) \longrightarrow NH_4^+(g) + Cl^-(g) \quad : \quad \Delta H_3 = +683 \text{ kJ/mole}$$

$$H(g) \longrightarrow H^+(g) \quad : \quad \Delta H_4 = 1310 \text{ kJ/mole}$$

$$Cl(g) \longrightarrow Cl^-(g) \quad : \quad \Delta H_5 = -348 \text{ kJ/mole}$$

$$Cl_2(g) \longrightarrow 2Cl(g) \quad : \quad \Delta H_6 = 124 \text{ kJ/mole}$$

$$\frac{1}{2}N_2(g) + 2H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow NH_4Cl(s) \quad : \quad \Delta H_7 = -314 \text{ kJ/mole}$$

$$\Delta H = -\frac{1}{2}(\Delta H_1) - \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5 - \frac{1}{2}(\Delta H_6) + \Delta H_7$$

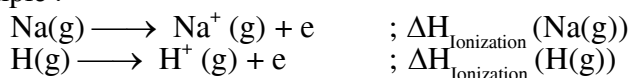
$$= -\frac{1}{2} \times 218 + 46 + 683 - 1310 + 348 - \frac{1}{2} \times 124 - 314$$

$$= -768 \text{ kJ/mole}$$

**7.8 IONISATION ENTHALPY,  $\Delta_i H$  :**

Enthalpy change when one mole of gaseous atom is converted into gaseous ion by removing one mole electron from ground state is called ionisation enthalpy.

Example :

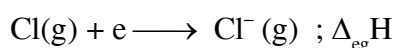


$$\Delta_i H = \text{I.E.} + \frac{5}{2} RT$$

**7.9 ELECTRON GAIN ENTHALPY,  $\Delta_{\text{eg}} H$  :**

Enthalpy change when 1 mole electrons are added to valence shell of gaseous atoms is called electron gain enthalpy.

Example :

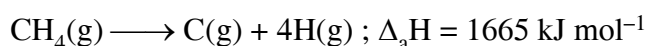
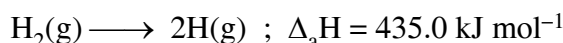


$$\Delta_{\text{eg}} H = -E_a - \frac{5}{2} RT$$

**7.10 ENTHALPY OF ATOMISATION,  $\Delta_a H$  :**

It is the enthalpy change (always positive) when one mole of a substance is completely dissociated into atoms in the gaseous state, under constant pressure and temperature condition.

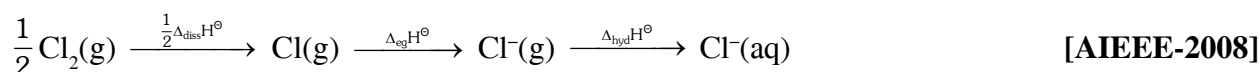
For example

**7.11 ENTHALPY OF TRANSITION (Enthalpy of allotropic form) ,  $\Delta_{\text{trs}} H$  :**

It is the enthalpy change when one mole of one allotropic form changes to another under conditions of constant temperature and pressure. For example

**EXERCISE-VI**

35. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:



The energy involved in the conversion of  $\frac{1}{2} \text{Cl}_2(\text{g})$  to  $\text{Cl}^-(\text{aq})$

(using the data  $\Delta_{\text{diss}} H_{\text{Cl}_2}^\circ = 240 \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{eg}} H_{\text{Cl}}^\circ = -349 \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{hyd}} H_{\text{Cl}^-}^\circ = -381 \text{ kJ mol}^{-1}$ ) will be:-

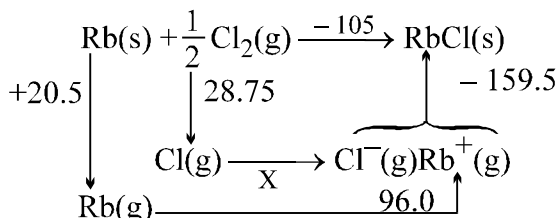
(A)  $-610 \text{ kJ mol}^{-1}$  (B)  $-850 \text{ kJ mol}^{-1}$  (C)  $+120 \text{ kJ mol}^{-1}$  (D)  $+152 \text{ kJ mol}^{-1}$

36. The lattice enthalpy of solid NaCl is  $772 \text{ kJ mol}^{-1}$  and enthalpy of solution is  $2 \text{ kJ mol}^{-1}$ . If the hydration enthalpy of  $\text{Na}^+$  &  $\text{Cl}^-$  ions are in the ratio of 3:2.5, what is the enthalpy of hydration of chloride ion?

(A)  $-140 \text{ kJ mol}^{-1}$  (B)  $-350 \text{ kJ mol}^{-1}$  (C)  $-351.81 \text{ kJ mol}^{-1}$  (D)  $-420 \text{ kJ/mol}$

37. The enthalpy of solution of anhydrous  $\text{CuSO}_4$  is  $-16 \text{ kcal}$  and that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is  $3 \text{ kcal}$ . Calculate the enthalpy of hydration of  $\text{CuSO}_4$ .

- 38 Calculate the electron gain enthalpy of fluorine atom using the following data . (All the values are in kJ mol<sup>-1</sup> at 25° C).  $\Delta H_{\text{diss}}(\text{F}_2) = 160$ ,  $\Delta_f H(\text{NaF(s)}) = -571$ , I.E.  $[\text{Na(g)}] = 494$ ,  $\Delta H_{\text{sub}}[\text{Na(s)}] = 101$ , Lattice enthalpy of  $\text{NaF(s)} = 894$ .
- 39 The Born–Haber cycle for formation of rubidium chloride (RbCl) is given below (the enthalpies are in k Cal mol<sup>-1</sup>)



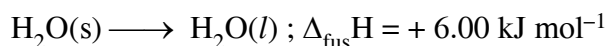
Find the value of X.

- 40 By using the following data, calculate the enthalpy change of hydration of (i) the chloride ion ; (ii) the iodide ion.
- enthalpy change of solution of  $\text{NaCl(s)} = -2$  kJ/mol.  
 enthalpy change of solution of  $\text{NaI(s)} = +2$  kJ/mol.  
 enthalpy change of hydration of  $\text{Na}^+(\text{g}) = -390$  kJ/mol.  
 lattice enthalpy of  $\text{NaCl} = -772$  kJ/mol.  
 lattice enthalpy of  $\text{NaI} = -699$  kJ/mol.

### 7.12 ENTHALPY CHANGES DURING PHASE TRANSFORMATIONS :

- (i) **Enthalpy of Fusion,  $\Delta_{\text{fus}} H$**  : It is the enthalpy change that accompanies melting of one mole of a solid substance at constant temperature (melting point of solid) and pressure.

For example,



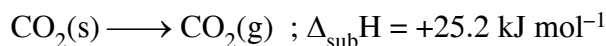
- (ii) **Enthalpy of Vaporisation,  $\Delta_{\text{vap}} H$**  :

It is the enthalpy change to vapourise one mole of a liquid substance at constant temperature (boiling point of liquid) and pressure for example :



- (iii) **Enthalpy of Sublimation,  $\Delta_{\text{sub}} H$**  :

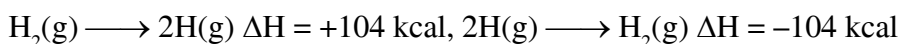
It is the amount of enthalpy change to sublime one mole of a solid substance at constant temperature (sublimation temperature of solid) and pressure. For example



## 8. LAWS OF THERMOCHEMISTRY

- (i) **Lavoisier and Laplace law :**

Heat absorbed or evolved in a process is equal to the heat evolved or absorbed when the process is reversed.



It follows from this law that thermochemical equation may be reversed.

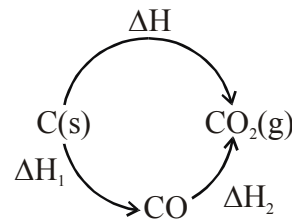
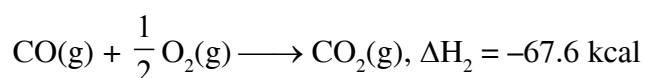
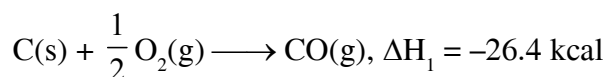
**(ii) Hess's law of constant heat summation :**

Heat change of a process is the same whether the process takes place in one step or several steps. It follows from this law that the thermochemical equation may be treated like algebraic equations. Hess's law is helpful in calculating those heat changes which cannot be determined experimentally. It has been experimentally verified and is also a consequence of the law of conservation of energy.

For example : Carbon can be converted into  $\text{CO}_2$  in 1 step



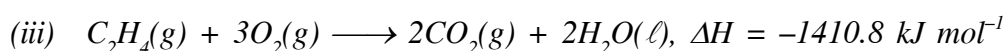
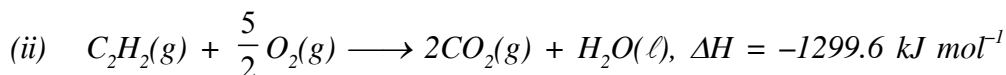
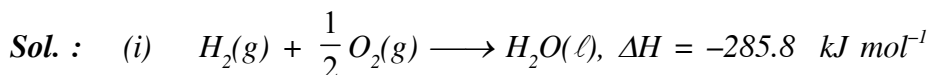
Or in two steps



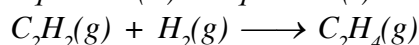
According to Hess's law :  $\Delta H = \Delta H_1 + \Delta H_2 = -26.4 - 67.6 = -94 \text{ kcal}$ .

**Ex.9.** Calculate the heat of reaction for the hydrogenation of acetylene to ethylene at constant volume at  $25^\circ\text{C}$  from the following data.

- (i) Enthalpy of formation of water =  $-285.8 \text{ kJ mol}^{-1}$
- (ii) Enthalpy of combustion of acetylene =  $-1299.6 \text{ kJ mol}^{-1}$
- (iii) Enthalpy of combustion of ethylene =  $-1410.8 \text{ kJ mol}^{-1}$



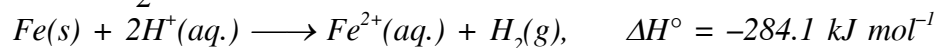
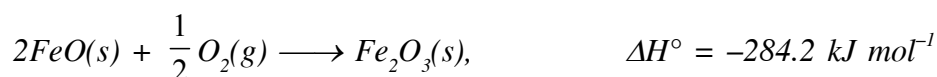
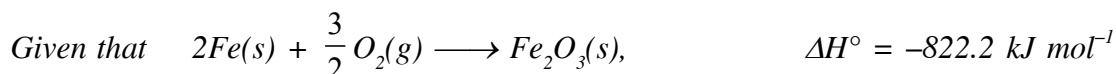
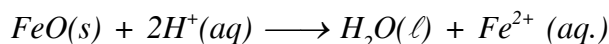
Equation (ii) + equation (i) - equation (iii), we get



$$\Delta H = -1299.6 - 285.8 + 1410.8 = -174.6 \text{ kJ mol}^{-1}$$

$$\Delta E = -174.6 - (-1)(8.314 \times 10^{-3})(298) = -172.12 \text{ kJ mol}^{-1}$$

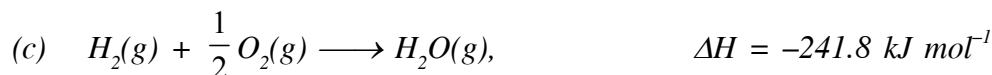
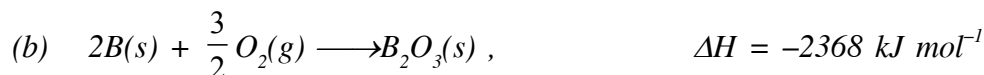
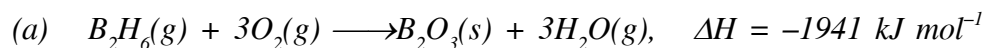
**Ex.10.** Calculate  $\Delta H^\circ$  for the reaction



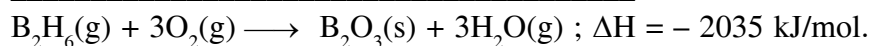
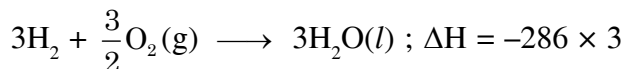
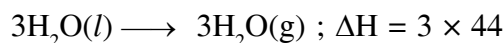
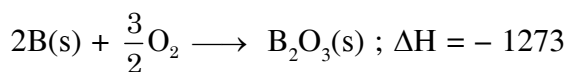
Sol. Eq.(iii) + Eq.(iv) -  $\frac{1}{2}$  × Eq. (i) +  $\frac{1}{2}$  × Eq.(ii).

$$\Delta H_{\text{required}}^{\circ} = (-286.0) + (-284.1) - \frac{1}{2} (-822.2) + \frac{1}{2} (-284.2) = -301.1 \text{ kJ/mol.}$$

**Ex.11.** From the following data, determine  $\Delta H_f^{\circ}(\text{B}_2\text{H}_6)$  at 298 K;



**Sol. Sol.**  $\text{B}_2\text{H}_6(\text{g}) \longrightarrow 2\text{B}(\text{s}) + 3\text{H}_2(\text{g}); \Delta H = -36$



For eq.(a),

$$(-1941) = [(-2368) + 3(-241.8)] - [\Delta_f H_{\text{B}_2\text{H}_6(\text{g})}^{\circ} + 3 \times 0]$$

$$\therefore [\Delta_f H_{\text{B}_2\text{H}_6(\text{g})}^{\circ}] = -1152.4 \text{ kJ/mol.}$$

**ANSWER KEY****EXERCISE-I**

1. Ans.(D)                      2. Ans.(A)                      3. Ans. (D)                      4. Ans.(B)  
 5. Ans.(B)                      6. Ans.  $-741.5 \text{ kJ/mole}$   
 7. Ans.  $-3.502 \text{ kJ}$

**EXERCISE-II**

8. Ans.  $602.49 \text{ kJ}$                       9. (i)  $-885 \text{ kJ/mol}$  (ii)  $-889.99 \text{ kJ/mol}$   
 10.  $W = 0, \Delta U = -31.723 \text{ J}$

**EXERCISE-III**

11. Ans.(D)                      12. Ans.(D)                      13. Ans.(B)                      14. Ans. (B)  
 15. Ans. (D)                      16. Ans.(C)                      17. Ans.(D)                      18. Ans.(D)  
 19. Ans.(D)                      20.  $129 \text{ kJ}$                       21.  $-1560.1 \text{ kJ mol}^{-1}$

**EXERCISE-IV**

21. Ans.(C)                      22. Ans.(+  $20.6 \text{ kcal/mol.}$ )  
 23. Ans. ( $400 \text{ kJ/mole}$ )                      24. Ans.  $-119 \text{ kJ/mol}$   
 25. Ans.(B)                      26. Ans.(C)                      27. Ans.(C)  
 28.  $213 \text{ kJ / mol}$                       29. Ans.(B)                      30. Ans.(D)  
 31. Ans  $132.5 \text{ kJ/mol}$                       32.  $-207.5 \text{ kJ mol}^{-1}$

**EXERCISE-V**

33. Ans.(6)                      34. Ans.(B)

**EXERCISE-VI**

35. Ans.(A)                      36. Ans.(B)                      37.  $-19 \text{ kcal / mole}$   
 38.  $-352 \text{ kJ mol}^{-1}$                       39.  $-90.75 \text{ kcal mol}^{-1}$   
 40. for  $\text{Cl}^-$   $-384 \text{ kJ mol}^{-1}$ , for  $\text{I}^-$   $-307 \text{ kJ mol}^{-1}$

## MISCELLANEOUS PREVIOUS YEARS QUESTION

Q.1 Which of the following is not an endothermic reaction?

- (A) Combustion of methane  
 (B) Decomposition of water  
 (C) Dehydrogenation of ethene to acetylene  
 (D) Conversion of graphite to diamond

[JEE 1999]

**Q.1 Ans.(A)**

**Sol.** Combustion reaction is always an exothermic reaction

Q.2 Estimate the average S–F bond enthalpy in SF<sub>6</sub>. The ΔH<sub>f</sub><sup>0</sup> values of SF<sub>6</sub>(g), S(g), and F(g) are –1100, 275 and 80 kJ/mol respectively. [JEE 99, 5]

Q.2 309.16 kJ/mol

**Sol.** SF<sub>6</sub>(g) → S(g) + 6F(g)

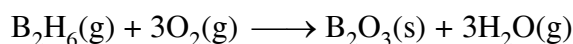
$$\Delta H_{\text{rxn}}^0 = \Delta H_{\text{f}}^0[\text{S}(\text{g})] + 6\Delta H_{\text{f}}^0[\text{F}(\text{g})] - \Delta H_{\text{f}}^0[\text{SF}_6(\text{g})]$$

$$\Delta H_{\text{rxn}}^0 = 275 + (6 \times 80) + 1100$$

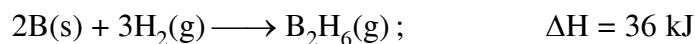
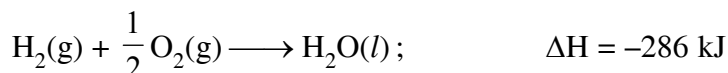
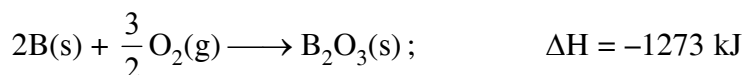
$$\Delta H_{\text{rxn}}^0 = 1855$$

$$(\text{S} - \text{F}) = \frac{\Delta H_{\text{rxn}}^0}{6} = \frac{1855}{6} = 309.166 \text{ kJ/mol.}$$

Q.3 Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

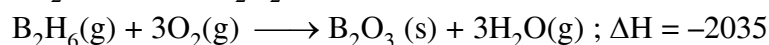
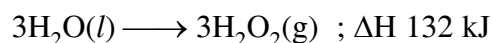
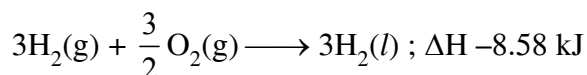
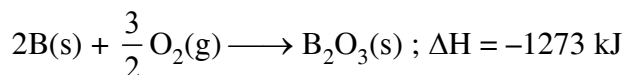


From the following data, calculate the enthalpy change for the combustion of diborane : [JEE 2000]

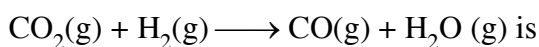


**Q.3 –2035 kJ mol<sup>-1</sup>**

**Sol.** B<sub>2</sub>H<sub>6</sub>(g) → 2B(s) + 3H<sub>2</sub>(g); ΔH = –36 kJ



Q.4  $\Delta H_f^\circ$  for  $\text{CO}_2(\text{g})$ ,  $\text{CO}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are  $-393.5$ ,  $-110.5$  and  $-241.8$   $\text{kJ mol}^{-1}$  respectively. The standard enthalpy change (in kJ) for the reaction



- (A) 524.1                      (B) 41.2                      (C)  $-262.5$                       (D)  $-41.2$  [JEE 2000]

Q.4 Ans.(B)

Sol.  $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$

$$\Delta H_{\text{rxn}}^\circ = (\Delta H_f^\circ[\text{CO}(\text{g})] + \Delta H_f^\circ[\text{H}_2\text{O}(\text{g})]) - (\Delta H_f^\circ[\text{CO}_2(\text{g})] + \Delta H_f^\circ[\text{H}_2(\text{g})])$$

$$\Delta H_{\text{rxn}}^\circ = (-110.5 - 241.8) - (-393.5 + 0)$$

$$= +41.2 \text{ kJ/mol}$$

Q.5 Which of the following reactions defines  $\Delta H_f^\circ$ ?

- (A)  $\text{C}_{(\text{diamond})} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$                       (B)  $1/2 \text{H}_2(\text{g}) + 1/2 \text{F}_2(\text{g}) \longrightarrow \text{HF}(\text{g})$   
 (C)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3$                       (D)  $\text{CO}(\text{g}) + 1/2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  [JEE 2003]

Q.5 Ans.(B)

Sol. In the formation reaction, 1 mole products should be formed from its elements and elements must be in their most abundance state this condition is fulfilled by options (B)

Q.6 In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5  $\text{kJ K}^{-1}$ , the numerical value for the enthalpy of combustion of the gas in  $\text{kJ mol}^{-1}$  is

[JEE 2009]

Q.6 Ans.(9)

Sol.  $q = (2.5)(0.45) = 1.125$

$$\Delta U_{\text{combination}} = (1.125) \left( \frac{28}{3.5} \right) = -9 \text{ kJ/mol}$$



## EXERCISE (S-I)

Relationship between  $\Delta H$  &  $\Delta U$ 

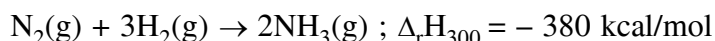
Q.1 The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of  $H_2$  at 1.5 bar pressure is  $\Delta H = -0.31$  KJ. What is the  $\Delta U$  ? **TC0001**

Q.2 Ethyl chloride ( $C_2H_5Cl$ ), is prepared by reaction of ethylene with hydrogen chloride:



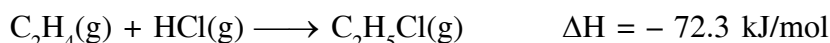
What is the value of  $\Delta E$  (in kJ), if 98 g of ethylene and 109.5 g of HCl are allowed to react at 300 K. **TC0002**

Q.3 Determine the amount of heat (in kcal) given off at constant volume when 0.5 mol of  $N_2$  & 1.5 mol of  $H_2$  reacted according to equation at 300 K.



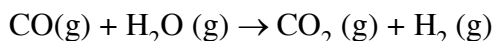
(Given :  $R = 2 \text{ cal / mol-K}$ ) **TC0003**

Q.4 Ethyl chloride ( $C_2H_5Cl$ ), is prepared by reaction of ethylene with hydrogen chloride :



What is the value of  $\Delta U$  (in kJ), if 70 g of ethylene and 73 g of HCl are allowed to react at 300 K. **TC0004**

Q.5 Determine  $\Delta H$  for the following reaction at 500K and constant pressure :



use the following data :

Substance	$C_p$ (J/mol K)	$\Delta_f H$ (300K) (kJ/mol)
CO (g)	29	-110
$H_2O$ (g)	33	-241
$CO_2$ (g)	37	-393
$H_2$ (g)	29	0

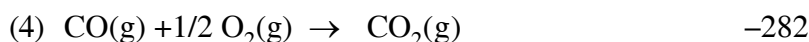
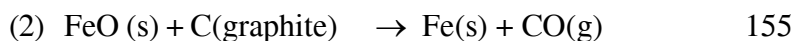
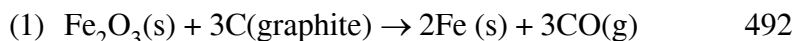
**TC0005**

## Enthalpy of formation and combustion

Q.6 When 2 moles of  $C_2H_6(g)$  are completely burnt, 3120 kJ of heat is liberated . Calculate the enthalpy of formation, of  $C_2H_6(g)$  . Given  $\Delta_f H$  for  $CO_2(g)$  &  $H_2O(l)$  are  $-395$  &  $-286$  kJ respectively. **TC0006**

Q.7 From the following data at  $25^\circ C$ , Calculate the standard enthalpy of formation of  $FeO(s)$  and of  $Fe_2O_3(s)$ .

**Reaction**  **$\Delta_r H^\circ$  (kJ/mole)**



**TC0007**

Q.8 At 300 K, the standard enthalpies of formation of  $C_6H_5COOH(s)$ ,  $CO_2(g)$  &  $H_2O(l)$  are  $-408$ ,  $-393$  &  $-286$  kJ mol $^{-1}$  respectively . Calculate the heat of combustion of benzoic acid at : (i) constant pressure (ii) constant volume. **TC0008**

- Q.9 A cylinder of gas is assumed to contain 11.6 kg of butane. If a normal family needs 26,500 kJ of energy per day for cooking, how long will the cylinder last if the enthalpy of combustion,  $\Delta H = -2650$  kJ/mole for butane. **TC0009**
- Q.10 0.821 l sample of a mixture of  $\text{CH}_4(\text{g})$  &  $\text{O}_2(\text{g})$  measured at  $27^\circ\text{C}$  & 760 torr was allowed to react at constant pressure in a calorimeter which together with its contents had a heat capacity of 1200 Cal/K. The complete combustion of methane to  $\text{CO}_2$  &  $\text{H}_2\text{O}$  caused a temperature rise, in the calorimeter, of 0.25 K. What was the mole percent of  $\text{CH}_4$  in the original mixture?  
 $\Delta H^\circ_{\text{comb}}(\text{CH}_4) = -200$  kcal mol $^{-1}$ . **TC0010**

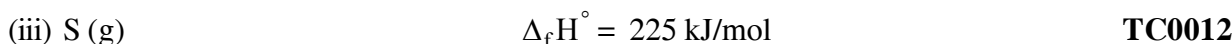
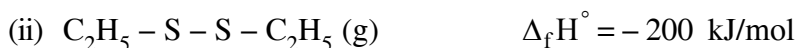
**Bond Enthalpy**

- Q.11 Compute the enthalpy of formation of liquid methyl alcohol in kJ mol $^{-1}$ , using the following data. Enthalpy of vaporisation of liquid  $\text{CH}_3\text{OH} = 38$  kJ/mol. Enthalpy of formation of gaseous atoms from the elements in their standard states are  
 $\text{H} \rightarrow 218$  kJ/mol ;  $\text{C} \rightarrow 715$  kJ/mol ;  $\text{O} \rightarrow 249$  kJ/mol.

Bond Enthalpies

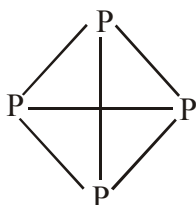


- Q.12 Find the enthalpy of S-S bond from the following data.

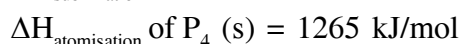
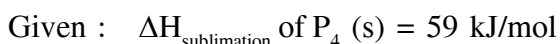


- Q.13 The polymerisation of ethylene to linear polyethylene is represented by the reaction  
 $n \text{CH}_2 = \text{CH}_2(\text{g}) \rightarrow (-\text{CH}_2 - \text{CH}_2)_n (\text{g})$   
 where n has a large integral value. Given that the average enthalpies of bond dissociation for C=C & C-C at 298 K are +590 & +331 kJ mol $^{-1}$  respectively. Calculate the enthalpy of polymerisation per mole of ethylene at 298 K. **TC0013**

- Q.14 White phosphorus is a tetra-atomic solid  $\text{P}_4 (\text{s})$  at room temperature.



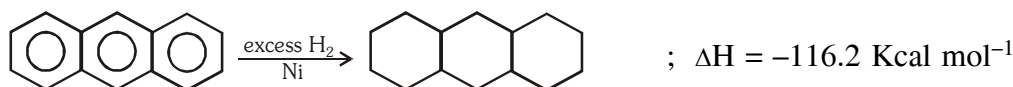
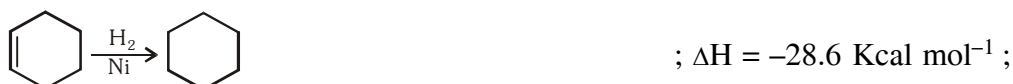
Find average (P-P) bond enthalpy in kJ/mol.

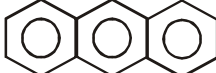


- Q.15 Calculate enthalpy of combustion of propane [ $\text{C}_3\text{H}_8 (\text{g})$ ] in kJ/mol at 298 K.



Q.16 Use the following data to answer the questions below :



Calculate the resonance energy of anthracene,  **TC0016**

Q.17 Calculate the magnitude of resonance enthalpy of  $\text{CO}_2(\text{g})$  from following data

$$\Delta H_{\text{combustion}}^{\circ}[\text{C}_{(\text{graphite})}] = -390 \text{ kJ/mol}$$

$$\Delta H_{\text{atomisation}}^{\circ}[\text{C}_{(\text{graphite})}] = 715 \text{ kJ/mol}$$

$$\Delta H_{\text{B.E.}}^{\circ}[\text{O}=\text{O}] = 500 \text{ kJ/mol}$$

$$\Delta H_{\text{B.E.}}^{\circ}[\text{C}=\text{O}] = 800 \text{ kJ/mol} \quad \text{TC0017}$$

*Other types of Enthalpy of reaction*

Q.18  $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} \quad ; \Delta H^{\circ} = -57 \text{ kJ/mol}$

$$\Delta H_{\text{ionisation}}^{\circ}[\text{HCN}] = 45 \text{ kJ/mol}$$

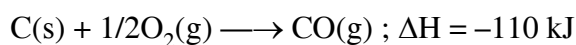
If 200 ml, 1/10 M  $\text{Ba}(\text{OH})_2$  solution is mixed with 500 ml, 1/10M HCN, then evolved heat will be. **TC0018**

Q.19 The enthalpies of neutralization of NaOH &  $\text{NH}_4\text{OH}$  by HCl are  $-13680 \text{ Cal/Eq}$  and  $-12270 \text{ Cal/Eq}$ . respectively. What would be the enthalpy change if one gram equivalent of NaOH is added to one gram equivalent of  $\text{NH}_4\text{Cl}$  in solution? Assume that  $\text{NH}_4\text{OH}$  and NaCl are quantitatively obtained. **TC0019**

Q.20 Two solutions initially at  $25^{\circ}\text{C}$  were mixed in an adiabatic constant pressure calorimeter. One contains 400 ml of 0.2 M weak monoprotic acid solution. The other contain 100 ml of 0.80 M NaOH. After mixing temperature increased to  $26.2^{\circ}\text{C}$ . How much heat is evolved in the neutralization of 1 mole of acid? Assume density of solution  $1.0 \text{ g/cm}^3$ , and specific heat of solution  $4.2 \text{ J/g-K}$ . Neglect heat capacity of the calorimeter. **TC0020**

Q.21 If the enthalpy of formation of HCl (g) and  $\text{Cl}^- (\text{aq})$  are  $-90 \text{ kJ/mole}$  and  $-170 \text{ kJ/mol}$ , find the enthalpy of solution of hydrogen chloride gas. **TC0021**

Q.22 From the following data of  $\Delta H$  of the following reactions



Calculate the mole ratio of steam and oxygen on being passed over coke at  $1273 \text{ K}$ , keeping the reaction temperature constant. **TC0022**



## EXERCISE (S-II)

- Q.1 The enthalpy of formation of  $C_2H_5OH(l)$  is  $-66$  k Cal/mol. The enthalpy of combustion of  $CH_3-O-CH_3$  is  $-348$  k Cal/mol. Given that the enthalpies of formation of  $CO_2(g)$  and  $H_2O(l)$  are  $-94$  k Cal/mol &  $-68$  kcal/mol respectively, calculate  $\Delta H$  for the isomerisation of ethanol to methoxymethane. All data are at  $25^\circ C$ . **TC0026**
- Q.2 Calculate the mass of mercury which can be liberated from  $HgO$  at  $27^\circ C$  by the treatment of excess  $HgO$  with  $9$  kJ of heat at (a) constant pressure, (b) constant volume  
Given :  $\Delta H_f^\circ (HgO, s) = -90$  kJ mol $^{-1}$  & Molar mass of  $(Hg) = 200$  g mol $^{-1}$ . **TC0027**
- Q.3 A stoichiometric mixture of ferric oxide & Al is used as solid rocket fuel. Calculate the fuel value per gm & fuel value per CC of the mix. Enthalpy of formation & densities are :  
 $\Delta H_f^\circ (Al_2O_3) = -399$  k Cal/mole ;  $\Delta H_f^\circ (Fe_2O_3) = -199$  kcal / mole,  
density of  $Fe_2O_3 = 5.2$  g/cc ; density of Al =  $2.7$  g/cc. **TC0028**
- Q.4 Calculate the enthalpy change for the reaction :  $XeF_4 \longrightarrow Xe^+ + F^- + F_2 + F$ .  
The average Xe-F bond enthalpy is  $34$  kcal/mol, first I.E. of Xe is  $279$  kcal/mol, electron affinity of F is  $85$  kcal/mol & bond dissociation enthalpy of  $F_2$  is  $38$  kcal/mol. **TC0029**
- Q.5 Calculate the bond enthalpy of the O-H bond in water at  $298K$  using the data/information given below :-  
(A)  $\Delta_f H^\circ [H(g)] = 218$  kJ/mol  
(B)  $\Delta_f H^\circ [O(g)] = 249.2$  kJ/mol  
(C)  $\Delta_f H^\circ [H_2O(g)] = -241.8$  kJ/mol  
The bond enthalpy of the O-H bond in water is defined as one-half of the enthalpy change for the reaction  $H_2O(g) \rightarrow 2H(g) + O(g)$ .  
Also, determine the  $\Delta U$  of the O-H bond in water at  $298K$ . Assume ideal gas behaviour.  
**Given :**  $(8.314 \times 0.298 = 2.5)$  **TC0091**
- Q.6 (i) From the following data :  
Enthalpy of formation of  $C_2H_6 = -83$  kJ/mol  
Enthalpy of sublimation of graphite =  $719$  kJ/mol  
Enthalpy of bond dissociation of  $H_2 = 435$  kJ/mol  
C-H bond enthalpy =  $414$  kJ/mol  
Calculate the bond enthalpy of C - C  
(ii) By using data of above question calculate bond enthalpy of  $C \equiv N$  if enthalpy of formation of  $CH_3CN = 87$  kJ/mol and enthalpy of bond dissociation of nitrogen =  $945$  kJ/mol **TC0092**
- Q.7 Calculate the enthalpy change when infinitely dilute solution of  $CaCl_2$  and  $Na_2CO_3$  are mixed  $\Delta_f H^\circ$  for  $Ca^{2+}(aq)$ ,  $CO_3^{2-}(aq)$  and  $CaCO_3(s)$  are  $-129$ ,  $-161$ ,  $-288$  kcal mol $^{-1}$  respectively. **TC0030**

- Q.8 The enthalpy of formation of ethane(g), ethylene(g) and benzene(g) from the gaseous atoms are –2840, –2275 and –5530 kJmol<sup>-1</sup> respectively. Calculate the magnitude of resonance energy of benzene. The bond enthalpy of C–H bond is given as equal to +410 kJ/mol. **TC0031**
- Q.9 Calculate the enthalpy of combustion of methyl alcohol (*l*) at 298 K from the following data
- | Bond                                 | C – H | C – O | O – H | O = O | C = O |
|--------------------------------------|-------|-------|-------|-------|-------|
| Bond Enthalpy(kJ mol <sup>-1</sup> ) | 414   | 351.5 | 464.5 | 494   | 711   |
- Resonance energy of CO<sub>2</sub> = –143 kJ mol<sup>-1</sup>  
 Latent heat of vaporisation of methyl alcohol = 35.5 kJ mol<sup>-1</sup>.  
 Latent heat of vaporisation of water = 40.6 kJ mol<sup>-1</sup>. **TC0032**
- Q.10 The bond enthalpies of C–C, C=C & C≡C bonds are 348, 610 & 835 kJ/mol respectively at 298K & 1 bar. What is of the enthalpy change of polymerisation at 298K & 1 bar per mole of 2-butyne?  
 $n\text{CH}_3\text{-C}\equiv\text{C-CH}_3(\text{g}) \rightarrow (-\text{CH}_2\text{-CH=CH-CH}_2\text{-})_n(\text{g})$   
 ['n' is a large integral value] **TC0033**

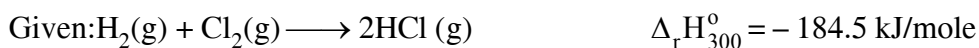
## EXERCISE (O-I)

Relationship of  $\Delta H$  &  $\Delta U$ 

- Q.1 For a reaction,  $2X(s) + 2Y(s) \rightarrow 2C(l) + D(g)$   
The  $q_p$  at  $27^\circ\text{C}$  is  $-28 \text{ Kcal mol}^{-1}$ , the  $q_v$  is -----  $\text{Kcal mol}^{-1}$   
(A)  $-27.4$  (B)  $+27.4$  (C)  $-28.6$  (D)  $28.6$  **TC0034**
- Q.2 Consider the reaction at  $300 \text{ K}$   
 $\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{HCl}(g) \quad \Delta H = -185 \text{ kJ/mol}$   
Calculate  $\Delta U$  if  $3$  mole of  $\text{H}_2$  completely react with  $3$  mole of  $\text{Cl}_2$  to form  $\text{HCl}$ .  
(A)  $0$  (B)  $-185 \text{ kJ}$  (C)  $555 \text{ kJ}$  (D)  $-555 \text{ kJ}$  **TC0035**

## Enthalpy of formation and combustion

- Q.3 Study the following thermochemical equations :  
 $A \rightarrow B$  ;  $\Delta H = +100 \text{ kcal}$   
 $B \rightarrow C$  ;  $\Delta H = -80 \text{ kcal}$   
The correct order of enthalpies of formation of A, B and C is -  
(A)  $A < B < C$  (B)  $A < C < B$  (C)  $C < A < B$  (D)  $B < C < A$  **TC0036**
- Q.4  $\text{N}_2(g) + 2\text{O}_2(g) \rightarrow 2\text{NO}_2$   $\Delta H = +x \text{ kJ}$   
 $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$   $\Delta H = +y \text{ kJ}$   
The enthalpy of formation of  $\text{NO}$  is  
(A)  $(2x - 2y) \text{ kJ/mol}$  (B)  $(x - y) \text{ kJ/mol}$  (C)  $\frac{1}{2}(y - x) \text{ kJ/mol}$  (D)  $\frac{1}{2}(x - y) \text{ kJ/mol}$  **TC0037**
- Q.5  $2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$  ;  $\Delta U_f^\circ [\text{N}_2\text{O}_4(g)] = 2 \text{ kcal/mole}$  and  $\Delta U_{\text{reaction}}^\circ = -16 \text{ kcal/mole}$  then calculate  $\Delta H_{\text{formation}}^\circ$  of  $\text{NO}_2$  at  $727^\circ\text{C}$   
(A)  $9 \text{ kcal/mole}$  (B)  $4.5 \text{ kcal/mole}$  (C)  $8 \text{ kcal/mole}$  (D)  $10 \text{ kcal/mole}$  **TC0038**
- Q.6 Find  $\Delta_r U^\circ$  for the reaction  $4\text{HCl}(g) + \text{O}_2(g) \rightarrow 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g)$  at  $300 \text{ K}$ . Assume all gases are ideal.



- (A)  $111.5 \text{ kJ/mole}$  (B)  $-109.01 \text{ kJ/mole}$  (C)  $-111.5 \text{ kJ/mole}$  (D)  $-114 \text{ kJ/mole}$  **TC0039**

- Q.7 What amount of heat energy (kJ) is released in the combustion of  $12.0 \text{ g}$  of  $\text{C}_3\text{H}_4$  at  $1 \text{ atm}$  constant pressure.  
 $\text{C}_3\text{H}_4(g) + 4 \text{ O}_2(g) \rightarrow 3 \text{ CO}_2(g) + 2 \text{ H}_2\text{O}(l)$  ;  $\Delta H^\circ = -1939 \text{ kJ}$   
(A)  $696.3$  (B)  $1939$  (C)  $6463.3$  (D)  $581.7$  **TC0040**
- Q.8  $\text{NH}_3(g) + 3\text{Cl}_2(g) \rightarrow \text{NCl}_3(g) + 3\text{HCl}(g)$  ;  $\Delta H_1$   
 $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$  ;  $\Delta H_2$   
 $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$  ;  $\Delta H_3$

The enthalpy of formation of  $\text{NCl}_3(\text{g})$  in the terms of  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  is

(A)  $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(B)  $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(C)  $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(D)  $\Delta H_f = \Delta H_1 + \Delta H_2 - \Delta H_3$

TC0041

### Bond enthalpy

Q.9 The bond dissociation energy of gaseous  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 104, 58 and 103 kcal mol<sup>-1</sup> respectively. The enthalpy of formation for  $\text{HCl}$  gas will be :-

- (A) -44.0 kcal/mol (B) -22.0 kcal/mol (C) 22.0 kcal/mol (D) 44.0 kcal/mol

TC0042

Q.10 The reaction  $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$  has  $\Delta H = -25$  kcal.

Bond	Bond Enthalpy kCal
$\epsilon_{\text{C-Cl}}$	84
$\epsilon_{\text{H-Cl}}$	103
$\epsilon_{\text{C-H}}$	x
$\epsilon_{\text{Cl-Cl}}$	y
$x : y = 9 : 5$	

From the given data, what is the bond enthalpy of  $\text{Cl-Cl}$  bond

- (A) 70 kcal/mol (B) 80 kcal/mol (C) 67.75 kcal/mol (D) 57.86 kcal/mol

TC0043

Q.11 If  $x_1$ ,  $x_2$  and  $x_3$  are enthalpies of  $\text{H-H}$ ,  $\text{O=O}$  and  $\text{O-H}$  bonds respectively, and  $x_4$  is the enthalpy of vapourisation of water, estimate the standard enthalpy of combustion of hydrogen

- (A)  $x_1 + \frac{x_2}{2} - 2x_3 + x_4$  (B)  $x_1 + \frac{x_2}{2} - 2x_3 - x_4$  (C)  $x_1 + \frac{x_2}{2} - x_3 + x_4$  (D)  $2x_3 - x_1 - \frac{x_2}{2} - x_4$

TC0044

Q.12 If bond enthalpy of  $\text{C-C}$  and  $\text{C=C}$  are 348 kJ/mole and 615 kJ/mole respectively then calculate enthalpy change (in kJ/mole) which occurs during the isomerisation of cyclopropane (g) into propene(g)

- (A) -267 (B) 81 (C) -81 (D) 267

TC0045

Q.13 If enthalpy change for hydrogenation of ethylene is -132 kJ/mole and enthalpy of formation 1,3-butadiene (g) and butane (g) are 115 kJ and -140 kJ/mole respectively then calculate resonance energy of 1,3-butadiene (in kJ).

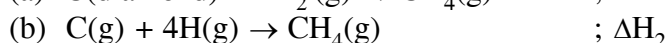
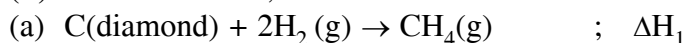
- (A) 9 (B) 18 (C) 4 (D) 10

TC0046

Q.14 Given the correct order of initials **T** (true) or **F** (false) for following statements.

(i) For the reaction  $\text{CaCO}_3(\text{Calcite}) \rightarrow \text{CaCO}_3(\text{aragonite})$ ;  $\Delta H = -1127.75$  kJ/mol, then Calcite form is more stable at standard conditions.

(ii) For the reaction,



then more heat is evolved in reaction (b)

(iii)  $\Delta_f H^\circ(\text{I}_2, \text{g}) = \Delta_{\text{sub}} H[\text{I}_2, \text{s}]$  at 25°C



(iv) For the exothermic reaction  $2\text{Ag}(s) + 1/2 \text{O}_2(g) \rightarrow 2\text{Ag}_2\text{O}(s)$  at 298 K.  $\Delta H < \Delta U$

(A) FTTT (B) TTFT (C) TFTF (D) TTTT **TC0047**

Q.15  $\Delta_r H$  of which of the following reactions is zero ?

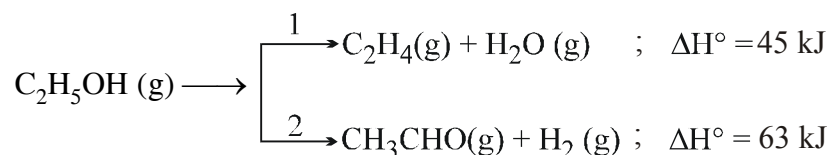
(A)  $\text{H}_2(g) \rightarrow 2\text{H}^+(g) + 2e^-$  (B)  $2\text{H}(g) + \text{aq} \rightarrow 2\text{H}^+(\text{aq}) + 2e^-$   
 (C)  $2\text{H}(g) \rightarrow 2\text{H}^+(g) + 2e^-$  (D)  $\text{H}_2(g) + \text{aq} \rightarrow 2\text{H}^+(\text{aq}) + 2e^-$  **TC0048**

Q.16  $\Delta H_f^0$  of water is  $-285.8 \text{ kJ mol}^{-1}$ . If enthalpy of neutralisation of monoacid strong base and mono basic strong acid is  $-57.3 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^0$  of  $\text{OH}^-$  ion will be

(A)  $-228.5 \text{ kJ mol}^{-1}$  (B)  $228.5 \text{ kJ mol}^{-1}$  (C)  $114.25 \text{ kJ mol}^{-1}$  (D)  $-114.25 \text{ kJ mol}^{-1}$

**TC0049**

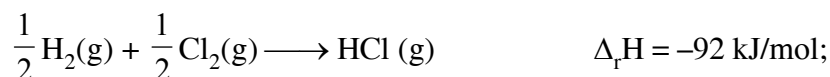
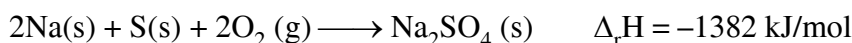
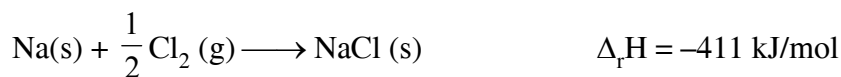
Q.17 Ethanol can undergoes decomposition to form two sets of products



if the molar ratio of  $\text{C}_2\text{H}_4$  to  $\text{CH}_3\text{CHO}$  is 8 : 1 in a set of product gases, then the enthalpy involved in the decomposition of 1 mole of ethanol is

(A) 423 kJ (B) 47 kJ (C) 61 kJ (D) 549 kJ **TC0050**

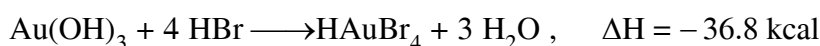
Q.18 The enthalpy changes of the following reactions at  $27^\circ\text{C}$  are



from these data, the heat change of reaction at constant volume ( in kJ/mol) at  $27^\circ\text{C}$  for the process  $2\text{NaCl}(s) + \text{H}_2\text{SO}_4(l) \longrightarrow \text{Na}_2\text{SO}_4(s) + 2\text{HCl}(g)$  is ( $R = 8.3 \text{ J/K-mol}$ )

(A) 67 (B) 62.02 (C) 71.98 (D) 64.51 **TC0051**

Q.19 Reactions involving gold have been of particular interest to a chemist . Consider the following reactions,



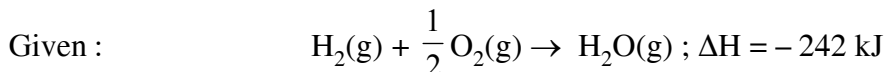
In an experiment there was an absorption of 0.44 kcal when one mole of  $\text{HAuBr}_4$  was mixed with 4 moles of  $\text{HCl}$  . What is the percentage conversion of  $\text{HAuBr}_4$  into  $\text{HAuCl}_4$  ?

(A) 0.5 % (B) 0.6 % (C) 5 % (D) 50 % **TC0052**

## EXERCISE (O-II)

## Single Correct :

- Q.1 What is the ratio of the enthalpy yield on combustion of hydrogen atoms to steam to the yield on combustion of an equal mass of hydrogen molecules to steam?



B.E. (H – H) = 436 kJ

- (A) 0.80 : 1                      (B) 1 : 0.80                      (C) 1.80 : 1                      (D) 2.80 : 1                      **TC0053**

- Q.2 For the allotropic change represented by the equation  $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$ ,  $\Delta H = 1.9 \text{ kJ}$ . If 6 g of diamond and 6 g of graphite are separately burnt to yield  $\text{CO}_2$ , the heat liberated in first case is

- (A) less than in the second case by 1.9 kJ                      (B) more than in the second case by 11.4 kJ  
(C) more than in the second case by 0.95 kJ                      (D) less than in the second case by 11.4 kJ

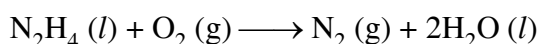
**TC0054**

- Q.3 (i) Cis-2 – butene  $\rightarrow$  trans – 2 – butene,  $\Delta H_1$   
(ii) Cis – 2 – butene  $\rightarrow$  1 – butene,  $\Delta H_2$   
(iii) Enthalpy of combustion of 1 – butene,  $\Delta H = -649.8 \text{ kcal/mol}$   
(iv)  $9\Delta H_1 + 5 \Delta H_2 = 0$   
(v) Enthalpy of combustion of trans 2 – butene,  $\Delta H = -647.0 \text{ kcal/mol}$ .

The value of  $\Delta H_1$  &  $\Delta H_2$  in Kcal/mole are

- (A) -1.0, 1.8                      (B) 1.8, -1.0                      (C) -5, 9                      (D) -2, 3.6                      **TC0055**

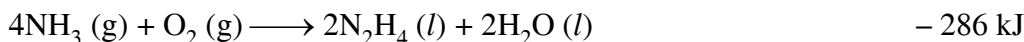
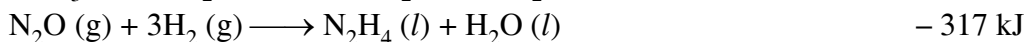
- Q.4 Hydrazine, a component of rocket fuel, undergoes combustion to yield  $\text{N}_2$  and  $\text{H}_2\text{O}$ .



What is the enthalpy change of combustion of  $\text{N}_2\text{H}_4$  (kJ/mole)

## Given Reaction

$\Delta H/\text{kJ}$



- (A) -620.5                      (B) -622.75                      (C) 1167.5                      (D) +622.75                      **TC0056**

- Q.5 The enthalpy change for the reaction,



Calculate the temperature at which  $\Delta_r H$  for the reaction will be zero.

[Given :  $C_{p,m}(\text{CH}_4, g) = 38 \text{ J/K mol}$  ;  $C_{p,m}(\text{CO}, g) = 31 \text{ J/K mol}$  &  $C_{p,m}(\text{CH}_3\text{CHO}, g) = 52 \text{ J/K mol}$  ]

- (A) 1300°C                      (B) 1027°C                      (C) 700°C                      (D) 754°C                      **TC0057**

More than one may correct

Q.6 Select the correct option -

- (A)  $\Delta H_f(H(g))$  is equal to  $\Delta H_{\text{atomisation}}$  of  $H_2(g)$
- (B)  $\Delta H_{BE}(H-H)$  is equal to  $\Delta H_f$  of  $H(g)$
- (C)  $\Delta H_{BE}(H-H)$  is equal to  $\Delta H_{\text{atomisation}}$  of  $H_2(g)$
- (D)  $\Delta H_{\text{combustion}} [H_2(g)]$  is equal to  $\Delta H_f [H_2O(l)]$  at 300K

TC0058

Q.7 Which of the following statement is (are) correct ?

- (A) for any reaction  $\Delta_r H^\circ = \sum \Delta_f H^\circ_{\text{product}} - \sum \Delta_f H^\circ_{\text{reactant}}$
- (B)  $\Delta H_f^\circ$  of  $CO_2(g)$  is same as the  $\Delta H_{\text{comb.}}^\circ$  of carbon graphite
- (C) All exothermic gaseous reactions,  $\sum (B.E.)_{\text{reactants}} > \sum (B.E.)_{\text{products}}$
- (D) for a reaction  $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ , the heat at constant pressure and the heat at constant volume at a given temperature are same

TC0059

Q.8 Which of the following do(es) not represent  $\Delta H^\circ$  formation of the product.

- (A)  $H_2(g) + I_2(s) \longrightarrow 2HI(g)$
- (B)  $\frac{2}{3} O_3(g) \longrightarrow O_2(g)$
- (C)  $NH_4^+(g) + Cl^-(g) \longrightarrow NH_4Cl(s)$
- (D)  $P_4(\text{black}) + 5O_2(g) \longrightarrow P_4O_{10}(s)$
- (E) Reaction representing  $\Delta H_{\text{combustion}}^\circ$  of C (graphite).

TC0060

Q.9 From the following data at 25°C

Reaction	$\Delta_r H^\circ$	kJ/mol
$\frac{1}{2} H_2(g) + \frac{1}{2} O_2(g) \longrightarrow OH(g)$	42	
$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$	-242	
$H_2(g) \longrightarrow 2H(g)$	436	
$O_2(g) \longrightarrow 2O(g)$	495	

Which of the following statement(s) is/are correct:

- (A)  $\Delta_r H^\circ$  for the reaction  $H_2O(g) \longrightarrow 2H(g) + O(g)$  is 925.5 kJ/mol
- (B)  $\Delta_r H^\circ$  for the reaction  $OH(g) \longrightarrow H(g) + O(g)$  is 502 kJ/mol
- (C) Enthalpy of formation of  $H(g)$  is -218 kJ/mol
- (D) Enthalpy of formation of  $OH(g)$  is 42 kJ/mol

TC0061

Match the column :

Q.10

Column-I

- (A)  $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$
- (B)  $C(\text{graphite}) \rightarrow C(\text{gas})$
- (C)  $CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$
- (D)  $CH_4(g) \rightarrow C(g) + 4H(g)$

Column-II

- (P)  $\Delta H_{\text{formation}}^\circ$
- (Q)  $\Delta H_{\text{combustion}}^\circ$
- (R)  $\Delta H_{\text{atomization}}^\circ$
- (S)  $\Delta H_{\text{neutralization}}^\circ$

TC0062

**Match list :**

Q.11 Match the enthalpy change ( $\Delta H$ ) mentioned in list-II for 16 gm  $O_2$  with the various reaction in list-I.

<b>List-I</b>		<b>List-II (<math>\Delta H</math> in kJ)</b>	
(P)	$2C_2H_2 + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l), \Delta H = -2601 \text{ kJ}$	(A)	-285.8
(Q)	$H_2(g) + 1/2O_2(g) \longrightarrow H_2O(g), \Delta H = -285.8 \text{ kJ}$	(B)	-196.75
(R)	$3FeO(s) + 1/2O_2(g) \longrightarrow Fe_3O_4(s), \Delta H = -302.4 \text{ kJ}$	(C)	-260.1
(S)	$C_{\text{graphite}} + O_2(g) \longrightarrow CO_2(g), \Delta H = -393.5 \text{ kJ}$	(D)	-302.4

**TC0063****Code :**

	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>
(A)	4	1	3	2
(B)	3	1	4	2
(C)	3	4	1	2
(D)	2	3	1	4

**Passage (Q. 12 to Q.13)**

Bond dissociation enthalpy of the first H-S bond in hydrogen sulphide is 376 kJ/mole. The enthalpies of formation of  $H_2S(g)$  and  $S(g)$  are  $-20.0$  and  $277.0$  kJ/mole respectively. The enthalpy of formation of gaseous hydrogen atom is 218 kJ/mole. Using above information, answer following questions :

Q.12 The enthalpy of formation of free radical HS is

- (A) 138 kJ/mole                      (B)  $-138$  kJ/mole                      (C)  $-10$  kJ/mole                      (D) 357 kJ/mole

**TC0064**

Q.13 The bond dissociation enthalpy of the free radical HS is

- (A) 138 kJ/mole                      (B) 276 kJ/mole                      (C) 357 kJ/mole                      (D) 376 kJ/mole

**TC0064****Paragraph for Q.14 to Q.15**

Amount of heat evolved during complete combustion of liquid benzene can be calculated from the following data.

(i) 18 gm of graphite on complete combustion evolve 591 kJ heat

(ii)  $\Delta H_f^\circ(H_2O, \ell) = -286 \text{ kJ/mol}$

(iii) The heat of formation of liquid benzene is 50 kJ /mole

Q.14 Heat of formation of  $CO_2(g)$  from following data is-

- (A)  $-286$  kJ/mole                      (B)  $-590$  kJ/mole                      (C)  $-394$  kJ/mole                      (D)  $-3268$  kJ/mole

**TC0065**

Q.15 Find heat evolved from combustion of 78 gm benzene

- (A) 3272 kJ                      (B) 6345 kJ                      (C) 4536 kJ                      (D) 5364 kJ

**TC0065**

**Table Type Question :**

Column-I (Reactions)	Column-II (Characteristics)	Column-III (Characteristics)
(I) $C(s) + O_2(g) \rightarrow CO_2(g)$	(i) $\Delta H = +ve$	(P) $\Delta H > \Delta E$
(II) $SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$	(ii) $\Delta n_g = +ve$	(Q) $ \Delta H  >  \Delta E $
(III) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$	(iii) $\Delta n_g = -ve$	(R) $\Delta H < \Delta E$
(IV) $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$	(iv) $\Delta H = -ve$	(S) $ \Delta H  <  \Delta E $

Q.16 Which of the following is only correct match ?

- (A) I , i , P                      (B) II , ii , Q                      (C) III , iii , S                      (D) IV , iv , R

**TC0066**

Q.17 Which of the following is only incorrect match ?

- (A) II , i , P                      (B) III , iv , R                      (C) IV , iii , S                      (D) II , ii , Q

**TC0066**

Q.18 Which of the following is only correct match ?

- (A) I , ii , Q                      (B) II , iii , Q                      (C) III , iv , S                      (D) IV , ii , P

**TC0066**

## EXERCISE-J-MAIN

1. Consider the reaction : [AIEEE-2011]  
 $4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}_5(\text{g}), \Delta_r H = -111\text{kJ}$   
 If  $\text{N}_2\text{O}_5(\text{s})$  is formed instead of  $\text{N}_2\text{O}_5(\text{g})$  in the above reaction, the  $\Delta_r H$  value will be :-  
 (given,  $\Delta H$  of sublimation for  $\text{N}_2\text{O}_5$  is  $54\text{ kJ mol}^{-1}$ )  
 (1)  $-165\text{ kJ}$                       (2)  $+54\text{ kJ}$                       (3)  $+219\text{ kJ}$                       (4)  $-219\text{ kJ}$                       **TC0067**
2. The value of enthalpy change ( $\Delta H$ ) for the reaction  
 $\text{C}_2\text{H}_5\text{OH}_{(\text{l})} + 3\text{O}_{2(\text{g})} \rightarrow 2\text{CO}_{2(\text{g})} + 3\text{H}_2\text{O}_{(\text{l})}$   
 at  $27^\circ\text{C}$  is  $-1366.5\text{ kJ mol}^{-1}$ . The value of internal energy change for the above reaction at this temperature will be :- [AIEEE-2011]  
 (1)  $-1371.5\text{ kJ}$                       (2)  $-1369.0\text{ kJ}$                       (3)  $-1364.0\text{ kJ}$                       (4)  $-1361.5\text{ kJ}$                       **TC0068**
3. The enthalpy of neutralisation of  $\text{NH}_4\text{OH}$  with  $\text{HCl}$  is  $-51.46\text{ kJ mol}^{-1}$  and the enthalpy of neutralisation of  $\text{NaOH}$  with  $\text{HCl}$  is  $-55.90\text{ kJ mol}^{-1}$ . The enthalpy of ionisation of  $\text{NH}_4\text{OH}$  is:  
[JEE-MAINS (online) 2012]  
 (1)  $+107.36\text{ kJ mol}^{-1}$                       (2)  $-4.44\text{ kJ mol}^{-1}$                       (3)  $-107.36\text{ kJ mol}^{-1}$                       (4)  $+4.44\text{ kJ mol}^{-1}$   
**TC0069**
4. Given [JEE-MAINS (online) 2013]  

Reaction	Energy Change (in kJ)
$\text{Li}(\text{s}) \longrightarrow \text{Li}(\text{g})$	161
$\text{Li}(\text{g}) \longrightarrow \text{Li}^+(\text{g})$	520
$\frac{1}{2}\text{F}_2(\text{g}) \longrightarrow \text{F}(\text{g})$	77
$\text{F}(\text{g}) + \text{e}^- \longrightarrow \text{F}^-(\text{g})$	(Electron gain enthalpy)
$\text{Li}^+(\text{g}) + \text{F}^-(\text{g}) \longrightarrow \text{LiF}(\text{s})$	$-1047$
$\text{Li}(\text{s}) + \frac{1}{2}\text{F}_2(\text{g}) \longrightarrow \text{LiF}(\text{s})$	$-617$

Based on data provided, the value of electron gain enthalpy of fluorine would be :  
 (1)  $-300\text{ kJ mol}^{-1}$                       (2)  $-328\text{ kJ mol}^{-1}$                       (3)  $-350\text{ kJ mol}^{-1}$                       (4)  $-228\text{ kJ mol}^{-1}$                       **TC0070**

5. Given : [JEE-MAINS (online) 2013]  
 (1)  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}); \Delta H_{298\text{K}}^\circ = -285.9\text{ kJ mol}^{-1}$   
 (2)  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}); \Delta H_{298\text{K}}^\circ = -241.8\text{ kJ mol}^{-1}$   
 The molar enthalpy of vapourisation of water will be :-  
 (1)  $241.8\text{ kJ mol}^{-1}$                       (2)  $527.7\text{ kJ mol}^{-1}$                       (3)  $44.1\text{ kJ mol}^{-1}$                       (4)  $22.0\text{ kJ mol}^{-1}$                       **TC0071**

6. The standard enthalpy of formation ( $\Delta_f H_{298}^\circ$ ) for methane,  $\text{CH}_4$  is  $-74.9\text{ kJ mol}^{-1}$ . In order to calculate the average energy given out in the formation of a C-H bond from this it is necessary to know which one of the following? [JEE-MAINS(online) 2014]  
 (1) the dissociation energy of the hydrogen molecule,  $\text{H}_2$ .  
 (2) the dissociation energy of  $\text{H}_2$  and enthalpy of sublimation of carbon (graphite).  
 (3) the first four ionisation energies of carbon and electron affinity of hydrogen.  
 (4) the first four ionisation energies of carbon. **TC0072**

7. For complete combustion of ethanol,  $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ , the amount of heat produced as measured in bomb calorimeter, is  $1364.47 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ . Assuming ideality the Enthalpy of combustion,  $\Delta_c H$ , for the reaction will be :- **[JEE-MAINS(offline)2014]**

$$(R = 8.314 \text{ J mol}^{-1})$$

- (1)  $-1460.50 \text{ kJ mol}^{-1}$  (2)  $-1350.50 \text{ kJ mol}^{-1}$  (3)  $-1366.95 \text{ kJ mol}^{-1}$  (4)  $-1361.95 \text{ kJ mol}^{-1}$

TC0073

8. The heats of combustion of carbon and carbon monoxide are  $-395.5$  and  $-285.5 \text{ kJ mol}^{-1}$ , respectively. The heat of formation (in kJ) of carbon monoxide per mole is :- **[JEE-MAINS(offline)2016]**

- (1)  $-110.5$  (2)  $110.5$  (3)  $676.5$  (4)  $-676.5$  **TC0074**

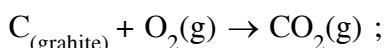
9. The enthalpy change on freezing of 1 mol of water at  $5^\circ\text{C}$  to ice at  $-5^\circ\text{C}$  is :

$$(\text{Given } \Delta_{\text{fus}} H = 6 \text{ kJ mol}^{-1} \text{ at } 0^\circ\text{C}, C_p(\text{H}_2\text{O}, l) = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}, C_p(\text{H}_2\text{O}, s) = 36.8 \text{ J mol}^{-1} \text{ K}^{-1})$$

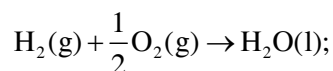
**[JEE-MAINS(online)2017]**

- (1)  $6.56 \text{ kJ mol}^{-1}$  (2)  $5.81 \text{ kJ mol}^{-1}$  (3)  $6.00 \text{ kJ mol}^{-1}$  (4)  $5.44 \text{ kJ mol}^{-1}$  **TC0075**

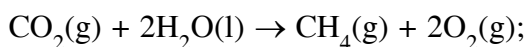
10. Given **[JEE-MAINS(offline)2017]**



$$\Delta_r H^\circ = -393.5 \text{ kJ mol}^{-1}$$

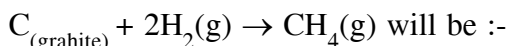


$$\Delta_r H^\circ = -285.8 \text{ kJ mol}^{-1}$$



$$\Delta_r H^\circ = +890.3 \text{ kJ mol}^{-1}$$

Based on the above thermochemical equations, the value of  $\Delta_r H^\circ$  at 298 K for the reaction



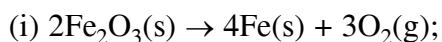
- (1)  $+74.8 \text{ kJ mol}^{-1}$  (2)  $+144.0 \text{ kJ mol}^{-1}$  (3)  $-74.8 \text{ kJ mol}^{-1}$  (4)  $-144.0 \text{ kJ mol}^{-1}$  **TC0076**

11. The combustion of benzene (l) gives  $CO_2(g)$  and  $H_2O(l)$ . Given that heat of combustion of benzene at constant volume is  $-3263.9 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ ; heat of combustion (in  $\text{kJ mol}^{-1}$ ) of benzene at constant pressure will be - **[JEE-MAINS(offline)2018]**

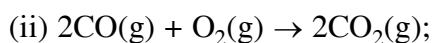
$$(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1})$$

- (1)  $-452.46$  (2)  $3260$  (3)  $-3267.6$  (4)  $4152.6$  **TC0077**

12. Given **[JEE-MAINS(online)2018]**

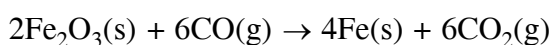


$$\Delta_r G^\circ = +1487.0 \text{ kJ mol}^{-1}$$



$$\Delta_r G^\circ = -514.4 \text{ kJ mol}^{-1}$$

Free energy change,  $\Delta_r G^\circ$  for the reaction



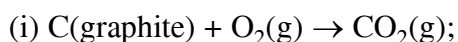
will be :-

- (1)  $-112.4 \text{ kJ mol}^{-1}$  (2)  $-56.2 \text{ kJ mol}^{-1}$  (3)  $168.2 \text{ kJ mol}^{-1}$  (4)  $208.0 \text{ kJ mol}^{-1}$

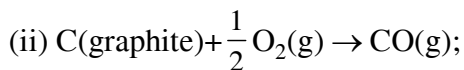
TC0078

13. Given :

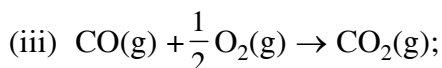
[JEE-MAINS(online)2019]



$$\Delta_r H^\circ = x \text{ kJ mol}^{-1}$$



$$\Delta_r H^\circ = y \text{ kJ mol}^{-1}$$



$$\Delta_r H^\circ = z \text{ kJ mol}^{-1}$$

Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct ?

(1)  $z = x + y$       (2)  $x = y - z$       (3)  $x = y + z$       (4)  $y = 2z - x$       **TC0079**

14. The difference between  $\Delta H$  and  $\Delta U$  ( $\Delta H - \Delta U$ ), when the combustion of one mole of heptane (1) is carried out at a temperature  $T$ , is equal to: [JEE-MAINS-(ONLINE)-2019]

(1)  $3RT$       (2)  $-3RT$       (3)  $-4RT$       (4)  $4RT$       **TC0080**

15. Enthalpy of sublimation of iodine is  $24 \text{ cal g}^{-1}$  at  $200^\circ\text{C}$ . If specific heat of  $I_2(s)$  and  $I_2(\text{vap})$  are  $0.055$  and  $0.031 \text{ cal g}^{-1}\text{K}^{-1}$  respectively, then enthalpy of sublimation of iodine at  $250^\circ\text{C}$  in  $\text{cal g}^{-1}$  is :

[JEE-MAINS(online)2019]

(1) 2.85      (2) 11.4      (3) 5.7      (4) 22.8      **TC0081**

16. The standard heat of formation ( $\Delta_f H_{298}^\circ$ ) of ethane in (kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are  $-1560$ ,  $-393.5$  and  $-286 \text{ kJ/mol}$ , respectively is \_\_\_\_\_

[JEE-MAINS(online)2020]

**TC0082**

17. If enthalpy of atomisation for  $Br_{2(1)}$  is  $x \text{ kJ/mol}$  and bond enthalpy for  $Br_2$  is  $y \text{ kJ/mol}$ , the relation between them :

[JEE-MAINS(online)2020]

(1) is  $x = y$       (2) is  $x < y$       (3) does not exist      (4) is  $x > y$       **TC0083**



## EXERCISE (J-ADVANCE)

Q.1 Using the data provided, calculate the multiple bond energy ( $\text{kJ mol}^{-1}$ ) of a  $\text{C}\equiv\text{C}$  bond in  $\text{C}_2\text{H}_2$ . That energy is (take the bond energy of a  $\text{C-H}$  bond as  $350 \text{ kJ mol}^{-1}$ ). [JEE 2012]



(A) 1165 (B) 837 (C) 865 (D) 815 TC0087

Q.2. The standard enthalpies of formation of  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  and glucose(s) at  $25^\circ\text{C}$  are  $-400 \text{ kJ/mol}$ ,  $-300 \text{ kJ/mol}$  &  $-1300 \text{ kJ/mol}$ , respectively. The standard enthalpy of combustion per gram of glucose at  $25^\circ\text{C}$  is - [JEE 2013]

(A) + 2900 kJ (B) - 2900 kJ (C) -16.11 kJ (D) + 16.11 kJ TC0088

## Paragraph For Questions 3 and 4

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of  $5.7^\circ\text{C}$  was measured for the beaker and its contents. (**Expt-1**). Because the enthalpy of neutralisation of a strong acid with a strong base is a constant ( $-57.0 \text{ kJ mol}^{-1}$ ), this experiment could be used to measure the calorimeter constant. In a second experiment (**Expt-2**), 100 mL of 2.0 M acetic acid ( $K_a = 2.0 \times 10^{-5}$ ) was mixed with 100 mL of 1.0M NaOH (under identical conditions to (**Expt-1**)) where a temperature rise of  $5.6^\circ\text{C}$  was measured. (Consider heat capacity of all solutions as  $4.2 \text{ J g}^{-1} \text{ K}^{-1}$  and density of all solutions as  $1.0 \text{ g mL}^{-1}$ ) [JEE 2015]

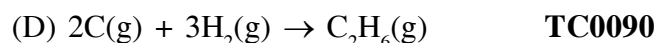
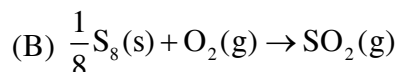
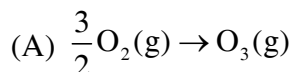
Q.3 Enthalpy of dissociation (in  $\text{kJ mol}^{-1}$ ) of acetic acid obtained from the **Expt-2** is

(A) 1.0 (B) 10.0 (C) 24.5 (D) 51.4 TC0089

Q.4 The pH of the solution after **Expt-2**

(A) 2.8 (B) 4.7 (C) 5.0 (D) 7.0 TC0089

Q.5 Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation. [JEE 2019]



**ANSWER-KEY****EXERCISE (S-I)**

- |   |                                |
|---|--------------------------------|
| Q.1 Ans. – 0.3025 kJ  | Q.2 Ans. –209.41               |
| Q.3 Ans. 189.4 kcal   | Q.4 –139.6                     |
| Q.5 $\Delta H = -41.2$ kJ                                     | Q.6 – 88 kJ/mol                |
| Q.7 –266 kJ/mol and –825 kJ/mol                               |                                |
| Q.8 (i) -3201 kJ/mol (ii) -3199.75 kJ/mol                     | Q.9 20 days                    |
| Q.10 4.5%   | Q.11 -266 kJ mol <sup>-1</sup> |
| Q.12 275 kJ/mol   | Q.13 -72 kJ mol <sup>-1</sup>  |
| Q.14 Ans. 201   | Q.15 Ans. (-2669)              |
| Q.16 Ans. (-84 kcal / mol )                                   | Q.17 Ans. (5 kJ/mol)           |
| Q.18 Ans. (480 J)   | Q.19 — 1410 Cal                |
| Q.20 31.5 kJ/mole   | Q.21 – 80 kJ/mole              |
| Q.22 22 : 13  | Q.23 Ans. 178 kJ               |
| Q.24 Ans. $\Delta U = -39.03$ kJ ; q = –36.5 kJ; w = –2.53 kJ |                                |
| Q.25 1000 Cal   |                                |

**EXERCISE (S-II)**

- |   |  |
|---|--|
| Q.1 22 kcal mol <sup>-1</sup>                               | Q.2 (a) 20 g (b) 20.28 g   |
| Q.3 0.935 kcal g <sup>-1</sup> , 3.94 kcal cm <sup>-3</sup> | Q.4 292 kcal/mol   |
| Q.5 E(O–H) = 463.5 kJ/mol $\Delta U = 461$ kJ/mol           | Q.6 (i) 342 kJ/mol <sup>-1</sup> ; (ii) 892 kJ/mol <sup>-1</sup> |
| Q.7 2 kcal  | Q.8 25 kJ/mol  |
| Q.9 – 669.7 kJ mol <sup>-1</sup>                            |  |
| Q.10 Ans. –123 kJ/mol                                       |  |
| $\Delta H = 835 - 610 = 348$                                |  |
| = – 123   |  |

**EXERCISE (O-I)**

- |               |               |               |               |
|---------------|---------------|---------------|---------------|
| Q.1 Ans.(C)   | Q.2 Ans.(D)   | Q.3 Ans.(B)   | Q.4 Ans.(D)   |
| Q.5 Ans. (C)  | Q.6 Ans.(C)   | Q.7 Ans.(D)   | Q.8 Ans.(B)   |
| Q.9 Ans.(B)   | Q.10 Ans.(D)  | Q.11 Ans.(B)  | Q.12 Ans. (B) |
| Q.13 Ans. (A) | Q.14 Ans. (A) | Q.14 Ans. (D) | Q.16 Ans.(A)  |
| Q.17 Ans.(B)  | Q.18 Ans.(B)  | Q.19 Ans.(C)  |               |

**EXERCISE (O-II)**

---

Q.1	Ans.(D)	Q.2	Ans.(C)	Q.3	Ans.(A)	Q.4	Ans.(A)
Q.5	Ans.(B)	Q.6	Ans.(C, D)	Q.7	Ans.(A, B, D)	Q.8	Ans.(A,B,C,D)
Q.9	Ans.(A,D)						
Q.10	Ans. (A) P, Q ; (B) P, R ; (C) S, D - (R)	Q.11	Ans.(B)				
Q.12	Ans. (A)	Q.13	Ans.(C)	Q.14	Ans.(C)	Q.15	Ans.(A)
Q.16	Ans.(B)	Q.17	Ans.(C)	Q.18	Ans.(D)		

**EXERCISE-J-MAIN**

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Q.1.	Ans.(4)	Q.2.	Ans.(3)	Q.3.	Ans.(4)	Q.4.	Ans.(2)
Q.5.	Ans.(3)	Q.6.	Ans.(2)	Q.7.	Ans.(3)	Q.8.	Ans.(1)
Q.9.	Ans.(1)	Q.10.	Ans.(3)	Q.11.	Ans.(3)	Q.12.	Ans.(2)
Q.13	Ans.(3)	Q.14.	Ans.(3)	Q.15	Ans.(4)		
Q.16.	(-192.50)	Q.17.	Ans.(4)				

**EXERCISE (J-ADVANCE)**

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Q.1	Ans.(D)	Q.2	Ans.(C)	Q.3	Ans. (A)	Q.4	Ans. (B)
Q.5	Ans.(A,B)						

## THERMODYNAMICS-01

### 1. INTRODUCTION

Thermodynamics is concerned with energy and its transformation in various forms in different physical and chemical processes.

Thermodynamics  $\equiv$  Thermo + dynamics

Dynamics  $\equiv$  Study of change due to a driving force

Thermo  $\equiv$  Thermal which is related to temperature or energy.

The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state.

### 2. SOME BASIC DEFINITIONS (Thermodynamic terms)

#### 2.1 SYSTEM :

The macroscopic part of the universe under study is called a **system**. Rest of the universe outside the system is called **surroundings**. The actual or imaginary surface that separates the system from the surroundings is called the **boundary**.

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

##### 2.1.1 Types of boundary :

- (i) Real or imaginary
- (ii) Rigid (fixed) or movable (flexible)
- (iii) Permeable (allow mass transfer) or impermeable (does not allow mass transfer).
- (iv) Diathermal (allow heat transfer) or Adiabatic (does not allow heat transfer).

##### 2.1.2 Types of systems :

- (i) **Isolated system** : A system is said to be isolated if it cannot exchange both matter and energy with the surroundings. Example : coffee in a thermos flask.
- (ii) **Closed system** : A system is said to be closed if it can exchange energy but not matter. Example : Coffee in a closed stainless steel flask.
- (iii) **Open system** : A system is said to be open if it can exchange matter and energy. Example : A thermos flask or a steel flask if not closed.

**Note** : A perfectly isolated system is only a theoretical system.

**2.2 State of system** : A system is called in a particular state where all the macroscopic properties of the system have definite value.

**2.3 Properties of system** : The state of a system is defined by a particular set of its measurable quantities called properties. They can be categorised into extensive and intensive properties.

Intensive property is one whose value is independent of the size (or mass) of the system. An extensive property is one whose value depends on the size (or mass) of the system.

\* Extensive properties are additive but intensive properties are non additive.

\* Ratio of two extensive property gives an intensive property.

**Extensive Properties**

Volume  
 Number of moles  
 Mass  
 Free Energy (G)  
 Entropy (S)  
 Enthalpy (H)  
 Internal energy (E & U)  
 Heat capacity

**Intensive Properties**

Molar volume  
 Density  
 Refractive index  
 Surface tension  
 Viscosity  
 Free energy per mole  
 Specific heat  
 Pressure  
 Temperature  
 Boiling point, freezing point etc

**2.4 State function or state variable :** Variables like P, V, T are State Functions or State Variables because their values depend only on the present state of a system and not on how the state was reached

**Condition for a function to be a state function :**

(i) If  $\phi$  is state function,  $\int_A^B d\phi = \phi_B - \phi_A$

(ii) If  $\phi$  is a state function,  $\oint d\phi = 0$

**2.5 Path function :** Function which depends on the path, i.e. how the process is carried out e.g. work & heat.

**2.6 Thermodynamic process :** A thermodynamic process involves change of a system from one state to another state.

### EXERCISE-I

1. Which of the following are extensive and which are intensive properties ?

Temperature, boiling point, melting point, pressure, density, viscosity, surface tension, refractive index, molar volume, free energy/mole, specific heat, Specific volume, Mass, Volume, number of moles, Heat capacity, internal energy, enthalpy, entropy,  $\Delta G$ , concentration, dipole moment, pH, gas constant, vapour pressure, specific gravity, E.M.F. of the dry cell, molarity, molality.

**Sol. Intensive property :** Temperature, (boiling point, melting point), pressure, density, viscosity, surface tension, refractive index, molar volume, free energy/mole, specific heat, Specific volume, concentration, dipole moment, pH, gas constant, vapour pressure, specific gravity, E.M.F. of the dry cell, molarity, molality.

**Extensive property :** Mass, Volume, number of moles, Heat capacity, internal energy, enthalpy, entropy

2. Which of the following are state function & path function ?

Pressure, Volume, Enthalpy, Work, Heat, Gibbs energy, temperature, Internal energy, Entropy,

Sol. **State function :** Pressure, volume, enthalpy, Gibbs energy, temperature, Internal energy, Entropy,

**Path function :** Work, Heat

3. A state function is that :

- (A) which is used in thermochemistry
- (B) which obeys all laws of thermodynamics
- (C) quantity whose value depends only upon the state of the system
- (D) quantity which is used in measuring thermal change

Ans. (C)

4. Which amongst the following is an extensive property of the system -

- (A) Temperature
- (B) Volume
- (C) Viscosity
- (D) Refractive index

Ans. (B)

5. Which of the following is not a state function of thermodynamic system -

- (A) Internal energy(E)
- (B) Free energy(G)
- (C) Enthalpy(H)
- (D) Work(W)

Ans. (D)

6. What is true for a cyclic process [E = internal energy]

- (A)  $W = 0$
- (B)  $\Delta E = 0$
- (C)  $\Delta H = 0$
- (D) B & C both

Ans. (D)

7. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy ? [AIIEEE-2003]

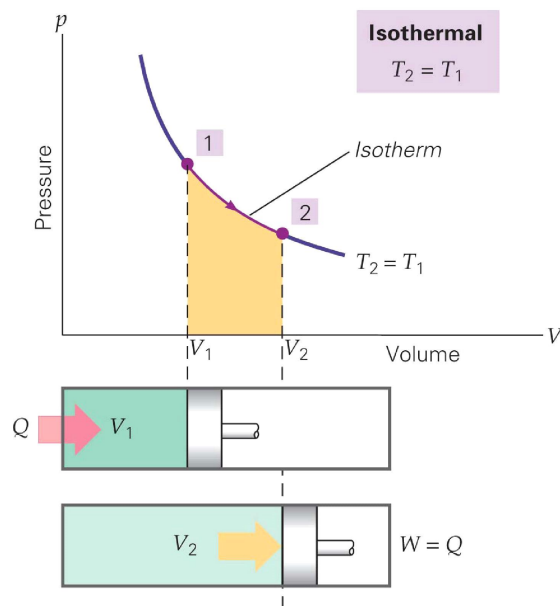
- (A) < 40 kJ
- (B) Zero
- (C) 40 kJ
- (D) > 40 kJ

Ans.(B)

Type of process :

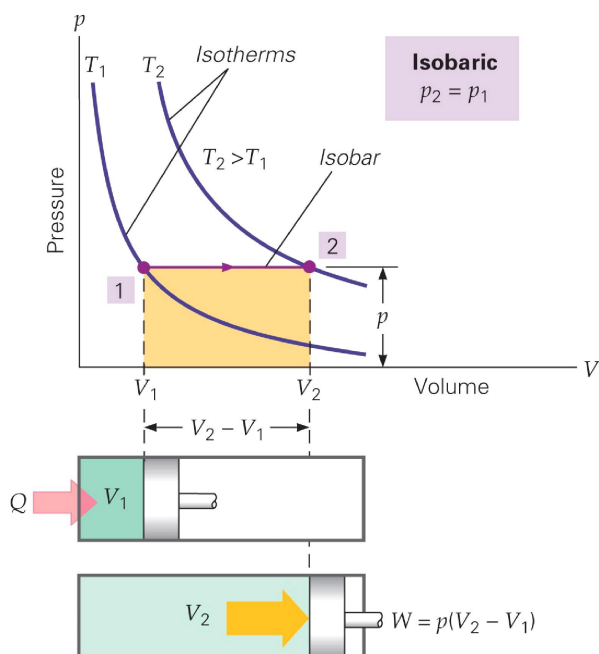
(i) **Isothermal process :**

A process in which temperature of the system remains constant is called isothermal process.



(ii) **Isobaric process :**

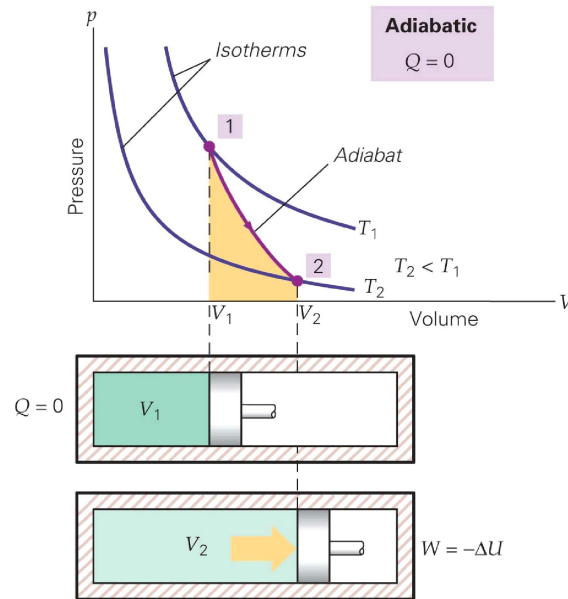
A process in which pressure of the system remains constant is called isobaric process. Temperature and volume of the system may change.



**Ex.** All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at constant pressure (1 atm.)

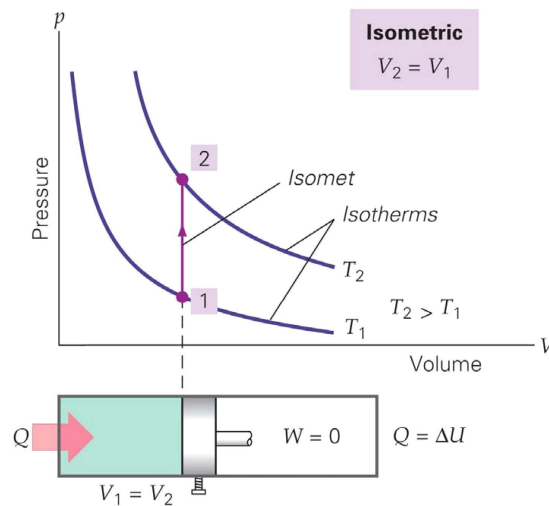
**(iii) Adiabatic process :**

A process in which no heat exchange takes place is called adiabatic process. Adiabatic process occurs in systems with insulated walls.



**(iv) Isochoric process :**

The process for which volume of the system remains constant is called isochoric process i.e., Heating of gas in closed or rigid vessel.



**(v) Cyclic process :** It is combination of two or more process in which the final state of system, becomes identical to the initial. The net change in all thermodynamic properties of system must be zero.

$$\Delta T = \Delta P = \Delta V = \Delta H = \Delta S = \Delta G \dots\dots = 0$$

However  $Q_{\text{net}}$  or  $W_{\text{net}}$  may or may not be zero.

**(vi) Reversible or Irreversible process :** If the initial state may be received just by reversing the direction of process at any state, process is called reversible. In irreversible process the initial state can never be achieved just by reversing the direction of process.



In the reversible process, the driving force is only infinitesimally greater than the opposing force. In the irreversible process, they differ largely.

A perfectly reversible process is a theoretical process because it takes infinite time but reversible processes are important because it results maximum efficiency in any machine. The actual process occurring in the machine is quasi static which may tend to reversible or irreversible process.

During irreversible process, one of the equation of state like  $PV = nRT$ , is valid. Such equation is valid only at initial & final state. However during reversible process such equation are valid throughout the process.

A process is reversible when the system throughout remain in thermodynamic equilibrium with the surrounding.

A system is said in thermodynamic equilibrium when it simultaneously satisfy the following equilibria.

- (a) **Thermal equilibrium:** Same temperature throughout (No heat transfer within the system)
- (b) **Mechanical equilibrium :** Same pressure or force throughout the system (No work should be performed by one part on the other)
- (c) **Material equilibrium :** No change in the composition of system with time. No mass transfer within the system.

If a system is in thermodynamic equilibrium there is no net energy or mass transfer within the system.

### 3. WORK

Thermodynamically, work may be defined as the form of energy which appears only when, there is some change in the boundary of the system. Such work is called mechanical or PV work.

Work may also be non-mechanical like electric work.

Presently, we will discuss only mechanical work.

- (i) It is not thermodynamic property of system.
- (ii) It depends on the quantity of system.
- (iii) Sign convention, work on system = (+)ve.

In physics, work is calculate from the force applied by system, but in chemistry due to external force.

$W = \int_{V_1}^{V_2} P \cdot dV = - \int_{V_1}^{V_2} P_{\text{ext}} dV$
<div style="display: flex; justify-content: space-around;"> <span>Physics</span> <span>Chemistry</span> </div>

### 4. HEAT

Heat is defined as the energy that flows into or out of a system because of a difference in temperature between the system and its surrounding.

According to IUPAC convention

**heat lost by system is expressed with -ive sign**

**heat given to system is expressed with +ive sign**

\*  $q_v = nC_{v,m} dT$

\*  $q_p = nC_{p,m} dT$

- \*  $C_{p,m} - C_{v,m} = R$  (for ideal gas)
- \*  $C_v$  &  $C_p$  depends on temperature even for an ideal gas. ( $C = a + bT + cT^2$ .....)

General values of  $C_v$  &  $C_p$  for an ideal gas can be taken as follows.

Atomicity	$n_{tr}$	$n_{Rot}$	$n_{Vib}$	$C_v$		$C_p$		$\gamma$		
				Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib	
Mono	3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$	
Di	3	2	1	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$	
Tri	Linear	3	2	4	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	Non Linear	3	3	3	3R	6R	4R	7R	$\frac{4}{3}$	$\frac{7}{6}$

### 5. INTERNAL ENERGY (E & U)

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy.

$$U = U_{Kinetics} + U_{Potential} + U_{Electronic} + U_{nuclear} + \dots$$

U is a state function & is an extensive property.

$$\Delta U = U_{final} - U_{initial}$$

For a given closed system

$$U = f(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

### 6. ENTHALPY

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function **Enthalpy** (H) as.

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta(PV)$$

at constant pressure

$$\Delta H = \Delta U + P \Delta V$$

combining with first law.

$$\Delta H = q_p$$

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

#### 6.1 RELATIONSHIP BETWEEN $\Delta H$ & $\Delta U$ :

The difference between  $\Delta H$  &  $\Delta U$  becomes significant only when gases are involved (insignificant in solids and liquids)

$$\Delta H = \Delta U + \Delta(PV)$$

If substance is not undergoing chemical reaction or phase change.

$$\Delta H = \Delta U + nRT$$

In case of chemical reaction

$$\Delta H = \Delta U + (\Delta n_g)RT$$

**7. ZEROth LAW OF THERMODYNAMICS**

Two system in thermal equilibrium with a third system are also in thermal equilibrium with each other. It introduces temperature as a state function.

**8. FIRST LAW OF THERMODYNAMICS**

"Total energy of universe remains constant." It is law of conservation of energy.

Let us consider a system whose internal energy is  $U_1$ . If the system is supplied with heat  $q$ , the internal energy of the system increases to  $U_1 + q$ . If work ( $w$ ) is done on the system, the internal energy in the final state of the system,  $U_2$  is given by

$$U_2 = U_1 + q + w$$

or  $U_2 - U_1 = q + w$

$$\Delta U = q + w$$

According to IUPAC, heat added to the system and work done on the system are assigned positive values as both these modes increase the internal energy of the system.

**EXERCISE -2**

8. Represent the following observations in terms of proper IUPAC symbol?

- Heat absorbed by a system is 20 Joule.
- Work done by a system is 40 Joule.
- Work done on a system is 5 Joule.
- Heat given out by system is 50 Joule.

**Ans.** It is standard practice to represent both types of heat and work (in/out or on/by) by single symbols  $q$  and  $w$  -

(a)  $q = +20$  Joule.      (b)  $w = -40$  Joule.

(c)  $w = +5$  Joule.      (d)  $q = -50$  Joule.

9. For certain processes the heat and work exchanged between system and surrounding is given in standard format. Describe the physical interpretation of each observation.

(a)  $q = +10$  kJ

(b)  $w = -20$  kJ

**Ans. (a)  $q = +10$  kJ :**

Since numerical value of  $q$  is positive, this shows heat is absorbed by the system from surrounding resulting in gain of energy by system.

**(b)  $w = -20$  kJ :**

Since numerical value of work is negative, this shows work is done by the system on surrounding resulting in loss of energy of system.

10. Predict sign of work done in following reactions at constant pressure.

Initial state	→	Final state
(i) $\text{H}_2\text{O}(\text{g})$	→	$\text{H}_2\text{O}(\ell)$
(ii) $\text{H}_2\text{O}(\text{s})$	→	$\text{H}_2\text{O}(\text{g})$
(iii) $\text{H}_2\text{O}(\ell)$	→	$\text{H}_2\text{O}(\text{s})$
(iv) $\text{CaCO}_3(\text{s})$	→	$\text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

Ans. (i) + , (ii) − , (iii) − , (iv) −

11. Explain why variation of enthalpy for a process involving an ideal gas is given by  $dH = nC_p dT$ , irrespective of process ?

Sol. Because

$$H_{\text{ideal gas}} = f(T), \text{ independent of pressure or volume}$$

12. The heat capacity of a molecule depends upon complexity of the molecule. Explain ?

Sol. The heat capacity can be defined as energy needed to raise the temperature of a body by  $1^\circ\text{C}$ . The molecule which have large number of degree's of freedom requires larger quantity of heat to raise the temperature by  $1^\circ\text{C}$ . This is because energy supplied is distributed in each degree of freedom equally.

13. If work done by the system is 300 joule when 100 cal heat is supplied to it. The change in internal energy during the process is :-

- (A) − 200 Joule (B) 400 Joule  
(C) 720 Joule (D) 120 Joule

Ans. (D)

14. One mole of a gas absorbs 200J of heat at constant volume. Its temperature rises from 298 K to 308 K. The change in internal energy is :-

- (A) 200 J (B) −200 J (C)  $200 \times \frac{308}{298}$  J (D)  $200 \times \frac{298}{308}$  J

Ans. (A)

15. A system has internal energy equal to  $U_1$ , 450 J of heat is taken out of it and 600 J of work is done on it. The final energy of the system will be -

- (A)  $(U_1 + 150 \text{ J})$  (B)  $(U_1 + 1050 \text{ J})$  (C)  $(U_1 - 150 \text{ J})$  (D)  $(U_1 - 1050 \text{ J})$

Ans. (A)

16. The work done by a system is 8J when 40J heat is supplied to it. The change in internal energy of the system during the process :

- (A) 32 J (B) 40 J (C) 48 J (D) −32 J

Ans. (A)

17. Two moles of an ideal gas expand spontaneously into vacuum. The work done is :-

- (A) Zero (B) 2 J (C) 4 J (D) 8 J

Ans. (A)

18. The work done during the expansion of a gas from a volume of 4 dm<sup>3</sup> to 6 dm<sup>3</sup> against a constant external pressure of 3 atm is -

- (A) -608 J (B) +304 J (C) -304 J (D) -6 J

Ans. (A)

19. Assuming that water vapour is an ideal gas, the internal energy change ( $\Delta U$ ) when 1 mol of water is vapourised at 1 bar pressure and 100°C, (Given : Molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol<sup>-1</sup> and R = 8.3 J mol<sup>-1</sup> K<sup>-1</sup> will be) :- [AIEEE-2007]

- (A) 4.100 kJ mol<sup>-1</sup> (B) 3.7904 kJ mol<sup>-1</sup> (C) 37.904 kJ mol<sup>-1</sup> (D) 41.00 kJ mol<sup>-1</sup>

Ans.(3)

20. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :- [JEE-MAIN-2013]

(R = 8.314 J/mol K) (ln 7.5 = 2.01)

- (A) q = + 208 J, w = - 208 J  
 (B) q = - 208 J, w = - 208 J  
 (C) q = - 208 J, w = + 208 J  
 (D) q = + 208 J, w = + 208 J

Ans.(A)

Sol.

q = + 208 Joule

for isothermal process

$$\Delta U = 0$$

∴ from 1<sup>st</sup> law of thermodynamics

$$\Delta U = q + w$$

$$0 = q + w$$

$$\Rightarrow w = -q = -208 \text{ Joule}$$

## 9. CALCULATION OF q, w, $\Delta U$ & $\Delta H$ IN VARIOUS PROCESS :

### 9.1 ISOTHERMAL EXPANSION OR COMPRESSION OF IDEAL GAS :

For isothermal process :  $\Delta T = 0$

$$\therefore \Delta U = n.C_{p,m}.\Delta T = 0$$

$$\Delta H = n.C_{p,m}.\Delta T = 0$$

$$\text{and } q = \Delta U - w = -w$$

Now, w depends on path (reversible or irreversible).

#### 9.1.1 Reversible process :

$$w_{\text{rev.}} = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV = - \int_{V_1}^{V_2} (P \pm dP) \cdot dV = - \int_{V_1}^{V_2} P \cdot dV = - \int_{V_1}^{V_2} \frac{nRT}{V} \cdot dV$$

$$\therefore w_{\text{rev.}} = -nRT \cdot \ln \frac{V_2}{V_1} = -nRT \cdot \ln \frac{P_1}{P_2}$$

**9.1.2 Irreversible process, against a constant external pressure :**

$$w_{\text{irr.}} = -P_{\text{ext}} \int_{V_1}^{V_2} dV = -P_{\text{ext}}(V_2 - V_1)$$

**9.1.3 Free expansion (or expansion in vacuum) :**

$$P_{\text{ext}} = 0 \text{ but } dV = \text{finite, Hence, } w = 0$$

**9.1.4 Comparison of magnitude of work :**

In expansion, magnitude of work =  $-w_{\text{exp}}$

In compression, magnitude of work =  $w_{\text{comp}}$

$$\begin{aligned} \text{Now, } w_{\text{rev}} - w_{\text{irr}} &= (-P \cdot dV) - (-P_{\text{ext}} \cdot dV) = (P_{\text{ext}} - P) \cdot dV \\ &= -ve, \text{ always} \end{aligned}$$

In expansion,  $P_{\text{ext}} < P$  and  $dV = +ve$

In compression,  $P_{\text{ext}} > P$  and  $dV = -ve$

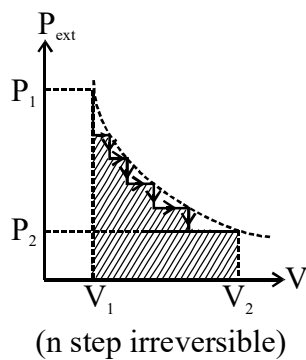
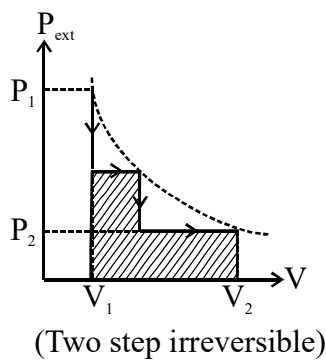
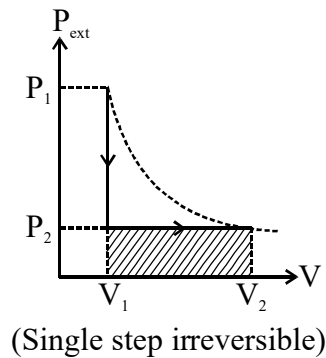
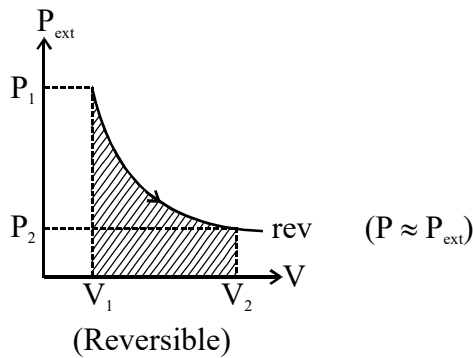
Hence,  $w_{\text{rev}} < w_{\text{irr}}$  (Always, with proper sign).

Now, as magnitude of work in expansion is  $-w_{\text{exp}}$ , hence,  $(-w_{\text{rev, exp}}) > (-w_{\text{irr, exp}})$ , i.e., magnitude of work is greater when expansion is reversible.

And, as magnitude of work in compression is  $w_{\text{comp}}$ , hence,  $(w_{\text{rev, comp}}) < (w_{\text{irr, comp}})$ , i.e., magnitude of work is greater when compression is irreversible.

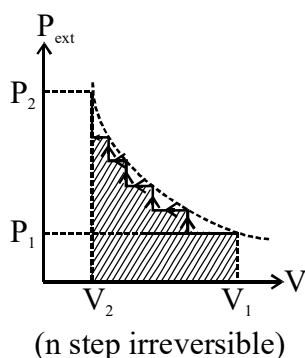
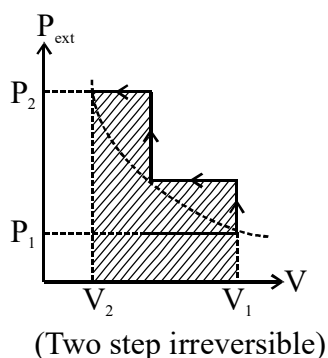
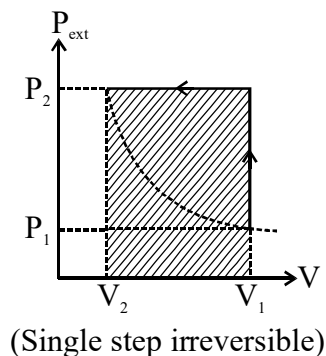
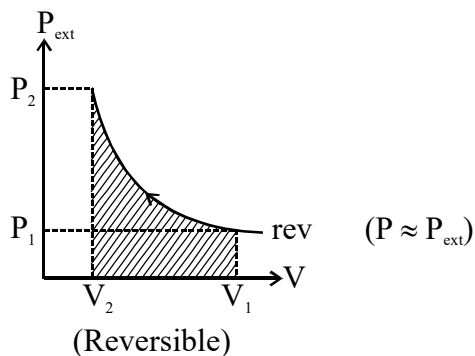
**9.1.5 Graphical comparison :**

**(a) Expansion :**



$$(-w_{\text{exp}}) : \text{Rev} > n \text{ step} > \dots > 2 \text{ step} > \text{single step}$$

(b) Compression :



( $w_{\text{comp}}$ ) : Rev < n step < ..... < 2 step < single step

**Ex.1** Two moles of an ideal gas undergoes isothermal expansion from 4L to 20L at 27°C. Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$ , if the process is performed.

(i) reversibly

(ii) irreversibly, against a constant external pressure of 1atm.

(iii) as free expansion

**Sol.** For isothermal process,  $\Delta T = 0$ . Hence,

$$\Delta U = n.C_{v,m}.\Delta T = 0$$

$$\Delta H = n.C_{p,m}.\Delta T = 0$$

$$(i) \quad w = -nRT \cdot \ln \frac{V_2}{V_1} = -2 \times 8.314 \times 300 \times \ln \frac{20}{4} = -8028.52 \text{ J}$$

$$\text{and } q = -w = 8028.52 \text{ J}$$

$$(ii) \quad w = -P_{\text{ext}}.(V_2 - V_1) = -1 \text{ atm}(20\text{L} - 4\text{L}) = -16\text{L}\cdot\text{atm}$$

$$= -16 \times 101.3 \text{ J} = -1620.8 \text{ J}$$

$$q = -w = 1620.8 \text{ J}$$

$$(iii) \quad w = 0 \text{ and } q = 0$$

## 9.2 ADIABATIC EXPANSION OR COMPRESSION OF IDEAL GAS :

$$q = 0$$

$$\therefore \Delta U = w = n.C_{v,m}.(T_2 - T_1)$$

$$\text{and } \Delta H = n.C_{p,m}.(T_2 - T_1)$$

The change in temperature may be calculated as

$$n \cdot \int_{T_1}^{T_2} C_{v,m} \cdot dT = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV$$

(a) If  $C_{v,m}$  is temperature independent and the process is reversible, then  
 $T \cdot V^{\gamma-1} = \text{constant}$

or,  $P \cdot V^{\gamma} = \text{constant}$

or,  $T^{\gamma} P^{1-\gamma} = \text{constant}$

(b) If  $C_{v,m}$  is temperature independent and the process is irreversible, then

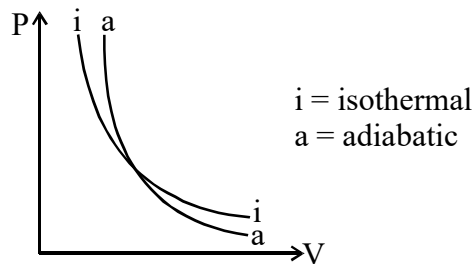
$$n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{\text{ext}} \cdot (V_2 - V_1)$$

(i) The temperature of ideal gas decreases in adiabatic expansion (except free expansion, which is isothermal too) and the temperature of ideal gas increases in adiabatic compression.

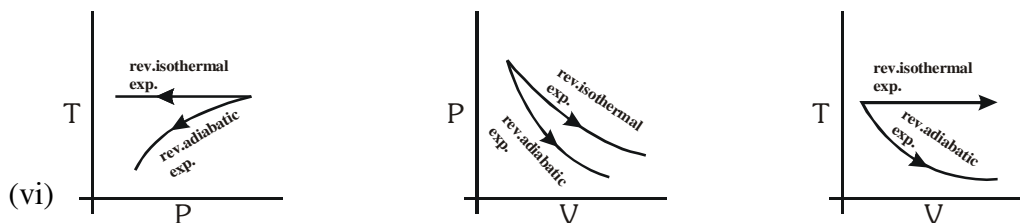
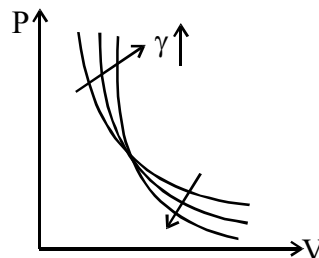
(ii) The final temperature of gas is always higher in irreversible process (expansion or compression) relative to reversible process, for the same change in volume.

(iii) Just like isothermal process, the magnitude of work is maximum when expansion is reversible and compression is irreversible (single step).

(iv) Work in reversible isothermal and adiabatic processes may be compared graphically.



(v) Work in reversible adiabatic process may be compared graphically.



**Comparison of reversible adiabatic expansion and reversible isothermal expansion on TP, PV and TV diagram**



**Ex.2.** Two moles of an ideal monoatomic gas undergoes adiabatic expansion from 5L, 127°C to 40L. Calculate  $q$ ,  $\Delta U$ ,  $w$  and  $\Delta H$ , if the process is performed.

- (i) reversibly  
 (ii) irreversibly, against a constant external pressure of 0.1 atm.  
 (iii) as free expansion

**Sol. :** For adiabatic process,  $q = 0$

$$(i) \quad T \cdot V^{\gamma-1} = \text{constant} \Rightarrow T_1 \cdot V_1^{\gamma-1} = T_2 \cdot V_2^{\gamma-1}$$

$$\therefore T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1} = 400 \times \left( \frac{5}{40} \right)^{\frac{5}{3}-1} = 100 \text{ K}$$

$$\text{Now, } w = \Delta U = nC_v \Delta T = -7482.6 \text{ J}$$

$$\Delta H = \gamma \Delta U = -12471 \text{ J}$$

$$(ii) \quad \Delta U = w = -P_{\text{ext}}(V_2 - V_1) = -0.1 \times (40 - 5) \times 101.3 = -354.55 \text{ J}$$

$$\text{and } \Delta H = \frac{5}{3} \cdot \Delta U = -590.92 \text{ J}$$

$$(iii) \quad \Delta U = w = 0$$

$$\text{and } \Delta H = 0$$

**Ex.3.** Five moles of an ideal monoatomic gas undergoes adiabatic expansion from 12 atm to 1 atm, against a constant external pressure of 1 atm. If the initial temperature of gas is 27°C, calculate the final temperature. Also calculate  $q$ ,  $\Delta U$ ,  $w$  and  $\Delta H$ .

**Sol. :**  $q = 0$

$$\Delta U = w$$

$$\text{or, } n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{\text{ext}} \cdot (V_2 - V_1)$$

$$\text{or, } n \cdot \frac{3}{2} R (T_2 - T_1) = -P_2 \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

$$\text{or, } \frac{3}{2} (T_2 - 300) = - \left( T_2 - 300 \times \frac{1}{12} \right) \Rightarrow T_2 = 190 \text{ K}$$

$$\text{or, } \Delta U = w = 5 \times \frac{3}{2} R \times (190 - 300) = -6859.05 \text{ J}$$

$$\text{and } \Delta H = \gamma \cdot \Delta U = -11431.75 \text{ J}$$

### 9.3 ISOBARIC PROCESS FOR AN IDEAL GAS :

$$q = \Delta H = n \cdot C_{v,m} \cdot \Delta T$$

$$\therefore \Delta U = n \cdot C_{v,m} \cdot \Delta T$$

$$w = -P \cdot (V_2 - V_1) = -nR \cdot \Delta T$$

**Ex.4.** One mole of an ideal diatomic undergoes isobaric expansion from  $27^\circ\text{C}$  to  $87^\circ\text{C}$ . Calculate  $q$ ,  $\Delta U$ ,  $w$  and  $\Delta H$ .

**Sol. :**  $q = \Delta H = n.C_{v,m}.\Delta T = 1 \times \frac{7}{2}R \times 60 = 1745.94 \text{ J}$

$$\Delta U = \frac{\Delta H}{\gamma} = 1247.1 \text{ J}$$

and  $w = -nR.\Delta T = -1 \times 8.314 \times 60 = -498.84 \text{ J}$

**9.4 ISOCHORIC PROCESS FOR AN IDEAL GAS :**

$$w = 0$$

$$q = \Delta U = n.C_{v,m}.\Delta T$$

$$\therefore \Delta U = n.C_{v,m}.\Delta T$$

**Ex.5.** Ten moles of an ideal gas ( $\gamma = 1.2$ ) is heated from  $27^\circ\text{C}$  to  $47^\circ\text{C}$  at constant volume. Calculate  $q$ ,  $\Delta U$ ,  $w$  and  $\Delta H$ .

**Sol. :**  $w = 0$

$$q = \Delta U = n.C_{v,m}.\Delta T = 2 \times \frac{R}{1.2-1} \times 20 = 200 R$$

$$\Delta H = \gamma.\Delta U = 240R$$

**9.5 POLYTROPIC PROCESS FOR AN IDEAL GAS :**

$$\Delta U = n.C_{v,m}.\Delta T$$

$$\therefore \Delta H = n.C_{p,m}.\Delta T$$

For ideal gas is reversible polytropic process and  $C_{v,m}$  temperature independent,

$$P.V^x = \text{constant}$$

or,  $T.V^{x-1} = \text{constant}$

where  $x = \text{polytropic index}$

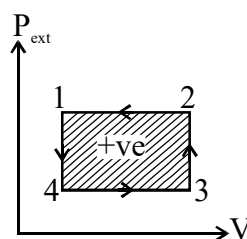
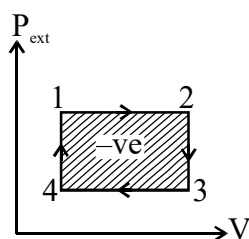
$$w_{\text{rev}} = \frac{P_2V_2 - P_1V_1}{1-x} = -\frac{nR(T_2 - T_1)}{1-x} \quad (x \neq 1)$$

$$= -nRT \cdot \ln \frac{V_2}{V_1} \quad (x = 1)$$

and  $q = n.C_m.\Delta T$

The molar heat capacity,  $C_m = C_{v,m} + \frac{P \cdot dV}{n \cdot dT} = C_{v,m} + \frac{R}{1-x}$

**9.6 CYCLIC PROCESS :**



## 9.7 CHANGE IN PHYSICAL STATE :

Solid  $\rightleftharpoons$  liquidLiquid  $\rightleftharpoons$  GasSolid  $\rightleftharpoons$  Gas

Changes in physical state occurs at constant pressure and temperature conditions.

$$\Delta U = q + w$$

$$q = \Delta H = m.L$$

$$\text{and } w = -P(V_{\text{final state}} - V_{\text{initial state}})$$

**Ex.6.** 90 gm water is completely converted into steam at 100°C and 1 atm. Calculate q,  $\Delta U$ , w and  $\Delta H$ . Latent heat of vaporisation of water at 100°C is 540 cal/gm.

**Sol. :**  $\Delta H = m.L = 90 \times 540 = 48600 \text{ cal}$

$$w = -P(V_{\text{vap}} - V_{\text{water}}) = -P.V_{\text{vap}} = -nRT = -\frac{90}{18} \times 2 \times 373 = -3730 \text{ cal}$$

$$\Delta U = q + w = 48600 + (-3430) = 44870 \text{ cal}$$

## EXERCISE-3

21. Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 27°C. ( $\ln 5 = 1.6$ )

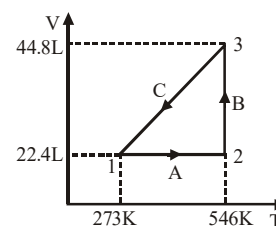
**Ans.**  $w = -3.99 \text{ kJ}$

22. Five moles of an ideal gas at 300 K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a constant external pressure of 1 atm. Calculate q, w,  $\Delta U$  &  $\Delta H$ . Calculate the corresponding value of all if the above process is carried out reversibly. ( $\ln 2 = 0.7$ )

**Ans.**  $w_{\text{irr}} = -1125 \text{ R}$ ,  $w_{\text{rev}} = -2100 \text{ R}$ ,  $\Delta U = \Delta H = 0$ ,  $q = -w$

23. One mole of an ideal monoatomic gas is carried through the reversible cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3. Fill in the blank space in the table given below assuming reversible steps.

Table-1			
State	P	V	T
1			
2			
3			



Step	Name of process	q	w	$\Delta U$	$\Delta H$
A					
B					
C					
overall					

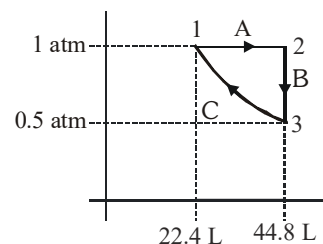
Table-1			
State	P	V	T
1	1 atm	22.4	273
2	2 atm	22.4	546
3	1 atm	44.8	546

Ans.

Step	Name of process	q	w	$\Delta E$	$\Delta H$
A	Isochoric	$3/2 R (273)$	0	$3/2 R (273)$	$5/2 R(273)$
B	Isothermal	$546 R \ln 2$	$-546 R \ln 2$	0	0
C	Isobaric	$-5/2 R(273)$	$R(273)$	$-3/2 R (273)$	$-5/2 R(273)$

24. One mole of an ideal monoatomic gas is put through reversible path as shown in figure. Fill in the blank in the tables given below.

Table-1			
State	P	V	T
1			
2			
3			



Step	Name of process	q	w	$\Delta U$	$\Delta H$
A					
B					
C					
	cyclic				

Table-1			
State	P	V	T
1	1 atm	22.4	273
2	1	44.8	546
3	0.5	44.8	273

Ans.

Step	Name of process	q	w	$\Delta E$	$\Delta H$
A	Isobaric	$5/2 R (273)$	$-R(273)$	$3/2 R (273)$	$5/2 R(273)$
B	Isochoric	$-3/2 R (273)$	0	$-3/2 R (273)$	$-5/2 R (273)$
C	Isothermal	$-273 R \ln 2$	$273 R \ln 2$	0	0
	Cyclic	$R(273) - 273 R \ln 2$	$-R(273) + 273 R \ln 2$	0	0

25.  $\frac{1}{22.4}$  mol of an ideal monoatomic gas undergoes a reversible process for which  $PV^2 = C$ . The gas is expanded from initial volume of 1 L to final volume of 2 L starting from initial temperature of 273 K. Find the heat exchanged q during the process. Express your answer in litre atm.

$$R = \frac{22.4}{273} \text{ L atm mole}^{-1} \text{ degree}^{-1}.$$

Ans. -0.25

26. An ideal gas is allowed to expand both adiabatic reversibly and adiabatic irreversibly. If  $T_i$  is the initial temperature and  $T_f$  is the final temperature, which of the following statements is correct :-

[AIEEE-2006]

- (1)  $T_f > T_i$  for reversible process but  $T_f = T_i$  for irreversible process
- (2)  $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
- (3)  $T_f = T_i$  for both reversible and irreversible processes
- (4)  $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$

26. Ans.(4)

27. Which of the following statements/relationships is not correct in thermodynamic changes ?

- (1)  $q = -nRT \ln \frac{V_2}{V_1}$  (isothermal reversible expansion of an ideal gas)[JEE-MAINS(online)-2014]
- (2) For a system at constant volume, heat involved merely changes to internal energy.
- (3)  $w = -nRT \ln \frac{V_2}{V_1}$  (isothermal reversible expansion of an ideal gas)
- (4)  $\Delta U = 0$  (isothermal reversible expansion of a gas)

27. Ans.(1)

10. SUMMARY

Process	Expression for w	Expression for q	$\Delta U$	$\Delta H$	Work on PV-graph
Reversible isothermal	$w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$	$q = nRT \ln \left( \frac{V_2}{V_1} \right)$ $q = nRT \ln \left( \frac{P_1}{P_2} \right)$	0 process	0	
Irreversible isothermal	$w = -P_{\text{ext}} (V_2 - V_1)$ $= -P_{\text{ext}} \left( \frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$	$q = P_{\text{ext}} (V_2 - V_1)$	0	0	
Isobaric process	$w = -P_{\text{ext}} (V_2 - V_1)$ $= -nR\Delta T$	$q = \Delta H = nC_p \Delta T$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Isochoric process	$w = 0$	$q = \Delta U = nC_v \Delta T$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Reversible adiabatic process	$w = nC_v (T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$ $PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Irreversible adiabatic process	$w = nC_v (T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$ $nC_v (T_2 - T_1) = -P_{\text{ext}} \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Polytropic	$w = \frac{P_2 V_2 - P_1 V_1}{n - 1}$ $w = \frac{R(T_2 - T_1)}{(n - 1)}$	$q = \int_{T_1}^{T_2} C_v dT$ $w = \frac{R(T_2 - T_1)}{(n - 1)}$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Cyclic Process	Area enclosed in PV-diagram For clockwise -ive For anticlockwise +ive	$q = -w$	0	0	

11. LIMITATION OF FIRST LAW :

It can predict the change in energy as a result of change in state or vice-versa, but can not predict the natural direction of change (whether a change can happen on it's own or not).

### MISCELLANEOUS PREVIOUS YEARS QUESTION

1. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm<sup>3</sup> to 2.50 dm<sup>3</sup>. Calculate the enthalpy change in this process.  $C_{v,m}$  for argon is 12.48 JK<sup>-1</sup> mol<sup>-1</sup>

[JEE 2000]

Ans.  $\Delta H \approx -115 \text{ J}$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

$$T_2 = 300 (1/2)^{8.3/12.48} \left[ \gamma^{-1} \frac{R}{C_{\gamma,m}} \right]$$

$$T_2 = 189.2 \text{ Kelvin.}$$

$$n = \frac{P_1 V_1}{RT_1} = \frac{(1)(1.25)}{(0.0821)(300)} = 0.507$$

$$\begin{aligned} \Delta H &= nC_{p,m} (T_2 - T_1) \\ &= 0.507 (20.78) (189.2 - 300) \\ &= -116.732 \text{ Joule.} \end{aligned}$$

2. Which of the following statement is false ?

[JEE 2001]

- (A) Work is a state function  
 (B) Temperature is a state function  
 (C) Change of state is completely defined when initial and final states are specified.  
 (D) Work appears at the boundary of the system

Ans. (A)

3. One mole of non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) to (4.0 atm, 5.0 L, 245 K) with a change in internal energy ( $\Delta U$ ) = 30.0 L-atm. The change in enthalpy ( $\Delta H$ ) of the process in L-atm.

[JEE 2002]

- (A) 40.0 (B) 42.3  
 (C) 44.0 (D) Not defined, because pressure is not constant

Ans. (C)

$$\Delta H = \Delta U + P_2 Y_2 - P_1 Y_1$$

$$\Delta H = 30 + 20 - 6$$

$$= 44$$

4. One mole of a liquid (1 bar, 100 ml) is taken in an adiabatic container and the pressure increases steeply to 100 bar. Then at a constant pressure of 100 bar, volume decrease by 1 ml. Find  $\Delta U$  and  $\Delta H$ .

[JEE 2004]

Ans.  $\Delta U = 10 \text{ J}$  ,  $\Delta H = 990 \text{ J}$

$$0 + w = \Delta U$$

$$\Delta U = -P_{\text{ext}} (V_2 - V_1)$$

$$= -100 \left( \frac{-1}{1000} \right)$$

$$= 0.1 \text{ bar litre.}$$

$$\Delta H = \Delta U + P_2 V_2 - P_1 V_1$$

$$\Delta H = 0.1 + \left[ \frac{100(99) - (1)(100)}{1000} \right]$$

$$\Delta H = 0.1 + 9.8$$

$$\Delta H = 9.9 \text{ bar. litre}$$

$$\Delta H = 990 \text{ Joules}$$

5. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in KJ) for the process is :- [JEE 2004]  
 (A) 11.4 kJ                      (B) - 11.4 kJ                      (C) 0 kJ                      (D) 4.8 kJ

Ans. (C)

In isothermal process  $\Delta T = 0$

$$\Delta H = nC_{v,m} \Delta T$$

$$\Delta H = 0$$

6. One mole of monoatomic ideal gas expands adiabatically at initial temp. T against a constant external pressure of 1 atm from one litre to two litre. Find out the final temperature. [JEE 2005]  
 (R = 0.0821 litre. atm K<sup>-1</sup> mol<sup>-1</sup>)

(A) T                      (B)  $\frac{T}{(2)^{\frac{5}{3}-1}}$                       (C)  $T - \frac{2}{3 \times 0.0821}$                       (D)  $T + \frac{2}{3 \times 0.0821}$

Ans. (C)

$$-P_{\text{ext}} (V_2 - V_1) = nC_{v,m} (T_2 - T_1)$$

$$-1(2 - 1) = 1 \left( \frac{3}{2} R \right) (T_2 - T)$$

$$T_2 = T - \frac{2}{3R}$$



7. The molar heat capacity of a monoatomic gas for which the ratio of pressure and volume is one.

- (A)  $\frac{4}{2}R$                       (B)  $\frac{3}{2}R$                       (C)  $\frac{5}{2}R$                       (D) zero [JEE 2006]

Ans. (A)

$$\frac{P}{V} = C$$

$$PV^{-1} = C$$

$$C_m = C_{v.m.} + \frac{R}{1 - (-1)}$$

$$= \frac{3}{2}R + \frac{R}{2} = \frac{4R}{2}$$

8. Among the following, the state function(s) is (are) [JEE 2009]

- (A) Internal energy                      (B) Irreversible expansion work  
(C) Reversible expansion work                      (D) Molar enthalpy

Ans. (A,D)

## EXERCISE # (S-I)

## BASIC

1. Find the work done in each case :
- (a) When one mole of ideal gas in 10 litre container at 1 atm is allowed to enter an very large evacuated bulb of capacity 100 litre.

TE0001

- (b) When 1 mole of gas expands from 1 litre to 5 litre against constant one atmospheric pressure.

TE0002

2. Find the work done in atm-litre when 18 mL of water is getting vapourised at 373 K against 1atm pressure.

(Assume the ideal behaviour of water vapour).

TE0003

3. Find total degree of freedom and break up as translational, rotational or vibrational degree of freedom in following cases.

- (i)  $\text{CO}_2$                       (ii)  $\text{SO}_2$                       (iii) He                      (iv)  $\text{NH}_3$

TE0004

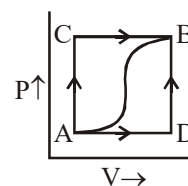
□ Problems related to First law of thermodynamics :

4. The gas is cooled such that it loses 65 J of heat. The gas contracts as it cools and work done on the system is equal to 20 J. What are q, w and  $\Delta U$  ?

TE0005

5. When a system is taken from state A to state B along the path ACB, 80J of heat flows into the system and the system does 30J of work.

- (a) How much heat flows into the system along path ADB if the work done by the system is 10J ?



TE0006

- (b) When the system is returned from state B to A along the curved path, the work done on the system is 20J. Does the system absorb or liberate heat, and how much ?

TE0007

- (c) If  $U_D - U_A = 40\text{J}$ , find the heat absorbed in the process AD and DB if work done by system in ADB is 10 Joule.

TE0008

6. An ideal gas undergoes expansion from A(10 atm, 1 litre) to B(1 atm, 10 litre), first against 5 atm and then against 1 atm, isothermally. Calculate the amount of heat absorbed (in litre. atm)

TE0009

7. 2 moles of an ideal gas is compressed from (1 bar, 2L) to 2 bar isothermally. Calculate magnitude of minimum possible work involved in the change (in Joules). (Given : 1 bar L = 100 J) ( $\ln 2 = 0.7$ )

TE0010

8. 2 mole of an ideal gas undergoes isothermal compression along three different paths if it's initial state is (2 bar, 4 litre) in all three process.

- (i) Reversible compression from till 20 bar.  
 (ii) A single stage compression against a constant external pressure of 20 bar  
 (iii) A two stage compression consisting initially of compression against a constant external pressure of 10 bar until  $P_{\text{gas}} = P_{\text{ext}}$ , followed by compression against a constant pressure of 20 bar until  $P_{\text{gas}} = P_{\text{ext}}$ .

Calculate the work (in bar. L) for each of these processes and for which of the irreversible processes is the magnitude of the work greater ? [Given : R = 0.08 bar. L/mole.K]

TE0011

9. A monoatomic ideal gas undergoing irreversible adiabatic compression from 4L to 1L against 1 bar pressure. Calculate the enthalpy change of gas. (Given: 1 bar-L = 100 J)

TE0012

10. Two mole of ideal diatomic gas ( $C_{V,m} = 5/2 R$ ) at 300K and 5 atm expanded irreversibly & adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm. Calculate q, w,  $\Delta H$  &  $\Delta U$ .

TE0013

11. Calculate the work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas ( $\gamma = 4/3$ ) from 400 K and pressure 10 atm to 1 atm.

TE0014

12. 1 mole of  $\text{CO}_2$  gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times.

- (a) What is the final temperature ?  
 (b) What is work done ?

Given  $\gamma = 1.33$  and  $C_V = 25.08 \text{ Jmol}^{-1}\text{K}^{-1}$  for  $\text{CO}_2$ .

TE0015

13. Molar heat capacity of an ideal gas at constant volume is given by  $C_V = (16.5 + 10^{-2}T) \frac{\text{J}}{\text{K} - \text{mol}}$ . If 2 moles of this ideal gas are heated at constant volume from 300K to 400K. Then the change in internal energy (in kJ) will be approximately.

TE0016

14. Three moles of an ideal gas at 200 K and 2.0 atm pressure undergoes reversible adiabatic compression until the temperature becomes 250 K. For the gas  $C_V$  is  $27.5 \text{ JK}^{-1} \text{ mol}^{-1}$  in this temperature range. Calculate q, w,  $\Delta U$ ,  $\Delta H$  and final V and final P.

$$\text{Given } \left(\frac{5}{4}\right)^{1/0.3} = 2.1, \left(\frac{5}{4}\right)^{35.8/8.3} = 2.61$$

[R = 8.3 Joule/mol.K or R = 0.0821 atm litre/mol.K]

TE0017

❑ Problem related to cyclic process

15. One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps :

(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with

T going from  $T_1$  to  $T_2$ . (BC) Cooling at constant volume to bring the gas to the original pressure and temperature. The steps are shown schematically in the figure shown.

(a) Calculate  $T_1$  and  $T_2$

TE0018

(b) Calculate  $\Delta U$ ,  $q$  and  $w$  (in calories) for the cycle.

[Given :  $\ln 10 = 2.3$ ,  $R = 0.0821 \text{ atm.litre/mol.K}$  or  $R = 2 \text{ cal/mol.K}$ ]

TE0019

16. The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas. Calculate the :

(a) Path along which magnitude of work done is least ABC or AC

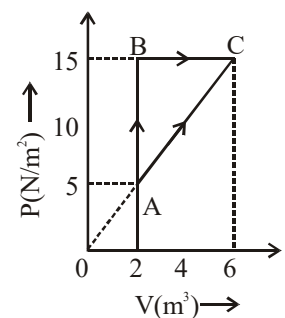
TE0020

(b) Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200J.

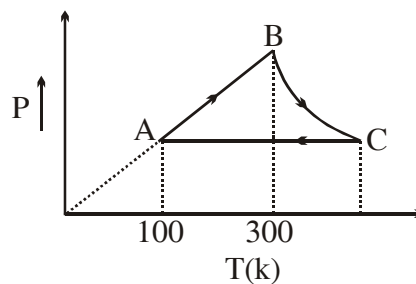
TE0021

(c) Amount of heat supplied to the gas to go from A to B, if internal energy change of gas from A to B is 10 J.

TE0022

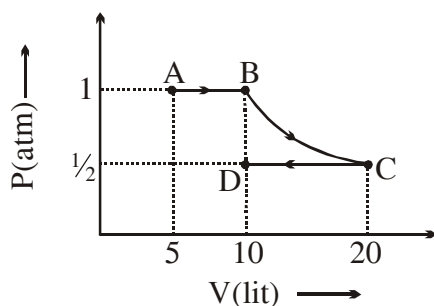


17. Calculate the net work done in the following cycle for one mol of an ideal gas (in calorie), where in process BC,  $PT = \text{constant}$ . ( $R = 2 \text{ cal/mol.K}$ ).



TE0023

18.



Calculate magnitude of total work done (in atm.lit) for the above process ABCD involving a monoatomic ideal gas.

[Given:  $\ln 2 = 0.7$ ]

TE0024

□ **Problem based on polytropic process**

19. For 1 mole of ideal monoatomic gas if  $\frac{P}{V^2} = \text{constant}$  and initial temperature is 100 K. If gas is expanded from 1 L to 2 L then find (a) heat capacity (b) total heat absorbed (c) work (d) change in internal energy.

(Assume  $R = 0.0821 \frac{\text{L-atm}}{\text{mole-k}}$ ,  $1 \text{ L-atm} = 24 \text{ cal}$ )

TE0025

20. One mole of an ideal monoatomic gas undergoes expansion along a straight line on P-V curve from initial state A(3L, 8 atm) to final state B(7.5 L, 2 atm). Calculate q for the above process in L atm.

TE0026

□ **Problems based on change in physical state :**

21. Water expands when it freezes. Determine amount of work done, in joules, when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.

TE0027

22. What is  $\Delta U$  when 2.0 mole of liquid water vaporises at  $100^\circ\text{C}$ ? The heat of vaporisation,  $\Delta H_{\text{vapour}}$  of water at  $100^\circ\text{C}$  is  $40.66 \text{ kJ mol}^{-1}$ .

TE0028

23. When 1 mole of ice melt at  $0^\circ\text{C}$  and at constant pressure of 1 atm, 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 litre respectively. Calculate  $\Delta H$  and  $\Delta U$  for the reaction.

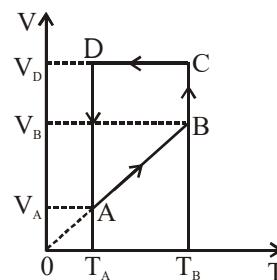
TE0029

EXERCISE # (S-II)

1. A monoatomic ideal gas of two moles is taken through a reversible

cyclic process starting from A as shown in figure. The volume ratios

are  $\frac{V_B}{V_A} = 2$  and  $\frac{V_D}{V_A} = 4$ . If the temperature  $T_A$  at A is  $27^\circ\text{C}$ , calculate:



(a) The temperature of the gas at point B.

TE0030

(b) Heat absorbed or released by the gas in each process.

TE0031

(c) The total work done by the gas during complete cycle. ( $\ln 2 = 0.7$ )

TE0032

2. One mole of an ideal gas (not necessarily monoatomic) is subjected to the following sequence of steps.

(a) It is heated at constant volume from 298 K to 373 K

(b) It is expanded freely into a vacuum to double volume at 373 K.

(c) It is cooled reversibly at constant pressure to 298K.

Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  for the overall process.

TE0033

3. Derive a mathematical expression for the work done when  $n$ -mole a gas that has the equation of state  $PV = nRT - \frac{n^2 a}{V}$  expands reversibly from  $V_i$  to  $V_f$  at constant temperature  $T$ .

TE0034

4.  $3 \text{ dm}^3$  of an ideal monoatomic gas at 600 K and 32 bar expands until pressure of the gas is 1bar Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  for the process if the expansion is :

(Use :  $R = 0.08 \text{ bar litre/mol-K} = 2 \text{ cal / mol-K}$ )

(i) Isothermal and reversible

TE0035

(ii) Adiabatic and reversible

TE0036

(iii) Isothermal and adiabatic

TE0037

(iv) Against 1 bar and adiabatic

TE0038

(v) Against 1 bar and isothermal.

TE0039

5. Pressure over 1000 mL of a liquid is gradually increased from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 mL, calculate  $\Delta U$  and  $\Delta H$  of the process, assuming linear variation of volume with pressure.

TE0040

6. At 500 kilobar pressure, density of diamond and graphite are 3 g/cc and 2 g/cc respectively, at certain temperature 'T'. Find the value  $|\Delta H - \Delta U|$  (kJ/mole) for the conversion of 1 mole of graphite to 1 mole of diamond at temperature 'T' :

TE0041

7. 2 mole of ideal monoatomic gas was subjected to reversible adiabatic compression from initial state of  $P = 1$  atm and  $T = 300$  K till the pressure is  $4\sqrt{2}$  atm and temperature is TK. The gas is then subjected to reversible isothermal expansion at TK till the internal pressure is one atm. The gas is now isobarically cooled to attain initial state. Find  $W_{\text{Net}}$  (in calorie) for whole process.

[Use  $\ln 2 = 0.7$ ,  $R = 2$  cal/K-mol]

TE0042

8. One mole of an ideal gas at 300 K is heated at constant volume ( $V_1$ ) until its temperature is doubled, then it is subjected to isothermal reversible expansion till it reaches the original pressure. Finally the gas is cooled at constant pressure till system reached to the half of original volume ( $V_1/2$ ). Determine total work done ( $|w|$ ) in cal. [Use :  $\ln 2 = 0.70$  ;  $R = 2$  Cal/K.mol.]

TE0043

9. How many times volume of diatomic gas should be expanded reversibly & adiabatically in order to reduce its r.m.s velocity to half.

TE0044

10. 0.5 mole each of two ideal gases A ( $C_v = \frac{3}{2}R$ ) and B ( $C_v = \frac{5}{2}R$ ) are taken in a container and expanded reversibly and adiabatically from  $V = 1$  L to  $V = 4$  L starting from initial temperature  $T = 300$  K. Find  $|\Delta H|$  for the process in (cal/mol).

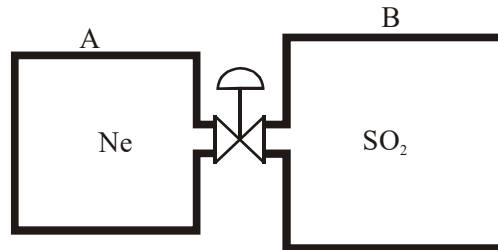
TE0045

11. 0.50 mol of an ideal gas initially at a temperature of 300 K and at a pressure of 2 atm is expanded isothermally in three steps. In each step, the pressure is dropped suddenly and held constant until equilibrium is re-established. The pressure at each of the three stages of expansion are 1.6, 1.2 and 1 atm. Calculate the work done ( $|W|$ ) (in atm -litre) in this process.

[Use  $R = 0.08$  atm litre/ mole. K ]

TE0046

12. Two rigid adiabatic vessels A and B which initially, contains two gases at different temperatures are connected by pipe line with valve of negligible volume. The vessel 'A' contains 2 moles Ne gas  $\left(C_{p,m} = \frac{5}{2}R\right)$  at 300 K, vessel 'B' contains 3 moles of  $SO_2$  gas  $(C_{p,m} = 4R)$  at 400 K. The volume of A & B vessel is 4 and 6 litre respectively. The final total pressure (in atm) when valve is opened and 12 Kcal heat supplied through it to vessels.  
[Use :  $R = 2 \text{ cal/mol. K}$  and  $R = 0.08 \text{ L. atm / mol K}$  as per desire]



TE0047

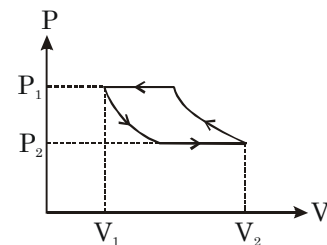
13. One mole of an ideal monoatomic gas initially at 1200 K and 64 atm is expanded to a final state at 300 K and 1.00 atm. To achieve change, a reversible path is constructed that involve an adiabatic expansion in the beginning followed by an isothermal expansion to the final state. Determine the magnitude of net work done by the gas, in cal. ( $R = 2 \text{ cal/K-mol}$ .  $\ln 2 = 0.7$ )

TE0048

14. An ideal gas is carried through a thermodynamic cycle.

$$P_1 = 2 \text{ bar} \quad V_1 = \frac{1}{\ln 10} \text{ litre}$$

$$P_2 = 1 \text{ bar} \quad V_2 = \frac{8}{\ln 10} \text{ litre}$$



Consisting of two isobaric and two isothermal processes. Calculate the net work in the entire cycle in litre bar. ( $\log_{10}^2 = 0.3$ )

TE0049



## EXERCISE # (O-I)

## BASIC

1. Out of boiling point (I), entropy (II), pH (III) and density (IV), intensive properties are  
 (A) I, II (B) I, II, III (C) I, III, IV (D) All of these  
**TE0050**
2. What is the change in internal energy when a gas is compressed from 377 ml to 177 ml under a constant pressure of 1520 torr, while at the same time being cooled by removing 124 J heat ?  
**[Take : (1L atm) = 100 J]**  
 (A) -24 J (B) - 84 J (C) - 164 J (D) - 248 J  
**TE0051**
3. One mole of an ideal monoatomic gas expanded irreversibly in two stage expansion.  
 State-1 (8.0 bar, 4.0 litre, 300 K)  
 State-2 (2.0 bar, 16litre, 300 K)  
 State-3 (1.0 bar, 32 litre, 300 K)  
 Total heat absorbed by the gas in the process is :  
 (A) 116J (B) 40 J (C) 4000 J (D) None of these  
**TE0052**
4. An ideal gas undergoes isothermal expansion from A(10 atm, 1l) to B(1 atm, 10 l) either by  
 (I) Infinite stage expansion or by  
 (II) First against 5 atm and then against 1 atm isothermally  
 Calculate  $\frac{q_I}{q_{II}}$   
 (A)  $\frac{1}{13 \times 2.303}$  (B)  $13 \times 2.303$  (C)  $\frac{13}{23.03}$  (D)  $\frac{23.03}{13}$   
**TE0053**
5. One mole of ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C. If the work done by the gas in the process is 3 kJ, the final temperature will be equal to ( $C_V = 20 \text{ J/K mol}$ )  
 (A) 100 K (B) 450 K (C) 150 K (D) 400 K  
**TE0054**
6. For an adiabatic process, which of the following relation must be correct -  
 (A)  $\Delta U = 0$  (B)  $P\Delta V = 0$  (C)  $q = 0$  (D)  $q = + W$   
**TE0055**

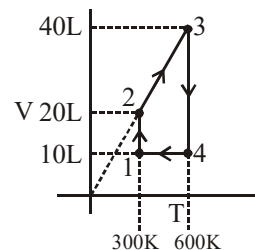
7. A system containing ideal gas is expanded under adiabatic process  
 (A) Temperature increases (B) Internal energy decreases  
 (C) Internal energy increases (D) None of these  
**TE0056**
8. A gas  $\left(C_{v,m} = \frac{5}{2}R\right)$  behaving ideally was allowed to expand reversibly and adiabatically from 1 litre to 32 litre. Its initial temperature was  $327^\circ\text{C}$ . The molar enthalpy change (in J/mole) for the process is :-  
 (A)  $-1125 R$  (B)  $-575 R$  (C)  $-1575 R$  (D) None of these  
**TE0057**
9. Two moles of an ideal gas  $(C_v = \frac{5}{2}R)$  was compressed adiabatically against constant pressure of 2 atm, which was initially at 350 K and 1 atm pressure. The work involve in the process is equal to -  
 (A) 250 R (B) 300 R (C) 400 R (D) 500 R  
**TE0058**
10. A gas is expanded from volume  $V_1$  to  $V_2$  through three different process :  
 (a) Reversible adiabatic (b) Reversible isothermal (c) Irreversible adiabatic  
 The correct statements is -  
 (A)  $(T_f)_{\text{Reversible Isothermal}} > (T_f)_{\text{Reversible adiabatic}} > (T_f)_{\text{Irreversible adiabatic}}$   
 (B)  $(T_f)_{\text{Reversible Isothermal}} > (T_f)_{\text{Irreversible adiabatic}} > (T_f)_{\text{Reversible adiabatic}}$   
 (C)  $W_{\text{Reversible Isothermal}} > W_{\text{Irreversible adiabatic}} > W_{\text{reversible adiabatic}}$   
 (D)  $(P_f)_{\text{Reversible Isothermal}} > (P_f)_{\text{Reversible adiabatic}} > (P_f)_{\text{Irreversible adiabatic}}$   
**TE0059**
11. What is the magnitude of work performed by one mole of an ideal gas when its volume increases eight times in irreversible adiabatic expansion if the initial temperature of the gas in 300 K ?  $C_v$  for the gas in 1.5 R. ( $R = 2 \text{ Cal / mol/ K}$ )  
 (A) 900 Cal (B) 450 Cal (C) 675 Cal (D) 331.58 Cal  
**TE0060**
12. For a process which follows the equation  $PV^3 = C$ , the work done when one mole of ideal gas was taken from 1 atm to  $2\sqrt{2}$  atm starting from initial temperature of 300 K is  
 (A) 300 R (B) 150 R (C) 600 R (D) 900 R  
**TE0061**

13. What is the net work done ( $w$ ) when 1 mole of monoatomic ideal gas undergoes in a process described by 1, 2, 3, 4 in given V-T graph

Use :  $R = 2\text{cal/mole K}$

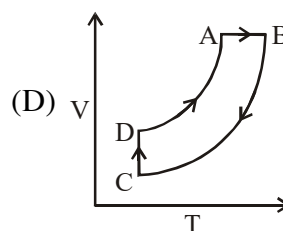
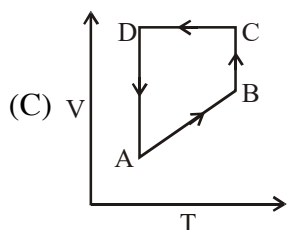
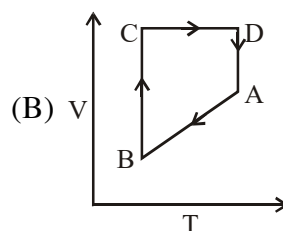
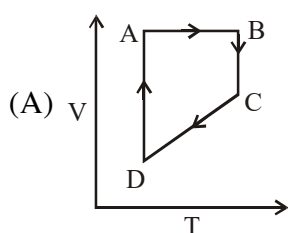
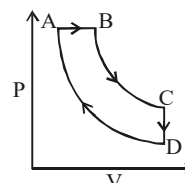
$\ln 2 = 0.7$

- (A)  $-600\text{ cal}$  (B)  $-660\text{ cal}$   
(C)  $+660\text{ cal}$  (D)  $+600\text{ cal}$



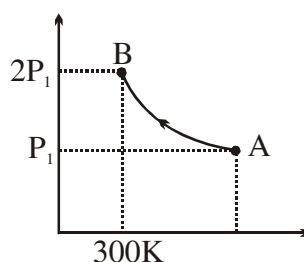
TE0062

14. A cyclic process ABCD is shown in PV diagram for an ideal gas. which of the following diagram represents the same process ?



TE0063

15. 2 moles of an ideal monoatomic gas is taken from state A to state B through a process AB in which  $PT = \text{constant}$ . The process can be represented on a P-T graph as follows:

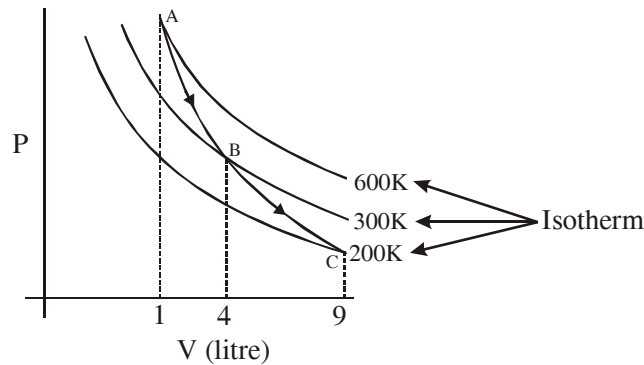


Select the incorrect option(s):

- (A) Heat evolved by the gas during process AB =  $2100 R$   
(B) Heat absorbed by the gas during process AB =  $2100 R$   
(C)  $\Delta U = -900 R$   
(D)  $W = 1200R$

TE0064

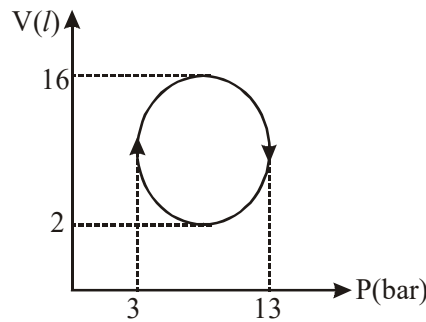
16. The given figure shows a polytropic process ABC for one mole of an ideal gas. Calculate the polytropic index ( $x$ ) for the process-



- (A)  $1/2$                       (B)  $-1/2$                       (C)  $3/2$                       (D) None

TE0065

17. Work (in kJ) in the following cyclic process is

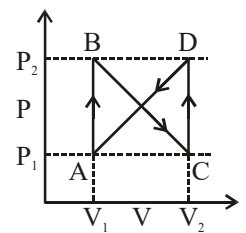


- (A)  $-11$                       (B)  $-11000$                       (C)  $11$                       (D)  $11000$

TE0066

18. An ideal gas is taken around the cycle ABCDA as shown in figure. The net work done during the cycle is equal to :-

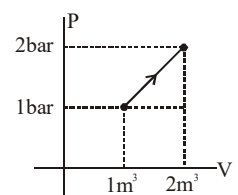
- (A) Zero  
(B) Positive  
(C) Negative  
(D) We cannot predict



TE0067

19. What is  $\Delta U$  for the process described by figure. Heat supplied during the process  $q = 200$  kJ.

- (A)  $+50$  kJ                      (B)  $-50$  kJ  
(C)  $-150$  kJ                      (D)  $+150$  kJ



TE0068

20. A diatomic ideal gas initially at 273 K is given 100 cal heat due to which system did 209 J work, Molar heat capacity ( $C_m$ ) of gas for the process is [1 cal = 4.18 Joule]

(A)  $\frac{3}{2}R$                       (B)  $\frac{5}{2}R$                       (C)  $\frac{5}{4}R$                       (D) 5R

TE0069

21. For an ideal monoatomic gas during any process  $T = kV$ , find out the molar heat capacity of the gas during the process. (Assume vibrational degree of freedom to be active)

(A)  $\frac{5}{2}R$                       (B) 3R                      (C)  $\frac{7}{2}$                       (D) 4R

TE0070

22. An amount  $Q$  of heat is added to a monoatomic ideal gas in a process in which the gas performs a work  $Q/2$  on its surrounding. The molar heat capacity of gas (in cal/K-mol) for the process is.

(A) 3R                      (B) 5R                      (C) 4R                      (D) 2R

TE0071

EXERCISE # (O-II)

❑ ONE OR MORE THAN ONE MAY BE CORRECT :

1. An insulated container of gas has two chambers separated by an insulating partition. One of the chambers has volume  $V_1$  and contains ideal gas at pressure  $P_1$  and temperature  $T_1$ . The other chamber has volume  $V_2$  and contains same ideal gas at pressure  $P_2$  and temperature  $T_2$ . If the partition is removed without doing any work on the gas, the final equilibrium temperature of the gas in the container will be :-

(A)  $\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1}$  (B)  $\frac{P_1 V_1 T_1 + P_2 V_2 T_2}{P_1 V_1 + P_2 V_2}$  (C)  $\frac{P_1 V_1 T_2 + P_2 V_2 T_1}{P_1 V_1 + P_2 V_2}$  (D)  $\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_1 + P_2 V_2 T_2}$

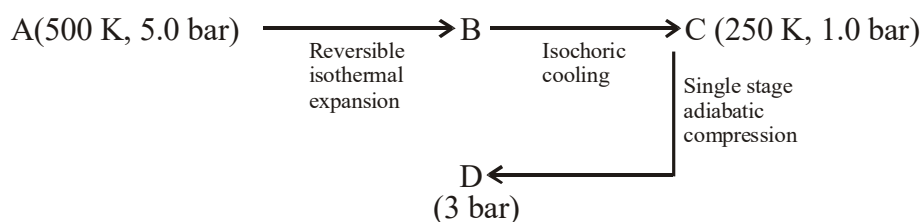
TE0072

2. The heat capacity of liquid water is 75.6 J/mol.K, while the enthalpy of fusion of ice is 6.0 kJ/mol. What is the smallest number of ice cubes at 0°C, each containing 9.0 g of water, needed to cool 500 g of liquid water from 20°C to 0°C ?

(A) 1 (B) 7 (C) 14 (D) 252

TE0073

3. Two moles of an ideal gas ( $C_{v,m} = \frac{3}{2}R$ ) is subjected to following change of state



The correct statement is/are

- (A) The pressure at B is 2.0 bar (B) The temperature at D is 450 K  
 (C)  $\Delta H_{CD} = 1000$  R (D)  $\Delta U_{BC} = 375$  R

TE0074

4. A real gas is subjected to an adiabatic process from (2 bar, 40 lit., 300 K) to (4 bar, 30 lit., 300 K) against a constant pressure 4 bar the enthalpy change for the process is

(A) Zero (B) 6000 J (C) 8000 J (D) 80 J

TE0075

5. Which of the following statement is/are correct ?

- (A) Enthalpy can be written as  $H = f(V, T)$  for a substance ( no physical or chemical change)  
 (B) Absolute value of enthalpy can not be determined  
 (C) The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero  
 (D) During compression of an ideal gas at constant pressure the temperature of gas decreases.

TE0076

6. Choose the correct statement(s)
- (A) During adiabatic expansion of an ideal gas, magnitude of work obtained is equal to  $\Delta H$  of gas.  
 (B) For same change in temperature of ideal gas through adiabatic process, magnitude of  $W$  will be same in reversible as well as irreversible process  
 (C) During an adiabatic reversible expansion of an ideal gas, temperature of the system increases.  
 (D) For same change in volume of ideal gas,  $\Delta U$  is less in adiabatic expansion than in isobaric expansion if expansion starts with same initial state.

TE0077

7. Choose the correct statement(s) among the following -
- (A) Internal energy of  $H_2O$  remains constant during conversion of liquid into its vapour at constant temperature.  
 (B) During fusion of ice into water, enthalpy change and internal energy change are almost same at constant temperature  
 (C) Molar heat capacity of gases are temperature dependent  
 (D) During boiling of  $H_2O$  at 1 atm,  $100^\circ C$ , average kinetic energy of  $H_2O$  molecules increases.

TE0078

8. Suppose that the volume of a certain ideal gas is to be doubled by one of the following processes :
- (A) isothermal expansion (B) adiabatic expansion  
 (C) free expansion in insulated condition (D) expansion at constant pressure.
- If  $E_1, E_2, E_3$  and  $E_4$  respectively are the changes in average kinetic energy of the molecules for the above four processes, then-
- (A)  $E_2 = E_3$  (B)  $E_1 = E_3$  (C)  $E_1 > E_4$  (D)  $E_4 > E_3$

TE0079

□ **Assertion / reason :**

9. **Statement-1** : There is no change in enthalpy of an ideal gas during compression at constant temperature.  
**Statement-2** : Enthalpy of an ideal gas is a function of temperature and pressure.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

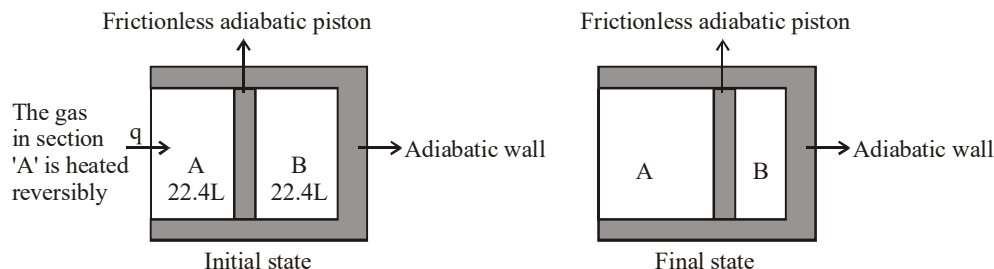
TE0080

10. **Statement-1** : Due to adiabatic expansion, the temperature of an ideal gas always decreases.  
**Statement-2** : For an adiabatic process,  $\Delta U = w$ .
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

TE0081

## Paragraph for Q.11 to Q.13

A cylindrical container of volume 44.8 litres is containing equal no. of moles (in integer no.) of an ideal monoatomic gas in two sections A and B separated by an adiabatic frictionless piston as shown in figure. The initial temperature and pressure of gas in both section is 27.3K and 1 atm. Now gas in section 'A' is slowly heated till the volume of section B becomes  $(1/8)^{\text{th}}$  of initial volume.



Given :  $R = 2 \text{ cal/mol-K}$ ,  $C_{v,m}$  of monoatomic gas  $= \frac{3}{2} R$ ,

At 1 atm &  $0^\circ\text{C}$  ideal gas occupy 22.4 litre.

11. What will be the final pressure in container B.  
 (A) 2 atm                      (B) 8 atm                      (C) 16 atm                      (D) 32 atm  
TE0082
12. Final temperature in container A will be  
 (A) 1638 K                      (B) 6988 K                      (C) 3274 K                      (D) 51 K  
TE0083
13. Change in enthalpy for section A in Kcal  
 (A) 48.3                      (B) 80.53                      (C) 4.83                      (D) 8.05  
TE0084

## Paragraph for Q.14 to 16

As a result of the isobaric heating by  $\Delta T = 72\text{K}$ , one mole of a certain ideal gas obtains an amount of heat  $Q = 1.60 \text{ kJ}$ .

14. The work performed by the gas is -  
 (A) 8.60 kJ                      (B) 0.60 kJ                      (C) 16.60 kJ                      (D) 4.60 kJ  
TE0085
15. The increment of its internal energy ( in kJ) is  
 (A) 1.0                      (B) 1.6                      (C) 2.2                      (D) 2.0  
TE0086
16. The value of  $\gamma$  for the gas is -  
 (A) 0.6                      (B) 1.4                      (C) 1.6                      (D) 1.5  
TE0087



## MATCH THE COLUMN :

17. Match Column-I with Column-II

## Column-I (Ideal Gas)

- (A) Reversible isothermal process  
 (B) Reversible adiabatic process  
 (C) Irreversible adiabatic process  
 (D) Irreversible isothermal process

## Column-II (Related equations)

- (P)  $W = 2.303 n RT \log(P_2/P_1)$   
 (Q)  $W = nC_{V,m} (T_2 - T_1)$   
 (R)  $W = -2.303nRT \log(V_2/V_1)$   
 (S)  $W = -\int_{V_i}^{V_f} P_{\text{ext.}} dV$

TE0088

18. Match the column

## Column-I

- (A) Isothermal vaporisation of water at 100°C & 1 atm  
 (B) Isothermal reversible expansion of an ideal gas  
 (C) Adiabatic free expansion of ideal gas  
 (D) Isochoric heating of an ideal gas

## Column-II

- (P)  $\Delta T = 0$   
 (Q)  $\Delta U = 0$   
 (R)  $\Delta H = 0$   
 (S)  $q = 0$   
 (T)  $w = 0$

TE0089

## MATCH THE LIST :

19. Match the following, and select the correct code :-

## Column-I

- (P) Isothermal process (reversible)  
 (Q) Adiabatic process (reversible)  
 (R) Isochoric process  
 (S) Isothermal process (irreversible)

## Column-II

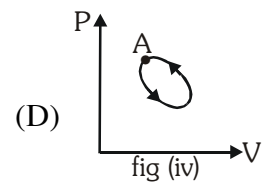
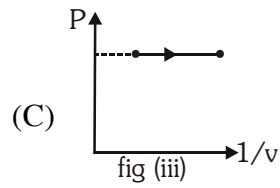
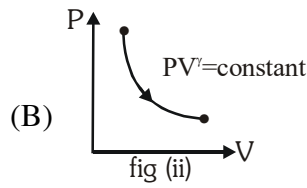
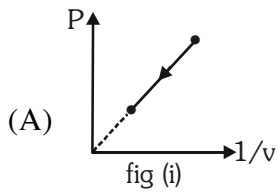
- (1)  $q = 2.303 nRT \log \frac{P_1}{P_2}$   
 (2)  $PV^\gamma = \text{const.}$   
 (3)  $q = P_{\text{ext.}} (V_2 - V_1)$   
 (4) Area under P-V curve is zero

Code:

	P	Q	R	S
(A)	2	1	4	3
(B)	1	2	4	3
(C)	2	1	3	4
(D)	1	2	3	4

TE0090

20. The figures given below depict different processes for a given amount of an ideal gas.



**Column-I**

- (P) In Fig (i)
- (Q) In Fig (ii)
- (R) In Fig (iii)
- (S) In Fig (iv)

**Column-II**

- (1) Net heat is absorbed by the system
- (2) Net work is done on the system
- (3) Net heat is rejected by the system
- (4) Net work is done by the system
- (5) Net internal energy change is zero

**Code:**

	P	Q	R	S
(A)	1, 4, 5	4	2, 3	2, 3, 5
(B)	1, 4, 5	4	2, 3	2, 3
(C)	1, 2, 4	2	1, 4	2, 3
(D)	1, 2	2	1, 4	3, 5

TE0091

## EXERCISE # (J-MAIN)

1. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of  $q$  and  $w$  for the process will be :- **[JEE-MAIN-2013]**

$$(R = 8.314 \text{ J/mol K}) (\ln 7.5 = 2.01)$$

- (1)  $q = + 208 \text{ J}$ ,  $w = - 208 \text{ J}$   
 (2)  $q = - 208 \text{ J}$ ,  $w = - 208 \text{ J}$   
 (3)  $q = - 208 \text{ J}$ ,  $w = + 208 \text{ J}$   
 (4)  $q = + 208 \text{ J}$ ,  $w = + 208 \text{ J}$

TE0092

2. Which of the following statements/relationships is not correct in thermodynamic changes ?

- (1)  $q = -nRT \ln \frac{V_2}{V_1}$  (isothermal reversible expansion of an ideal gas) **[JEE-MAINS(online)-2014]**  
 (2) For a system at constant volume, heat involved merely changes to internal energy.  
 (3)  $w = -nRT \ln \frac{V_2}{V_1}$  (isothermal reversible expansion of an ideal gas)  
 (4)  $\Delta U = 0$  (isothermal reversible expansion of a gas)

TE0093

3. A gas undergoes change from state A to state B. In this process, the heat absorbed and work done by the gas is 5 J and 8 J, respectively. Now gas is brought back to A by another process during which 3 J of heat is evolved. In this reverse process of B to A:- **[JEE-MAINS(online)-2017]**

- (1) 10 J of the work will be done by the surrounding on gas.  
 (2) 6 J of the work will be done by the surrounding on gas.  
 (3) 10 J of the work will be done by the gas.  
 (4) 6 J of the work will be done by the gas.

TE0094

4. The enthalpy change on freezing of 1 mol of water at 5°C to ice at -5°C is :

$$(\text{Given } \Delta_{\text{fus}}H = 6 \text{ kJ mol}^{-1} \text{ at } 0^\circ\text{C}, C_p(\text{H}_2\text{O}, l) = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}, C_p(\text{H}_2\text{O}, s) = 36.8 \text{ J mol}^{-1} \text{ K}^{-1})$$

**[JEE-MAINS(online)-2017]**

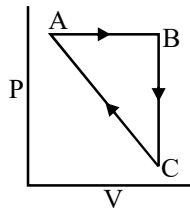
- (1)  $-6.56 \text{ kJ mol}^{-1}$       (2)  $-5.81 \text{ kJ mol}^{-1}$       (3)  $-6.00 \text{ kJ mol}^{-1}$       (4)  $-5.44 \text{ kJ mol}^{-1}$

TE0095

5.  $\Delta U$  is equal to [JEE-MAINS(online)-2017]  
 (1) Isochoric work (2) Isobaric work (3) Adiabatic work (4) Isothermal work

TE0096

6. An ideal gas undergoes a cyclic process as shown in figure. [JEE-MAINS(online)-2018]



$\Delta U_{BC} = -5 \text{ kJ mol}^{-1}$ ,  $q_{AB} = 2 \text{ kJ mol}^{-1}$

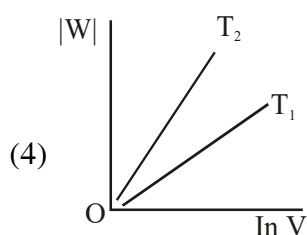
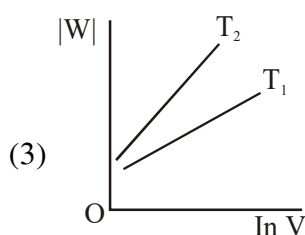
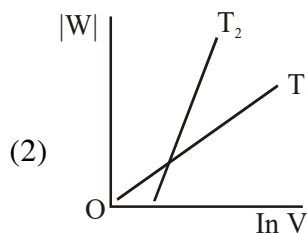
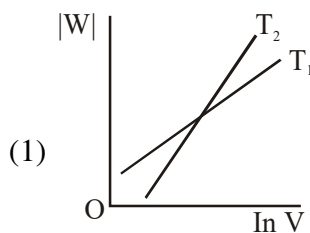
$W_{AB} = -5 \text{ kJ mol}^{-1}$ ,  $W_{CA} = 3 \text{ kJ mol}^{-1}$

Heat absorbed by the system during process CA is :-

- (1)  $18 \text{ kJ mol}^{-1}$  (2)  $+5 \text{ kJ mol}^{-1}$  (3)  $-5 \text{ kJ mol}^{-1}$  (4)  $-18 \text{ kJ mol}^{-1}$

TE0097

7. Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures  $T_1$  and  $T_2$  ( $T_1 < T_2$ ). The correct graphical depiction of the dependence of work done (w) on the final volume (V) is: [JEE-MAINS(online)-2019]



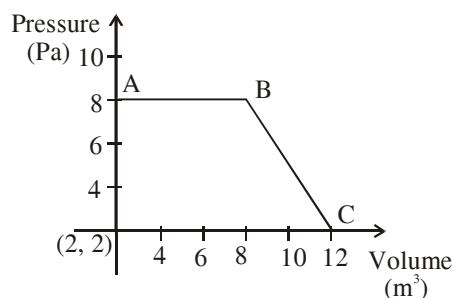
TE0098

8. An ideal gas undergoes isothermal compression from  $5 \text{ m}^3$  to  $1 \text{ m}^3$  against a constant external pressure of  $4 \text{ Nm}^{-2}$ . Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is  $24 \text{ J mol}^{-1} \text{ K}^{-1}$ , the temperature of Al increases by [JEE-MAINS(online)-2019]

- (1)  $\frac{3}{2} \text{ K}$  (2)  $\frac{2}{3} \text{ K}$  (3)  $1 \text{ K}$  (4)  $2 \text{ K}$

TE0099

9. The magnitude of work done by a gas that undergoes a reversible expansion along the path ABC shown in the figure is \_\_\_\_\_. [JEE-MAINS(online)-2020]



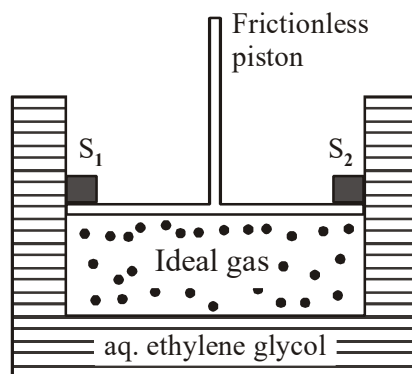
TE0100

10. At constant volume, 4 mol of an ideal gas when heated from 300 K to 500K changes its internal energy by 5000 J. The molar heat capacity at constant volume is \_\_\_\_\_. [JEE-MAINS(online)-2020]

TE0101

11. A cylinder containing an ideal gas (0.1 mol of 1.0 dm<sup>3</sup>) is in thermal equilibrium with a large volume of 0.5 molal aqueous solution of ethylene glycol at its freezing point. If the stoppers S<sub>1</sub> and S<sub>2</sub> (as shown in the figure) are suddenly withdrawn, the volume of the gas in litres after equilibrium is achieved will be \_\_\_\_\_. (Given, K<sub>f</sub> (water) = 2.0 K kg mol<sup>-1</sup>, R = 0.08 dm<sup>3</sup> atm K<sup>-1</sup> mol<sup>-1</sup>)

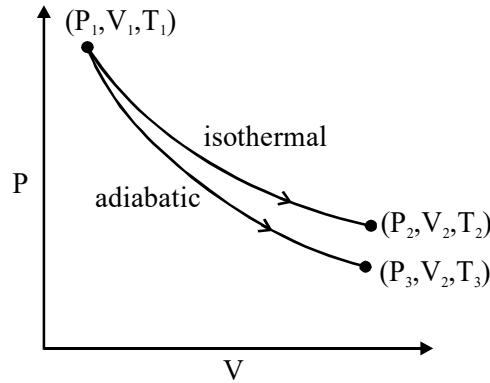
[JEE-MAINS(online)-2020]



TE0102

EXERCISE # (J-ADVANCED)

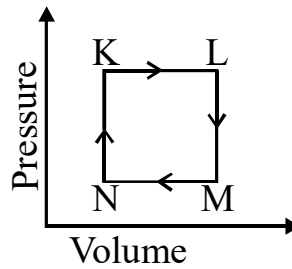
1. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct ? [JEE 2012]



- (A)  $T_1 = T_2$  (B)  $T_3 > T_1$   
 (C)  $w_{\text{isothermal}} > w_{\text{adiabatic}}$  (D)  $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

Paragraph for Question 2 and 3

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure. [JEE 2013]



TE0103

2. The pair of isochoric processes among the transformation of states is  
 (A) K to L and L to M (B) L to M and N to K  
 (C) L to M and M to N (D) M to N and N to K

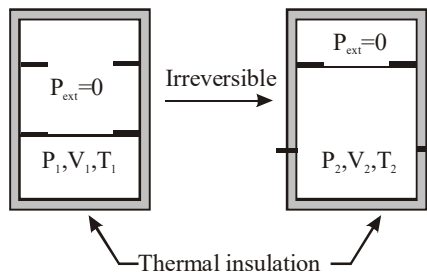
TE0104

3. The succeeding operations that enable this transformation of states are  
 (A) Heating, cooling, heating, cooling  
 (B) cooling, heating, cooling, heating  
 (C) Heating, cooling, cooling, heating  
 (D) Cooling, heating, heating, cooling

TE0105

4. An ideal gas in thermally insulated vessel at internal pressure =  $P_1$ , volume =  $V_1$  and absolute temperature =  $T_1$  expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are  $P_2$ ,  $V_2$  and  $T_2$ , respectively. For this expansion,

[JEE 2014]



- (A)  $q = 0$  (B)  $T_2 = T_1$   
 (C)  $P_2V_2 = P_1V_1$  (D)  $P_2V_2^\gamma = P_1V_1^\gamma$

TE0106

5. An ideal gas is expanded from  $(p_1, V_1, T_1)$  to  $(p_2, V_2, T_2)$  under different conditions. The correct statement(s) among the following is(are) :-

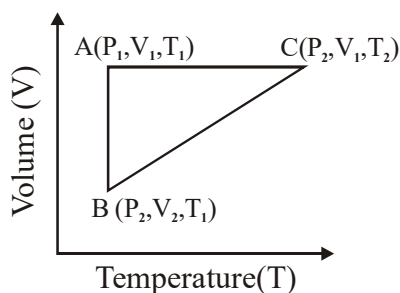
[JEE 2017]

- (A) The work done on the gas is maximum when it is compressed irreversibly from  $(p_2, V_2)$  to  $(p_1, V_1)$  against constant pressure  $p_1$   
 (B) The work done by the gas is less when it is expanded reversibly from  $V_1$  to  $V_2$  under adiabatic conditions as compared to that when expanded reversibly from  $V_1$  to  $V_2$  under isothermal conditions.  
 (C) The change in internal energy of the gas (i) zero, if it is expanded reversibly with  $T_1 = T_2$ , and (ii) positive, if it is expanded reversibly under adiabatic conditions with  $T_1 \neq T_2$   
 (D) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic

TE0107

6. A reversible cyclic process for an ideal gas is shown below. Here,  $P$ ,  $V$  and  $T$  are pressure, volume and temperature, respectively. The thermodynamic parameters  $q$ ,  $w$ ,  $H$  and  $U$  are heat, work, enthalpy and internal energy, respectively.

[JEE 2018]



The correct option(s) is (are)

- (A)  $q_{AC} = \Delta U_{BC}$  and  $w_{AB} = P_2(V_2 - V_1)$  (B)  $w_{BC} = P_2(V_2 - V_1)$  and  $q_{BC} = \Delta H_{AC}$   
 (C)  $\Delta H_{CA} < \Delta U_{CA}$  and  $q_{AC} = \Delta U_{BC}$  (D)  $q_{BC} = \Delta H_{AC}$  and  $\Delta H_{CA} > \Delta U_{CA}$

TE0108

**ANSWER KEY****EXERCISE # (S-I)**

1. Ans. (a) 0 (b)  $W = -P\Delta V = -1(5 - 1) = -4$  litre-atm.
2. Ans.  $-3.1$  kJ
3. Ans. (i) 9, 3, 2, 4 (ii) 9, 3, 3, 3 (iii) 3, 3, 0, 0 (iv) 12, 3, 3, 6
4. Ans.  $q = -65$  J;  $w = 20$  J;  $\Delta U = -45$  J
5. Ans. (a)  $+60$  J (b)  $-70$  J (c),  $+50$  J,  $+10$  J
6. Ans. (13)
7. Ans. (140)
8. Ans. (i) 18.42 bar.L; (ii) 72 bar.L; (iii) 40 bar.L
9. Ans. (500 J)
10. Ans.  $\Delta U = w = -150$  R,  $\Delta H = -210$ R,  $q = 0$ 11. Ans. 2244.78 Joule
12. Ans.  $T_2 = 100$ K;  $w = -5.016$  kJ
13. Ans. (4)
14. Ans.  $q = 0$ ,  $w = \Delta U = 4.125$  kJ;  $\Delta H = 5.372$  kJ;  $V_f = 11.8$  dm<sup>3</sup>;  $P = 5.22$  atm
15. Ans. (a)  $T_1 = 243.60$  K;  $T_2 = 2436$  K, (b)  $\Delta U = 0$ ;  $q = -w = 3264.24$  cal
16. Ans. (a) AC, (b) 170 J, (c) 10 J
17. Ans.  $[-800$  cal]
18. Ans. (7)
19. Ans. (a)  $\frac{11}{3}$  cal/K-mol. (b) 2566.67 cal (c)  $-466.67$  cal (d) 2100 cal
20. Ans. (9)
21. Ans.  $-10.13$  J
22. Ans.  $\Delta E = 75.12$  kJ
23. Ans.  $\Delta U \approx \Delta H = 1440$  calories

**EXERCISE # (S-II)**

1. Ans. (a) 600 K, (b) 3 kcal, 1.680 kcal,  $-1.8$  kcal,  $-1.680$  kcal (c)  $w = -1.2$  kcal
2. Ans.  $\Delta U$  &  $\Delta H = 0$ ;  $w = 623.55$  J ;  $q = -623.55$  J
3. Ans.  $w = -nRT \ln \frac{V_f}{V_i} - n^2 a \left( \frac{1}{V_f} - \frac{1}{V_i} \right)$
4. Ans. (i)  $w = -8400$  cal ,  $q = 8400$ cal ,  $\Delta U = \Delta H = 0$ .  
 (ii)  $w = -2700$  cal ,  $q = 0$ cal ,  $\Delta U = -2700$ ,  $\Delta H = -4500$  cal  
 (iii)  $w = 0$  cal ,  $q = 0$  cal ,  $\Delta U = 0$  ,  $\Delta H = 0$ .  
 (iv)  $w = -1395$  cal  $q = 0$ ,  $\Delta U = -1395$  cal ,  $\Delta H = -2325$  cal  
 (v)  $w = -2325$  cal  $q = 2325$  cal ,  $\Delta U = 0$  ,  $\Delta H = 0$
5. Ans.  $\Delta U = 501$  J;  $\Delta H = 99.5$  kJ



6. Ans. 100 KJ/mole
7. Ans. -1200 cal
8. Ans. 60 cal
9. Ans. (32)
10. Ans. (900 calorioes)
11. Ans. 7.4 atm litre
12. Ans. 35 atm
13. Ans. 3120
14. Ans. (1.8 bar-litre)

### EXERCISE # (O-I)

- |             |              |             |             |
|-------------|--------------|-------------|-------------|
| 1. Ans.(C)  | 2. Ans.(B)   | 3. Ans.(C)  | 4. Ans.(D)  |
| 5. Ans.(C)  | 6. Ans.(C)   | 7. Ans.(B)  | 8. Ans.(C)  |
| 9. Ans.(D)  | 10. Ans. (B) | 11. Ans.(D) | 12. Ans.(B) |
| 13. Ans.(C) | 14. Ans.(C)  | 15. Ans.(B) | 16. Ans.(C) |
| 17. Ans.(C) | 18. Ans.(A)  | 19. Ans.(A) | 20. Ans.(D) |
| 21. Ans.(A) | 22. Ans.(A)  |             |             |

### EXERCISE # (O-II)

- |   |                |                 |               |
|---|----------------|-----------------|---------------|
| 1. Ans. (A)   | 2. Ans.( C)    | 3. Ans. (A,B,C) | 4. Ans. (C)   |
| 5. Ans. (A,B,C,D)   | 6. Ans. (B, D) | 7. Ans. (B,C)   | 8. Ans. (B,D) |
| 9. Ans. (C)   | 10. Ans. (D)   | 11. Ans. (D)    | 12. Ans. (A)  |
| 13. Ans. (B)  | 14. Ans. (B)   | 15. Ans.( A)    | 16. Ans. (C)  |
| 17. Ans. (A) → (P,R,S) ; (B) → (Q, S) ; (C) → (Q,S) ; (D) → (S) |                |                 |               |
| 18. Ans. (A)-P; (B)-P,Q,R ; (C)-P,Q,R,S,T ; D-T                 |                |                 |               |
| 19. Ans. (B)  | 20. Ans. (A)   |                 |               |

### EXERCISE # (J-MAIN)

- |                 |                 |                         |             |
|-----------------|-----------------|-------------------------|-------------|
| 1. Ans. (1)     | 2. Ans. (1)     | 3. Ans. (2)             | 4. Ans. (1) |
| 5. Ans. (3)     | 6. Ans. (2)     | 7. Ans. (2)             | 8. Ans. (2) |
| 9. Ans. (48.00) | 10. Ans. (6.25) | 11. Ans. (2.17 to 2.23) |             |

### EXERCISE # (J-ADVANCED)

- |                 |               |             |                |
|-----------------|---------------|-------------|----------------|
| 1. Ans. (A,D)   | 2. Ans. (B)   | 3. Ans. (C) | 4. Ans.(A,B,C) |
| 5. Ans. (A,B,D) | 6. Ans. (B,C) |             |                |



## THERMODYNAMICS-02

### 1. LIMITATION OF FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics can evaluate the value of  $\Delta U$  and  $\Delta H$  (i.e. energy difference between two states), but can not predict the feasibility of a process. Many processes can take place on their own and many others require an external force to carry out the process. The first law is clueless about why some processes happens on their own and why some others do not.

#### ❖ Importance of Second law :

What is the driving force for a process which takes system from one state to other on it's own? Why such processes (*called spontaneous process*) take place at all? Answers to these questions are given by second law.

### 2. SPONTANEOUS PROCESS

A spontaneous process is the one which takes place on its own & can drive some other process as well. However, in some cases, initiation may be required.

**Ex :**

- (i) Mixing of two gases.
- (ii) Cooling of a hot object by transferring heat to surrounding.
- (iii) Water flowing down the hill.
- (iv) Rusting of iron.
- (v) Burning of coal, coke, hydrocarbons.
- (vi) Volcanic eruptions.

The synonyms of spontaneous processes are **natural processes** and irreversible processes.

It is a common observation that natural processes occur with finite rate. All spontaneous processes take place due to a finite driving force (which can be temperature difference, height difference, potential energy difference, etc.). Also the change brought about by a spontaneous process can not be restored without making some effort (which brings about permanent change in surrounding). Hence it is quite natural to call these processes as irreversible processes.

**Ex :**

When water flows from a dam, a part of the potential energy is converted into electrical energy and a part is converted into kinetic energy. The kinetic energy part is lost as heat energy. This loss of extra work is the permanent change in universe, because this heat energy lost cannot be completely converted back into P.E. of water.

### 3. Disorder :

The term 'disorder' is related to randomness. Any macroscopic property of a system is an average of large number of microscopic forces which are random in nature. Greater the randomness associated with microscopic forces, greater is the uncertainty about exact microscopic description of a macroscopic state and greater will be the disorder associated with the macroscopic state.

**As a rule :**

- (i) Greater the number of molecules in which a given energy is distributed, greater is the disorder.
- (ii) Greater the spread of given number of molecules with given energy in space, greater will be the disorder.

### 4. SECOND LAW OF THERMODYNAMICS

The entropy of the universe increases in course of every spontaneous process. The entropy of system is a state function. The change in entropy of a system is given by -

$$dS = \frac{dq_{rev}}{T} \quad \text{where ; } dq_{rev} = \text{heat exchanged by system in a very small step (reversibly).}$$

#### 4.1 Entropy :

Entropy is a measure of disorder. The entropy is a state function and a basic quantity directly defined by second law. In every spontaneous process, entropy of universe increases.

There are three types of entropy changes :

- (i)  $\Delta S_{\text{System}}$  : Entropy change of system
  - (ii)  $\Delta S_{\text{Surrounding}}$  : Entropy change of surrounding
  - (iii)  $\Delta S_{\text{Total}}$  : Entropy change of universe
- $$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = \Delta S_{\text{universe}} = \Delta S_{\text{total}} = \Delta S_{\text{isolated}}$$

Normally,  $\Delta S$  means entropy change of system.

#### 4.2 Second law in terms of entropy of universe :

For any spontaneous process (irreversible process) -

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

During a reversible process -

$$\Delta S_{\text{universe}} = 0$$

Thus during irreversible process, entropy of universe increases while during reversible process, entropy of universe remains constant.

#### 4.3 Physical significance of quantity $\frac{dq_{rev}}{T}$ :

$dq_{rev}$  = heat absorbed by the system,  $T$  = absolute temperature at which heat is absorbed. Suppose, similar quantity of heat is absorbed at two different temperatures  $T_1$  and  $T_2$  ( $T_2 \gg T_1$ ). When heat is supplied at high temperature, the % age increase in kinetic energy is less compared to heat supplied at low temperature. Hence, disorder will increase by greater value, when heat is supplied at lower temperature.

4.4 Determining ' $\Delta S_{\text{surr.}}$ ' for irreversible processes :

The change in entropy is given by :  $\frac{\text{heat absorbed by an entity}}{\text{Exact temperature at which heat is absorbed}}$

The irreversible processes are fast and uncontrolled. The exact temperature of system during exchange of heat cannot be known. Hence, reversible path is needed to evaluate the entropy of system. Along reversible path, the heat exchange and exact temperature both are known.

Surrounding is generally a big entity and heat absorbed by surrounding is comparatively very small as compared to its size. Hence, internal equilibrium of surrounding is not disturbed during exchange of heat.

$\therefore$  Actual heat exchange of system is reversible heat exchange of surroundings

$\therefore (q_{\text{rev}})_{\text{surr}} = -q_{\text{irr}}$  [ $q_{\text{irr}}$  = Actual heat gained by system in a irreversible process.]

Hence, exact temperature and heat exchange both are known as far as surrounding is concerned even for an irreversible process.

$\therefore$  For irreversible process :  $\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T}$

	$\Delta S_{\text{system}}$	$\Delta S_{\text{surrounding}}$
(i)	<p><b>For reversible process :</b></p> $\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}$	<p><b>For reversible process :</b></p> $\Delta S_{\text{surr}} = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T} = -\Delta S_{\text{system}}$
(ii)	<p><b>For irreversible process :</b></p> $\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}$ <p>[Where ; <math>dq_{\text{rev}}</math> = heat gained by system for imaginary reversible path between same states]</p>	<p><b>For irreversible process :</b></p> $\Delta S_{\text{surr}} = -\frac{q_{\text{irr}}}{T}$
(iii)	<p>Always evaluated along reversible path (for both reversible and irreversible process)</p>	<p>For reversible process, <math>\Delta S_{\text{surr}}</math> is evaluated along reversible path, while for irreversible process, irreversible heat is used to calculate <math>\Delta S_{\text{surr}}</math>.</p>
(iv)	<p>Since no actual process is reversible, <math>\Delta S_{\text{system}}</math> is always evaluated by hypothetical path.</p>	<p>For hypothetical process, <math>\Delta S_{\text{surr}}</math> is evaluated by hypothetical heat, while for real irreversible process, it is evaluated by heat exchanged in irreversible process.</p>

## 5. SECOND LAW (IN TERMS OF ENGINE)

- (i) No cyclic engine is possible whose only effect is complete conversion of heat into work without making any change in surrounding on its own.
- (ii) Heat can not flow from cold body to hot body on it's own without external intervention.
- (iii) Complete conversion of heat (taken from a single source) into work is not possible in a cyclic process while complete conversion of work into heat is possible in a cyclic process. Thus, heat and work are not equivalent from the view point of II law.

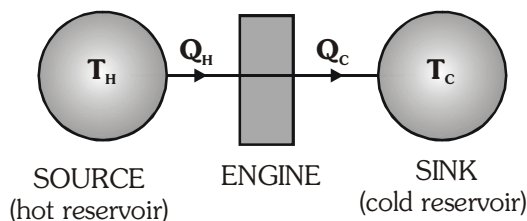
All above statements can be easily justified by realising that heat is a disordered form of energy while work is an ordered form of energy.

Complete conversion of [**Heat**  $\longrightarrow$  **Work**] on it's own without any external assistance means [**Disorder**  $\longrightarrow$  **Order**] on it's own - which is impossible.

### 5.1 Heat engine :

A heat engine is a device which can work continuously and cyclically without any external help absorbing heat from a source and rejecting a part of heat into sink. The net heat absorbed by engine (heat absorbed from source – heat given out to sink) is converted into work.

$\Rightarrow$  Heat engine must work in cycles , otherwise it can not work continuously.



$Q_H$  = Heat gained by engine per cycle

$Q_C$  = Heat rejected by engine per cycle

$$\text{Efficiency of engine : } \eta = \frac{Q_H - Q_C}{Q_H} = \frac{W_{by}}{Q_H}$$

$W_{by}$  = Work done by engine per cycle.

During operation of heat engine, heat is transferred from source (high temperature reservoir) to sink (low temperature reservoir) thus degrading the quality of energy. Note that net energy of universe remains conserved, but it's quality is degraded (i.e. more disordered energy) when heat engine runs spontaneously.

### 5.2 CARNOT ENGINE

A carnot engine (a hypothetical engine) runs in reversible manner. Thus during expansion (work producing process) maximum work is done. However during compression (work requiring process) minimum work need to be done. Thus no engine can be more efficient than carnot engine.

The carnot engine works in following steps. (Assume ideal gas as working material).

- (i) Reversible isothermal expansion  $(P_1, V_1, T_2 \rightarrow P_2, V_2, T_2)$
- (ii) Reversible adiabatic expansion  $(P_2, V_2, T_2 \rightarrow P_3, V_3, T_1)$
- (iii) Reversible isothermal compression  $(P_3, V_3, T_1 \rightarrow P_4, V_4, T_1)$
- (iv) Reversible adiabatic compression  $(P_3, V_3, T_1 \rightarrow P_1, V_4, T_2)$

Now:  $Q_{NET} = -W_{NET}$

$$W_{NET} = w_{12} + w_{23} + w_{34} + w_{41}$$

$$w_{12} = -nRT_H \ln\left(\frac{V_2}{V_1}\right)$$

$$w_{23} = nC_V(T_C - T_H)$$

$$w_{34} = -nRT_C \ln\left(\frac{V_4}{V_3}\right)$$

$$w_{41} = -nC_V(T_H - T_C)$$

.....(i)

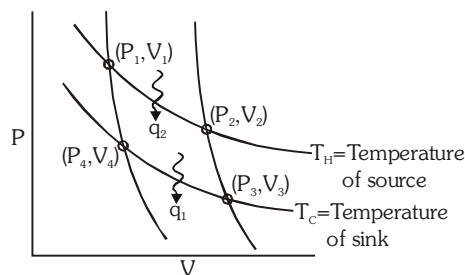
.....(ii)

.....(iii)

.....(iv)

.....(v)

.....(vi)



Also since process 2 – 3 and 4 – 1 are reversible adiabatic process.

$$T_H V_2^{\gamma-1} = T_C V_3^{\gamma-1}$$

$$T_C V_1^{\gamma-1} = T_H V_4^{\gamma-1}$$

from above equations

$$\left(\frac{V_2}{V_1}\right) = \left(\frac{V_3}{V_4}\right)$$

.....(vii) for process 2 – 3

.....(viii) for process 1 – 4

.....(ix)

Substituting the value of  $\left(\frac{V_4}{V_3}\right)$  in eq.(v) and adding w in individual step.

$$W_{NET} = -nRT_H \ln\left(\frac{V_2}{V_1}\right) + nC_V(T_C - T_H) - nRT_C \ln\left(\frac{V_4}{V_3}\right) - nC_V(T_C - T_H)$$

$$W_{NET} = -nRT_H \ln\left(\frac{V_2}{V_1}\right) - nRT_C \ln\left(\frac{V_1}{V_2}\right)$$

$$W_{NET} = -nR [T_C - T_H] \ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow \text{Efficiency } \eta = -\frac{W_{NET}}{q_2}$$

$$\eta = \frac{nR \ln\left(\frac{V_2}{V_1}\right) [T_H - T_C]}{nRT_H \ln\left(\frac{V_2}{V_1}\right)}$$

$$\therefore \eta = \frac{T_H - T_C}{T_H}$$

Thus efficiency of carnot engine depends only upon temperature of source and sink.

Note : If working substance is changed (eg. ideal gas by real gas) efficiency of carnot engine remains unaffected.

## EXERCISE-1

- A heat engine absorbs 760 kJ heat from a source at 380K. It rejects (i) 650 kJ, (ii) 560 kJ, (iii) 504 kJ of heat to sink at 280K. State which of these represent a reversible, an irreversible or an impossible cycle.
- The maximum efficiency of a heat engine operating between 100°C and 25°C is :-  
(A) 20.11% (B) 22.2% (C) 25.17% (D) None
- A carnot engine operating between 227°C and 27°C absorbs 2 Kcal of heat from the 227°C reservoir reversibly per cycle. The amount of work done in one cycle is :-  
(A) 0.4 Kcal (B) 0.8 Kcal (C) 4 Kcal (D) 8 Kcal
- An ideal gas heat engine operates in carnot's cycle between 227°C and 127°C. It absorbs  $6 \times 10^4$  cal of heat at high temperature. Amount of heat converted to work is :  
(A)  $2.4 \times 10^4$  cal (B)  $4.8 \times 10^4$  cal (C)  $1.2 \times 10^4$  cal (D)  $6.0 \times 10^4$  cal

## 6. ENTROPY CHANGE OF AN IDEAL GAS

From definition of entropy of system -

$$dS_{\text{system}} = \frac{dq_{\text{rev}}}{T} \quad \text{.....(i)}$$

from first law,  $dq_{\text{rev}} = dU + PdV$

For a reversible change involving an ideal gas -

$$dq_{\text{rev}} = nC_{V,m} \cdot dT + \frac{nRT}{V} \cdot dV \quad \text{.....(ii)}$$

$$\Rightarrow \int_1^2 \frac{dq_{\text{rev}}}{T} = \int_1^2 \frac{nC_{V,m} dT}{T} + \int_{V_1}^{V_2} nR \frac{dV}{V}$$

$$\Delta S_{\text{system}} = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ln \left( \frac{V_2}{V_1} \right) = nC_{P,m} \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

Note : This formula is applicable to all ideal gas process.

## 6.1 Ideal gas processes :

## (i) For isothermal change :

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_1^2 dq_{\text{rev}} \quad (\because T = \text{constant})$$

$$\Rightarrow \Delta S = \frac{q_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1} \quad \left[ \because q_{\text{rev}} = nRT \ln \left( \frac{V_2}{V_1} \right) \right]$$

## (ii) For isochoric change :

$$\Delta S = \int_1^2 \frac{dq_v}{T} = \int_1^2 \frac{nC_{V,m} dT}{T} = nC_{V,m} \int_1^2 \frac{dT}{T} \quad [\because dq_v = nC_{V,m} \cdot dT]$$

$$\Rightarrow \Delta S = nC_{V,m} \ln \frac{T_2}{T_1}$$

## (iii) For isobaric change :

$$\Delta S = \int_1^2 \frac{dq_p}{T} = \int_1^2 \frac{nC_{P,m} dT}{T} = nC_{P,m} \int_1^2 \frac{dT}{T} \quad [\because dq_p = nC_{P,m} dT]$$

$$\Rightarrow \Delta S = nC_{P,m} \ln \left( \frac{T_2}{T_1} \right)$$



**(iv) Reversible adiabatic process :**

$$q_{\text{rev}} = 0$$

$$\Rightarrow \Delta S = \underbrace{nC_V \ln \frac{T_2}{T_1}}_{\text{entropy change due to change in temperature}} + \underbrace{nR \ln \frac{V_2}{V_1}}_{\text{entropy change due to change in volume}} = 0$$

**(a) During reversible adiabatic expansion :**

$$T_2 < T_1 \text{ and } V_2 > V_1$$

$\Rightarrow$  Sign of two terms are opposite and magnitudes are same because for reversible adiabatic process -

$$nC_{V,m} \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1}$$

$\Rightarrow$  +ive and -ive term cancel out each other and hence,  $\Delta S = 0$

Thus, decrease in entropy during expansion due to decrease in temperature is exactly cancelled out by increase in entropy due to increase in volume of system in reversible adiabatic expansion.

**(b) During reversible adiabatic compression :**

$$T_2 > T_1 \text{ and } V_2 < V_1$$

$$\Rightarrow \Delta S_{\text{Total}} = \underbrace{nC_{V,m} \ln \frac{T_2}{T_1}}_{\text{+ive}} + \underbrace{nR \ln \frac{V_2}{V_1}}_{\text{? ive}} = 0$$

Thus, increase in entropy due to increase in temperature is compensated by decrease in entropy due to decrease in volume of system in reversible adiabatic compression.

Hence,  $\Delta S = 0$  for reversible adiabatic compression.

**(v) Irreversible adiabatic process :**

Since process is irreversible,  $\Delta S_{\text{Total}} > 0$ .

$$\Rightarrow \Delta S_{\text{system}} + \Delta S_{\text{surr}} > 0$$

$$\because \Delta S_{\text{surr}} = 0$$

$$\because \Delta S_{\text{system}} > 0$$

The physical interpretation is -

**(a)** During irreversible adiabatic compression, large quantity of heat is produced while decrease in volume is less.

Thus, increase in entropy due to rise in temperature exceeds the decrease in entropy due to decrease in volume. Hence net entropy change is positive.

**(b)** During irreversible adiabatic expansion, due to sudden decrease in external pressure, the system remains less challenged during expansion. Hence system does less work - resulting in lesser decrease in temperature.

The increase in volume of system is relatively larger (because system was less challenged)

Thus increase in entropy due to increase in volume exceeds decrease in entropy due to decrease in temperature. The net change in entropy is positive in both processes  $\Delta S_{\text{surr.}} = 0$  ( $\because$  no heat is exchanged with surrounding) and  $\Delta S_{\text{total}} > 0$ .

**(vi) Free expansion of an ideal gas against vacuum :**

Free expansion of an ideal gas is an example of irreversible adiabatic as well as irreversible isothermal process.

During free expansion, the  $P_{\text{ext.}} = 0$ . Hence, the ideal gas is not challenged at all during expansion. The kinetic energy of ideal gas remains constant. Hence, no temperature difference is created during expansion between system and surrounding.

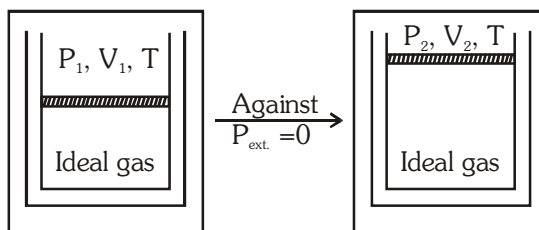
$\because \Delta T = 0$ , the heat absorbed during the process = 0

Since,  $V_f > V_i$  and  $T = \text{constant}$ ,  $\Delta S_{\text{system}} > 0$

The free expansion is an example where  $q_{\text{actual}} = 0$ , still  $\Delta S_{\text{system}} > 0$ .

This is reasonable, because :  $\Delta S_{\text{system}} = \int \frac{dq_{\text{rev.}}}{T}$

This, example clearly shows that even if  $q_{\text{actual}}$  between two states is zero, this does not mean that  $\int_1^2 \frac{dq_{\text{rev.}}}{T}$  between two states is zero. This outlines the importance of reversible path and  $q_{\text{rev.}}$  in calculation of entropy of system.



$$q_{\text{irr}} = 0 ; w_{\text{irr}} = 0$$

$$\Delta S_{\text{system}} = \int_1^2 \frac{dq_{\text{rev.}}}{T} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{surr.}} = \frac{-q_{\text{irr}}}{T} = 0$$

$$\Delta S_{\text{total.}} = nR \ln \frac{V_2}{V_1} > 0$$

ENTROPY CALCULATION

Process	$\Delta S_{\text{Sys.}}$	$\Delta S_{\text{Surr.}}$
Isothermal reversible	$\Delta S_{\text{Sys.}} = nR \ln \frac{V_2}{V_1}$	$\Delta S_{\text{Surr.}} = -\Delta S_{\text{Sys.}}$
Isothermal irreversible	$\Delta S_{\text{Sys.}} = nR \ln \frac{V_2}{V_1}$	$\Delta S_{\text{Surr.}} = \frac{-q_{\text{Sys}}}{T} = \frac{W_{\text{Sys}}}{T} = \frac{-P_{\text{ext}}(V_2 - V_1)}{T}$
Adiabatic reversible	$\Delta S_{\text{Sys.}} = 0$	$\Delta S_{\text{Surr.}} = 0$
Adiabatic irreversible	$\Delta S_{\text{Sys.}} = nC_{P,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$	$\Delta S_{\text{Surr.}} = 0$
Isochoric reversible	$\Delta S_{\text{Sys.}} = nC_{V,m} \ln \frac{T_2}{T_1}$	$\Delta S_{\text{Surr.}} = -\Delta S_{\text{Sys.}}$
Isochoric irreversible	$\Delta S_{\text{Sys.}} = nC_{V,m} \ln \frac{T_2}{T_1}$	$\Delta S_{\text{Surr.}} = \frac{-q_{\text{sys}}}{T_{\text{surr}}} = \frac{-nC_{V,m} \Delta T}{T_{\text{final}}}$

**Ex.1** Three moles of an ideal gas is expanded isothermally from 2L to 10L, at 27°C. Calculate  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{univ.}}$ , if the process is preformed.

(i) Reversibly

(ii) Irreversibly, against a constant external pressure of 1 atm

(iii) As free expansion

**Sol:** (i)  $\Delta S_{\text{univ.}} = 0$ ,  $\Delta S_{\text{surr.}} = -\Delta S_{\text{sys.}}$

$$\text{and } \Delta S_{\text{sys}} = nR \ln \frac{V_2}{V_1} = 3R \cdot \ln \frac{10}{2} = 40.14 \text{ J/K}$$

(ii)  $\Delta S_{\text{sys}} = 40.14 \text{ J/K}$

$$\Delta S_{\text{surr.}} = -\frac{P_{\text{ext.}}(V_2 - V_1)}{T} = -\frac{1 \times (10 - 2) \times 101.3}{300} = -2.7 \text{ J/K}$$

$$\text{and } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 37.44 \text{ J/K}$$

(iii)  $\Delta S_{\text{sys}} = 40.14 \text{ J/K}$

$$\Delta S_{\text{surr.}} = 0 \quad \text{as } P_{\text{ext}} = 0$$

$$\text{and } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 40.14 \text{ J/K}$$

**Ex.2.** Two moles of an ideal monoatomic gas is expanded adiabatically from 10L, 27°C to 80L. Calculate  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{univ}}$ , if the process is performed.

(i) Reversibly

(ii) Irreversibly, against a constant external pressure of 0.1 atm.

(iii) As free expansion

**Sol.:**  $\Delta S_{\text{surr}} = 0$  for all

(i)  $\Delta S_{\text{sys}} = \Delta S_{\text{surr}} = \Delta S_{\text{univ}} = 0$

(ii)  $n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{\text{ext}}(V_2 - V_1)$

$$\text{or } 2 \times \frac{3}{2} \times 0.0821 \times (T_2 - 300) = -0.1 \times (80 - 10) \Rightarrow T_2 = 271.58 \text{ K}$$

$$\text{Now, } \Delta S_{\text{sys}} = n \cdot C_{v,m} \cdot \ln \frac{T_2}{T_1} + nR \cdot \ln \frac{V_2}{V_1}$$

$$= 2 \times \frac{3}{2} R \times \ln \frac{271.58}{300} + 2 \times R \times \ln \frac{80}{10} = 32.90 \text{ J/K}$$

and  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}}$

$$\text{(iii) } T_1 = T_2 \Rightarrow \Delta S_{\text{sys}} = nR \cdot \ln \frac{V_2}{V_1} = 2 \times R \times \ln \frac{80}{10} = 34.58 \text{ J/K}$$

## 6.2 Entropy change of solids and liquids upon heating :

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \int \frac{mS \cdot dT}{T} = mS \cdot \ln \frac{T_2}{T_1} \quad [S = \text{specific heat of solid/ liquid}]$$

For molar change in entropy,  $m = M(\text{g/mole})$ ; where  $M = \text{molar mass}$ .

Note, for solids and liquids ( $MS \cong C_p \cong C_v$ )

**Ex.3** Two blocks of equal masses and heat capacity but at different temperatures are taken in an adiabatic vessel. Show that total change in entropy when both attain thermal equilibrium is always positive.

**Sol.** Let the temperature of hot body be  $T_H$ , temperature of cold body be  $T_C$  & the final temperature be  $T_F$ .

Now, net heat exchanged by two bodies must be zero.

$$\Rightarrow m \cdot S (T_F - T_H) + mS (T_F - T_C) = 0$$

$$\Rightarrow T_F = \frac{T_H + T_C}{2}$$

Since both bodies are of finite mass, entropy of both bodies are evaluated by reversible paths.

$$\Delta S_{\text{Hot}} = \int_{T_H}^{T_F} mS \cdot \frac{dT}{T} = mS \cdot \ln \frac{T_F}{T_H}$$

$$\Delta S_{\text{Cold}} = \int_{T_C}^{T_F} mS \cdot \frac{dT}{T} = mS \cdot \ln \frac{T_F}{T_C}$$

$$\Rightarrow \Delta S_{\text{total}} = (mS) \ln \left( \frac{T_F^2}{T_H T_C} \right)$$

$$\Rightarrow T_H^2 + T_C^2 + 2T_H T_C - 4T_H T_C = (T_H - T_C)^2 > 0$$

$$\Rightarrow (T_H + T_C)^2 > 4T_H T_C$$

$$\Rightarrow \Delta S_{\text{total}} > 0$$

6.3 Reversible phase transitions :

Reversible phase transitions are always isothermal & isobaric.

$$\Delta S_{\text{system, P,T}} = \frac{q_{\text{rev.}}}{T} = \frac{\Delta H_{\text{P,T}}}{T_{\text{Transition}}}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{P,T}}}{T_{\text{Transition}}}$$

$$\Delta S_{\text{total}} = 0$$

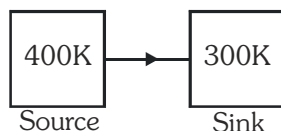
Thus,  $\Delta S_{\text{vaporisation}}$  at boiling point =  $\frac{\Delta H_{\text{vaporisation}}}{T_{\text{vaporisation}}}$

$$\Delta S_{\text{fusion}}$$
 at melting point =  $\frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$

$$\Delta S_{\text{sublimation}}$$
 at sublimation point =  $\frac{\Delta H_{\text{sublimation}}}{T_{\text{sublimation}}}$

$$\Delta S_{\text{allotropic modification}} = \frac{\Delta H_{\text{allotropic modification}}}{T_{\text{transition}}}$$

Ex.4 100 kJ heat is transferred from a larger heat reservoir at 400 K to another large heat reservoir at 300 K. Suppose there is no change in temperature due to exchange of heat :



Find  $\Delta S_{\text{source}}$ ,  $\Delta S_{\text{sink}}$  and  $\Delta S_{\text{total}}$ . Comment on spontaneity of process.

Ans. (i)  $\Delta S_{\text{source}} = \frac{\text{heat absorbed by source}}{\text{Temperature of source}}$

$$\Delta S_{\text{source}} = \frac{-100\text{kJ}}{400} = -250\text{J/K}$$

(ii)  $\Delta S_{\text{sink}} = \frac{\text{heat absorbed by sink}}{\text{Temperature of sink}}$

$$= \frac{+100000\text{J}}{300} = 333.33\text{J/K}$$

(iii)  $\Delta S_{\text{Total}} = \Delta S_{\text{source}} + \Delta S_{\text{sink}} = +83.33\text{J/K}$

Ex.5 Trouton's rule states that the ratio of the molar heat of vaporisation of a liquid to its normal boiling point is approximately the same for all liquids,  $\frac{\Delta H_{\text{vap}}}{T_{\text{bp}}} = 88\text{JK}^{-1}\text{mol}^{-1} = \Delta S_{\text{vap}}$ .

Which of the following liquids do not follow Trouton's rule :  $\text{NH}_3$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , Hg. Explain.

Ans.  $\text{NH}_3$ , due to H-bonding :  $\Delta S_{\text{vap}} > 88\text{J/K-mol}$

## EXERCISE-2

5. Identify the correct statement regarding a spontaneous process :- [AIEEE-2007]  
 (A) For a spontaneous process in an isolated system, the change in entropy is positive  
 (B) Endothermic processes are never spontaneous  
 (C) Exothermic processes are always spontaneous  
 (D) Lowering of energy in the reaction process is the only criterion for spontaneity
6. Find the change in entropy (in cal/k) of 1 mole of  $O_2$  gas ( $C_V = 5/2 R$ ), when it is  
 (a) heated from 300 K to 400 K isobarically  
 (b) heated from 300 K to 400 K isochorically (Given :  $\ln 3 = 1.1$ ,  $\ln 2 = 0.7$ )
7. One mole of  $NaCl(s)$  on melting at its melting point absorbed 32.76 kJ of heat and its entropy is increased by  $30 JK^{-1}$ . What is the melting point of sodium chloride ?
8. The entropy change when two moles of ideal monoatomic gas is heated from  $200^\circ C$  to  $300^\circ C$  reversibly and isochorically :-  
 (A)  $\frac{3}{2}R \ln\left(\frac{300}{200}\right)$  (B)  $\frac{5}{2}R \ln\left(\frac{573}{273}\right)$  (C)  $3R \ln\left(\frac{573}{473}\right)$  (D)  $\frac{3}{2}R \ln\left(\frac{573}{473}\right)$
9. Predict the sign entropy change for the following processes:  
 (A)  $O_2(g) \rightarrow 2O(g)$   
 (B)  $2O_3(g) \rightarrow 3O_2(g)$   
 (C)  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$   
 (D)  $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$   
 (E)  $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$   
 (F)  $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
10. 5 mole of an ideal gas expands reversibly from a volume of  $8 dm^3$  to  $80 dm^3$  at a constant temperature of  $27^\circ C$ . The change in entropy is :-  
 (A)  $41.57 JK^{-1}$  (B)  $-95.73 JK^{-1}$  (C)  $95.73 JK^{-1}$  (D)  $-41.57 JK^{-1}$
11.  $\Delta S$  for the reaction ;  $MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$  will be :  
 (A) 0 (B) -ve (C) +ve (D)  $\infty$
12. Change in entropy is negative for :-  
 (A) Bromine ( $\ell$ )  $\longrightarrow$  Bromine (g)  
 (B)  $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$   
 (C)  $(C) N_2(g, 10 \text{ atm}, 298 \text{ K}) \longrightarrow N_2(g, 1 \text{ atm}, 298K)$   
 (D)  $Fe(\text{at } 400 \text{ K}) \longrightarrow Fe(\text{at } 300 \text{ K})$
13. For which reaction from the following,  $\Delta S$  will be maximum ?  
 (A)  $Ca(s) + \frac{1}{2}O_2(g) \longrightarrow CaO(s)$  (B)  $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$   
 (C)  $C(s) + O_2(g) \longrightarrow CO_2(g)$  (D)  $N_2(g) + O_2(g) \longrightarrow 2NO(g)$
14. When two gases are mixed the entropy :-  
 (A) Remains constant (B) Decreases (C) Increases (D) Becomes zero
15. For the process,  $CO_2(s) \longrightarrow CO_2(g)$  :  
 (A) Both  $\Delta H$  and  $\Delta S$  are +ve (B)  $\Delta H$  is -ve and  $\Delta S$  is +ve  
 (C)  $\Delta H$  is +ve and  $\Delta S$  is -ve (D) Both  $\Delta H$  and  $\Delta S$  are -ve

7. THIRD LAW OF THERMODYNAMICS

“At absolute zero, the entropy of a perfectly crystalline substance is zero”, which means that at absolute zero, every crystalline solid is in a state of perfect order and its entropy should be zero.

By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

$$S_T - S_{0K} = \int_0^T \frac{q_{rev}}{T}$$

Since  $S_{0K} = 0$

$$S_T = \int_0^T \frac{q_{rev}}{T}$$

The variation of entropy of a substance with temperature is given by graph :

At 1, entropy of substance is zero.

- **from 1-2 ;** The temperature of solid increases upon heating -

$$\Rightarrow S_2 - S_1 = \int \frac{C_{P,solid}}{T} dT \quad \dots\dots(i)$$

- **from 2-3 ;** The temperature remains constant during phase transition

$$\Rightarrow S_3 - S_2 = \Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f} \quad \dots\dots(ii)$$

- **from 3-4 ;** The temperature of liquid increases

$$\Rightarrow S_4 - S_3 = \int_{T_3}^{T_4} \frac{C_{P,liquid} \cdot dT}{T} \quad \dots\dots(iii)$$

- **from 4-5 ;** Reversible vaporisation takes place at constant temperature -

$$\Rightarrow S_5 - S_4 = \Delta S_{vap.} = \frac{\Delta H_{vap.}}{T_b} \quad \dots\dots(iv)$$

- **from 5-6 ;** The gas is heated -

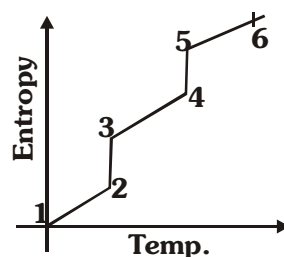
$$\Rightarrow S_6 - S_5 = \int_{T_5}^{T_6} \frac{C_{P,gas} \cdot dT}{T} \quad \dots\dots(v)$$

$$\Delta S_{1-6} = (S_2 - S_1) + (S_3 - S_2) + (S_4 - S_3) + (S_5 - S_4) + (S_6 - S_5) = S_6 - S_1 \quad [\because S_1 = 0]$$

$\therefore S_6 =$  absolute entropy at 6.

$$= \int_{T_1}^{T_2} \frac{C_{P,Solid} dT}{T} + \frac{\Delta H_{fusion}}{T_f} + \int_{T_3}^{T_4} \frac{C_{P,liquid} dT}{T} + \frac{\Delta H_{vap}}{T_b} + \int_{T_5}^{T_6} \frac{C_{P,gas} dT}{T}$$

- **Comment :** Absolute entropy of a substance can be calculated using third law by reversible path.



Change in entropy of a pure substance with temperature at constant pressure.

**7.1 Standard absolute molar entropy :**

It is the entropy in one mole of substance at standard temperature at 1 bar.

It is calculated assuming that substance is heated isobarically and reversibly at 1 bar from 0 K to standard temperature.

**7.2 Comparing absolute entropies of substance :**

(i) The absolute entropies of substance follow the order,

$$S(g) \gg S(l) > S(s)$$

(ii) Entropy increases when solid and liquid is dissolved into solvent,

e.g.	CH <sub>3</sub> OH(l)	S° = 127 J/K-mole
	CH <sub>3</sub> OH(aq)	S° = 132.3 J/K-mole
	NaCl(s)	S° = 72.4 J/K-mole
	NaCl(aq.)	S° = 115.4 J/K-mole

(iii) The entropy of dissolved gas is less than pure gas.

e.g.	HCl(g)	S° = 186.7 J/K-mole
	HCl(aq)	S° = 55.2 J/K-mole

(iv) Entropy rises with increasing mass, (if other factors are similar).

e.g.	F <sub>2</sub> (g)	S° = 203 J/K-mole
	Cl <sub>2</sub> (g)	S° = 223 J/K-mole
	Br <sub>2</sub> (g)	S° = 245 J/K-mole

(v) Entropy is lower in covalently bonded solids, with strong directional bonds, than in solids with partial metallic character.

e.g.	C(diamond)	S° = 2.44 J/K-mole
	C(graphite)	S° = 5.69 J/K-mole
	Sn(gray)	S° = 44.8 J/K-mole
	Sn(white)	S° = 51.5 J/K-mole

(vi) Entropy increases with increasing softness and with weakness of bonds between atoms.

e.g.	C(diamond)	Be(s)	S <sub>1</sub> O <sub>2</sub> (s)	Pb(s)	Hg(l)
	2.44	9.54	41.8	64.9	77.4
	diamond	hard metal	quartz	soft metal	liquid

(vii) Entropy increases with chemical complexity

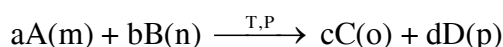
Sub.	NaCl	MgCl <sub>2</sub>	AlCl <sub>3</sub>	
	72.4	89.5	167	
For CuSO <sub>4</sub> .nH <sub>2</sub> O				
	n = 0	n = 1	n = 3	n = 5
	S° = 113	150	225	305

**Note : Above data is given in SI unit.**

**7.3 Entropy change ( $\Delta_r S$ ) of a chemical reaction :**

The change in entropy when reactants turn into products according to a balanced chemical reaction with specified physical state of each reactant and product is called entropy of reaction.

• **Consider a reaction :**



where m, n, o, p are physical states at temperature T and pressure P.

$$\Delta_r S = \sum S(\text{products}) - \sum S(\text{reactants})$$

$$\Delta_r S = cS_C + dS_D - aS_A - bS_B$$

$S_A$ ,  $S_B$ ,  $S_C$  and  $S_D$  are absolute molar entropies at temperature T and pressure P (**from third law**)

So,  $\Delta_r S$  is evaluated from table of data of third law entropies of various substances.



**7.4  $\Delta S_{\text{Surrounding}}$  for chemical reaction :**

$\Delta_r H = q_p =$  heat absorbed by the system during chemical reaction.

$\Rightarrow -\Delta_r H = -q_p = q_{\text{surr}} =$  heat absorbed by the surrounding.

Now,

$$\Delta S_{\text{Surr}} = \frac{q_{\text{surr}}}{T} = -\frac{\Delta_r H}{T}$$

If  $\Delta_r H = -\text{ive}$  (exothermic) heat is lost by the system and gained by the surrounding. Hence,  $\Delta S_{\text{surr}}$  increases.

If  $\Delta_r H = +\text{ive}$  (endothermic process), entropy of surrounding decreases.

$$\therefore \Delta S_{\text{surr}} = -\frac{\Delta_r H}{T} = -\text{ive}$$

- We can not comment on entropy change of system from knowledge of  $\Delta_r H$ . The entropy change of system ( $\Delta_r S$ ) is estimated by third law.

**7.5 Driving force of a spontaneous chemical process :**

The driving force of a spontaneous chemical process is increase in entropy of universe.

In simple terms, negative value of  $\Delta_r H$  and positive value of  $\Delta_r S$  favours the chemical process.

If  $\Delta_r H$  is positive, the enthalpy factor don't support the forward process. Under these conditions,  $\Delta_r S$  should be sufficiently positive to drive the reaction in forward direction. If  $\Delta_r H$  is +ive and  $\Delta_r S$  is -ive, under a given situation, the process become non-spontaneous because both factors tends to decrease the entropy of the universe.

**7.6 Prediction the sign of  $\Delta_r S$  by inspecting a balanced chemical reaction.**

(i) If more no. of gaseous moles are present on product side,  $\Delta_r S$  will be +ive (since gas is more disordered than solid or liquid).

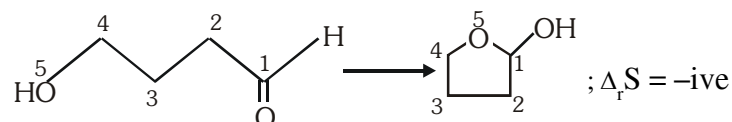
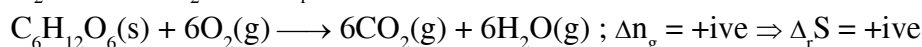
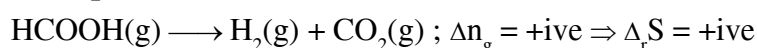
- (ii) If
- solid  $\longrightarrow$  liquid
  - solid  $\longrightarrow$  gas
  - liquid  $\longrightarrow$  gas

then,  $\Delta_r S = +\text{ive}$ .

(iii) If a molecule is undergoing cyclisation, it's rotational modes of motion are replaced by vibrational modes of motion.

Since quantum energy separation of rotational motion is closely spaced compared to vibrational energy state, rotational energy is more disordered. Hence,  $\Delta_r S = -\text{ive}$ .

**Example :**



### 7.7 Table for spontaneity of chemical process and sign of $\Delta_r H$ , $\Delta_r S$ and dependence on temperature.

Sign of $\Delta H$	Sign of $\Delta S$	Comment	Example	$\Delta H_{298}^\circ$	$\Delta S_{298}^\circ$
-	+	Spontaneous at all temperature	$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ $C(s) + O_2(g) \rightarrow CO_2(g)$	-185 -394	14.1 3
-	-	Spontaneous at low temperature	$H_2(g) + 1/2 O_2(g) \rightarrow H_2O(l)$ $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	-44 -198	-119 -187
+	+	Spontaneous at high temperature	$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$ $N_2(g) + O_2(g) \rightarrow 2NO(g)$	176 180	284 25
+	-	Non spontaneous at all temperature	$3O_2 \rightarrow 2O_3$ $2H_2O(l) + O_2(g) \rightarrow 2H_2O_2(l)$	286 196	-137 -126

### 7.8 State of equilibrium :

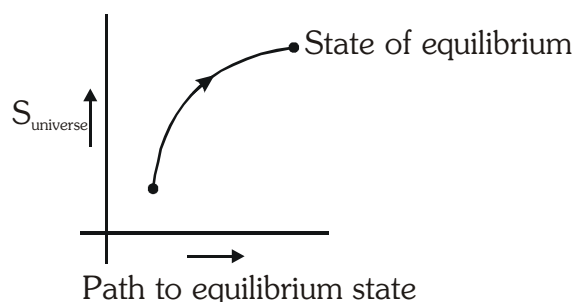
A system at equilibrium is a stable system. Hence, its state variables become constant (do not vary with time) at equilibrium.

If a system is in non-equilibrium state, it moves spontaneously in the direction of equilibrium (because the equilibrium state is stable). During the spontaneous movement towards equilibrium, the entropy of universe increases.

As the system gets closer to equilibrium state, the driving force to attain equilibrium become small and so does the increase in disorder of universe. At equilibrium, the driving force to move ahead finishes and entropy of the universe can not increase further.

In nutshell, when a system attains equilibrium, its capacity to increase the disorder of universe is lost.

- At equilibrium, the entropy of universe is maximum.



## 8. GIBB'S FUNCTION

Gibb's function 'G' is defined as  $G = H - TS$ .

Since 'G' is a combination of state variables (a compound state variable), it is a state function. The dimension of Gibb's function is the dimension of energy. 'G' is an extensive quantity.

Gibb's function provide a very useful criteria for spontaneity of a process taking place at constant temperature and pressure (isobaric, isothermal process).

The entropy of universe is also a very useful criteria of spontaneity, but it is based on properties of system as well as surrounding.

The Gibb's function provides criteria for spontaneity based only on the properties of system.

$$\Delta G = \Delta H - \Delta(TS)$$

$$\Delta G = \Delta H - T\Delta S$$

(Isothermal process)

**Ex.6** The thermodynamic stability of a substance is dependent upon the value of Gibb's function. Explain the stability of solid at low temperature and stability of gas at very high temperature.

**Sol.** Any stable state tries to minimise its enthalpy while maximising its entropy.

$$\text{For solids - } G_{\text{solid}} = H_{\text{solid}} - TS_{\text{solid}} \quad (\text{at certain T \& P})$$

$$\text{For liquids - } G_{\text{liquid}} = H_{\text{liquid}} - TS_{\text{liquid}} \quad (\text{at certain T \& P})$$

$$\text{For gas - } G_{\text{gas}} = H_{\text{gas}} - TS_{\text{gas}} \quad (\text{at certain T \& P})$$

$$\text{At any given T and P, } H_{\text{solid}} < H_{\text{liquid}} < H_{\text{gas}}$$

$$\text{and } S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$

At very low temperature, TS term contributes very little towards Gibb's function. Hence -

$$G_{\text{solid}} < G_{\text{liquid}} < G_{\text{gas}} \quad (\text{at very low temperature}).$$

This explains why solids are most stable at low temperature.

At very high temperature, TS term is very important. Since  $S_{\text{gas}}$  is large, for gas TS term becomes very large at large temperature. Hence -

$\Rightarrow G_{\text{solid}} > G_{\text{liquid}} > G_{\text{gas}}$  (at very high temperature). Thus, gaseous state is most stable at high temperature.

Hence, the low enthalpies of solid are responsible for stability of solid at low temperature, while high entropy of gas is responsible for stability of gas at high temperature.

### 8.1 $\Delta G_{T,P}$ and $\Delta S_{\text{universe}}$

Decrease in Gibb's function at constant temperature and pressure is related to  $\Delta S_{\text{total}}$  (total entropy change of system and surrounding).

$$-\Delta G = T(\Delta S_{\text{total}})$$

**At constant P, T**

**if  $\Delta G < 0 \Rightarrow$  spontaneous process**

**if  $\Delta G > 0 \Rightarrow$  non-spontaneous process**

**if  $\Delta G = 0 \Rightarrow$  reversible process**

**At constant P, T, Gibbs energy of a system spontaneously decreases.**

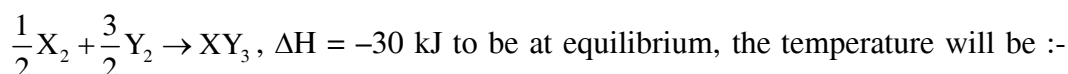
## EXERCISE-3

16. Animals operate under conditions of constant pressure and most of the processes that maintain life are electrical (in a broad sense). How much energy is available for sustaining this type of muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37°C (blood temperature) ? The entropy change is + 210 JK<sup>-1</sup> for the reaction as stated.

$$\Delta H_{\text{combustion [glucose]}} = -2808 \text{ kJ / mol.}$$

17. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?  
 (A) endothermic and decreasing disorder      (B) exothermic and increasing disorder  
 (C) endothermic and increasing disorder      (D) exothermic and decreasing disorder

18. Standard entropy of X<sub>2</sub>, Y<sub>2</sub> and XY<sub>3</sub> are 60, 40 and 50 JK<sup>-1</sup>mol<sup>-1</sup>, respectively. for the reaction,



- (A) 1250 K      (B) 500 K      (C) 750 K      (D) 1000 K

19. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T<sub>e</sub> is the temperature at equilibrium, then reaction would be spontaneous when :-

[AIIEE-2010]

- (A) T = T<sub>e</sub>      (B) T<sub>e</sub> > T      (C) T > T<sub>e</sub>      (D) T<sub>e</sub> is 5 times T

20. For a reaction at 25°C, enthalpy change (ΔH) and entropy change (ΔS) are -11.7 × 10<sup>3</sup> J mol<sup>-1</sup> and -105 J mol<sup>-1</sup> K<sup>-1</sup> respectively. The reaction is :

- (A) Spontaneous      (B) Non spontaneous      (C) At equilibrium      (D) Can't say anything

21. Identify the correct statement for change of Gibbs energy for a system at constant temperature and pressure.

- (A) If ΔG<sub>system</sub> > 0, the process is spontaneous.  
 (B) If ΔG<sub>system</sub> = 0, the system has attained equilibrium.  
 (C) If ΔG<sub>system</sub> = 0, the system is still moving in a particular direction.  
 (D) If ΔG<sub>system</sub> < 0, the process is non spontaneous.

22. In conversion of lime-stone to lime, CaCO<sub>3</sub>(s) → CaO(s) + CO<sub>2</sub>(g)

the values of ΔH° and ΔS° are +179.1 kJ mol<sup>-1</sup> and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is :-

[AIIEE-2007]

- (A) 1008 K      (B) 1200 K      (C) 845 K      (D) 1118 K

## 8.2 CALCULATE ΔG FOR VARIOUS PROCESSES

- (i) **Ideal gas subjected to isothermal compression or expansion :**

For isothermal process :

$$\Delta G = \Delta H - T\Delta S$$

For ideal gas, ΔH = nC<sub>p,m</sub>ΔT = 0

(As ΔT = 0, for isothermal change)

$$\& \quad \Delta S = nR \ln \frac{V_2}{V_1}$$

(for isothermal change)

$$\therefore \quad \Delta G = -nRT \ln \frac{V_2}{V_1}$$

Hence, during isothermal expansion Gibb's function decreases while during isothermal compression Gibb's function increases.

(ii) **Isothermal and isobaric phase transitions :**

At transition temperature, the stability (or Gibb's functions) of two phases are equal. Hence, there is no driving force for conversion of one phase into other. This means phase transitions are examples of reversible processes at transition temperature.

Now, for reversible, isothermal and isobaric change,  $\Delta G = 0$

$\Rightarrow \Delta G = 0$ , for phase transitions at transition temperature.

Thus,  $\Delta G_{\text{vap}} = 0$  at boiling point :

$$\Rightarrow \Delta H_{\text{vap}} = T_b \Delta S_{\text{vap}}$$

$$\Rightarrow T_b = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}}$$

Also,  $\Delta G_{\text{fusion}} = 0$  at melting point :

$$\Rightarrow \Delta H_{\text{fusion}} = T_f \Delta S_{\text{fusion}}$$

$$T_f = \frac{\Delta H_{\text{fusion}}}{\Delta S_{\text{fusion}}}$$

**Ex.7** The enthalpy of vaporization of a liquid is  $30 \text{ kJ mol}^{-1}$  and entropy of vaporization is  $75 \text{ J mol}^{-1} \text{ K}^{-1}$ . The boiling point of the liquid at 1 atm is :

- (A) 250 K                      (B) 400 K                      (C) 450 K                      (D) 600 K

**Ans. [B]**

**Sol.**  $T = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}} = \frac{30 \times 10^3}{75} = 400 \text{ K}$

**Ex.8** At what minimum temperature would a given reaction become spontaneous if  $\Delta H = +119 \text{ kJ}$  and  $\Delta S = +263 \text{ J/K}$ ?

- (A) 452 K                      (B) 2210 K                      (C) 382 K                      (D) 2.21 K

**Ans. [A]**

**Sol.**  $T = \frac{\Delta H}{\Delta S} = \frac{119 \times 10^3}{263} = 452.47 \text{ K}$

**iii.  $\Delta_r G$  for a chemical reaction.**



The change in Gibb's function for a chemical reaction is change in  $\Delta G$  when reactants react according to a given balanced chemical reaction with specified physical state of each reactant and product at given temperature and pressure.

$$\Delta_r G = cG_C + dG_D - aG_A - bG_B \quad \text{.....(i)}$$

Where  $G_A, G_B, G_C$  and  $G_D$  are molar Gibb's function of A, B, C and D respectively at given T and P.  
also,

$$\left. \begin{aligned} G_A &= H_A - TS_A \\ G_B &= H_B - TS_B \\ G_C &= H_C - TS_C \\ G_D &= H_D - TS_D \end{aligned} \right\} \dots\dots(ii)$$

Substituting (ii) in (i)

$$\Delta_r G = (cH_C + dH_D - aH_A - bH_B) - T(cS_C + dS_D - aS_A - bS_B)$$

$$\Rightarrow \boxed{\Delta_r G = \Delta_r H - T\Delta_r S}$$

$(\Delta H)_{T,P}$	$(\Delta S)_{T,P}$	$(\Delta G)$	Remarks
- ve	+ ve	Always -ve	Reaction is spontaneous
+ ve	- ve	Always +ve	Reaction non-spontaneous
+ ve	+ ve	At low temperature, $\Delta G = + ve$ At high temperature, $\Delta G = - ve$	Non-spontaneous Spontaneous
- ve	- ve	At low temperature, - ve	Spontaneous
- ve	- ve	At high temperature, + ve	Non spontaneous

#### (iv) Gibb's functions of pure substances :

Consider a pure substance having a Gibb's function as follows :

$$G = H - TS = U + PV - TS$$

Let, the pressure and temperature are varied by infinitesimally small value :

$$dG = dU + PdV + VdP - TdS - SdT$$

As,  $dU = dq - PdV$  and  $TdS = dq$  [Assume only PV- work and reversible process.]

$$dG = VdP - SdT$$

(a) If pressure is varied keeping temperature constant -

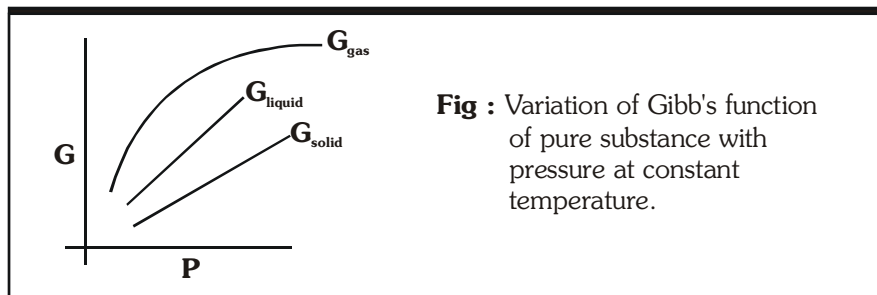
$$dG = VdP \Rightarrow \left( \frac{dG}{dP} \right)_T = V$$

The physical significance of above relation is when pressure over a substance is increased, it's Gibb's function increases & the increase is proportional to molar volume. Since molar volume of gas, liquid and solid are in order, as follows :

$$V_{\text{Gas}} > V_{\text{Liquid}} > V_{\text{Solid}}$$

Hence, Gibb's function of gases increases most rapidly on increasing pressure.

That's why, gas phase becomes unstable at high pressure.



**Fig :** Variation of Gibb's function of pure substance with pressure at constant temperature.

(b) If temperature is changed keeping pressure constant -

$$dG = -SdT \Rightarrow \left(\frac{dG}{dT}\right)_P = -S$$

Since entropy of pure substances are always positive, the slope of G vs T curve is negative. Also since,

$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$$

⇒ the slope is more negative for gas.

Thus, on increasing temperature, the Gibb's function of pure substances decreases, but this decrement is maximum for gaseous phase. Thus, gas phase acquire stability on increasing temperature.

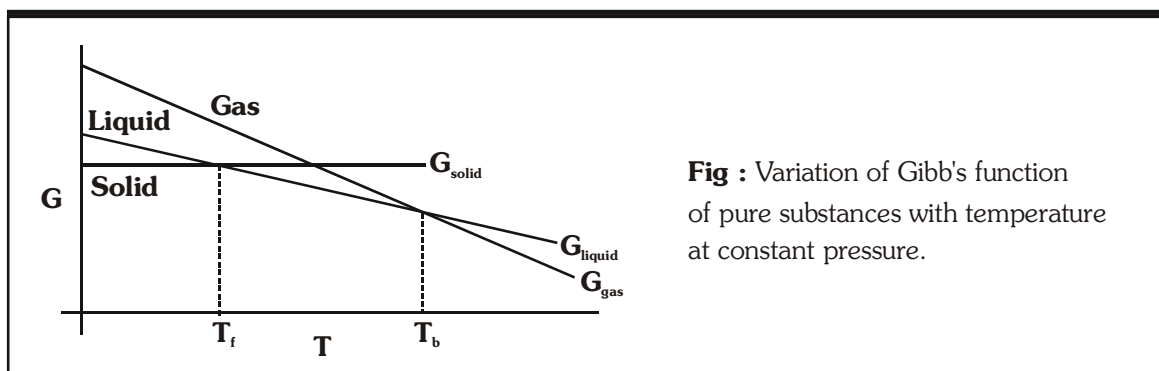
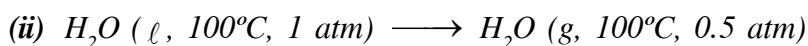
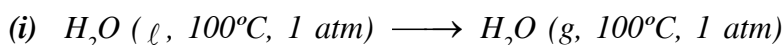
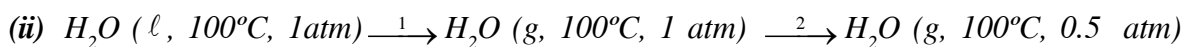


Fig : Variation of Gibb's function of pure substances with temperature at constant pressure.

Ex. 9. Calculate  $\Delta G_m$  for the following process:



Sol. : (i)  $\Delta G = 0$  (Equilibrium condition)



$$\Delta G_1 = 0$$

$$\Delta G_2 = nRT \cdot \ln \frac{P_2}{P_1} = 1 \times R \times 373 \times \ln \frac{0.5}{1} = -2149.5 \text{ J}$$

$$\therefore \Delta G = \Delta G_1 + \Delta G_2 = -2149.5 \text{ J}$$

### 8.3 APPLICATION OF GIBB'S ENERGY (AS MEASURE OF NON-PV WORK)

For a pure substance

$$dG = d(H - TS) = dH - TdS - SdT$$

also  $dH = dU + PdV + VdP$

also  $dU = dq - PdV - w_{\text{non-PV}}$

( $w_{\text{non-PV}}$  = non-PV work done by system)

$$\Rightarrow dG = dq - PdV - w_{\text{non-PV}} + PdV + VdP - TdS - SdT$$

for a reversible change at constant T and P.

$$dq = TdS ; \text{ and } SdT \text{ and } VdP \text{ term vanishes.}$$

$$\Rightarrow dG = TdS - w_{\text{non-PV}} - TdS$$

$$(dG)_{T,P} = -w_{\text{non-PV}}$$

$$\Rightarrow \boxed{-(dG)_{T,P} = w_{\text{non-PV}}}$$

Thus decrease in Gibb's function at constant temperature and pressure is equal to maximum non-PV work obtainable from system.

## 9. Chemical equilibrium :

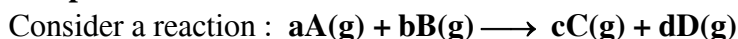
The state of chemical equilibrium is characterised by constant value of temperature, pressure and composition of a closed system. The state of equilibrium represent most stable state acquired by chemical system under given conditions.

The characteristics of state of equilibrium are :

- (i) The equilibrium is attained in closed system.
- (ii) At equilibrium, the chemical system is at minimum value of Gibb's function possible under given conditions.
- (iii) A state of equilibrium is attained spontaneously.
- (iv) At equilibrium, the rate of change of Gibb's function with progress of reaction under given conditions becomes zero  $\Rightarrow \Delta_r G = 0$ .
- (v) At state of equilibrium, the total Gibb's function of products becomes equal to total Gibb's function of reactants.

### 9.1 EQUILIBRIUM CONSTANT

#### Gas phase reactions :



Now molar Gibb's functions of A, B, C and D are given by :

$$G_A = G_A^\circ + RT \ln \left( \frac{P_A}{P_0} \right)$$

$$G_B = G_B^\circ + RT \ln \left( \frac{P_B}{P_0} \right)$$

$$G_C = G_C^\circ + RT \ln \left( \frac{P_C}{P_0} \right)$$

$$G_D = G_D^\circ + RT \ln \left( \frac{P_D}{P_0} \right)$$

$$\text{Now, } \Delta_r G = cG_C + dG_D - aG_A - bG_B$$

Substituting value of  $G_A$ ,  $G_B$ ,  $G_C$  and  $G_D$  in above equation :

$$\Delta_r G = (cG_C^\circ + dG_D^\circ - bG_B^\circ - aG_A^\circ) + RT \ln \left[ \frac{\left( \frac{P_C}{P_0} \right)^c \left( \frac{P_D}{P_0} \right)^d}{\left( \frac{P_A}{P_0} \right)^a \left( \frac{P_B}{P_0} \right)^b} \right]$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

$$\text{Where, } Q = \left( \frac{P_C \cdot P_D}{P_A \cdot P_B} \right) \left( \frac{1}{P_0} \right)^{(c+d-a-b)}$$



At equilibrium,  $\Delta_r G = 0$  and  $Q = K_p = \left(\frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}\right) \left(\frac{1}{P_0}\right)^{\Delta n_g}$

$$\Delta_r G^\circ = -RT \ln K_p$$

**Note :**  $Q$  contains partial pressures at that moment but  $K_p$  contain partial pressures at equilibrium.

### 10. RELATIONSHIP BETWEEN, $\Delta G^\circ$ AND EQUILIBRIUM CONSTANT

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq}$$

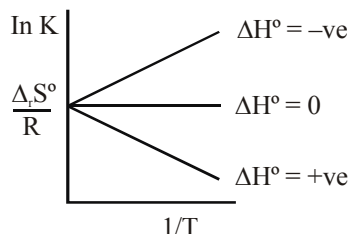
$$\ln K_{eq} = \frac{-\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$$

$$\ln K_1 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_1}$$

$$\ln K_2 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_2}$$

[where  $K_1$  &  $K_2$  are values of  $K_p$  at temperature  $T_1$ K &  $T_2$ K respectively]

$$\ln \left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (\text{Van't Hoff's equation})$$



### EXERCISE-4

23. In a irreversible process taking place at constant  $T$  and  $P$  and in which only pressure-volume work is being done the change in Gibbs free energy ( $dG$ ) and change in entropy ( $dS$ ) satisfy the criteria:-  
 (A)  $(dS)_{V,E} = 0$ ,  $(dG)_{T,P} = 0$  (B)  $(dS)_{V,E} = 0$ ,  $(dG)_{T,P} > 0$  [AIEEE-2003]  
 (C)  $(dS)_{V,E} < 0$ ,  $(dG)_{T,P} < 0$  (D)  $(dS)_{V,E} > 0$ ,  $(dG)_{T,P} < 0$
24. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant  $K_c$  is :- [AIEEE-2003]  
 (A)  $\Delta G^\circ = RT \ln K_c$  (B)  $-\Delta G^\circ = RT \ln K_c$  (C)  $\Delta G = RT \ln K_c$  (D)  $-\Delta G = RT \ln K_c$
25. For the reaction at 298 K  
 $A(g) + B(g) \rightleftharpoons C(g) + D(g)$   
 $\Delta H^\circ = -29.8 \text{ kcal}$ ;  $\Delta S^\circ = -0.1 \text{ kcal/K}$   
 Calculate  $\Delta G^\circ$  and  $K$ .
26. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant  $K$  is :-  
 (A)  $-\Delta G^\circ = RT \ln K$  (B)  $\Delta G = RT \ln K$   
 (C)  $-\Delta G = RT \ln K$  (D)  $\Delta G^\circ = RT \ln K$

**ANSWER KEY****EXERCISE-1**

1. Ans. (i) irreversible, (ii) reversible, (iii) impossible  
 2. Ans.(A)                      3. Ans.(B)                      4. Ans.(C)

**EXERCISE-2**

5. Ans.(A)  
 6. Ans. (a) 2.1 cal/K , (b) 1.5 cal/K                      7. Ans 819°C  
 8. Ans.(C)  
 9. Ans.  
 (A) (+ive)                      (B) (+ive)                      (C)  $\approx 0$                       (D) (+ive)  
 (E) (+ive)                      (F) (-ive)  
 10. Ans.(C)                      11. Ans.(C)                      12. Ans.(D)                      13. Ans.(B)  
 14. Ans.(C)                      15. Ans.(A)

**EXERCISE-3**

16. Ans. -2873.1 kJ                      17. Ans. (B)                      18. Ans.(C)                      19. Ans.(C)  
 20. Ans.(B)                      21. Ans.(B)                      22. Ans.(D)

**EXERCISE-4**

23. Ans.(D)                      24. Ans.(B)                      25. Ans.  $\Delta G^\circ = 0$ ;  $K = 1$   
 26. Ans.(A)

MISCELLANEOUS SOLVED QUESTION

1. When 1-pentyne(A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne(B) & 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate  $\Delta G^\circ$  for the following equilibria.



From the calculated value of  $\Delta G_1^\circ$  &  $\Delta G_2^\circ$  indicate the order of stability of A, B & C. Write a reasonable reaction mechanism sharing all intermediate leading to A, B & C. [JEE 2001]

2. Show that the reaction  $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$  at 300 K is spontaneous and exothermic, when the standard entropy is  $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$ . The standard Gibbs free energies of formation for  $CO_2$  and CO are  $-394.4$  and  $-137.2 \text{ kJ mol}^{-1}$ , respectively. [JEE 2001]

3.  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

This reaction is carried out at 298 K and 20 bar. 5 mol each of  $N_2O_4$  and  $NO_2$  are taken initially.

Given :  $(\Delta G_f^\circ)_{N_2O_4} = 100 \text{ kJ mol}^{-1}$ ;  $(\Delta G_f^\circ)_{NO_2} = 50 \text{ kJ mol}^{-1}$

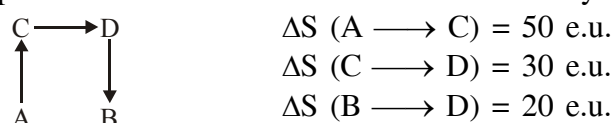
(i) Find  $\Delta G$  for reaction at 298 K under given condition.

(ii) Find the direction in which the reaction proceeds to achieve equilibrium. [JEE 2004]

4. The enthalpy of vapourization of a liquid is  $30 \text{ kJ mol}^{-1}$  and entropy of vapourization is  $75 \text{ J mol}^{-1} \text{ K}^{-1}$ . The boiling point of the liquid at 1 atm is :- [JEE 2004]

(A) 250 K (B) 400 K (C) 450 K (D) 600 K

5. A process  $A \longrightarrow B$  is difficult to occur directly instead it takes place in three successive steps.



[JEE 2006]

Where e.u. is entropy unit.

Then the entropy change for the process  $\Delta S (A \longrightarrow B)$  is :-

(A) + 100 e.u. (B) - 60 e.u. (C) - 100 e.u. (D) + 60 e.u.

6. For the process  $H_2O(l) (1 \text{ bar}, 373 \text{ K}) \longrightarrow H_2O(g) (1 \text{ bar}, 373 \text{ K})$ , the correct set of thermodynamic parameters is :- [JEE 2007]

(A)  $\Delta G = 0, \Delta S = +ve$  (B)  $\Delta G = 0, \Delta S = -ve$   
 (C)  $\Delta G = +ve, \Delta S = 0$  (D)  $\Delta G = -ve, \Delta S = +ve$

7. **Statement-1** : There is a natural asymmetry between converting work to heat and converting heat to work.

**Statement-2** : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

[JEE 2008]

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

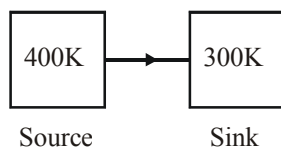
8. **Statement-1** : For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.  
**Statement-2** : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. [JEE 2008]

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

## EXERCISE (S-I)

## □ Carnot Cycle

- The efficiency of a carnot cycle is  $1/6$ . On decreasing the temperature of the sink by  $65^\circ\text{C}$ , the efficiency increases to  $1/3$ . Calculate the temperature of source and sink. **TD0001**
- A carnot cycle has an efficiency of 40%. Its low temperature reservoir is at  $9^\circ\text{C}$ . What is the temperature of source ? **TD0002**
- A diatomic ideal gas is expanded isothermally to 32 times of its initial volume then it is cooled to restore to initial entropy at constant volume. Calculate ratio of initial temperature to final temperature **TD0003**
- One mole of an ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate  $\Delta S_{\text{system}}$ ,  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{total}}$ 
  - when the process is carried out reversibly
  - when the process is carried out irreversibly (one step) **TD0004**
- 100 kJ heat is transferred from a large heat reservoir at 400 K to another large heat reservoir at 300 K. Suppose there is no change in temperature due to exchange of heat and combinedly source and sink form isolated system.

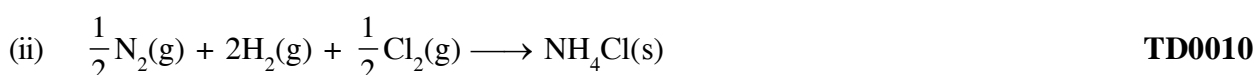
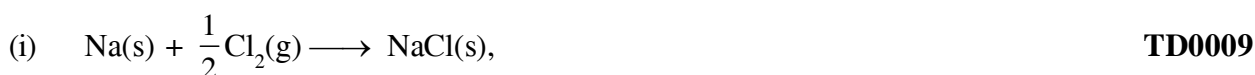


Find (a)  $\Delta S_{\text{source}}$ , (b)  $\Delta S_{\text{sink}}$  and (c)  $\Delta S_{\text{total}}$ . Also comment on spontaneity of process. **TD0005**

- A system of 100 kg mass undergoes a process in which its specific entropy increases from  $0.3 \text{ kJkg}^{-1}\text{K}^{-1}$  to  $0.4 \text{ kJkg}^{-1}\text{K}^{-1}$ . At the same time, the entropy of the surrounding decreases from  $80 \text{ kJ}^{-1}$  to  $75 \text{ kJ}^{-1}$ . Find the  $(\Delta S)_{\text{universe}}$  in  $\text{kJK}^{-1}$ . **TD0006**
- Calculate  $(\Delta S)_{\text{universe}}$  (in  $\text{cal/K}$ ) when 1kg water at 300K is brought into contact with a heat reservoir at 600K. Specific heat capacity of water is  $1 \text{ cal/gm}^\circ\text{C}$ . Assume no change in physical state of water.  $(\ln 2 = 0.7)$  **TD0007**
- 1 mole of ideal monoatomic gas is heated by supplying 5 kJ heat from a reservoir maintained at 400 K from 300 K to 400 K. In the process volume of gas increased from 1 L to 10 L. Find  $\Delta S_{\text{total}}$  (in  $\text{J/K-mol}$ ) in the process

Use :  $\ln \left(\frac{4}{3}\right) = 0.3$ ,  $\ln 10 = 2.3$ ,  $R = 8.3 \text{ J/K-mol}$  and  $\ln x = 2.3 \log x$  **TD0008**

- Calculate  $\Delta S_r^\circ$  at 298K of



The values of  $S^\circ$  of Na,  $\text{Cl}_2$ , NaCl,  $\text{NH}_4\text{Cl}$ ,  $\text{N}_2$ ,  $\text{H}_2$  diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 &  $5.69 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively.

10. Identify the substance in each of the following pairs of samples that has the higher entropy?

- (A) Br<sub>2</sub>(l) or Br<sub>2</sub>(g) (B) C<sub>2</sub>H<sub>6</sub>(g) or C<sub>3</sub>H<sub>8</sub>(g)  
 (C) MgO(s) or NaCl(s) (D) KOH(s) or KOH(aq)

TD0012

□ **Gibb's Function**

11. Calculate the  $\Delta G^\circ$  change at 300 K for the reaction;

Br<sub>2</sub>(l) + Cl<sub>2</sub>(g) → 2BrCl(g). For the reaction  $\Delta H^\circ = 29.3$  kJ & the standard entropies of Br<sub>2</sub>(l), Cl<sub>2</sub>(g) & BrCl(g) at the 300 K are 150, 220, 240 J mol<sup>-1</sup>K<sup>-1</sup> respectively. **TD0013**

12. The standard entropies of H<sub>2</sub>(g) and H(g) are 130 and 115 J mol<sup>-1</sup>K<sup>-1</sup> respectively at 300K. Using the data given below calculate the bond energy of H<sub>2</sub>(in kJ/mol) :-

H<sub>2</sub>(g) → 2H(g) ;  $\Delta G^\circ = 406$  kJ/mol **TD0014**

13. 5 mole H<sub>2</sub>O(l) at 373K and 1 atm is converted into H<sub>2</sub>O(g) at 373K and 5 atm. Calculate  $\Delta G$  for this process. [Given : R = 2Cal/K-mol, ln 5 = 1.6] **TD0015**

14. Calculate  $\Delta G$  (in bar-L) when a definite mass of a monoatomic ideal gas at 1 bar & 27°C is expanded adiabatically against vacuum from 10 L to 20 L (ln2 = 0.7) **TD0016**

15. Find  $(\Delta S)_{\text{universe}}$  (in Joule/mole/K) at 1 bar for a chemical reaction at 300 K if  $\Delta H_{300\text{K}}^\circ = 75$  kJ / mol  $\Delta S_{300\text{K}}^\circ = 300$  J/K **TD0017**

16. A liquid freezes into a solid ( $\Delta H = -1000$  J/mole) at 200 K and 1 atm, (it's normal melting point).

(i) What is the value of  $\Delta G$  at 200 K ?

(ii) What is the  $\Delta S$  value at 200 K ?

(iii) Will the freezing be spontaneous at 150 K and 1 atm ? Calculate  $\Delta S_{\text{total}}$ .

(iv) What is the value of  $\Delta G$  at 250 K and 1 atm ?

(And it is assumed that  $\Delta S$  and  $\Delta H$  do not depend on temperature)

TD0018

□ **Thermodynamic and equilibrium constant**

17.  $\alpha$ -D Glucose undergoes mutarotation to  $\beta$ -D-Glucose in aqueous solution. If at 300K there is 60% conversion. Calculate  $\Delta G^\circ$  of the reaction. (ln2 = 0.7, ln 3 = 1.1)

$\alpha$ -D-Glucose  $\rightleftharpoons$   $\beta$ -D-Glucose **TD0019**

18. The equilibrium constant of the reaction  $2\text{C}_3\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{C}_4\text{H}_8(\text{g})$  is found to fit the expression

$$\ln K = -1.04 - \frac{1088\text{K}}{T}$$

Calculate the standard reaction enthalpy and entropy at 400 K. **TD0020**

19. For the reaction  $\text{SO}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$  ;  $\Delta H_{300}^\circ = -95$  kJ/mole,  $\Delta S_{300}^\circ = -95.0$  J/K mole. Find the value of  $\ln k_p$  for this reaction at 300 K. **TD0021**

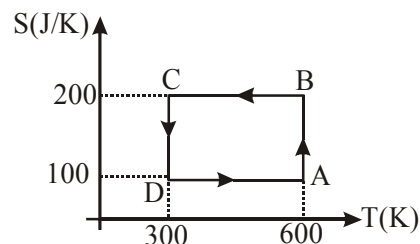
## EXERCISE-(S-II)

1. From the given T-S diagram of a reversible carnot engine, find

(i) work delivered by engine in one cycle **TD0022**

(ii) heat taken from the source in each cycle. **TD0023**

(iii)  $\Delta S_{\text{sink}}$  in each cycle. **TD0023**

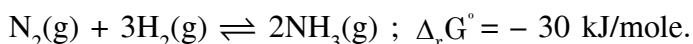


2. At 300 K,  $\Delta H^{\circ}_{\text{combustion}}(\text{sucrose}) = -5000 \text{ KJ/mol}$  &  $\Delta G^{\circ}_{\text{combustion}}(\text{sucrose}) = -6000 \text{ KJ/mol}$ . Estimate additional non-PV work that is obtained by raising temperature to 309 K. Assume  $\Delta_r C_p = 0$  for this temperature change. **TD0024**

3. The  $K_p$  for reaction  $A + B \rightleftharpoons C + D$  is 2.0 at  $27^{\circ}\text{C}$  and 8.0 at  $127^{\circ}\text{C}$ . Determine the standard free energy change of this reaction at each temperature and  $\Delta H^{\circ}$  for the reaction over this range of temperature ( $\ln 2 = 0.7$ ) ? **TD0025**

4. Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 atm against constant external pressure without change in temperature. If surrounding temperature (300 K) and pressure (1 atm) always remains constant then calculate total entropy change ( $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ ) for given process. **TD0026**

5. What is  $\Delta_r G$  for synthesis of ammonia at 300 K at following sets of partial pressure :



[Take  $R = \frac{25}{3} \text{ J/K mole}$ ,  $\ln 2 = 0.7$ ,  $\ln 3 = 1.1$ ,  $\ln 5 = 1.6$ ]

Gas	$\text{N}_2$	$\text{H}_2$	$\text{NH}_3$	
Pressure (atm)	1	3	0.02	<b>TD0027</b>

6.  $2\text{A}(\text{s}) \rightleftharpoons \text{B}(\text{g}) + 2\text{C}(\text{g}) + 3\text{D}(\text{g})$

Total pressure developed in a closed container by decomposition of A at equilibrium is 12 bar at  $727^{\circ}\text{C}$ . Calculate  $|\Delta G^{\circ}|$  (in kcal) of the reaction at  $727^{\circ}\text{C}$  ( $R = 2 \text{ cal/mole-K}$ ,  $\ln 2 = 0.7$ ,  $\ln 3 = 1.1$ ) **TD0028**

7. Find  $\Delta G(\text{J/mol})$  for the reaction at 300kPa &  $27^{\circ}\text{C}$  when all gases are in stoichiometric ratio of moles.  $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$  [ $\ln 2 = 0.7$ ]

Given :  $\Delta G_f^{\circ}(\text{N}_2\text{O}_4) = 100 \text{ kJ/mol}$

$\Delta G_f^{\circ}(\text{NO}_2) = 50 \text{ kJ/mol}$

$R = 8 \text{ J/mol-K}$  **TD0029**

8. Oxygen is heated from 300 to 600 K at a constant pressure of 1 bar. What is the increase in molar entropy? The molar heat capacity (in  $\text{JK}^{-1}\text{mol}^{-1}$ ) for the  $\text{O}_2$  is (Given :  $\ln 2 = 0.7$ )

$$C_{P,m} = 10 + 10^{-2}T$$

TD0030

9. Calculate the molar entropy of a substance at 600 K and 1 bar using the following data.

- (i) Heat capacity of solid from 0K to normal melting point 200 K

$$C_{P,m}(s) = 0.035 T \text{ JK}^{-1}\text{mol}^{-1}.$$

- (ii) Enthalpy of fusion =  $7.5 \text{ kJ mol}^{-1}$ ,

- (iii) Enthalpy of vaporisation =  $30 \text{ kJ mol}^{-1}$ ,

- (iv) Heat capacity of liquid from 200K to normal boiling point 300K

$$C_{P,m}(l) = 60 + 0.016T \text{ JK}^{-1}\text{mol}^{-1}.$$

- (v) Heat capacity of gas from 300K to 600K at 1 atm

$$C_{P,m}(g) = 50.0 \text{ JK}^{-1}\text{mol}^{-1}.$$

TD0031

10. For a reaction :  $2A(s) + B(g) \longrightarrow 3C(l)$ , standard entropy change of reaction is  $-2 \text{ kJ/mol-K}$  and standard enthalpy of combustion of  $A(s)$ ,  $B(g)$  and  $C(l)$  are  $-100$ ,  $-60$   $-285 \text{ kJ/mol}$  respectively, then find the maximum useful work that can be obtained at  $27^\circ\text{C}$  and 1 bar pressure from the reaction (in  $\text{kJ/mol}$ ).

TD0032

## EXERCISE (O-I)

1. A reversible heat engine A (based on Carnot cycle) absorbs heat from a reservoir at 1000 K and rejects heat to a reservoir at  $T_2$ . A second reversible engine B (based on Carnot cycle) absorbs the same amount of heat as rejected by the engine A, from the reservoir at  $T_2$  and rejects energy to a reservoir at 360 K.

If the efficiencies of engines A and B are the same then the temperature  $T_2$  is :-

- (A) 680 K                      (B) 640 K                      (C) 600 K                      (D) 670 K      **TD0033**

2. Which of the following is incorrect for a closed system in which an irreversible process is occurring?

- (A)  $Q_{\text{sys}} + Q_{\text{surr}} = 0$       (B)  $W_{\text{sys}} + W_{\text{surr}} = 0$       (C)  $\Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0$       (D)  $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

**TD0034**

3. For conversion C(graphite)  $\rightarrow$  C(Diamond), the  $\Delta S$  is :-

- (A) Zero    (B) Positive  
(C) Negative    (D) Can not be predicted      **TD0035**

4. Considering entropy (S) as a thermodynamic parameter, the criteria for the spontaneity of any process is :-

- (A)  $\Delta S_{\text{system}} - \Delta S_{\text{surroundings}} > 0$       (B)  $\Delta S_{\text{system}} > 0$  only  
(C)  $\Delta S_{\text{surroundings}} > 0$  only      (D)  $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$       **TD0036**

5. If  $\Delta H_{\text{vaporisation}}$  of substance X( $\ell$ ) (molar mass = 30 g/mol) is 300 J/g at its boiling point 300 K, then molar entropy change for reversible condensation process is :-

- (A) 30 J/mol.K                      (B) -300 J/mol.K                      (C) -30 J/mol.K                      (D) -10 J/mol.K

**TD0037**

6. For 1 mole of an ideal monoatomic gas on moving from one state to other, the temperature is doubled but pressure becomes  $\sqrt{2}$  times. Then entropy change in the process will be ( $R = 2 \text{ Cal/mol}\cdot\text{K}$ )

- (A)  $R \ln 2$                       (B)  $2R \ln 2$                       (C)  $3R \ln 2$                       (D)  $\frac{R}{2} \ln 2$       **TD0038**

7. If  $S^0$  for  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 0.13, 0.22 and 0.19  $\text{kJ K}^{-1} \text{mol}^{-1}$  respectively. The total change in standard entropy for the reaction,  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$  is :

- (A)  $30 \text{ JK}^{-1} \text{mol}^{-1}$                       (B)  $40 \text{ JK}^{-1} \text{mol}^{-1}$                       (C)  $60 \text{ JK}^{-1} \text{mol}^{-1}$                       (D)  $20 \text{ JK}^{-1} \text{mol}^{-1}$

**TD0039**

8. For a perfectly crystalline solid  $C_{p,m} = aT^3$ , where a is constant. If  $C_{p,m}$  is 0.42 J/K-mol at 10 K, molar entropy at 10 K is

- (A) 0.42 J/K-mol                      (B) 0.14 J/K-mol                      (C) 4.2 J/K-mol                      (D) Zero      **TD0040**



9. Identify the correct statement regarding entropy.

- (A) At absolute zero, the entropy of perfectly crystalline substance is taken to be +ve
- (B) At absolute zero, entropy of perfectly crystalline substance is taken to be zero.
- (C) At 0 °C, the entropy of a perfectly crystalline substance is taken to be zero.
- (D) At absolute zero, the entropy of all crystalline substances is taken to be zero.

**TD0041**

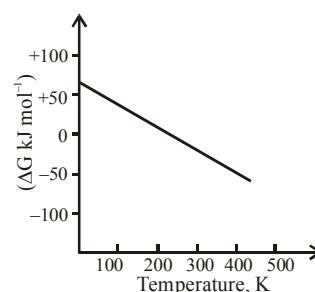
10. In which of the following reactions do you expect to have a decrease in entropy?

- (A)  $\text{Fe(s)} \longrightarrow \text{Fe(l)}$
- (B)  $2 \text{Fe(s)} + 3/2 \text{O}_2\text{(g)} \longrightarrow \text{Fe}_2\text{O}_3\text{(s)}$
- (C)  $\text{HF(l)} \longrightarrow \text{HF(g)}$
- (D)  $2 \text{H}_2\text{O}_2\text{(l)} \longrightarrow 2 \text{H}_2\text{O(l)} + \text{O}_2\text{(g)}$

**TD0042**

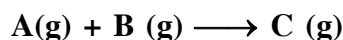
11. What can be concluded about the values of  $\Delta H$  and  $\Delta S$  from this graph?

- (A)  $\Delta H > 0, \Delta S > 0$
- (B)  $\Delta H > 0, \Delta S < 0$
- (C)  $\Delta H < 0, \Delta S > 0$
- (D)  $\Delta H < 0, \Delta S < 0$



**TD0043**

12. For the reaction at 300 K



$$\Delta U = -3.0 \text{ kcal} \quad ; \quad \Delta S = -10.0 \text{ cal/K}$$

value of  $\Delta G$  is ?

- (A) -600 cal
- (B) -6600 cal
- (C) -6000 cal
- (D) none

**TD0044**

13. For the reaction that taking place at certain temperature  $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{S(g)}$ , if equilibrium pressure is X bar, then  $\Delta_r G^\circ$  would be :-

- (A)  $-2 RT \ln X$
- (B)  $-RT (\ln X - \ln 2)$
- (C)  $-2 RT (\ln X - \ln 2)$
- (D)  $-0.5 RT (\ln X - \ln 2)$

**TD0045**

14. What is the free energy change ( $\Delta G$ ) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure ?

- (A) 80 cal
- (B) 540 cal
- (C) 620 cal
- (D) zero

**TD0046**

15. What is the free energy change ( $\Delta G$ ) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 2 atm pressure ?

- (A) Zero
- (B) 540 cal
- (C) 517.13 cal
- (D) 510 cal

**TD0047**

16. If  $\Delta G^\circ > 0$  for a gaseous reaction then :

- (A)  $K_p > 1$   
 (B)  $K_p < 1$   
 (C) The products predominate in the equilibrium mixture  
 (D) Mole of product must be less than mole of reactant

TD0048

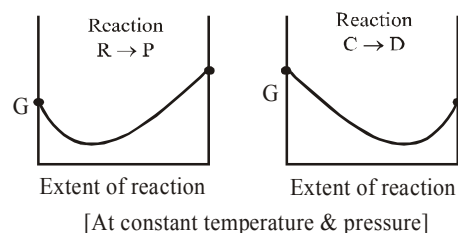
17. Heat liberated for an ideal gas undergoing reversible isothermal process is 1200 cal at 300 K. What will be Gibb's free energy change for the process ?

- (A) 1200 cal                      (B) -1200 cal                      (C) 400 cal                      (D) -400 cal

TD0049

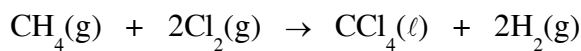
18. With the help of given curves select the correct statement.

- (A) C will partially convert into D.  
 (B) R will not convert into P  
 (C) R will be completely converted into P.  
 (D) C will be completely converted in D.



TD0050

19. Evaluate  $\Delta S^\circ$  for the reaction below at  $25^\circ\text{C}$ .



Given :

	$\text{CH}_4(\text{g})$	$\text{Cl}_2(\text{g})$	$\text{CCl}_4(\text{l})$	$\text{H}_2(\text{g})$
$\Delta H_f^\circ$ (kJ/mol)	-74.81	0	-135.4	0
$\Delta G_f^\circ$ (kJ/mol)	-50.75	0	-65.27	0

- (A) -360 J/K                      (B) -66.9 J/K                      (C) -155 J/K                      (D) -487 J/K                      **TD0051**

20. All of the following have  $\Delta G_f^\circ = 0$ , except -

- (A)  $\text{O}_2(\text{g})$                       (B)  $\text{Br}_2(\text{g})$                       (C)  $\text{H}_2(\text{g})$                       (D)  $\text{Ca}(\text{s})$                       **TD0052**

## EXERCISE (O-II)

Single correct :

1. When two equal sized pieces of the same metal at different temperatures  $T_h$  (hot piece) and  $T_c$  (cold piece) are brought into thermal contact and isolated from its surrounding. The total change in entropy of system is given by ? Suppose heat capacity of each piece is  $C$ .

(A)  $C \ln \frac{T_c + T_h}{2T_c}$       (B)  $C \ln \frac{T_2}{T_1}$       (C)  $C \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c}$       (D)  $C \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$

TD0053

2. The change in entropy of 2 moles of an ideal gas upon isothermal expansion at 243.6 K from 20 litre until the pressure becomes 1 atm, is :-

(A) 1.385 cal/K      (B) - 1.2 cal/K      (C) 1.2 cal/K      (D) 2.77 cal/K

TD0054

3. For the hypothetical reaction,  $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ ,  $\Delta_r G$  and  $\Delta_r S$  are 20 kJ/mole and  $-20 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively at 200 K. If  $\Delta_r C_p$  is  $20 \text{ JK}^{-1} \text{ mol}^{-1}$  then  $\Delta_r H$  at 400 K is :-

(A) 20 kJ/mole      (B) 7.98 kJ/mole      (C) 28 kJ/mole      (D) 16 kJ/mole

TD0055

4. 1 mole of ice at  $0^\circ\text{C}$  is converted in steam at  $100^\circ\text{C}$  then calculated  $\Delta S$ , in the process. enthalpy of vapourisation and fusion are  $540 \text{ cal gm}^{-1}$  and  $80 \text{ cal gm}^{-1}$  respectively. Use the average heat capacity of liquid water as  $1 \text{ cal gm}^{-1} \text{ degree}$ .

(A)  $18 \left( \frac{80}{373} + \frac{540}{373} + \ln \frac{373}{273} \right)$       (B)  $18 \left( \frac{80}{273} + \frac{540}{373} + \ln \frac{373}{273} \right)$

(C)  $18 \left( \frac{80}{273} + \frac{540}{373} + \ln \frac{273}{373} \right)$       (D)  $18 \left( \frac{80}{273} + \frac{540}{373} + 100 \right)$

TD0056

5. The value of  $\Delta G_f^\circ$  of gaseous mercury is 38 kJ/mole. At what total external pressure mercury start boiling at  $27^\circ\text{C}$ . ( $R \cdot \ln 10 = 19 \text{ J/K-mol}$ )

(A)  $10^{-6.67}$       (B)  $10^{-1.67}$       (C)  $10^{-13.33}$       (D)  $10^{-3.33}$       TD0057

6. If molar internal energy for a gas in a closed rigid vessel given by

$$U = a + bT + cT^2$$

find the entropy change (in J/K) at constant volume when 1 mol of gas are heated from 200 K to 400K. [Given :  $a = 20 \text{ J/mol}$ ;  $b = 10 \text{ J/K-mol}$ ;  $c = 2 \times 10^{-2} \text{ J/K}^2\text{-mol}$ ] ( $\ln 2 = 0.7$ )

(A) 15      (B) 30      (C) 60      (D) 9.78      TD0058

7. Statement - 1 : When process  $\text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l)$ , reaches equilibrium in a closed system at constant temperature and pressure, Gibb's function of  $\text{H}_2\text{O}(s)$  &  $\text{H}_2\text{O}(l)$  become same.

Statement - 2 : For reversible phase change at constant temperature & pressure, change in Gibb's free energy will be zero.

- (A) Statement-1 is true, statement- 2 is true and statement- 2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false  
 (D) Statement-1 is false, statement-2 is true.

TD0059

8. Statement- 1 : Absolute entropy of an ion in aqueous solution at 298 K may be negative.  
Statement -2 : Absolute entropy at 298 K of any substance can never be negative.  
(A) Statement-1 is true, statement- 2 is true and statement- 2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false  
(D) Statement-1 is false, statement-2 is true. **TD0060**

9. **Statement-1** : Net heat absorbed in a cyclic process must be always equal to net work done by the system in the cyclic process.

**Statement-2** : Internal energy of system is a function of state.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true. **TD0061**

10. **Statement-1** : Entropy change in reversible adiabatic expansion of an ideal gas is zero.

**Statement-2** : The increase in entropy due to volume increase just compensate the decrease in entropy due to fall in temperature.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true. **TD0062**

**MORE THAN ONE MAY BE CORRECT :**

11. Select the correct statement(s).

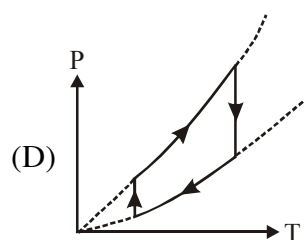
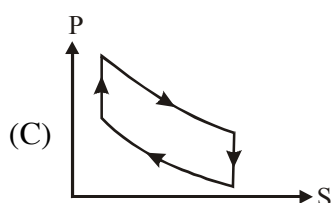
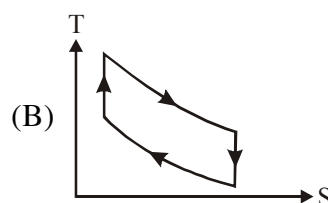
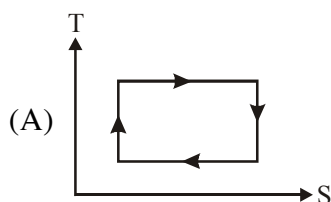
- (A) In a reversible process,  $\Delta G$  is always zero in a closed system.  
(B) In a reversible process,  $\Delta S_{\text{univ}}$  is always zero in a closed system.  
(C) In a reversible process,  $\Delta S_{\text{sys}}$  is always zero in a closed system.  
(D) In a reversible process,  $\Delta S_{\text{sys}}$  is always zero in an isolated system. **TD0063**

12. Which of the following statement (s) is/ are correct ?

- (A) The quantities E, H and G have the same dimension  
(B) Gibb's free energy of 10 gm ice at 0° C and 1.0 atm is less than the Gibb's free energy of 10 gm water at 0° C and 1 atm.  
(C)  $\Delta S_{\text{sys}} = 0$  for every adiabatic process in a closed system.

- (D) For every reversible process in a closed system,  $\Delta S_{\text{sys}} = \frac{\Delta H_{\text{sys}}}{T}$  **TD0064**

13. Which of the following represents the carnot cycle-



**TD0065**

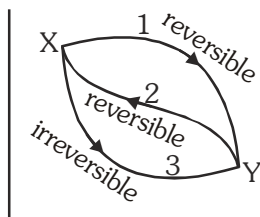
14. The normal boiling point of a liquid 'A' is 350 K.  $\Delta H_{\text{vap}}$  at normal boiling point is 35 kJ/mole. Pick out the correct statement(s). (Assume  $\Delta H_{\text{vap}}$  to be independent of pressure).
- (A)  $\Delta S_{\text{vaporisation}} > 100 \text{ J/K mole}$  at 350 K and 0.5 atm  
 (B)  $\Delta S_{\text{vaporisation}} < 100 \text{ J/K mole}$  at 350 K and 0.5 atm  
 (C)  $\Delta S_{\text{vaporisation}} < 100 \text{ J/K mole}$  at 350 K and 2 atm  
 (D)  $\Delta S_{\text{vaporisation}} = 100 \text{ J/K mole}$  at 350 K and 2 atm TD0066

15. In isothermal ideal gas compression :
- (A)  $w$  is + ve                      (B)  $\Delta H$  is zero                      (C)  $\Delta S_{\text{gas}}$  is + ve                      (D)  $\Delta G$  is + ve TD0067

16. Which of the following statement (s) is/are false :
- (A)  $\Delta_r S$  for  $\frac{1}{2} \text{N}_2(\text{g}) \longrightarrow \text{N}(\text{g})$  is positive  
 (B)  $\Delta G_{\text{system}}$  is always zero for a reversible process in a closed system  
 (C)  $\Delta G^\circ$  for an ideal gas is a function of temperature and pressure  
 (D) Entropy of a closed system is always maximized at equilibrium TD0068

17. Which of the following processes are spontaneous ?
- (A) Burning of fossil fuel  
 (B) Decomposition of water into  $\text{H}_2$  and  $\text{O}_2$  gas at room temperature  
 (C) Spreading of perfume in a room  
 (D) Diffusion of gas from high pressure to low pressure TD0069

18. Suppose a system make a transition from state X to state Y.



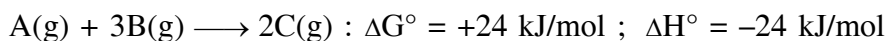
Given :  $\Delta S_{\text{XY}} = 10 \text{ J/K}$

- (A) The state Y is more disordered than state X.  
 (B)  $\Delta S_{\text{XY}}$  for path 1 and 3 is same.  
 (C)  $\Delta S_{\text{YX}} = -10 \text{ J/K}$   
 (D) The transition  $X \rightarrow Y$  must be spontaneous. TD0070
19. In which of the following processes involving an ideal gas, entropy of system remains constant?
- (A) Reversible isothermal expansion                      (B) Irreversible adiabatic expansion  
 (C) Reversible adiabatic expansion                      (D) Free expansion TD0071
20. In which of the following process involving ideal gas, entropy of surrounding remains constant ?
- (A) Reversible isobaric heating                      (B) Reversible adiabatic expansion  
 (C) Irreversible adiabatic compression                      (D) Free expansion TD0072

### Paragraph for Question 21 to 22

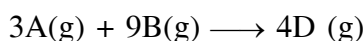
The reactions whose  $\Delta G^\circ$  are positive can not take place under standard state conditions. However another reaction whose  $\Delta G^\circ$  is negative can be coupled with the former type of reaction to give overall spontaneous process.

Consider the given reactions whose  $\Delta G^\circ$  at 300 K are provided to answer following questions.



All data at 300 K temperature.

21. What is  $\Delta S^\circ$  at 300 K of reaction (in J/Kmole) :



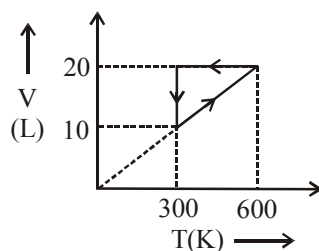
- (A) -640 (B) -480 (C) +640 (D) -240 **TD0073**

22. Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  do not vary with temperature. At what **minimum** temperature reaction  $A(g) + 3B(g) \longrightarrow 2C(g)$  become spontaneous-

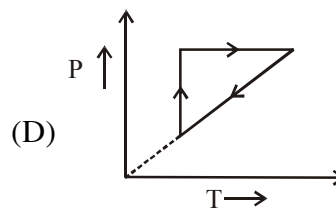
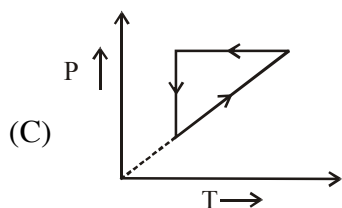
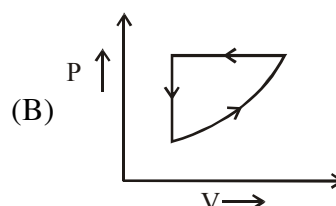
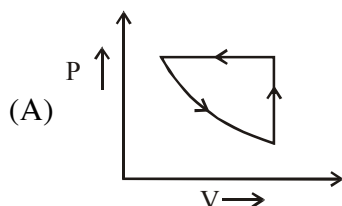
- (A) 6250 K (B) 625 K (C) 150 K (D) 1000 K **TD0074**

### Paragraph for Q.23 to Q.24

One mol of ideal monoatomic gas undergo the state change as shown in the following graph ( $\ln 2 = 0.7$ )



23. Correct graph for the process in paragraph is -



**TD0075**

24. Efficiency of the cycle will be -

- (A) 50% (B) 25% (C) 13.63% (D) 12% **TD0076**

**Table type question :**

Column-I	Column-II	Column-III
(A) Combustion of butane gas at S.T.P.	(P) Entropy change of universe constant	(I) Low temperature conditions favourable
(B) Dissolution of sodium chloride in water at STP	(Q) Entropy change of system positive	(II) More spontaneous at high temperature
(C) Adding carbon dioxide gas to water to form carbonated water at high pressure and 298K	(R) Enthalpy change of system negative	(III) High pressure condition favourable
(D) Vaporisation of liquid water at 1 atm and 373K	(S) Entropy change of universe positive	(IV) More spontaneous at low pressure

25. Which of following option is incorrect -

- (A) A – S – I                      (B) B – Q – IV                      (C) C – R – I                      (D) D – P – IV

**TD0077**

26. In column-I (A) if the reaction was carried at 400 K which option would be correct -

- (A) A – P – II                      (B) A – Q – III                      (C) A – S – IV                      (D) A – R – III

**TD0078**

27. In column-I (D), if vaporisation is carried out at 15 atm which option is correct -

- (A) D – P – IV                      (B) D – S – II                      (C) D – R – I                      (D) D – Q – II

**TD0079**

**MATCH THE LIST :**

28. Match the Column :

Column-I	Column-II
(P) $\text{H}_2\text{O} (l, 1 \text{ atm}, 363 \text{ K}) \rightarrow \text{H}_2\text{O} (g, 1 \text{ atm}, 363 \text{ K})$	(1) $\Delta_r S > 0$
(Q) $\text{H}_2\text{O} (s, 1 \text{ atm}, 373 \text{ K}) \rightarrow \text{H}_2\text{O} (g, 1 \text{ atm}, 373 \text{ K})$	(2) $\Delta_r G > 0$
(R) $\text{H}_2\text{O} (l, 1 \text{ atm}, 273 \text{ K}) \rightarrow \text{H}_2\text{O} (s, 1 \text{ atm}, 273 \text{ K})$	(3) $\Delta_r H < 0$
(S) $\text{H}_2\text{O} (s, 1 \text{ atm}, 353 \text{ K}) \rightarrow \text{H}_2\text{O} (l, 1 \text{ atm}, 353 \text{ K})$	(4) $\Delta_r U > 0$

**TD0080**

**Code:**

	P	Q	R	S
(A)	2	4	1	3
(B)	4	2	3	1
(C)	2	1	3	4
(D)	4	3	1	2

## MATCH THE COLUMN :

## 29. Column-I

- (A) Reversible adiabatic compression  
 (B) Reversible vaporisation  
 (C) Adiabatic free expansion of ideal gas in vacuum  
 (D) Dissociation of  
 $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

## Column-II

- (P)  $\Delta S_{\text{system}} > 0$   
 (Q)  $\Delta S_{\text{system}} < 0$   
 (R)  $\Delta S_{\text{surrounding}} < 0$   
 (S)  $\Delta S_{\text{surrounding}} = 0$

TD0081

## 30. Column-I

## (Related to process)

- (A) Fusion at melting point  
 (B) Vapourisation at boiling point  
 (C) Condensation at triple point  
 (D) Melting at normal boiling point

## Column-II

## (Related to system)

- (P)  $\Delta G = 0$   
 (Q)  $\Delta G < 0$   
 (R)  $\Delta S > 0$   
 (S)  $\Delta H \approx \Delta U$

TD0082



EXERCISE (J-MAIN)

1. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm<sup>3</sup> to a volume of 100 dm<sup>3</sup> at 27°C is :- [AIEEE-2011]
- (1) 32.3 J mol<sup>-1</sup> K<sup>-1</sup> (2) 42.3 J mol<sup>-1</sup> K<sup>-1</sup>  
 (3) 38.3 J mol<sup>-1</sup> K<sup>-1</sup> (4) 35.8 J mol<sup>-1</sup> K<sup>-1</sup> **TD0083**
2. The incorrect expression among the following is :- [AIEEE-2012]
- (1)  $K = e^{-\Delta G^\circ/RT}$   
 (2)  $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$   
 (3) In isothermal process,  $W_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$   
 (4)  $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$  **TD0084**
3. The entropy (S°) of the following substances are : [JEE-MAINS-(online) 2014]
- CH<sub>4</sub> (g) 186.2 J K<sup>-1</sup> mol<sup>-1</sup>  
 O<sub>2</sub> (g) 205.0 J K<sup>-1</sup> mol<sup>-1</sup>  
 CO<sub>2</sub> (g) 213.6 J K<sup>-1</sup> mol<sup>-1</sup>  
 H<sub>2</sub>O (l) 69.9 J K<sup>-1</sup> mol<sup>-1</sup>
- The entropy change (ΔS°) for the reaction  
 CH<sub>4</sub>(g) + 2O<sub>2</sub>(g) → CO<sub>2</sub>(g) + 2H<sub>2</sub>O (l) is:-
- (1) -312.5 JK<sup>-1</sup> mol<sup>-1</sup> (2) -37.6 JK<sup>-1</sup> mol<sup>-1</sup> (3) -108.1 JK<sup>-1</sup> mol<sup>-1</sup> (4) -242.8 JK<sup>-1</sup> mol<sup>-1</sup> **TD0085**
4. The molar heat capacity (C<sub>p</sub>) of CD<sub>2</sub>O is 10 cal at 1000 K. The change in entropy associated with cooling of 32 g of CD<sub>2</sub>O vapour from 1000 K to 100 K at constant pressure will be [JEE-MAINS-(online) 2014]
- (D = deuterium, at. mass = 2u)
- (1) -23.03 cal deg<sup>-1</sup> (2) 2.303 cal deg<sup>-1</sup> (3) 23.03 cal deg<sup>-1</sup> (4) -2.303 cal deg<sup>-1</sup> **TD0086**
5. Δ<sub>f</sub>G° at 500 K for substance 'S' in liquid state and gaseous state are + 100.7 kcal mol<sup>-1</sup> and + 103 kcal mol<sup>-1</sup>, respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to : [JEE-MAINS-(online) 2018]
- (R = 2 cal K<sup>-1</sup> mol<sup>-1</sup>) -
- (1) 0.1 atm (2) 10 atm (3) 100 atm (4) 1 atm **TD0087**
6. For which of the following processes, ΔS is negative? [JEE-MAINS-(online) 2018]
- (1) C(diamond) → C(graphite) (2) N<sub>2</sub>(g, 273 K) → N<sub>2</sub>(g, 300K)  
 (3) H<sub>2</sub>(g) → 2H(g) (4) N<sub>2</sub>(g, 1 atm) → N<sub>2</sub>(g, 5 atm) **TD0088**

7. At 320 K, a gas  $A_2$  is 20% dissociated to  $A(g)$ . The standard free energy change at 320 K and 1 atm in  $J\ mol^{-1}$  is approximately : [JEE-MAINS-(online) 2018]

( $R = 8.314\ JK^{-1}\ mol^{-1}$ ;  $\ln 2 = 0.693$ ;  $\ln 3 = 1.098$ )

- (1) 4281 (2) 4763 (3) 2068 (4) 1844 TD0089

8. Two blocks of the same metal having same mass and at temperature  $T_1$  and  $T_2$ , respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy,  $\Delta S$ , for this process is : [JEE-MAINS-(online) 2019]

- (1)  $2C_p \ln\left(\frac{T_1+T_2}{4T_1T_2}\right)$  (2)  $2C_p \ln\left[\frac{(T_1+T_2)^{\frac{1}{2}}}{T_1T_2}\right]$  (3)  $C_p \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$  (4)  $2C_p \ln\left[\frac{T_1+T_2}{2T_1T_2}\right]$

TD0090

9. For the chemical reaction  $X \rightleftharpoons Y$ , the standard reaction Gibbs energy depends on temperature  $T$  (in K) as : [JEE-MAINS-(online) 2019]

$$\Delta_r G^\circ \text{ (in kJ mol}^{-1}\text{)} = 120 - \frac{3}{8}T$$

The major component of the reaction mixture at  $T$  is :

- (1) X if  $T = 315\ K$  (2) X if  $T = 350\ K$  (3) Y if  $T = 300\ K$  (4) Y if  $T = 280\ K$

TD0091

10. For the equilibrium, [JEE-MAINS-(online) 2019]

$2H_2O \rightleftharpoons H_3O^+ + OH^-$ , the value of  $\Delta G^\circ$  at 298 K is approximately :-

- (1)  $-80\ kJ\ mol^{-1}$  (2)  $-100\ kJ\ mol^{-1}$  (3)  $100\ kJ\ mol^{-1}$  (4)  $80\ kJ\ mol^{-1}$

TD0092

11. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature  $T$  is given by

$$\Delta_r G^\circ = A - BT$$

Where  $A$  and  $B$  are non-zero constants. Which of the following is TRUE about this reaction ?

- (1) Exothermic if  $B < 0$  [JEE-MAINS-(online) 2019]

(2) Exothermic if  $A > 0$  and  $B < 0$

(3) Endothermic if  $A < 0$  and  $B > 0$

(4) Endothermic if  $A > 0$

TD0093

12. The reaction,  $MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$ , for which  $\Delta_r H^\circ = +491.1\ kJ\ mol^{-1}$  and  $\Delta_r S^\circ = 198.0\ JK^{-1}\ mol^{-1}$ , is not feasible at 298 K. Temperature above which reaction will be feasible is :-

[JEE-MAINS-(online) 2019]

- (1) 1890.0 K (2) 2480.3 K (3) 2040.5 K (4) 2380.5 K

TD0094

13. A process has  $\Delta H = 200 \text{ J mol}^{-1}$  and  $\Delta S = 40 \text{ JK}^{-1}\text{mol}^{-1}$ . Out of the values given below, choose the minimum temperature above which the process will be spontaneous : **[JEE-MAINS-(online) 2019]**
- (1) 5 K                      (2) 4 K                      (3) 20 K                      (4) 12 K                      **TD0095**
14. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is : **[JEE-MAINS-(online) 2019]**
- (Specific heat of water liquid and water vapour are  $4.2 \text{ kJ K}^{-1} \text{ kg}^{-1}$  and  $2.0 \text{ kJ K}^{-1} \text{ kg}^{-1}$ ; heat of liquid fusion and vapourisation of water are  $344 \text{ kJ kg}^{-1}$  and  $2491 \text{ kJ kg}^{-1}$ , respectively).
- ( $\log 273 = 2.436$ ,  $\log 373 = 2.572$ ,  $\log 383 = 2.583$ )
- (1)  $7.90 \text{ kJ kg}^{-1} \text{ K}^{-1}$       (2)  $2.64 \text{ kJ kg}^{-1} \text{ K}^{-1}$       (3)  $8.49 \text{ kJ kg}^{-1} \text{ K}^{-1}$       (4)  $9.26 \text{ kJ kg}^{-1} \text{ K}^{-1}$                       **TD0096**
15. The process with negative entropy change is : **[JEE-MAINS-(online) 2019]**
- (1) Dissolution of iodine in water  
(2) Synthesis of ammonia from  $\text{N}_2$  and  $\text{H}_2$   
(3) Dissolution of  $\text{CaSO}_4(\text{s})$  to  $\text{CaO}(\text{s})$  and  $\text{SO}_3(\text{g})$   
(4) Sublimation of dry ice                      **TD0097**
16. For the reaction ; **[JEE-MAINS-(online) 2020]**
- $\text{A}(\text{l}) \rightarrow 2\text{B}(\text{g})$
- $\Delta U = 2.1 \text{ kcal}$  ,  $\Delta S = 20 \text{ cal K}^{-1}$  at 300 K
- Hence  $\Delta G$  in kcal is \_\_\_\_\_ . **TD0098**

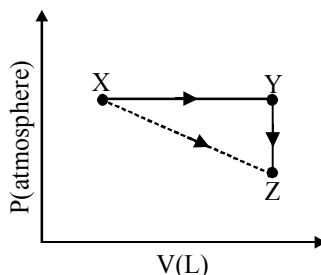
## EXERCISE (J-ADVANCE)

1. Match the transformations in **Column-I** with appropriate option in **Column-II** [JEE 2011]

Column-I	Column-II
(A) $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$	(p) phase transition
(B) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	(q) allotropic change
(C) $2\text{H}\cdot \rightarrow \text{H}_2(\text{g})$	(r) $\Delta H$ is positive
(D) $\text{P}_{(\text{white, solid})} \rightarrow \text{P}_{(\text{red, solid})}$	(s) $\Delta S$ is positive
	(t) $\Delta S$ is negative

TD0099

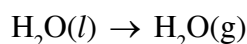
2. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [take  $\Delta S$  as change in entropy and w as work done] [JEE 2012]



- |  |   |
|--|---|
| (A) $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$ | (B) $W_{x \rightarrow z} = W_{x \rightarrow y} + W_{y \rightarrow z}$       |
| (C) $W_{x \rightarrow y \rightarrow z} = W_{x \rightarrow y}$                              | (D) $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$ |

TD0100

3. For the process



at  $T = 100^\circ\text{C}$  and 1 atmosphere pressure, the correct choice is

- |   |   |
|---|---|
| (A) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$ | (B) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$ |
| (C) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$ | (D) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$ |

TD0101

4. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. [JEE 2015]

**Column - I**

- (A) Freezing of water at 273 K and 1 atm
- (B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions
- (C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container
- (D) Reversible heating of  $\text{H}_2(\text{g})$  at 1 atm from 300 K to 600 K followed by reversible cooling to 300 K at 1 atm

**Column - II**

- (P)  $q = 0$
- (Q)  $w = 0$
- (R)  $\Delta S_{\text{sys}} < 0$
- (S)  $\Delta U = 0$
- (T)  $\Delta G = 0$

TD0102

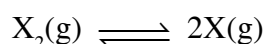
5. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings ( $\Delta S_{\text{surr}}$ ) in  $\text{J K}^{-1}$  is - [JEE 2016]

(1 L atm = 101.3 J)

- (A) 5.763 (B) 1.013 (C) -1.013 (D) -5.763 TD0103

**Paragraph for Q.6 & Q.7**

Thermal decomposition of gaseous  $X_2$  to gaseous X at 298 K takes place according to the following equation : [JEE 2016]



The standard reaction Gibbs energy,  $\Delta_r G^\circ$ , of this reaction is positive. At the start of the reaction, there is one mole of  $X_2$  and no X. As the reaction proceeds, the number of moles of X formed is given by  $\beta$ . Thus,  $\beta_{\text{equilibrium}}$  is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given :  $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$ )

6. The equilibrium constant  $K_p$  for this reaction at 298 K, in terms of  $\beta_{\text{equilibrium}}$ , is

- (A)  $\frac{8\beta_{\text{equilibrium}}^2}{2-\beta_{\text{equilibrium}}}$  (B)  $\frac{8\beta_{\text{equilibrium}}^2}{4-\beta_{\text{equilibrium}}^2}$  (C)  $\frac{4\beta_{\text{equilibrium}}^2}{2-\beta_{\text{equilibrium}}}$  (D)  $\frac{4\beta_{\text{equilibrium}}^2}{4-\beta_{\text{equilibrium}}^2}$

TD0104

7. The **INCORRECT** statement among the following for this reaction is

- (A) Decrease in the total pressure will result in formation of more moles of gaseous X  
 (B) At the start of the reaction, dissociation of gaseous  $X_2$  takes place spontaneously  
 (C)  $\beta_{\text{equilibrium}} = 0.7$   
 (D)  $K_c < 1$

TD0105

8. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at  $T = 298 \text{ K}$  are [JEE 2017]

$$\Delta_f G^\circ [\text{C}(\text{graphite})] = 0 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ [\text{C}(\text{diamond})] = 2.9 \text{ kJ mol}^{-1}$$

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by  $2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ . If C(graphite) is converted to C(diamond) isothermally at  $T = 298 \text{ K}$ , the pressure at which C(graphite) is in equilibrium with C(diamond), is

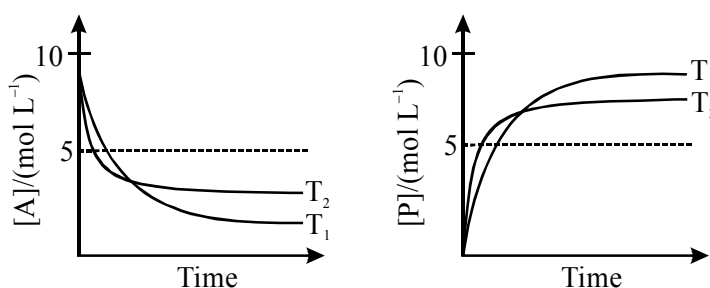
[Useful information :  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ ;  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$ ;  $1 \text{ bar} = 10^5 \text{ Pa}$ ]

- (A) 14501 bar (B) 29001 bar (C) 58001 bar (D) 1405 bar TD0106

9. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant  $K$  in terms of change in entropy is described by
- With increase in temperature, the value of  $K$  for exothermic reaction decreases because the entropy change of the system is positive
  - With increase in temperature, the value of  $K$  for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases
  - With increase in temperature, the value of  $K$  for exothermic reaction decreases because favourable change in entropy of the surroundings decreases
  - With increase in temperature, the value of  $K$  for endothermic reaction increases because the entropy change of the system negative
10. For a reaction,  $A \rightleftharpoons P$ , the plots of  $[A]$  and  $[P]$  with time at temperatures  $T_1$  and  $T_2$  are given below.

TD0107

[JEE 2018]



If  $T_2 > T_1$ , the correct statement(s) is (are)

(Assume  $\Delta H^\theta$  and  $\Delta S^\theta$  are independent of temperature and ratio of  $\ln K$  at  $T_1$  to  $\ln K$  at  $T_2$  is greater than  $\frac{T_2}{T_1}$ . Here  $H$ ,  $S$ ,  $G$  and  $K$  are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

(A)  $\Delta H^\theta < 0$ ,  $\Delta S^\theta < 0$

(B)  $\Delta G^\theta < 0$ ,  $\Delta H^\theta > 0$

(C)  $\Delta G^\theta < 0$ ,  $\Delta S^\theta < 0$

(D)  $\Delta G^\theta < 0$ ,  $\Delta S^\theta > 0$

TD0108

11. The surface of copper gets tarnished by the formation of copper oxide.  $N_2$  gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the  $N_2$  gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below
- $$2\text{Cu(s)} + \text{H}_2\text{O(g)} \rightarrow \text{Cu}_2\text{O(s)} + \text{H}_2\text{(g)}$$
- $p_{\text{H}_2}$  is the minimum partial pressure of  $\text{H}_2$  (in bar) needed to prevent the oxidation at 1250 K. The value of  $\ln(p_{\text{H}_2})$  is \_\_\_\_.

(Given : total pressure = 1 bar,  $R$  (universal gas constant) =  $8 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $\ln(10) = 2.3$ .  $\text{Cu(s)}$  and  $\text{Cu}_2\text{O(s)}$  are mutually immiscible.)

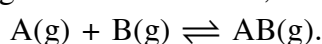
At 1250 K :  $2\text{Cu(s)} + 1/2\text{O}_2\text{(g)} \rightarrow \text{Cu}_2\text{O(s)}$ ;  $\Delta G^\theta = -78,000 \text{ J mol}^{-1}$

$\text{H}_2\text{(g)} + 1/2\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(g)}$ ;  $\Delta G^\theta = -1,78,000 \text{ J mol}^{-1}$ ;  $G$  is the Gibbs energy) [JEE 2018]

TD0109

[JEE 2018]

12. Consider the following reversible reaction,



The activation energy of the backward reaction exceeds that of the forward reaction by  $2RT$  (in  $\text{J mol}^{-1}$ ). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of  $\Delta G^\theta$  (in  $\text{J mol}^{-1}$ ) for the reaction at 300 K is \_\_\_\_.

(Given ;  $\ln(2) = 0.7$ ,  $RT = 2500 \text{ J mol}^{-1}$  at 300 K and  $G$  is the Gibbs energy)

TD0110

ANSWER KEY

EXERCISE (S-I)

1. Ans. 117°C, 52°C
2. Ans. 197°C
3. Ans. (4)
4. Ans. (i)  $\Delta S_{\text{syst}} = 28.72 \text{ J/K}$  ;  $\Delta S_{\text{surr}} = -28.72 \text{ J/K}$  ;  $\Delta S_{\text{total}} = 0$   
(ii)  $\Delta S_{\text{syst}} = 28.72 \text{ J/K}$  ;  $\Delta S_{\text{surr}} = -11.22 \text{ J/K}$  ,  $\Delta S_{\text{total}} = 17.50 \text{ J/K}$
5. Ans. (a) -250 J/K (b) 333.33 J/K (c) +83.33 J/K. Process is spontaneous.
6. Ans.(5)
7. Ans (200)
8. Ans. 10.325
9. Ans. (i) -90.5 (ii) -374.5 (iii) -3.26 (all in  $\text{J mol}^{-1} \text{ K}^{-1}$ )
10. Ans. [A] - II ; [B] - II ; [C] - II ; [D] - II
11. Ans. -3.7 kJ
11. Ans 436 kJ
13. Ans. 5.968 kcal
14. Ans.(-7)
15. Ans. (50)
16. Ans.  
(i)  $\Delta G = 0$   
(ii)  $\Delta S = -5 \text{ J/mole.K}$   
(iii)  $\Delta S_{\text{total}} = +1.66 \text{ J/ mole. K}$  ; process in spontaneous  
(iv)  $\Delta S_{\text{total}} = - \text{ J/mole. K} = \Delta G = +250 \text{ J/mole. K}$  ]
17. Ans. -997.68 J/mol
18. Ans.  $\Delta H^\circ = 9.04 \text{ kJ/mol}$ ;  $\Delta S^\circ = -8.64 \text{ J/mol}^{-1} \text{ K}^{-1}$
19. Ans. 26.7

EXERCISE-(S-II)

1. Ans. (i) 30 kJ (ii) 60 kJ (iii) 100 J/K
2. Ans. 30 kJ/mole
3. Ans. -1745.94 J/mol; -6983.76 J/mol and 13.97 kJ/mol
4. Ans. (16.66 J/K)
5. Ans. (- 327.75 kJ/ mol)
6. Ans. (17.8)
7. Ans.(3360)
8. Ans 10 J/K
9. Ans. 205.08  $\text{JK}^{-1}\text{mol}^{-1}$
10. Ans.(1195 kJ/mole)

**EXERCISE (O-I)**

- |             |              |              |             |
|-------------|--------------|--------------|-------------|
| 1. Ans.(C)  | 2. Ans.(D)   | 3. Ans.(C)   | 4. Ans.(D)  |
| 5. Ans.(C)  | 6. Ans.(B)   | 7. Ans.(A)   | 8. Ans.(B)  |
| 9. Ans.(B)  | 10. Ans.(B)  | 11. Ans.(A)  | 12. Ans.(A) |
| 13. Ans.(C) | 14. Ans.(D)  | 15. Ans.(C)  | 16. Ans.(B) |
| 17. Ans.(A) | 18. Ans. (A) | 19. Ans. (C) | 20. Ans.(B) |

**EXERCISE (O-II)**

- |  |                 |                 |                 |
|--|-----------------|-----------------|-----------------|
| 1. Ans.(D)   | 2. Ans.(D)      | 3. Ans.(A)      | 4. Ans.(B)      |
| 5. Ans.(A)   | 6. Ans.(A)      | 7. Ans.(A)      | 8. Ans.(C)      |
| 9. Ans.(A)   | 10. Ans.(A)     | 11. Ans.(B,D)   | 12. Ans.(A)     |
| 13. Ans. (A,C,D)   | 14. Ans.(A,C)   | 15. Ans.(A,B,D) | 16. Ans.(B,C,D) |
| 17. Ans.[A,C,D]  | 18. Ans.[A,B,C] | 19. Ans.[C]     | 20. Ans.[B,C,D] |
| 21. Ans.(A)  | 22. Ans.(C)     | 23. Ans.(D)     | 24. Ans.(D)     |
| 25. Ans.(B)  | 26. Ans.(C)     | 27. Ans.(D)     | 28. Ans.(C)     |
| 29. Ans. (A) - S ; (B) - P,R ; (C) - P, S (D) - P, R     |                 |                 |                 |
| 30. Ans. (A) - P,S,R ; (B) - P,R ; (C) - P (D) - Q, R, S |                 |                 |                 |

**EXERCISE (J-MAIN)**

- |                          |             |             |             |
|--------------------------|-------------|-------------|-------------|
| 1. Ans.(3)               | 2. Ans.(4)  | 3. Ans.(4)  | 4. Ans.(1)  |
| 5. Ans.(1)               | 6. Ans.(4)  | 7. Ans.(2)  | 8. Ans.(3)  |
| 9. Ans.(1)               | 10. Ans.(4) | 11. Ans.(4) | 12. Ans.(2) |
| 13. Ans.(1)              | 14. Ans.(4) | 15. Ans.(2) |             |
| 16. Ans.(-2.70 to -2.71) |             |             |             |

**EXERCISE (J-ADVANCE)**

- |   |               |                 |                |
|---|---------------|-----------------|----------------|
| 1. Ans.(A)→(p, r, s) ; (B)→(r, s) ; (C)→(t) ; (D)→(p, q, t)           |               |                 |                |
| 2. Ans.(A), (C)   | 3. Ans. (B)   |                 |                |
| 4. Ans. (A) → R, T ; (B) → P, Q, S ; (C) → P, Q, S ; (D) → P, Q, S, T |               |                 |                |
| 5. Ans. (C)   | 6. Ans.(B)    | 7. Ans.(C)      | 8. Ans.(A)     |
| 9. Ans.(BC)   | 10. Ans.(A,C) | 11. Ans.(-14.6) | 12. Ans.(8500) |



## IONIC EQUILIBRIUM

### 1. INTRODUCTION

Ionic equilibrium deals with the equilibrium of any substance with its ions in solution. The substance producing ions are called electrolytes.

According to conductivity, substances are of two types :

(i) **Non-Conductor :**

Those substances which do not show the flow of current or electricity.

**Ex.** Non - metals, plastic rubber, wood, etc.

Exception – Graphite is a non-metal but shows conductivity due to motion of free electrons.

(ii) **Conductors :**

Those substances which show conductivity or flow of current are called conductors. These are of 2 types :

(a) **Metallic or electronic conductors :**

Those conductor which show conductivity due to motion of free electrons. Resistance increases with temperature.

**Ex.** All metals, Graphite

(b) **Ionic or electrolytic conductors :**

Those conductors which show conductivity due to movement of free ions. Ions are in free state in the solutions of ionic compounds. On passing electric current through the solution, ions move towards oppositely charged electrodes, i.e., the cation moves towards cathode (negative electrode) and the anion moves towards anode (positive electrode).

The current flows through the solution due to the movement of the ions. Resistance decrease with temperature.

According to strength, ionic conductors are of two types :

(i) **Strong electrolyte :** Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolyte.

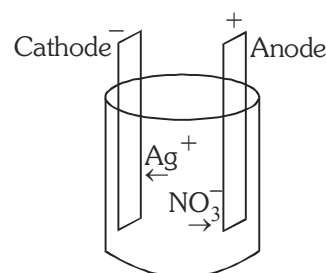
For strong electrolyte the value of degree of dissociation is 100%.

**i.e. :  $\alpha = 1$**

- Ex.** (a) Strong acid  $\rightarrow$   $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_5$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HBrO}_4$ ,  $\text{HIO}_4$ ,  $\text{RSO}_3\text{H}$   
 (b) Strong base  $\rightarrow$   $\text{KOH}$ ,  $\text{NaOH}$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{CsOH}$ ,  $\text{RbOH}$   
 (c) All soluble salts  $\rightarrow$   $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CuSO}_4$ .....

(ii) **Weak electrolytes :** Those electrolytes which are partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of  $\alpha$  is less than one.

- Ex.** (a) **Weak acid :**  $\text{HCN}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{HCOOH}$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{H}_3\text{PO}_2$ , etc.  
 (b) **Weak base :**  $\text{NH}_4\text{OH}$ ,  $\text{Cu}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ , etc.



## 1.2 DEGREE OF DISSOCIATION / IONISATION

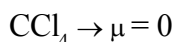
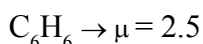
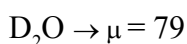
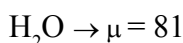
- When an electrolyte is dissolved in a solvent ( $H_2O$ ), it spontaneously dissociates into ions.
- It may dissociate partially ( $\alpha < 1$ ) or sometimes completely ( $\alpha \cong 1$ )
- The degree of dissociation ( $\alpha$ ) of an electrolyte is the fraction of mole of the electrolyte that has dissociated under the given conditions.

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{No. of moles taken initially}}$$

## 1.3 FACTORS AFFECTING THE VALUE OF DEGREE OF DISSOCIATION:

- (i) **Dilution** :  $\alpha \propto \sqrt{V}$ . So on dilution,  $\alpha$  increases
- (ii) **Temperature** : On increasing temperature, ionization increases so,  $\alpha$  increases
- (iii) **Nature of electrolyte** :
- (a) Strong electrolyte (b) Weak electrolyte
- $\alpha = 100\%$   $\alpha \ll 100\%$
- (iv) **Nature of solvent** :

If dielectric constant,  $\mu$ , of solvent increases, then the value of  $\alpha$  increases.



**Ex.1** Which one has greater  $\alpha_1$  or  $\alpha_2$  for the following equation :



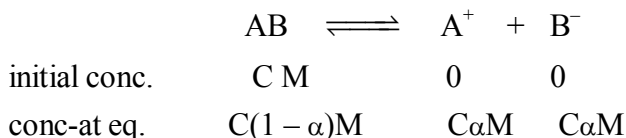
**Sol.** Dielectric constant of  $H_2O$  is more than that of  $D_2O$ , so  $\alpha_1 > \alpha_2$

(v) **Mixing of Ions** :

Common ion Effect	Odd ion Effect
$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ On mixing $NH_4Cl$ $NH_4Cl \rightarrow NH_4^+ + Cl^-$ Due to mixing of common ion, concentration of ammonium ion will increase therefore equilibrium will shift in backward direction means $\alpha$ decreases.	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ On mixing $HCl$ $HCl \rightarrow H^+ + Cl^-$ Due to reaction of $OH^-$ ions with $H^+$ ion, concentration of $OH^-$ will decrease $\therefore$ Equilibrium will shift in forward direction means $\alpha$ increases.

1.4 OSTWALD'S DILUTION LAW (FOR WEAK ELECTROLYTE)

- For a weak electrolyte  $A^+B^-$  dissolved in water, if  $\alpha$  is the degree of dissociation then



Then according to law of mass action,

$$K_{diss} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

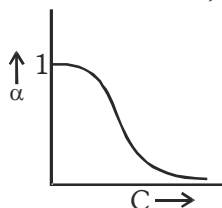
= dissociation constant of the weak electrolyte.

$$\left[ C = \frac{1}{V}, \text{ then } V = 1/C \text{ (volume of solution in which 1 mole is present) is called dilution, so } K_{diss} = \frac{\alpha^2}{(1-\alpha)V} \right]$$

If  $\alpha$  is negligible in comparison to unity,  $1 - \alpha \approx 1$ . so  $K_{diss} = \alpha^2 C \Rightarrow \alpha = \sqrt{\frac{K_{diss}}{C}} = \sqrt{K_{diss} V}$

$$\alpha \propto \frac{1}{\sqrt{\text{concentration}}}$$

- As concentration increases  $\Rightarrow \alpha$  decreases
- At infinite dilution  $\alpha$  reaches its maximum value, unity.

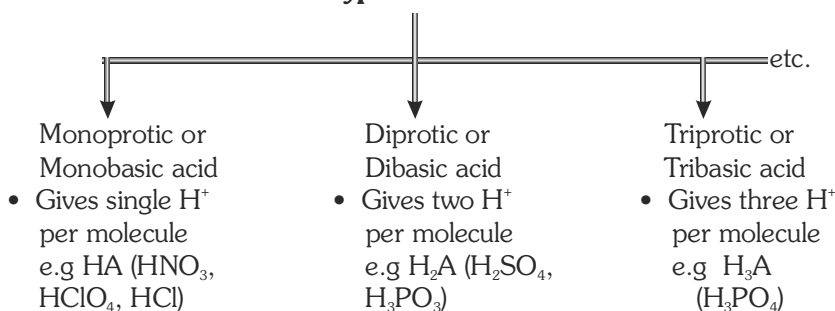


2. ACIDS BASES AND SALTS

2.1 Arrhenius concept :

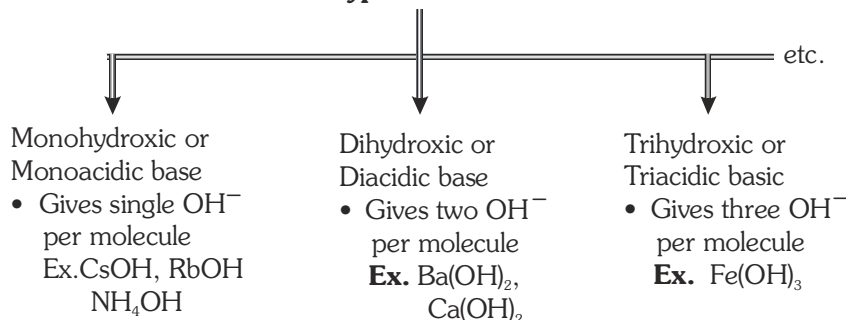
- (i) **Arrhenius Acid** : Substance which gives  $H^+$  ion on dissolving in water ( $H^+$  donor)  
 Ex.  $HNO_3, HClO_4, HCl, HI, HBr, H_2SO_4, H_3PO_4$  etc.

**Types of acids**



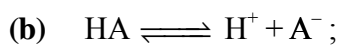
- (ii) **Arrhenius base** : Any substance which releases  $OH^-$  (hydroxyl) ion in water ( $OH^-$  ion donor)

**Types of bases**



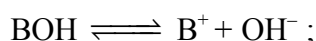
**(iii) Strength of Acid or Base :**

(a) Strength of acids or bases depends on the extent of its ionisation. Hence equilibrium constant  $K_a$  or  $K_b$  respectively of the following equilibria give a quantitative measurement of the strength of the acid or base.



$$K_a = \frac{[H^+][A^-]}{[HA]} = \text{dissociation or ionisation constant of acid.}$$

(c) Similarly



$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \text{dissociation or ionisation constant of base}$$

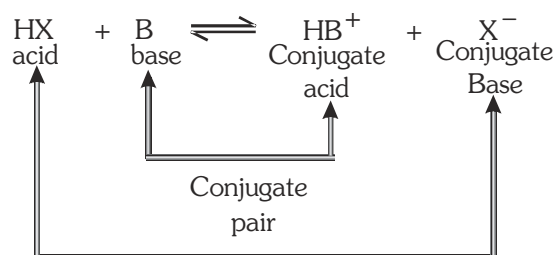
(d) Larger the value of  $K_a$  or  $K_b$ , stronger is the acid or base respectively.

**2.2 Bronsted - Lowry concept : (Conjugate acid - base concept) (Protonic concept)**

(i) **Acid** : substances which donate  $H^+$  are Bronsted Lowry acids ( $H^+$  donor)

(ii) **Base** : substances which accept  $H^+$  are Bronsted Lowry bases ( $H^+$  acceptor)

(iii) **Conjugate acid - base pairs** : In a typical acid base reaction,  $HX + B \rightleftharpoons X^- + HB^+$

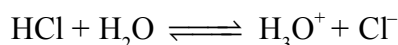


- Forward reaction - Here HX being a proton donor is an acid  
B being a proton acceptor is a base.
- Backward reaction - Here  $HB^+$  being a proton donor is an acid  
 $X^-$  being a proton acceptor is a base.

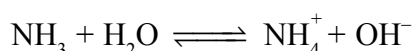
Acid	Base		Conjugate Acid	+	Conjugate Base
• HCl	+ H <sub>2</sub> O	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup>	+	Cl <sup>-</sup>
• HSO <sub>4</sub> <sup>-</sup>	+ NH <sub>3</sub>	$\rightleftharpoons$	NH <sub>4</sub> <sup>+</sup>	+	SO <sub>4</sub> <sup>-2</sup>
• [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	+ H <sub>2</sub> O	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup>	+	[Fe(H <sub>2</sub> O) <sub>5</sub> (OH)] <sup>2+</sup>
•	Conjugate acid - base pair differ by only one proton.				
•	Strong acid will have weak conjugate base and vice versa.				

Acid	Conjugate base	Base	Conjugate acid
HCl	Cl <sup>-</sup>	NH <sub>3</sub>	NH <sub>4</sub> <sup>+</sup>
H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>
HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	RNH <sub>2</sub>	RNH <sub>3</sub> <sup>+</sup>
H <sub>2</sub> O	OH <sup>-</sup>		

(iv) **Amphoteric (amphiprotic)** : Substances which can act as acid as well as base are known as amphoteric



base



acid

(v) **Classification of Bronsted - Lowery Acids and Bases :**

Bronsted - Lowery acids and bases can be

- (i) Molecular      (ii) Cationic and      (iii) Anionic

**Table - 1**

Type	Acid	Base
Molecular	HCl, HNO <sub>3</sub> , HClO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> O etc.	NH <sub>3</sub> , N <sub>2</sub> H <sub>4</sub> , Amines, H <sub>2</sub> O, Alcohol, Ethers, etc.
Cationic	NH <sub>4</sub> <sup>+</sup> , N <sub>2</sub> H <sub>5</sub> <sup>+</sup> , PH <sub>4</sub> <sup>+</sup> , [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> , [Al(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> etc.	[Fe(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup> [Al(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup> etc.
Anionic	HS <sup>-</sup> , HSO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HSO <sub>4</sub> <sup>-</sup> HCO <sub>3</sub> <sup>-</sup> , HPO <sub>4</sub> <sup>2-</sup> , etc. all amphiprotic anions	Cl <sup>-</sup> , Br <sup>-</sup> , OH <sup>-</sup> , HSO <sub>4</sub> <sup>-</sup> , CN <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> , NH <sub>2</sub> <sup>-</sup> , CH <sub>3</sub> COO <sup>-</sup> , etc. all amphiprotic anions

**2.3 Lewis concept (electronic concept) :**

(i) **Acid** : An acid is a molecule/ion which can accept an electron pair with the formation of a coordinate bond.

**Ex.** Electron deficient molecules : BF<sub>3</sub>, AlCl<sub>3</sub>, etc.

Cations : H<sup>+</sup>, Fe<sup>2+</sup>, Na<sup>+</sup>, etc.

Molecules with vacant orbitals : SF<sub>4</sub>, PF<sub>3</sub>

(ii) **Base** : A base is any molecule/ion which has a pair of electrons which can be donated.

**Ex.** Molecules with lone pairs : NH<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub>O, CH<sub>3</sub>OH

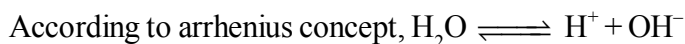
Anions : OH<sup>-</sup>, H<sup>-</sup>, NH<sub>2</sub><sup>-</sup>, etc.

### 3. PROPERTIES OF WATER

#### (i) Molar concentration / Molarity of water :

$$\text{Molarity} = \text{No. of moles/litre} = \frac{1000 \text{ g/litre}}{18 \text{ g/mole}} = 55.55 \text{ mole/litre} = \mathbf{55.55 \text{ M}}$$
 (density = 1 g/cc)

#### (ii) Ionic product of water :



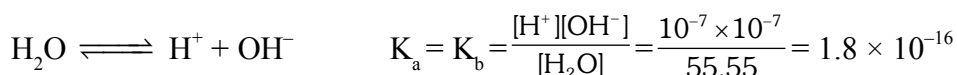
So, ionic product of water,  $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$  at  $25^\circ$  (experimental)

Dissociation of water is endothermic, so on increasing temperature  $K_w$  increases.

#### (iii) Degree of dissociation of water :

$$\begin{aligned} \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \Rightarrow \alpha &= \frac{\text{decrease in concentration}}{\text{initially concentration}} \\ &= \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7}\% \quad [\text{at } 25^\circ\text{C}] \end{aligned}$$

#### (iv) Dissociation or ionisation constant of water :



$$\text{So, } pK_a = pK_b = -\log(1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$$

**Ex.2.** At dissociation constant of heavy water is  $4 \times 10^{-15}$  at  $35^\circ\text{C}$ . If its density is  $1.04 \text{ g/mL}$ . Calculate its ionic product & degree of dissociation.

$$\text{Sol. } K_w = K_d[D_2O] = \left(4 \times 10^{-15} \times \frac{1040}{20}\right) = 2.08 \times 10^{-13}$$

$$d = \sqrt{\frac{K_w}{C}} = \sqrt{\frac{2.08 \times 10^{-13}}{52}} = 12.64 \times 10^{-8}$$

**Ex.3** Calculate ionic product of  $\text{H}_2\text{O}$  at  $50^\circ\text{C}$ .

$$\text{Sol. } \Delta H = 13.7 \times 10^3 \text{ cal}$$

$$\log \frac{K_2}{10^{-14}} = \frac{13.7 \times 10^3}{2} \left( \frac{1}{298} - \frac{1}{323} \right)$$

**Ex.4** The hydronium ion conc. in an aq.  $\text{H}_2\text{CO}_3$  solution is  $4 \times 10^{-4} \text{ M}$  at  $25^\circ\text{C}$   $\text{OH}^-$  ion conc. in the solution is :

- (A) 0                      (B)  $2.5 \times 10^{-10}$                       (C)  $2.5 \times 10^3$                       (D)  $2.5 \times 10^{-11} \text{ M}$

Answer : (D)

**Ex.5** Select the correct option from the following ?

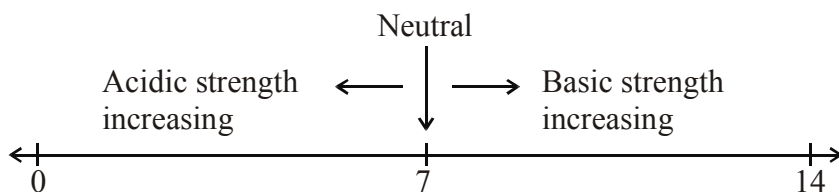
- (A)  $pK_w$  increases with increase of temperature  
 (B)  $pK_w$  decreases with increase of temperature  
 (C)  $pK_w = 14$  at all temperatures  
 (D)  $pK_w = pH$  at all temperatures

Sol. (B)

4. Acidity and pH scale :

- (i) Acidic strength means the tendency of an acid to give  $H_3O^+$  or  $H^+$  ions in water.  
So greater then tendency to give  $H^+$ , more will be the acidic strength of the substance.
- (ii) Basic strength means the tendency of a base to give  $OH^-$  ions in water.  
So greater the tendency to give  $OH^-$  ions, more will be basic strength of the substance.
- (iii) The concentration of  $H^+$  ions is written in a simplified form introduced by **Sorenson** known as pH scale. pH is defined as negative logarithm of activity of  $H^+$  ions.  
 $\therefore$  **pH = -log a<sub>H<sup>+</sup></sub>** (where a<sub>H<sup>+</sup></sub> is the activity of  $H^+$  ions)
- (iv) Activity of  $H^+$  ions is the molar concentration of free  $H^+$  ions or  $H_3O^+$  ions in a dilute solution, but unitless.
- (v) Now  $pH = -\log[H^+] = 7$  and  $pOH = -\log[OH^-] = 7$  for water at 25°C (experimental)
 

$pH = 7 = pOH$	$\Rightarrow$ neutral	}	at 25 °C
$pH < 7$ or $pOH > 7$	$\Rightarrow$ acidic		
$pH > 7$ or $pOH < 7$	$\Rightarrow$ Basic		

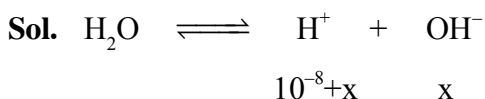


4.1 pH Calculation of different Types of solutions :

(a) Strong acid solution :

- (i) If concentration of  $H^+$  ions is greater than  $10^{-6}$  M,  $H^+$  ions coming from water can be neglected,  
So  $[H^+] =$  normality of strong acid solution
- (ii) If concentration is less than  $10^{-6}$  M,  $H^+$  ions coming from water cannot be neglected. So  
 $[H^+] =$  normality of strong acid +  $H^+$  ions coming from water in presence of this strong acid

**Ex.6 Calculate pH of  $10^{-8}$  M HCl solution.**



$$k_w = [H^+][OH^-]$$

$$10^{-14} = x(x + 10^{-8})$$

$$\Rightarrow x^2 + x \times 10^{-8} - 10^{-14} = 0$$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = \frac{-10^{-8} + 10^{-7} \sqrt{4 + \frac{1}{100}}}{2} = \frac{(\sqrt{401} - 1)10^{-8}}{2} = 0.95 \times 10^{-7}$$

$$[H^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$$

$$pH = -\log [H^+]$$

$$pH = 7 - \log 1.05 \approx 6.98$$

**4.2 Strong base solution :**

Calculate the  $[\text{OH}^-]$  which will be equal to normality of the strong base solution and then use

$$K_w = [\text{H}^+] \times [\text{OH}^-] = 10^{-14}, \text{ to calculate } [\text{H}^+]$$

**Ex.7 Calculate pH of  $10^{-7} \text{ M}$  of NaOH solution**

**Sol.**  $[\text{OH}^-]$  from NaOH =  $10^{-7}$

$[\text{OH}^-]$  from water =  $x < 10^{-7} \text{ M}$  (due to common ion effect)



$$- \quad \quad \quad (x + 10^{-7}) \quad \quad x$$

$$K_w = [\text{H}^+] [\text{OH}^-] = 10^{-14} = x(x + 10^{-7})$$

$$x^2 + 10^{-7}x - 10^{-14} = 0$$

$$\Rightarrow x = \frac{\sqrt{5}-1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \quad (\sqrt{5} = 2.236)$$

$$[\text{OH}^-] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$$

$$\text{pOH} = 7 - \log(1.618) = 6.79$$

$$\text{pH} = 14 - 6.79 = 7.21$$

**4.3 pH of mixture of two strong acids :** If  $V_1$  volume of a strong acid solution of normality  $N_1$  is mixed with  $V_2$  volume of another strong acid solution of normality  $N_2$ , then

$$\text{Number of } \text{H}^+ \text{ ions from I-solution} = N_1 V_1$$

$$\text{Number of } \text{H}^+ \text{ ions from II-solution} = N_2 V_2$$

If final normality is  $N$  and final volume is  $V$ , then

$$NV = N_1 V_1 + N_2 V_2$$

[dissociation equilibrium of none of these acids will be disturbed as both are strong acid]

$$[\text{H}^+] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \quad \left[ \begin{array}{l} \text{where } N = M \times n \\ n = \text{Basicity of acid} \end{array} \right]$$

**4.4 pH of mixture of two strong bases :**

Similar to above calculation

$$[\text{OH}^-] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \quad [\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]}$$

$$\left[ \begin{array}{l} \text{where } N = M \times n \\ n = \text{Acidity of base} \end{array} \right]$$

**Ex.8 Calculate pH of mixture of (400 mL,  $\frac{1}{200} \text{ M H}_2\text{SO}_4$ ) + (400 mL,  $\frac{1}{100} \text{ M HCl}$ ) + (200 mL of water)**

**Sol.**  $N_1 V_1 = \frac{1}{200} \times \frac{400}{1000} \times 2 = \frac{4}{1000}$ ,  $N_2 V_2 = \frac{4}{1000}$ ,  $\text{H}^+$  ions from water will be neglected

$$N_1 V_1 + N_2 V_2 = 8 \times 10^{-3} \quad [\text{H}^+] = \frac{8 \times 10^{-3}}{1} = 8 \times 10^{-3}$$

$$\text{pH} = 3 - \log 8 = 2.1$$



**Ex.9** 500 mL of  $10^{-5}$  M NaOH is mixed with 500 mL of  $2.5 \times 10^{-5}$  M of  $Ba(OH)_2$ . To the resulting solution 99 L water is added. Calculate pH.

**Sol.**  $[OH^-] = \frac{500 \times 10^{-5} + 500 \times 2 \times 2.5 \times 10^{-5}}{1000} = 3 \times 10^{-5}$  M

$$M_1 = 3 \times 10^{-5} \text{ M}$$

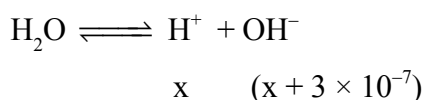
$$V_2 + V_1 = 1 \text{ L}$$

$$V_F = 100 \text{ L}$$

no. of moles of  $[OH^-]$  initially = no. of moles of  $[OH^-]$

$$3 \times 10^{-5} = M_2 \times 100$$

$$\therefore M_2 = 3 \times 10^{-7} < 10^{-6}$$



$$K_w = x(x + 3 \times 10^{-7}) = 10^{-14}$$

$$\therefore x = \left( \frac{\sqrt{13} - 3}{2} \right) \times 10^{-7}$$

$$x = 0.302 \times 10^{-7}$$

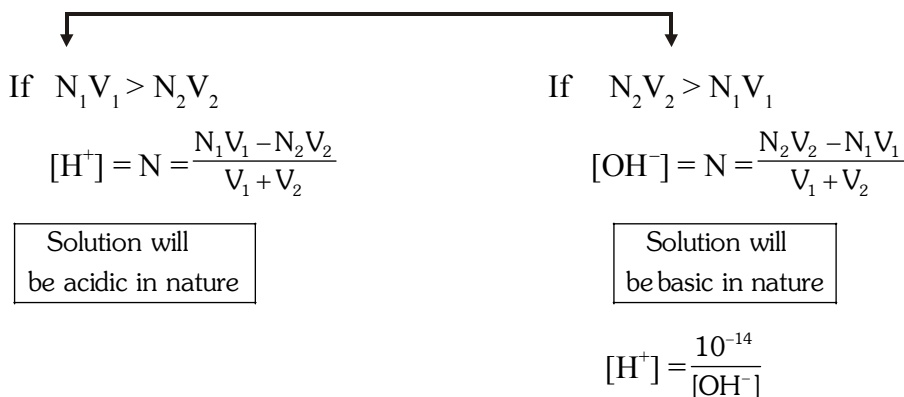
$$[OH^-]_{Net} = 3.302 \times 10^{-7}$$

#### 4.5 pH of mixture of a strong acid and a strong base :

- Acid Base neutralisation reaction will take place.
- The solution will be acidic or basic depending on which component has been taken in excess.
- If  $V_1$  volume of a strong acid solution of normality  $N_1$  is mixed with  $V_2$  volume of a strong base solution of normality  $N_2$ , then

$$\text{Number of } H^+ \text{ ions from I-solution} = N_1 V_1$$

$$\text{Number of } OH^- \text{ ions from II-solution} = N_2 V_2$$



**Ex.10** Calculate pH of mixture of (400 mL,  $\frac{1}{200}$  M Ba(OH)<sub>2</sub>) + (400 mL,  $\frac{1}{50}$  M HCl) + (200 mL of water)

**Sol.**  $[H^+] = \frac{400 \times \frac{1}{50} - 400 \times \frac{1}{200} \times 2}{1000} = 4 \times 10^{-3}$ , so  $pH = 3 - 2 \log 2 = 2.4$

**Ex.11** What will be the resultant pH when 150 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 350 mL of an aqueous solution of NaOH (pH = 12.0) ?

**Sol.** pH of HCl = 2

$\therefore [HCl] = 10^{-2}$  M

pH of NaOH = 12, pOH = 2  $\therefore [NaOH] = 10^{-2}$  M

	HCl	+	NaOH	→	NaCl	+	H <sub>2</sub> O
Meq. initial	$150 \times 10^{-2}$		$350 \times 10^{-2}$		0		0
	= 1.5		= 3.5				
Meq. final	0		2		1.5		1.5

$\therefore [OH^-] \text{ from NaOH} = \frac{2}{500} = 4 \times 10^{-3}$  M

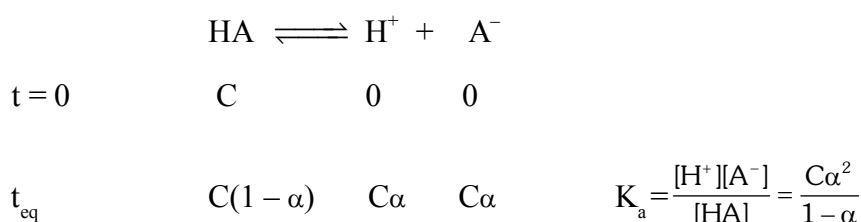
pOH =  $-\log[OH^-] = -\log(4 \times 10^{-3})$

$\therefore$  pOH = 2.3979

$\therefore$  pH = 14 - pOH = 14 - 2.3979 = 11.6021

#### 4.6 pH of a weak acid or weak base (monoprotic) Solution :

- Weak acid does not dissociated 100 % therefore we have to calculate the percentage dissociation using  $K_a$  dissociation constant of the acid.
- We have to use Ostwald's Dilution law (as have been derived earlier)



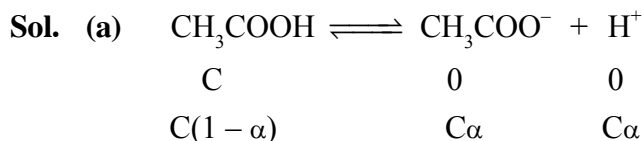
If  $\alpha \ll 1 \Rightarrow (1 - \alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$  (is valid if  $\alpha < 0.1$  or 10%)

$[H^+] = C\alpha = C \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C}$  So  $pH = \frac{1}{2}(pK_a - \log C)$

On increasing the dilution  $\Rightarrow C \downarrow = \alpha \uparrow$  and  $[H^+] \downarrow \Rightarrow pH \uparrow$

**Ex.12 Calculate pH of : (a)  $10^{-1}$  M  $CH_3COOH$  (b)  $10^{-3}$  M  $CH_3COOH$  (c)  $10^{-6}$  M  $CH_3COOH$**

Take  $K_a = 2 \times 10^{-5}$



$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}} \quad (\alpha \ll 0.1)$$

So,  $[H^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow \text{pH} = 3 - \frac{1}{2} \log 2 = 2.85$

**(b)**  $\alpha = \sqrt{\frac{K_a}{C}} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-3}}} = \sqrt{2 \times 10^{-2}} \quad (\alpha > 0.1)$

So we have to do the exact calculations

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow 2 \times 10^{-5} = \frac{10^{-3} \times \alpha^2}{1-\alpha} \Rightarrow \alpha = 13.14 \%$$

$$[H^+] = 10^{-3} \times 0.1314 = 1.314 \times 10^{-4} \Rightarrow \text{pH} = 4 - \log(1.314) \approx 3.8$$

**(c)** If approximation is used the,  $\alpha = \sqrt{\frac{2 \times 10^{-5}}{10^{-6}}} = \sqrt{20} > 1$ ,

So we have to do the exact calculation,  $2 \times 10^{-5} = 10^{-6} \frac{\alpha^2}{1-\alpha} \Rightarrow \alpha \approx 0.95$  or 95%

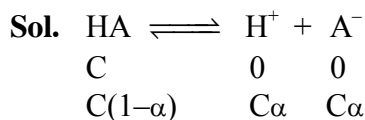
$$[H^+] = 0.95 \times 10^{-6} = 9.5 \times 10^{-7} \Rightarrow \text{pH} = 7 - \log(9.5) = 6.022$$

- At very low concentration (at infinite dilution) weak electrolyte will be almost 100% dissociate, so behave as strong electrolyte.

(pH) of  $10^{-6}$  M HCl  $\approx$  pH of  $10^{-6}$  M  $CH_3COOH \approx 6$

**Ex.13  $K_a$  for acid HA is  $2.5 \times 10^{-8}$  calculate for its decimolar solution at  $25^\circ\text{C}$ .**

**(i) % dissociation (ii) pH (iii)  $OH^-$  ion concentration**



$$K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \approx C\alpha^2$$

**(i)**  $\therefore \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2.5 \times 10^{-8}}{1/10}} \quad (C = 1/10 \text{ M})$   
 $= 5 \times 10^{-4} = 0.05\%$

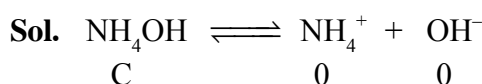
**(ii)**  $[H^+] = C\alpha = \frac{1}{10} \times 5 \times 10^{-4} = 5 \times 10^{-5} \text{ mol/L}$

So  $\text{pH} = 5 - \log 5 = 4.30$

**(iii)**  $[H^+][OH^-] = 1 \times 10^{-14}$

$$\therefore [OH^-] = \frac{10^{-14}}{5 \times 10^{-5}} = 2 \times 10^{-10} \text{ mol/L}$$

**Ex.14** Determine the degree of dissociation of 0.05 M  $\text{NH}_4\text{OH}$  at  $25^\circ\text{C}$  in a solution of  $\text{pH} = 10$ .



Given,  $\text{pH} = 10$

$$[\text{H}^+] = 10^{-10}$$

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{1 \times 10^{-14}}{10^{-10}} = 10^{-4} = C\alpha$$

$$\therefore \alpha = \frac{[\text{OH}^-]}{C} = \frac{10^{-4}}{0.05} = 2 \times 10^{-3} \text{ or } 0.2 \%$$

**Ex.15** The concentration of  $[\text{H}^+]$  and  $[\text{OH}^-]$  of the  $10^{-1}$  M aqueous solution of 2% ionised weak acid is :

(A)  $2 \times 10^{-3}$  M and  $5 \times 10^{-12}$  M

(B)  $1 \times 10^{-3}$  M and  $3 \times 10^{-11}$  M

(C)  $2 \times 10^{-4}$  M and  $5 \times 10^{-11}$  M

(D)  $3 \times 10^{-2}$  M and  $4 \times 10^{-13}$  M

**Sol.** (A)

$$[\text{H}^+] = C\alpha = 2 \times 10^{-3} \text{ M or } [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} = 5 \times 10^{-12} \text{ M}$$

**Ex.16** When a 0.1 N solution of an acid at  $25^\circ\text{C}$  has a degree of ionisation of 4%, the concentration of  $\text{OH}^-$  present is :

(A)  $2.5 \times 10^{-3}$

(B)  $2.5 \times 10^{-11}$

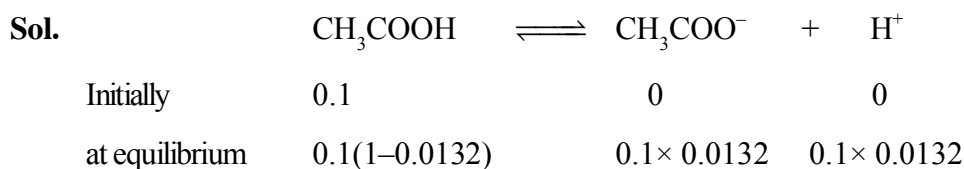
(C)  $2.5 \times 10^{-12}$

(D)  $2.5 \times 10^{-13}$

**Sol.** (C)

$$[\text{H}^+] = C\alpha = 0.1 \times 4 \times 10^{-2} = 4 \times 10^{-3} \text{ M or } [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} = 2.5 \times 10^{-12} \text{ N}$$

**Ex.17** The degree of dissociation of acetic acid in a 0.1 M solution is  $1.32 \times 10^{-2}$ . Calculate dissociation constant of acid and its  $\text{pK}_a$  value :



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{0.1 \times 0.0132 \times 0.1 \times 0.0132}{0.1(1-0.0132)} = 1.76 \times 10^{-5}$$

$$\text{pK}_a = -\log K_a = -\log (1.76 \times 10^{-5}) = 4.75$$

**4.7 pH of a mixture of weak acid (monoprotic) and a strong acid solution :**

- Weak acid and Strong acid both will contribute H<sup>+</sup> ion.
- For the first approximation we can neglect the H<sup>+</sup> ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.
- To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.
- If [SA] = C<sub>1</sub> and [WA] = C<sub>2</sub>, then [H<sup>+</sup>] from SA = C<sub>1</sub> the weak acid will dissociate as follows.



(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

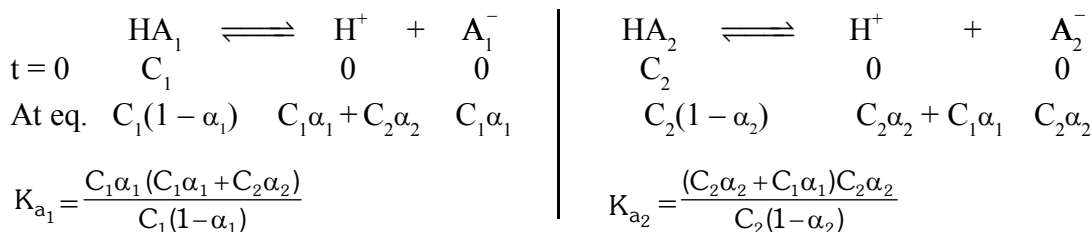
$$K_a = (C_2\alpha + C_1)\alpha$$

Total H<sup>+</sup> ion concentration = C<sub>1</sub> + C<sub>2</sub>α

- If the total [H<sup>+</sup>] from the acid is more than 10<sup>-6</sup> M, then contribution from the water can be neglected, if not then we have to take [H<sup>+</sup>] from the water also.

**4.8 pH of a mixture of two weak acid (both monoprotic) solution :**

- Both acids will dissociate partially.
- Let the acid are HA<sub>1</sub> & HA<sub>2</sub> and their final concentrations are C<sub>1</sub> & C<sub>2</sub> respectively, then



(Since α<sub>1</sub>, α<sub>2</sub> both are small in comparison to unity)

$$K_{a1} = (C_1\alpha_1 + C_2\alpha_2)\alpha_1 ; K_{a2} = (C_1\alpha_1 + C_2\alpha_2)\alpha_2 \Rightarrow \frac{K_{a1}}{K_{a2}} = \frac{\alpha_1}{\alpha_2}$$

$$\begin{aligned}
 [\text{H}^+] = C_1\alpha_1 + C_2\alpha_2 &= \frac{C_1K_{a1}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} + \frac{C_2K_{a2}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} \Rightarrow [\text{H}^+] \\
 &= \sqrt{C_1K_{a1} + C_2K_{a2}}
 \end{aligned}$$

- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

$$\text{So, } [\text{H}^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$$

**Ex.18** Calculate pH of solution obtained by mixing equal vol. of 0.02 M HOCl & 0.2 M CH<sub>3</sub>COOH solution given that  $K_{a_1}(\text{HOCl}) = 2 \times 10^{-4}$ ,  $K_{a_2}(\text{CH}_3\text{COOH}) = 2 \times 10^{-5}$

Also calculate OH<sup>-</sup>, OCl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>

**Sol.** Final solution volume become double

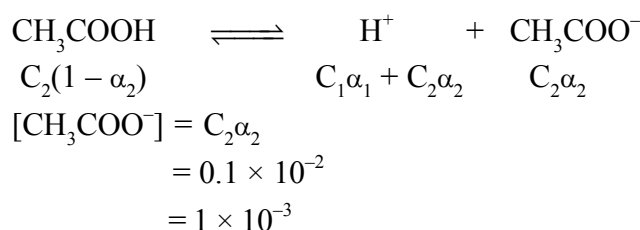
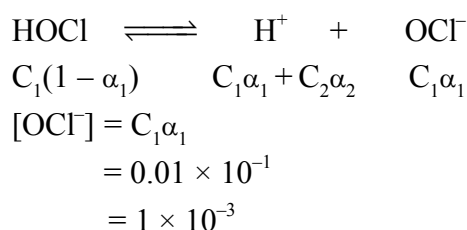
$$C_1 = 0.01, \quad C_2 = 0.1$$

$$[\text{H}^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2} = \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1}$$

$$= \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3}$$

$$\text{pH} = 3 - \log 2 = 3 - 0.3010 = 2.69$$

$$\alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 10^{-1} \quad \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 10^{-2}$$



$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 0.5 \times 10^{-11} = 5 \times 10^{-12} \text{ M}$$

$$[\text{HOCl}] = 10^{-2}(1 - 0.1) = 9 \times 10^{-3} \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 10^{-1}(1 - 0.01) \approx 10^{-1}$$

#### 4.9 pH of a solution of a polyprotic weak acid :

- Diprotic acid is the one, which is capable of giving 2 protons per molecule in water. Let us take a weak diprotic acid (H<sub>2</sub>A) in water whose concentration is c M.

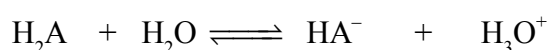
In an aqueous solution, following equilibria exist.

If

$\alpha_1$  = degree of ionization of H<sub>2</sub>A in presence of HA<sup>-</sup>       $K_{a_1}$  = first ionisation constant of H<sub>2</sub>A

$\alpha_2$  = degree of ionisation of HA<sup>-</sup> in presence of H<sub>2</sub>A       $K_{a_2}$  = second ionisation constant of H<sub>2</sub>A

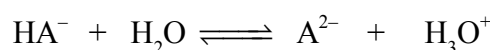
**I step**



at eq.  $c(1 - \alpha_1)$                        $c\alpha_1(1 - \alpha_2)$      $(c\alpha_1 + c\alpha_1\alpha_2)$

$$(K_{\text{eq}_1} [\text{H}_2\text{O}]) = \frac{[\text{H}_3\text{O}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} = K_{a_1}$$

**II step**



at eq.  $c\alpha_1(1 - \alpha_2)$                        $c\alpha_1\alpha_2$      $(c\alpha_1 + c\alpha_1\alpha_2)$

$$(K_{\text{eq}_2} [\text{H}_2\text{O}]) = \frac{[\text{H}_3\text{O}^+][\text{A}^{2-}]}{[\text{HA}^-]} = K_{a_2}$$

$$\therefore K_{a_1} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1(1-\alpha_2)]}{c(1-\alpha_1)} = \frac{[c\alpha_1(1+\alpha_2)][\alpha_1(1-\alpha_2)]}{1-\alpha_1} \dots\dots (i)$$

$$K_{a_2} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1\alpha_2]}{c\alpha_1(1-\alpha_2)} = \frac{[c\alpha_1(1+\alpha_2)]\alpha_2}{1-\alpha_2} \dots\dots (ii)$$

Knowing the values of  $K_{a_1}$ ,  $K_{a_2}$  and  $c$ , the values of  $\alpha_1$  and  $\alpha_2$  can be calculated using equations (i) and (ii) After getting the values of  $\alpha_1$  and  $\alpha_2$ ,  $[H_3O^+]$  can be calculated as

$$[H_3O^+]_T = c\alpha_1 + c\alpha_1\alpha_2$$

Finally, for calculation of pH

- If the total  $[H_3O^+] < 10^{-6}$  M, the contribution of  $H_3O^+$  from water should be added.
- If the total  $[H_3O^+] > 10^{-6}$  M, then  $[H_3O^+]$  contribution from water can be ignored.

Using this  $[H_3O^+]$ , pH of the solution can be calculated.

❖ **Approximation :**

For diprotic acids,  $K_{a_2} \ll K_{a_1}$  and  $\alpha_2$  would be even smaller than  $\alpha_1$

$$\therefore 1 - \alpha_2 \approx 1 \text{ and } 1 + \alpha_2 \approx 1$$

Thus, equation (i) can be reduced to 
$$K_{a_1} = \frac{C\alpha_1 \times \alpha_1}{1 - \alpha_1}$$

This is expression similar to the expression for a weak monoprotic acid.

- Hence, for a diprotic acid (or a polyprotic acid) the  $[H_3O^+]$  can be calculated from its first equilibrium constant expression alone provided  $K_{a_2} \ll K_{a_1}$ .

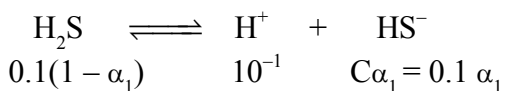
**Ex.19 Calculate pH of  $[HS^-]$ ,  $[S^{2-}]$ ,  $[Cl^-]$  in a solution which is 0.1 M HCl & 0.1 M  $H_2S$  given that  $K_{a_1}(H_2S) = 10^{-7}$ ,  $K_{a_2}(H_2S) = 10^{-14}$  also calculate  $\alpha_1$  &  $\alpha_2$ .**

**Sol.** HCl +  $H_2S$

$$0.1 \quad 0.1$$

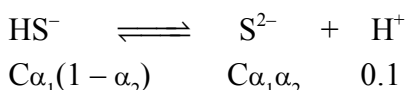
$$C_1 = C_2 = 0.1$$

$$\therefore \text{pH} = 1 \quad (\text{most of } [H^+] \text{ comes from HCl})$$



$$K_{a_1} = \frac{C\alpha_1 \times 10^{-1}}{C(1-\alpha_1)} = \frac{10^{-7}}{10^{-1}} = \alpha_1 \quad (\because 1 - \alpha_1 = 1)$$

$$\Rightarrow \alpha_1 = 10^{-6}$$



$$10^{-14} = 0.1 \times \alpha_2$$

$$\Rightarrow \alpha_2 = 10^{-13}$$

$$[S^{2-}] = C\alpha_1\alpha_2 = 10^{-6} \times 10^{-1} \times 10^{-13} = 10^{-20} \text{ M}$$

#### 4.10 ISOHYDRIC SOLUTIONS

- (i) Solutions of electrolytes are said to be isohydric if the concentration of the common ion present in them is the same and on mixing such solutions, there occurs no change in the degree of dissociation of either of the electrolyte.
- (ii) Let the isohydric solution is made by  $HA_1$  and  $HA_2$  acids, then  $[H^+]$  of both acids should be equal i.e.

$$\sqrt{K_{a_1} C_1} = \sqrt{K_{a_2} C_2} \quad \text{or} \quad \frac{K_{a_1}}{K_{a_2}} = \frac{C_2}{C_1}$$

#### 4.11 RELATIVE STRENGTH OF WEAK ACIDS AND BASES

For two acids of equimolar concentrations.

$$\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Similarly for bases, 
$$\frac{\text{Strength of base (I)}}{\text{Strength of base (II)}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

The modern method is to convert  $K_a$  as a power of 10 and express acid strength by power of 10 with sign changed and call this new unit  $pK_a$ . Thus, if  $K_a$  for acid is equal to  $10^{-4}$ ,  $pK_a = 4$ . So higher  $pK_a$  value means lower acid strength, that is,  $pK_a = -\log K_a$

Also,  $pK_b = -\log K_b$

### 5. SALTS

- (i) Salts are the ionic compounds formed when its positive part (Cation) come from a base and its negative part (Anion) come from an acid.
- (ii) Salts may taste salty, bitter or sweet or tasteless.
- (iii) Solution of salts may be acidic, basic or neutral.
- (iv) Fused salts and their aqueous solutions conduct electricity and undergo electrolysis.
- (v) The salts are generally crystalline solids.

#### 5.1 Classification of salts :

The salts may be classified into four categories.

##### (a) Normal salt :

- (i) The salt formed by the loss of all possible protons (replaceable  $H^+$  ions)

**Ex.**  $NaCl$ ,  $NaNO_3$ ,  $K_2SO_4$ ,  $Ca_3(PO_4)_2$ ,  $Na_3BO_3$ ,  $Na_2HPO_3$ ,  $NaH_2PO_2$  etc.

##### (b) Acid salts :

- (i) Salts formed by incomplete neutralisation of polybasic acids. Such salts contain one or more replaceable H atom.

**Ex.**  $NaHCO_3$ ,  $NaHSO_4$ ,  $NaH_2PO_4$ ,  $Na_2HPO_4$  etc.

- (ii) Above salts when neutralized by base form normal salts.

##### (c) Basic salts :



- (i) Salts formed by in complete neutralisation of poly acidic bases are called basic salts. These salt contain one or more hydroxyl groups.

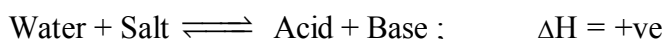
Ex.  $Zn(OH)Cl$ ,  $Mg(OH)Cl$ ,  $Fe(OH)_2 Cl$ ,  $Bi(OH)_2Cl$  etc.

- (ii) Above salts when neutralised by acids form normal salts.

## 5.2 HYDROLYSIS OF SALTS

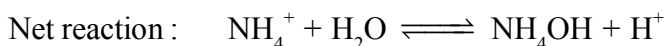
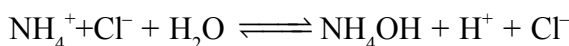
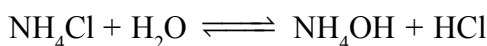
Salt hydrolysis is defined as the process in which water reacts with cation or anion or both of a salt to change the concentration of  $H^+$  and  $OH^-$  ions of water.

Salt hydrolysis is reverse process of neutralization.

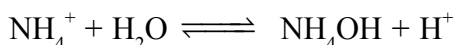


### 5.2.1 Hydrolysis of strong acid - weak base [SA - WB] type salt –

Ex.  $CaSO_4$ ,  $NH_4Cl$ ,  $(NH_4)_2SO_4$ ,  $Ca(NO_3)_2$ ,  $ZnCl_2$ ,  $CuCl_2$ ,  $CaCl_2$



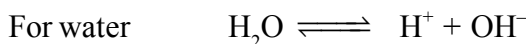
- (i) In this type of salt hydrolysis, cation reacts with  $H_2O$ , therefore called as *cationic hydrolysis*.  
 (ii) Solution is acidic in nature (SAWB) as  $[H^+]$  is increased.  
 (iii) pH of the solution is less than 7.  
 (iv) **Relation between  $K_h$ ,  $K_w$  &  $K_b$**



$$\text{Hydrolysis constant } K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \quad \dots(i)$$



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \dots(ii)$$



$$K_w = [OH^-][H^+] \quad \dots(iii)$$

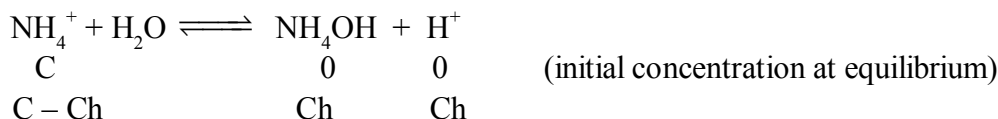
Now multiplying Eq. (1) & (2) = Eq. (3)

$$\frac{[NH_4OH][H^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} = [H^+][OH^-]$$

i.e.  $K_h \times K_b = K_w$

$$\boxed{K_h = \frac{K_w}{K_b}}$$

- (v) **Degree of hydrolysis – (Represented by h)**



$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{\text{Ch}^2}{(1-h)}$$

Since  $h \ll \ll \ll 1$

then  $(1-h) \approx 1$

$$\therefore K_h = \text{Ch}^2$$

$$\Rightarrow h = \sqrt{\frac{K_h}{C}}$$

$$\therefore \Rightarrow h = \sqrt{\frac{K_w}{K_b C}} \quad \Rightarrow \quad \boxed{h = \sqrt{\frac{K_w}{K_b \times C}}}$$

(vi) **pH of the solution :**

$$\text{pH} = -\log [\text{H}^+]$$

$$\Rightarrow [\text{H}^+] = \sqrt{\frac{K_w \times C}{K_b}}$$

On taking  $-\log$  on both sides

$$\text{pH} = -\log \left( \frac{K_w \times C}{K_b} \right)^{\frac{1}{2}}$$

$$\text{pH} = -\frac{1}{2} \log K_w - \frac{1}{2} \log C - \frac{1}{2} (-\log K_b)$$

$$\text{pH} = 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C$$

**Ex.20** Find out the  $K_h$  of centi normal [ $10^{-2}$  N] solution of  $\text{NH}_4\text{Cl}$  (SA - WB) if dissociation constant of  $\text{NH}_4\text{OH}$  is  $10^{-6}$  and  $K_w = 10^{-14}$ . Find out degree of hydrolysis and also find  $[\text{H}^+]$  and pH of solution?

(Given :  $K_w = 10^{-14}$  ;  $K_b = 10^{-6}$ )

**Sol.** (1)  $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

(2)  $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-8}}{10^{-2}}} = \sqrt{10^{-6}} = 10^{-3}$

(3)  $[\text{H}^+] = \text{Ch}$   
 $= 10^{-2} \times 10^{-3} = 10^{-5}$

(4)  $\text{pH} = -\log [\text{H}^+] = -\log [10^{-5}] = +5 \log 10 = +5 \times 1 = 5$

**Ex.21** How many grams of  $\text{NH}_4\text{Cl}$  should be dissolved per litre of solution to have a pH of 5.13 ?  $K_b$  for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ .

**Sol.**  $\text{NH}_4\text{Cl}$  is a salt of strong acid and weak base for solutions of such salts.

$$\text{pH} = \frac{1}{2} [\text{p}K_w - \log C - \text{p}K_b]$$

$$\Rightarrow 10.26 = 14 - \log C - 4.74$$

$$\Rightarrow \log C = 9.26 - 10.26 = -1.0$$

$$\therefore C = 10^{-1} \text{ M}$$

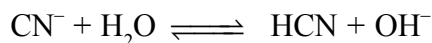
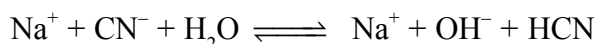
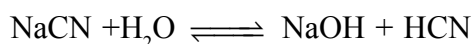
$$[\text{NH}_4\text{Cl}] = 10^{-1} \text{ M}$$

$$W_{\text{NH}_4\text{NO}_3} = 10^{-1} \times 53.5 \text{ gL}^{-1}$$

$$= 5.35 \text{ gL}^{-1}$$

### 5.2.2 Hydrolysis of [WA – SB] type salt :

**Ex.** KCN, NaCN,  $\text{K}_2\text{CO}_3$ ,  $\text{BaCO}_3$ ,  $\text{K}_3\text{PO}_4$

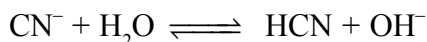


(i) In this type of salt hydrolysis anion reacts with water therefore called as anionic hydrolysis.

(ii) Solution is basic in nature as  $[\text{OH}^-]$  increases.

(iii) pH of the solution is greater than 7.

(iv) **Relation between  $K_h$ ,  $K_w$ ,  $K_a$**

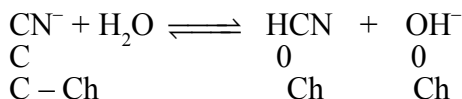


$$K_h = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} \quad \dots (i)$$

$$\frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} \times \frac{[\text{CN}^-][\text{H}^+]}{[\text{HCN}]} = [\text{H}^+][\text{OH}^-]$$

$$\boxed{K_h = \frac{K_w}{K_a}}$$

(v) **Degree of hydrolysis :**



Initial concentration at equilibrium

$$K_h = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

$$K_h = \frac{\text{Ch}^2}{(1-h)}$$

Since  $h \ll \ll \ll 1$ , therefore  $(1-h) \approx 1$

$$\therefore K_h = \text{Ch}^2$$

$$h^2 = \frac{K_h}{C} \quad \Rightarrow \quad \boxed{h = \sqrt{\frac{K_h}{C}}}$$

$$\boxed{h = \sqrt{\frac{K_w}{K_a \times C}}}$$

## (vi) pH of the solution

$$[\text{OH}^-] = Ch$$

$$[\text{OH}^-] = \sqrt{\frac{K_w \times C}{K_a}}$$

$$[\text{H}^+] = \frac{K_w}{\sqrt{\frac{K_w \times C}{K_a}}} \Rightarrow \boxed{[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{C}}}$$

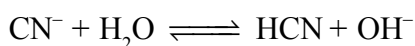
On taking  $-\log$  on both sides

$$\text{pH} = -\frac{1}{2} [\log K_w + \log K_a - \log C]$$

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$$

**Ex.22** Calculate the pH and degree of hydrolysis of 0.01 M solution of NaCN,  $K_a$  for HCN is  $6.2 \times 10^{-12}$ .

**Sol.** NaCN is a salt of strong base NaOH and weak acid HCN.  $\text{Na}^+$  does not react with water whereas  $\text{CN}^-$  reacts with water as here under



$$K_h = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{K_w}{K_a} = \frac{10^{-14}}{6.2 \times 10^{-12}} = 1.6 \times 10^{-3}$$

Let,  $x$  moles of salt undergo hydrolysis then concentrations of various species would be

$$[\text{CN}^-] = (0.01 - x) \approx 0.01, [\text{HCN}] = x$$

$$[\text{OH}^-] = x$$

$$\therefore K_h = \frac{x \cdot x}{0.01} = 1.6 \times 10^{-3}$$

$$\therefore x^2 = 1.6 \times 10^{-5}$$

$$\therefore x = 4 \times 10^{-3}$$

$$[\text{OH}^-] = x = 4 \times 10^{-3} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{4 \times 10^{-3}} = 0.25 \times 10^{-11}$$

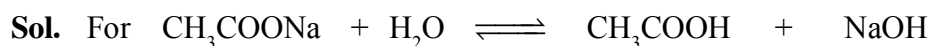
$$\text{pH} = -\log(0.25 \times 10^{-11}) = 11.6020$$

$$\text{Degree of hydrolysis} = \frac{x}{0.01} = \frac{4 \times 10^{-3}}{0.01} = 4 \times 10^{-1}$$

Ex.23. Calculate for 0.01 N solution of sodium acetate -

- (i) Hydrolysis constant
- (ii) Degree of hydrolysis
- (iii) pH

Given  $K_a$  of  $CH_3COOH = 1.9 \times 10^{-5}$ .



Initial	C	0	0
After	C(1-h)	Ch	Ch

(i)  $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}$

(ii)  $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5.26 \times 10^{-10}}{0.01}} = 2.29 \times 10^{-4} M$

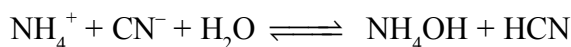
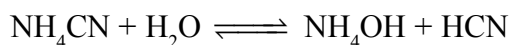
(iii)  $[OH^-]$  from NaOH, a strong base =  $Ch = 0.01 \times 2.29 \times 10^{-4} = 2.29 \times 10^{-6} M$

pOH = 5.64

$\therefore pH = 14 - 5.64 = 8.36$

### 5.2.3 Hydrolysis of (WA - WB) type salt :

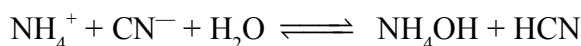
Ex.  $NH_4CN, CaCO_3, (NH_4)_2 CO_3, ZnHPO_3$



Solution is almost neutral but it may be acidic or basic depending upon the nature of acid & base & pH of the solution is near to 7.

For WA - WB types of salt :

	$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
1. Hydrolysis	Cationic-anionic	Anionic-cationic	Neutral hydrolysis
2. Nature	Acidic	Basic	Neutral
3. pH	$pH < 7$	$pH > 7$	$pH = 7$

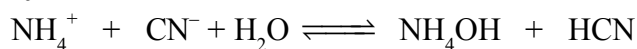
**(i) Relation between  $K_h$ ,  $K_w$ ,  $K_a$  &  $K_b$** 

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{HCN}]}{[\text{NH}_4^+][\text{CN}^-]} \quad \dots (i)$$

$$\frac{[\text{NH}_4\text{OH}][\text{HCN}]}{[\text{NH}_4^+][\text{CN}^-]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \times \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = [\text{H}^+][\text{OH}^-]$$

$$K_h \times K_b \times K_a = K_w$$

$$\boxed{K_h = \frac{K_w}{K_a \times K_b}}$$

**(ii) Degree of Hydrolysis :**

C	C	0	0	
C - Ch	C - Ch	Ch	Ch	Initial concentration at equilibrium

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{HCN}]}{[\text{NH}_4^+][\text{CN}^-]}$$

Since  $h \ll \ll \ll 1$

Then  $(1 - h) \approx 1$

$$\therefore \boxed{K_h = h^2} \quad \text{or} \quad h^2 = \frac{K_w}{K_a \times K_b}$$

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} \quad \dots (v)$$

**(iii) pH of the solution**

From eq. (iii)

$$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]}$$

$$[\text{H}^+] = \frac{K_a \times [\text{HCN}]}{[\text{CN}^-]}$$

$$[\text{H}^+] = \frac{K_a \times \text{Ch}}{\text{C} - \text{Ch}} = \frac{K_a \times h}{1 - h}$$

Since  $h \ll \ll \ll 1$ ,  $(1 - h) \approx 1$

$$[\text{H}^+] = K_a \times h \quad [\text{Now put the value of } h \text{ from eq. (5)}]$$

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$\boxed{[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{K_b}}}$$

On taking  $-\log$  on both sides

$$-\log [H^+] = -\log \left( \frac{K_w \times K_a}{K_b} \right)^{1/2}$$

$$pH = -\frac{1}{2} [\log K_w + \log K_a - \log K_b]$$

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

**Note :** Degree of hydrolysis of [WA – WB] type salt does not depend on the concentration of salt.

**Ex.24 Salt of weak acid and weak base**

(i) Calculate pH of the mixture (25 mL of 0.1 M  $NH_4OH$  + 25 mL of 0.1 M  $CH_3COOH$ ).

Given that  $K_a : 1.8 \times 10^{-5}$ , and  $K_b = 1.8 \times 10^{-5}$

<b>Sol.</b>	$NH_4OH$	+	$CH_3COOH$	$\rightarrow$	$CH_3COONH_4$	+	$H_2O$
Initial milli moles	$25 \times 0.1$		$25 \times 0.1$		0		0
	= 2.5		= 2.5		–		
Final milli moles	0		0		2.5		2.5

As salt is formed (salt of weak acid and weak base) and pH will be decided by salt hydrolysis

$$pH = \frac{pK_w + pK_a - pK_b}{2} = \frac{1}{2} (-\log 10^{-14} - \log 1.8 \times 10^{-5} + \log 1.8 \times 10^{-5}) = 7$$

**Ex.25 In the following which one has highest / maximum degree of hydrolysis.**

(1) 0.01 M –  $NH_4Cl$

(2) 0.1 M –  $NH_4Cl$

(3) 0.001 M –  $NH_4Cl$

(4) Same

**Sol.** [3]

$$\left( h = \sqrt{\frac{K_h}{C}} \quad \text{if } C \text{ decreases, } h \text{ increases} \right)$$

**Ex.26 In the following which one has lowest value of degree of hydrolysis.**

(1) 0.01 M –  $CH_3COONH_4$

(2) 0.1 M –  $CH_3COONH_4$

(3) 0.001 M –  $CH_3COONH_4$

(4) Same

**Sol.** [4]

**Ex.27 Find out the concentration of  $[H^+]$  in 0.1M  $CH_3COONa$  solution ( $K_a = 10^{-5}$ )**

**Sol.** Salt is [WA – SB] type

$$\therefore [H^+] = \sqrt{\frac{K_w \times K_a}{C}} = \sqrt{\frac{10^{-14} \times 10^{-5}}{10^{-1}}} = \sqrt{10^{-19} \times 10^{+1}} = \sqrt{10^{-18}} = 10^{-9}$$

**Ex.28** Calculate the degree of hydrolysis of a mixture containing 0.1N  $\text{NH}_4\text{OH}$  and 0.1N  $\text{HCN}$

$$K_a = 10^{-5} \quad \& \quad K_b = 10^{-5}$$

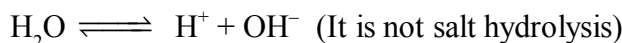
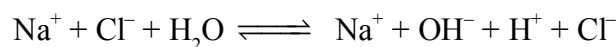
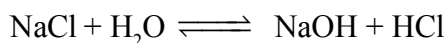
**Sol.** Salt is [WA – WB]

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 10^{-5}}}$$

$$= \sqrt{10^{-14} \times 10^{+10}} = \sqrt{10^{-4}} = 10^{-2}$$

### 5.2.4 Hydrolysis of [SA – SB] type salt :

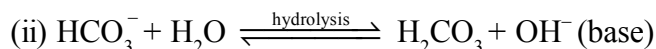
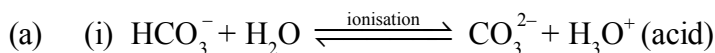
**Ex.**  $\text{NaCl}$ ,  $\text{BaCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KClO}_4$  etc.



- (1) Hydrolysis of salt of [SA – SB] is not possible
- (2) Solution is neutral in nature ( $\text{pH} = \text{pOH} = 7$ )
- (3) pH of the solution is 7

### 5.2.5 Hydrolysis of Amphiprotic Anion :

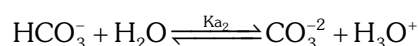
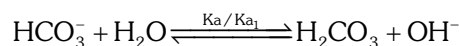
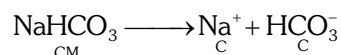
$\text{NaHCO}_3$ ,  $\text{NaHS}$ , etc., can undergo ionisation to form  $\text{H}^+$  ion and can undergo hydrolysis to form  $\text{OH}^-$  ( $\text{Na}^+$  ion is not hydrolysed)



$$\text{pH}(\text{HCO}_3^-) = \left( \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} \right)$$

(b) Similarly for  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  amphiprotic anions.

$$\text{pH}_{(\text{H}_2\text{PO}_4^-)} = \left( \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} \right) \quad \text{and} \quad \text{pH}_{(\text{HPO}_4^{2-})} = \left( \frac{\text{pK}_{a_2} + \text{pK}_{a_3}}{2} \right)$$



$\therefore \text{H}^+$  and  $\text{OH}^-$  also react

$\therefore$  We can safely assume that both reactions have nearly same degree of dissociation

$$\therefore [\text{H}_2\text{CO}_3] \approx [\text{CO}_3^{2-}] \quad \dots(1)$$

$$\frac{K_w}{K_{a_1}} = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} \Rightarrow \frac{1}{K_{a_1}} = \frac{[\text{H}_2\text{CO}_3]}{[\text{H}^+][\text{HCO}_3^-]} \quad \dots(2)$$

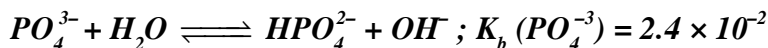


$$\frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = K_{a_2} \quad \dots(3)$$

Divide (2) by (3)

$$[\text{H}^+] = \sqrt{K_{a_1}K_{a_2}} \Rightarrow \text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2}$$

**Ex.29 Calculate the pH of 0.5 M  $\text{Na}_3\text{PO}_4$  in aqueous solution ?**



**Sol.**  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  are conjugate acid and base so  $K_a \times K_b = 10^{-14}$

$$K_a(\text{HPO}_4^{2-}) = \frac{10^{-14}}{2.4 \times 10^{-2}} = 4.17 \times 10^{-13}$$

$$\text{p}K_a = -\log K_a = 12.38$$

$$\text{or } \text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$$

$$\text{pH} = 13.04$$

## 6 BUFFER SOLUTIONS

A solution that resists change in pH value upon addition of small amount of strong acid or base or when solution is diluted is called buffer solution.

The capacity of a solution to resist alteration in its pH value is known as buffer capacity and the mechanism of buffer solution is called buffer action.

### 6.1 Types of buffer solutions

(A) Simple buffer solution

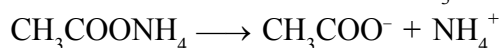
(B) Mixed buffer solution

### 6.2 SIMPLE BUFFER SOLUTION :

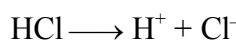
A salt of weak acid and weak base in water e.g.  $\text{CH}_3\text{COONH}_4$ ,  $\text{HCOONH}_4$ ,  $\text{AgCN}$ ,  $\text{NH}_4\text{CN}$ .

#### Buffer action of simple buffer solution

Consider a simple buffer solution of  $\text{CH}_3\text{COONH}_4$ , since it is a salt will dissociated completely.



If a strong acid such as HCl is added then

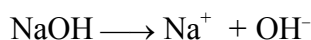


The  $\text{H}^+$  ions from the added acid (HCl) combine with  $\text{CH}_3\text{COO}^-$  ions to form  $\text{CH}_3\text{COOH}$ , which is a weak acid so will not further ionized.

Thus there is no rise in  $\text{H}^+$  ion concentration and the pH remains constant.



- If a strong base is added as NaOH



Thus change in  $\text{OH}^-$  ion concentration is resisted by  $\text{NH}_4^+$  ions by forming  $\text{NH}_4\text{OH}$  which is a weak base. So it will not further ionized and pH remains constant.

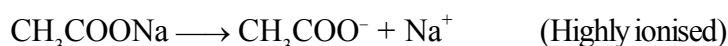
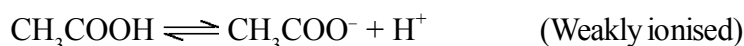
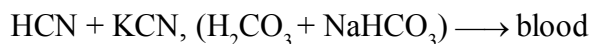
pH of a simple buffer solution :-

$$\text{pH} = 7 + \frac{1}{2} \text{p}k_a - \frac{1}{2} \text{p}k_b$$

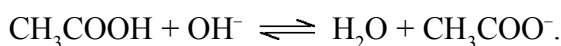
### 6.3 MIXED BUFFER SOLUTIONS :

#### 6.3.1 Acidic buffer solution :

An acidic buffer solution consists of solution of a weak acid and its salt with strong base. The best known example is a mixture of solution of acetic acid and its salt with strong base ( $\text{CH}_3\text{COONa}$ ). Other example :



When a few drops of an acid (HCl) are added to it, the  $\text{H}^+$  ions from the added acid (HCl) combine with the  $\text{CH}_3\text{COO}^-$  ions to form  $\text{CH}_3\text{COOH}$ . Thus there is no rise in  $\text{H}^+$  ion concentration and the pH of solution remains constant. On the other hand, when a few drops of base (NaOH) are added, the  $\text{OH}^-$  of the added base reacts with acetic acid to form unionise water and acetate ions.



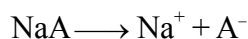
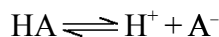
Thus there is no increase in  $\text{OH}^-$  ion concentration and hence the pH of the solution remains constant.

#### pH of a acidic buffer solution (Henderson equation) :

Consider a buffer mixture (acidic buffer)



where  $\text{A} = \text{CH}_3\text{COO}$ ,  $\text{A}^- = \text{CH}_3\text{COO}^-$



Applying law of mass action to dissociation equilibrium of HA

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} ; \text{ so } [\text{H}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$$

taking log,  $\log [\text{H}^+] = \log K_a + \log \frac{[\text{HA}]}{[\text{A}^-]}$

$$-\log [\text{H}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

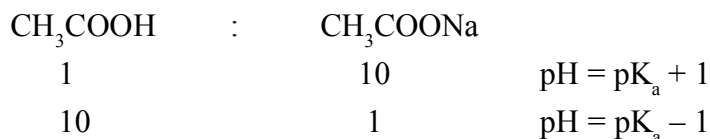
$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$[\text{A}^-]$  = Initial concentration of salt as it is mainly comes from salt.

$[\text{HA}]$  = Initial concentration of the acid.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad (\text{it is known as Henderson-Hasselbalch equation.})$$

**Note :** A solution can act as buffer only if ratio of concentration of salt to acid is between 0.1 to 10.



Thus pH range of an acidic buffer solution is  $(\text{pK}_a + 1)$  to  $(\text{pK}_a - 1)$

$$\text{pH range} = \text{pK}_a \pm 1$$

Maximum buffer action will be only when ratio of concentration of acid and salt is 1. So for maximum buffer action,  $\text{pH} = \text{pK}_a$

**Ex.30** How much volume of 0.2 M solution of acetic acid should be added to 100 mL of 0.2 M solution of sodium acetate to prepare a buffer solution of  $\text{pH} = 6.00$  ? ( $\text{pK}_a$  for acetic acid is 4.74)

**Sol.**  $\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

$$\log \frac{[\text{Salt}]}{[\text{Acid}]} = \text{pH} - \text{pK}_a = 6.00 - 4.74 = 1.26 \quad \therefore \frac{[\text{Salt}]}{[\text{Acid}]} = 18.2$$

Moles of  $\text{CH}_3\text{COONa}$  in solution  $\frac{100 \times 0.2}{1000} = 0.02$

Let, volume of 0.2 acetic acid added =  $V$  mL

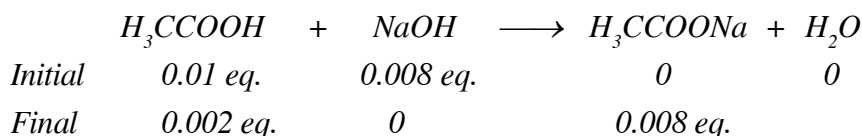
$$\therefore \text{Moles of acetic acid} = \frac{V \times 0.2}{1000}$$

$$\therefore \frac{0.02}{V \times \frac{0.2}{1000}} = 18.2$$

$$\therefore V = 5.49 \text{ mL}$$

**Ex.31** Calculate the pH after the addition of 80 mL and 100 mL respectively of 0.1 N NaOH to 100 mL, 0.1 N  $\text{CH}_3\text{COOH}$ . (Given  $\text{pK}_a$  for  $\text{CH}_3\text{COOH} = 4.74$ )

**Sol.** If 80 mL of 0.1 N NaOH is added to 100 mL of 0.1 N  $\text{CH}_3\text{COOH}$ , acidic buffer will form as



$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 4.74 + \log \frac{0.008}{0.002} = 5.342$$

If 100 mL of 0.1 N NaOH is added to 100 mL of 0.1 N  $\text{CH}_3\text{COOH}$ , complete neutralization takes place and the concentration of  $\text{H}_3\text{CCOONa} = \frac{0.1}{2} \text{ M} = 0.05 \text{ M}$

$$\text{Now, } \text{pH} = 7 + \frac{1}{2} \text{pK}_a + \frac{1}{2} \log C = 8.72$$

**Ex.32** Calculate the pH of a solution when 0.20 moles of HCl is added to one litre solution containing -

(a) 1 M each of acetic acid and acetate ion ?

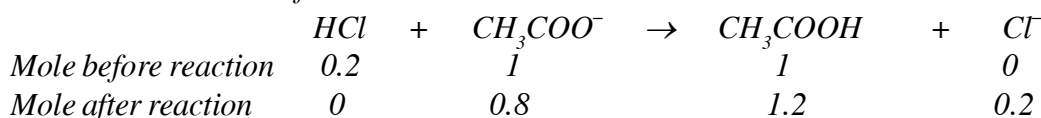
(b) 0.1 M each of acetic acid and acetate ion ?

Given  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ .

Sol. (a) Initially [Acetic acid] = 1 M

$$[\text{Acetate}] = 1 \text{ M}$$

Now 0.2 moles of HCl are added to it.



$$\therefore \text{New } [\text{CH}_3\text{COOH}] = 1.2 ; [\text{CH}_3\text{COO}^-] = 0.8$$

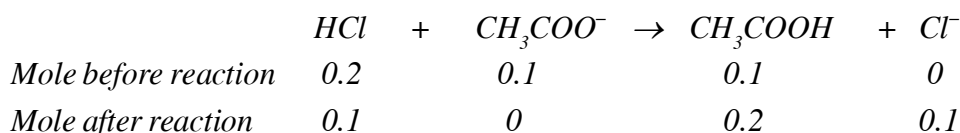
$$\therefore \text{pH} = \text{p}K_a + \log \frac{[\text{conjugate}]}{[\text{acid}]}$$

$$\therefore \text{pH} = -\log 1.8 \times 10^{-5} + \log \frac{0.8}{1.2} = 4.5686$$

(b) In II case initially [Acetic acid] = 0.1 M

$$[\text{Acetate}] = 0.1 \text{ M}$$

Now 0.2 mole of HCl are added to it



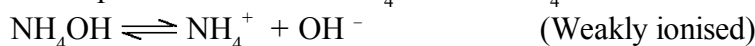
$$\therefore [\text{H}^+] \text{ from free HCl} = 0.1 \text{ M}$$

$$\therefore \text{pH} = 1$$

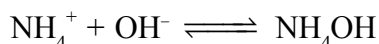
**Note:**  $\text{CH}_3\text{COOH}$  no doubt gives  $\text{H}^+$  but being weak acid as well as in presence of HCl does not dissociate appreciably and thus,  $\text{H}^+$  from  $\text{CH}_3\text{COOH}$  may be neglected.

### 6.3.2 Basic buffer solution :

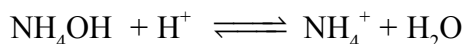
A basic buffer solution consists of a mixture of a weak base and its salt with strong acid. The best known example is a mixture of  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ .



When a few drops of a base (NaOH) are added, the  $\text{OH}^-$  ions from NaOH combine with  $\text{NH}_4^+$  ions to form feebly ionised  $\text{NH}_4\text{OH}$  thus there is no rise in the concentration of  $\text{OH}^-$  ions and hence the pH value remains constant.

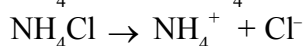
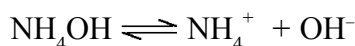


If a few drops of an acid (HCl) are added the  $\text{H}^+$  from acid combine with  $\text{NH}_4\text{OH}$  to form  $\text{H}_2\text{O}$  and  $\text{NH}_4^+$  ions.



Thus the addition of acid does not increase the  $\text{H}^+$  ion concentration and hence pH remains unchanged.

- **pH of basic buffer solution :**



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$[\text{OH}^-] = \frac{K_b [\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = \frac{K_b [\text{Base}]}{[\text{Salt}]}$$

( $\text{NH}_4^+$  mainly comes from salt)

taking  $-\log$  on both side

$$-\log \text{OH}^- = -\log \frac{K_b [\text{Base}]}{[\text{Salt}]} \Rightarrow \text{pOH} = -\log K_b - \log \frac{[\text{Base}]}{[\text{Salt}]}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \Rightarrow \text{pH} = 14 - \text{pOH}$$

❖ **pOH range :**

A solution can act as buffer solution only if ratio of concentration of salt to base is from 0.1 to 10.

$\text{NH}_4\text{OH}$	:	$\text{NH}_4\text{Cl}$	
1		10	$\text{pOH} = \text{p}K_b + 1$
10		1	$\text{pOH} = \text{p}K_b - 1$

So pOH range is  $\text{p}K_b \pm 1$

❖ **Condition for maximum buffer action :**

$[\text{NH}_4\text{OH}]$	:	$[\text{NH}_4\text{Cl}]$
1		1

$$\text{pOH} = \text{p}K_b + \log \frac{1}{1}$$

$$\text{pOH} = \text{p}K_b \quad \text{and} \quad \text{pH} = 14 - \text{p}K_b$$

Maximum buffer action because pH remains constant.

**Ex.33** An organic base  $B$  has  $K_b$  value equal to  $1 \times 10^{-8}$ . In what amounts should 0.01 M HCl and 0.01 M solution of  $B$  be mixed to prepare 1 L of a buffer solution having  $\text{pH} = 7.0$  ?

**Sol.**  $B + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[B]} = 1 \times 10^{-8}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{BH}^+]}{[B]}$$

$$\Rightarrow 7 = -\log (10^{-8}) + \log \frac{[\text{BH}^+]}{[B]} \Rightarrow 7 = 8 + \log \frac{[\text{BH}^+]}{[B]}$$

$$\log \frac{[\text{BH}^+]}{[B]} = -1$$

$$\therefore \frac{[\text{BH}^+]}{[\text{B}]} = 10^{-1} = 0.1$$

Let, volume of HCl taken = xL

$$\therefore \text{Volume of base taken} = (1 - x) \text{ L}$$

After the reaction, millimole of  $\text{BH}^+$  formed =  $0.01 \times (x)$

Millimoles of base left =  $0.01 (1 - 2x)$

$$\therefore \frac{[\text{BH}^+]}{[\text{B}]} = \frac{x}{[1 - 2x]} = 0.1$$

$$\therefore x = 0.083 \text{ L} = \text{Volume of HCl}$$

$$\therefore \text{Volume of base} = 0.917 \text{ L}$$

**Ex.34** Which of the following buffers containing  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$  show the lowest pH value?

	<i>conc. of</i> $\text{NH}_4\text{OH} (\text{mol L}^{-1})$	<i>conc. of</i> $\text{NH}_4\text{Cl} (\text{mol L}^{-1})$
(A)	0.50	0.50
(B)	0.10	0.50
(C)	0.50	1.50
(D)	0.50	0.10

**Sol. (B)**  $\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$  for  $\text{NH}_4\text{Cl} = 0.5$  and  $\text{NH}_4\text{OH} = 0.1$

pOH will be maximum and so pH will be minimum.

**Ex.35** A solution of weak base BOH was titrated with 0.1 N HCl. The pH of the solution was found to be 10.04 and 9.14 after the addition of 5 mL and 20 mL of the acid respectively. Find the dissociation constant of the base.

**Sol. Case I :**

	BOH	+	HCl	→	BCl	+	H <sub>2</sub> O
Millimole before reac.	a		$0.1 \times 5 = 0.5$		0		0
Millimole after reac.	$(a - 0.5)$		0		0.5		0.5

$$\therefore \text{pOH} = -\log K_b + \log \frac{[\text{BCl}]}{[\text{BOH}]} \dots\dots\dots(\text{i})$$

$$\therefore \text{pH} = 10.04 \quad \text{so} \quad \text{pOH} = 3.96$$

$$\therefore 3.96 = -\log K_b + \log \frac{0.5}{(a - 0.5)} \dots\dots\dots(\text{ii})$$

**Case II :**

	BOH	+	HCl	→	BCl	+	H <sub>2</sub> O
Millimole before reac.	a		$0.1 \times 20 = 2$		0		0
Millimole after reac.	$(a - 2)$		0		2		2

$$\therefore \text{pOH} = -\log K_b + \log \frac{[\text{BCl}]}{[\text{BOH}]} \dots\dots\dots(\text{iii})$$

$$\therefore \text{pH} = 9.14 \quad \therefore \text{pOH} = 4.86$$

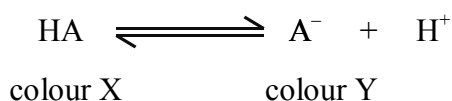
$$\therefore 4.86 = -\log K_b + \log \frac{2}{(a-2)} \dots\dots\dots(\text{iv})$$

Solving Eqs. (ii) and (iv),  $K_b = 1.81 \times 10^{-5}$

## 7. INDICATORS

The stage of titration when complete reaction occur between the solution is called **equivalent point**. The stage of titration when sudden change in colour of solution is observed is called **end point**. A perfect indicator response sudden colour change exactly on completion of reaction. An **indicator** is a substance which response sudden change in colour of solution at the end point or neutral point of the acid-base titration. **At end point**  $N_1V_1 = N_2V_2$

- (i) The indicators in acid-base titration changes colour on changing the pH of solution.
- (ii) All the acid-base indicators are either weak organic acid or base and having different colour for unionized and ionised form.
- (iii) A mixture of two colour is recognized in a single colour if the conc. of one is 10 times or more than that of others. (This 10 time is flexible)



$$\text{Diss. const. or (Ionisation const)} = K_a = K_m = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{p}K_m + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

(a) The solution will appear only of colour Y, if  $\frac{[\text{A}^-]}{[\text{HA}]} \geq 10 \Rightarrow \text{pH} \geq (\text{p}K + 1)$

(b) The solution will appear only of colour X, if  $\frac{[\text{A}^-]}{[\text{HA}]} \leq \frac{1}{10} \Rightarrow \text{pH} \leq (\text{p}K - 1)$

pH of solution below and above which solution appears in a single colour is called pH range of indicator.

Indicator	pH range	Colour change	pK <sub>a</sub>
Methyl orange	3.2 – 4.5	Pink to yellow	3.7
Methyl red	4.4 – 6.5	Red to yellow	5.1
Litmus	5.5 – 7.5	Red to blue	7.0
Phenol red	6.8 – 8.4	Yellow to red	7.8
Phenolphthalein	8.3 – 10.5	Colourless to pink	9.6

**Ex.36** The disso. const. of a basic indicator is  $2 \times 10^{-7}$ . Calculate its pH range.

**Sol.**  $5.7 - 7.7 = \text{pOH} \quad \therefore \quad \text{pH} = 6.3 - 8.3$

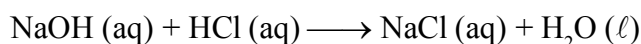
**Ex.37** The pH range of an acidic indicator  $\text{HIn}$  is 4.0 - 5.2. Calculate dissociation constant. Also

calculate  $\frac{\text{In}^-}{\text{HIn}}$  for the appearance of solution in single colour.

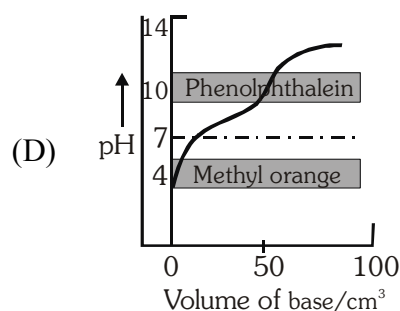
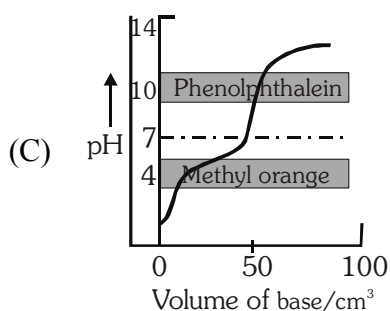
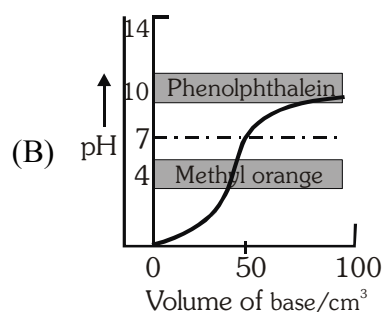
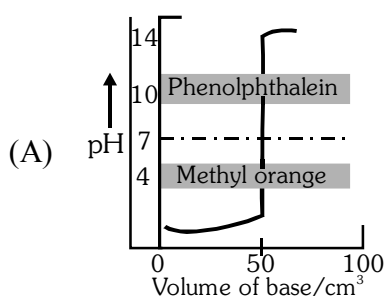
**Sol.** Diss. constant =  $2.5 \times 10^{-5}$ , 4

### 9.1 TITRATION OF STRONG ACID AGAINST STRONG ALKALI :

The graph (A) shows how pH changes during the titration of  $50 \text{ cm}^3$  of  $0.1 \text{ M HCl}$  with  $0.1 \text{ M NaOH}$ .



The pH of  $0.1 \text{ M}$  solution of  $\text{HCl}$  in the beginning would be 1. As alkali is added, the pH changes slowly in the beginning. However, at the equivalence point pH changes rapidly from about 3.5 to 10. It can be shown by simple calculations that pH of the solution is 3.7 when  $49.8 \text{ cm}^3$  of  $0.1 \text{ M NaOH}$  solution have been added. The pH suddenly changes to 10 after addition of  $50.1 \text{ cm}^3$  of the  $\text{NaOH}$  solution. Thus, any indicator having pH range between 3.5 to 10 will identify the equivalence point. This means that any one of phenolphthalein, methyl orange or bromothymol blue could be used as an indicator.

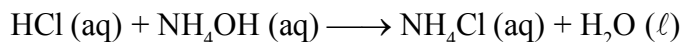


**Titration curves :** (A) strong base with strong acid ; (B) weak base with strong acid ; (C) strong base with weak acid ; (D) weak base with weak acid.



**7.2 TITRATION OF STRONG ACID AGAINST WEAK ALKALI :**

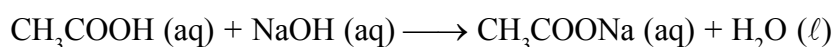
The graph (B) shows how pH changes during titration of 50 cm<sup>3</sup> of 0.1 M HCl with 0.1 M NH<sub>3</sub>.



In this case, the pH changes rapidly from 3.5 to 7.0 at the equivalence point. Methyl orange, methyl red and bromocresol green are suitable indicators for this type of titration. Phenolphthalein is unsuitable because its pH range lies outside the vertical portion of the curve.

**7.3 TITRATION OF WEAK ACID AGAINST STRONG BASE :**

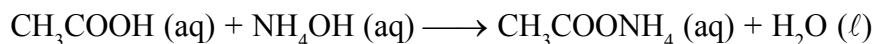
The graph (C) shows how pH changes during titration of 50 cm<sup>3</sup> of 0.1 M CH<sub>3</sub>COOH with 0.1 M NaOH.



The vertical portion of this titration curve lies between pH range 7 to 10.6. Phenolphthalein is suitable indicator for this titration. Methyl orange is not suitable for this titration because its pH range lies on the flat portion of the curve.

**7.4 TITRATION OF WEAK ACID AGAINST WEAK BASE :**

The graph (D) represents the titration curve obtained for titration of 50 cm<sup>3</sup> of 0.1 M CH<sub>3</sub>COOH with 0.1 M NH<sub>3</sub>.



For this type of titration there is no sharp increase in pH at the equivalence point. No indicator is suitable for this type of titration.

**Ex.38** Bromophenol blue is an indicator with a value of  $K_a = 6.84 \times 10^{-6}$ . At what pH it will work as an indicator? Also report the % of this indicator in its basic form at a pH of 5.84.

**Sol.**  $\text{HBPh} \rightleftharpoons \text{H}^+ + \text{BPh}^-$

$$K_a = \frac{[\text{H}^+][\text{BPh}^-]}{[\text{HBPh}]}, \text{ when } \text{BPh}^- = \text{HBPh}, \text{ indicator will work. Thus}$$

$$[\text{H}^+] = 6.84 \times 10^{-6}$$

$$\therefore \text{pH} = 5.165$$

Also if pH = 5.84

$$\text{or } [\text{H}^+] = 1.44 \times 10^{-6}, \text{ then}$$

$$K_a = \frac{[\text{H}^+][\text{BPh}^-]}{[\text{HBPh}]} \quad \text{or} \quad 6.84 \times 10^{-6} = \frac{1.44 \times 10^{-6} \cdot C\alpha}{C(1-\alpha)} \quad \text{or} \quad \alpha = 0.83 \text{ or } 83 \%$$

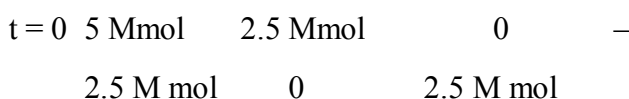
### 7.5 Titration of Poly protic acid v/s S.B. :

50 mL of 0.1 M  $\text{H}_3\text{PO}_4$  agent 0.1 M NaOH. Calculate pH when vol. of NaOH added is

- (a) 0 mL                      (b) 25 mL                      (c) 50 mL                      (d) 75 mL                      (e) 100 mL  
 (f) 125 mL                      (g) 150 mL                      (h) 200 mL                      (i) 90 mL

$$pK_{a1} = 3 \qquad pK_{a2} = 7, pK_{a3} = 11$$

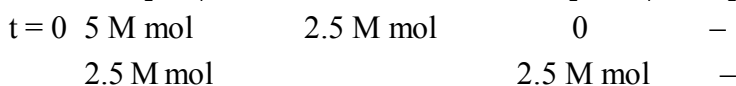
(a)  $\text{pH} = 1/2 (pK_{a1} - \log C) = 1/2 (3 + 1) = 2$



$$\text{pH} = pK_{a1} + \log 1/1 = pK_{a1} = 3$$

(c) Solution of  $\text{H}_2\text{PO}_4^-$  amphoteric species

$$\text{pH} = \frac{pK_{a1} + pK_{a2}}{2} = \frac{3 + 7}{2} = 5$$



$$\text{pH} = \log 1/1 + pK_{a2} = 7$$

(e)  $\text{HPO}_4^{2-}$  solution (amphoteric species)

$$\text{pH} = \frac{pK_{a2} + pK_{a3}}{2} = 9$$



$$\text{pH} = pK_{a3} + \log 1/1 = 11$$

(g) 3<sup>rd</sup> eq. pt  $\text{Na}_3\text{PO}_4$  solution

$$[\text{Na}_3\text{PO}_4] = 5/200 = 1/40$$

$$\text{pH} = 1/2 \{pK_w + pK_{a3} + \log C\} = 1/2 (14 + 11 - 2 + 0.4) = 11.7$$

(h) 200 mL

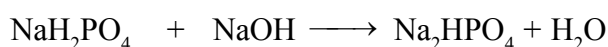
hydrolysis of  $\text{Na}_3\text{PO}_4$  can be neglected in presence of NaOH

$$[\text{NaOH}] = 5/250 = 1/50$$

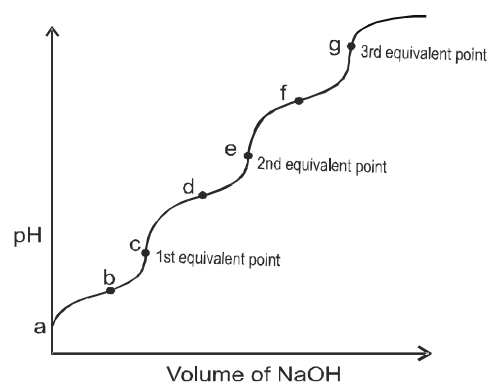
$$\text{pOH} = 1.7$$

$$\text{pH} = 12.3$$

(i) 90 mL



$$\text{pH} = pK_{a2} + \log 4 = 7.6$$



## 10. SOLUBILITY (s) & SOLUBILITY PRODUCT ( $K_{sp}$ )

### 10.1 SOLUBILITY :

At constant temperature, the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of saturated solution is called solubility.

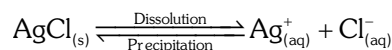
Solubility depends on the following –

- Temperature
- Presence of common ion
- Nature of solvent

### 10.2 SOLUBILITY PRODUCT ( $K_{sp}$ ) :

When a sparingly soluble salt such as AgCl is put into water, a very small amount of AgCl dissolves in water and most of the salt remains undissolved in its saturated solution.

- A solution which remains in contact with undissolved solute is said to be saturated.
- The salt AgCl is an electrolyte, its dissociation occurs in solution. Hence, the quantity of AgCl that dissolves in water dissociates into  $Ag^+$  and  $Cl^-$  ions. Thus, in the saturated solution of AgCl an equilibrium exists between undissolved solid AgCl and its ions,  $Ag^+$  and  $Cl^-$  ions.



according to law of mass action

$$K = \frac{[Ag^+] \cdot [Cl^-]}{[AgCl]}$$

Since, the concentration of undissolved solid AgCl is constant. Thus, the product  $K \cdot [AgCl]$  gives another constant which is designated as  $K_{sp}$

So,  $K \cdot [AgCl] = [Ag^+] \cdot [Cl^-]$

$\therefore K_{sp} = [Ag^+] \cdot [Cl^-]$

- $K_{sp}$  for  $CaCl_2$**   $CaCl_2(s) \rightleftharpoons Ca^{+2}(aq) + 2Cl^-(aq)$

Solubility product in terms of concentration of ions

$$K_{sp} = [Ca^{+2}] [Cl^-]^2$$

- $K_{sp}$  for  $AlCl_3$**   $AlCl_3(s) \rightleftharpoons Al^{+3}(aq) + 3Cl^-(aq)$

Solubility product in terms of concentration of ions  $K_{sp} = [Al^{+3}] [Cl^-]^3$

- General form**  $A_x B_y(s) \rightleftharpoons xA^{+y}(aq) + yB^{-x}(aq)$

$$K_{sp} = [A^{+y}]^x [B^{-x}]^y$$

**Thus, solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of ions given by the dissociation of electrolyte at a given temperature when the solution is saturated.**

### 10.3 APPLICATION OF SOLUBILITY PRODUCT ( $K_{sp}$ ) :

#### 10.3.1 To find out the solubility (S) :

- $K_{sp}$  of AB (Mono-mono, di-di, tri-tri valency) type salt –**

**Ex.** NaCl,  $BaSO_4$ ,  $CH_3COONa$ ,  $CaCO_3$ , NaCN, KCN,  $NH_4CN$ ,  $NH_4Cl$  etc.

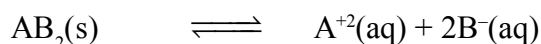


$$K_{sp} = [A^+] [B^-]$$

$$K_{sp} = s^2 \quad \text{or} \quad s = \sqrt{K_{sp}}$$

(ii)  $K_{sp}$  of  $AB_2$  or  $A_2B$  (Mono-di or di-mono valency) type salt –

Ex.  $CaCl_2$ ,  $CaBr_2$ ,  $K_2S$ ,  $(NH_4)_2SO_4$ ,  $K_2SO_4$ ,  $K_2CO_3$  etc.



$$K_{sp} = [A^{+2}] [B^-]^2$$

$$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$$

$$s = \left( \frac{K_{sp}}{4} \right)^{1/3}$$

(iii) General form :



$$K_{sp} = [A^{+y}]^x \cdot [B^{-x}]^y$$

$$K_{sp} = (xs)^x \cdot (ys)^y$$

$$K_{sp} = x^x \cdot y^y \cdot s^{(x+y)}$$

### 10.4 COMMON ION EFFECT ON SOLUBILITY :

Solubility of substances always decreases in the presence of common ion. According to Le-Chatelier's principle, on increasing common ion concentration equilibrium shifts in backward direction until the equilibrium is reestablished so, the solubility of substances decreases.

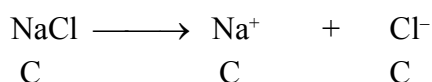
Ex. Find out the solubility of  $AgCl$  in water and in the presence of  $CM - NaCl$  solution?



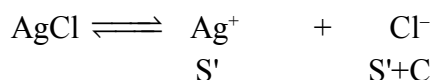
$$K_{sp} = [Ag^+] [Cl^-]$$

$$K_{sp} = S^2$$

In  $NaCl$  solution



Let solubility of AgCl in the presence of NaCl solution is  $S'$  mol  $L^{-1}$



$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-]$$

$$K_{sp} = S' (S' + C) = S'^2 + S'C \quad (\text{Neglecting the higher power terms of } S')$$

$$K_{sp} = S' C$$

$$\boxed{S' = \frac{K_{sp}}{C}}$$

### 10.5 SIMULTANEOUS SOLUBILITY :

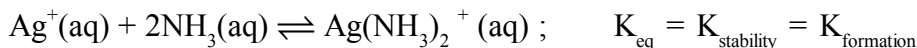
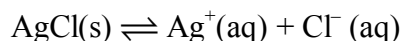
When two sparingly soluble salts are added in water simultaneously, there will be two simultaneous equilibria in the solution.

### 10.6 SOLUBILITY IN APPROPRIATE BUFFER SOLUTIONS :

Appropriate buffer means that the components of buffer should not interfere with the salt or only  $H^+$  or  $OH^-$  ions should be interacting with the ions of the salt.

### 10.7 EFFECT ON SOLUBILITY BECAUSE OF COMPLEX FORMATION :

Solubility of AgCl in aqueous  $NH_3$  is roughly 10,000 times as its solubility in water, due to complex formation.



$$\text{and } \frac{1}{K_{stability}} = K_{dissociation} = K_{instability}$$

### 10.8 CONDITION OF PRECIPITATION / IONIC PRODUCT (IP OR $Q_{sp}$ ) :

- Ionic product (IP) of an electrolyte is defined in the same way as  $K_{sp}$ . The only difference is that ionic product expression contains the initial concentration of ions or the concentration at any time whereas the expression of  $K_{sp}$  contains only equilibrium concentration. Thus, for AgCl.

$$IP = [\text{Ag}^+]_i [\text{Cl}^-]_i \quad \text{and} \quad K_{sp} = [\text{Ag}^+]_{eq} [\text{Cl}^-]_{eq}$$

- Ionic product changes with concentration but  $K_{sp}$  does not.
- To decide whether an ionic compound will precipitate, its  $K_{sp}$  is compared with the value of ionic product.

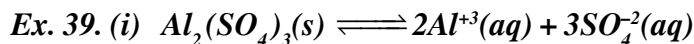
The following three cases arise :

- $IP < K_{sp}$  : The solution is unsaturated and precipitation will not occur.
- $IP = K_{sp}$  : The solution is saturated and solubility equilibrium exists.
- $IP > K_{sp}$  : The solution is supersaturated and hence precipitation of the compound will occur.

Thus, a salt is precipitated when its ionic product exceeds the solubility product of the salt.

## 10.9 SELECTIVE PRECIPITATION :

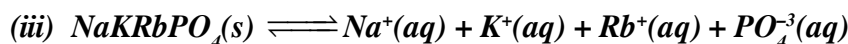
When the  $k_{sp}$  values differ then one of the salt can be selectively precipitated.



$$K_{sp} = 2^2 \times 3^3 \times (S)^{2+3} = 4 \times 27 \times S^5 = 108 S^5$$



$$K_{sp} = 2^2 \times 1^1 \times 1^1 (S)^{2+1+1} = 4S^4$$



$$K_{sp} = 1^1 \times 1^1 \times 1^1 \times 1^1 \times (S)^{1+1+1+1} = S^4$$

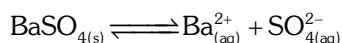
Ex. 40. If solubility product of the base  $M(OH)_3$  is  $2.7 \times 10^{-11}$ , the concentration of  $OH^-$  will be

- (1)  $3 \times 10^{-3}$       (2)  $3 \times 10^{-4}$       (3)  $10^{-3}$       (4)  $10^{-11}$

Answer : (3)

Ex. 41. The solubility of  $BaSO_4$  in water is  $1.07 \times 10^{-5} \text{ mol dm}^{-3}$ . Estimate its solubility product.

Sol. Solubility equilibrium for  $BaSO_4$  is

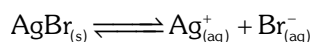


Now,  $S = 1.07 \times 10^{-5} \text{ M}$

Hence,  $K_{sp} = (1.07 \times 10^{-5})^2 = 1.145 \times 10^{-10}$

Ex. 42. The solubility product of  $AgBr$  is  $5.2 \times 10^{-13}$ . Calculate its solubility in  $\text{mol dm}^{-3}$  and  $\text{g dm}^{-3}$ . (Molar mass of  $AgBr$ . =  $187.8 \text{ g mol}^{-1}$ )

Sol. The solubility equilibrium of  $AgBr$  is



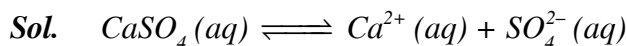
The molar solubility  $S$  of  $AgBr$  is given by

$$S = \sqrt{K_{sp}} = \sqrt{5.2 \times 10^{-13}} = 7.2 \times 10^{-7} \text{ mol dm}^{-3}$$

The solubility in  $\text{g dm}^{-3}$  = molar solubility ( $\text{mol dm}^{-3}$ )  $\times$  molar mass ( $\text{g mol}^{-1}$ )

$$= 7.2 \times 10^{-7} \times 187.8 = 1.35 \times 10^{-4} \text{ g dm}^{-3}$$

**Ex. 43.** What is the maximum volume of water required to dissolve 1 g of calcium sulphate at 25°C. For calcium sulphate,  $K_{sp} = 9.0 \times 10^{-6}$ .



If  $S$  is the solubility of  $\text{CaSO}_4$  in moles  $\text{L}^{-1}$

$$K_{sp} = [\text{Ca}^{2+}] \times [\text{SO}_4^{2-}] = S^2$$

$$\therefore S = \sqrt{K_{sp}} = \sqrt{9.0 \times 10^{-6}}$$

$$= 3 \times 10^{-3} \text{ mol L}^{-1}$$

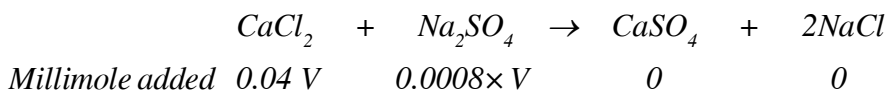
$$= 3 \times 10^{-3} \times 136 \text{ g L}^{-1} = 0.408 \text{ g L}^{-1}$$

For dissolving 0.408 g of  $\text{CaSO}_4$  water required = 1 L

$$\therefore \text{For dissolving 1g CaSO}_4 \text{ water required} = \frac{1}{0.408} \text{ L} = 2.45 \text{ L}$$

**Ex. 44.** Equal volumes of 0.04 M  $\text{CaCl}_2$  and 0.0008 M  $\text{Na}_2\text{SO}_4$  are mixed. Will a precipitate form?  $K_{sp}$  of  $\text{CaSO}_4 = 2.4 \times 10^{-5}$

**Sol.**



Suppose V mL of both are mixed

$$\therefore [\text{Ca}^{2+}] = \frac{0.04V}{2V}$$

$$[\text{SO}_4^{2-}] = \frac{0.0008V}{2V}$$

$$\therefore [\text{Ca}^{2+}][\text{SO}_4^{2-}] = \frac{0.04V}{2V} \times \frac{0.0008V}{2V} = 8 \times 10^{-6}$$

Thus,  $[\text{Ca}^{2+}][\text{SO}_4^{2-}]$  in solution  $< K_{sp}$

$$8 \times 10^{-6} < 2.4 \times 10^{-5}$$

$\therefore \text{CaSO}_4$  will not precipitate.

**Ex. 45.** Calculate simultaneous solubility of silverthiocyanate and silver bromide in water given that  $k_{sp}$  of silver thiocyanate =  $10^{-12}$  and  $k_{sp}$  of silver bromide =  $5 \times 10^{-13}$  respectively.

**Sol.** Let the solubility of  $\text{AgSCN}$  be  $x$  and that of  $\text{AgBr}$  is  $y$ , then



$$10^{-12} = x(x + y) \qquad \dots (i)$$

$$5 \times 10^{-13} = y(x + y) \qquad \dots (ii)$$

On solving we get,  $x = 2y$

$$\text{So} \qquad \qquad \qquad y = 4.08 \times 10^{-7} \quad \text{and} \quad x = 8.16 \times 10^{-7}$$

**Ex. 46.** What  $[H^+]$  must be maintained in saturated  $H_2S(0.1 M)$  to precipitate  $CdS$  but not  $ZnS$ , if  $[Cd^{2+}] = [Zn^{2+}] = 0.1$  initially ?

$$K_{sp} = (CdS) = 8 \times 10^{-27}$$

$$K_{sp} = (ZnS) = 1 \times 10^{-21}$$

$$K_a = (H_2S) = 1.1 \times 10^{-21}$$

**Sol.** In order to prevent precipitation of  $ZnS$

$$[Zn^{2+}][S^{2-}] < K_{sp}(ZnS) = 1 \times 10^{-21}$$

(ionic product)

$$\text{or } (0.1)[S^{2-}] < 1 \times 10^{-21}$$

$$\text{or } [S^{2-}] < 1 \times 10^{-20}$$

This is the maximum value of  $[S^{2-}]$  before  $ZnS$  will precipitate. Let  $[H^+]$  to maintain this  $[S^{2-}]$  be  $x$ .

Thus for  $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{x^2(1 \times 10^{-20})}{0.1} = 1.1 \times 10^{-21}$$

$$\text{or } x = [H^+] = 0.1 M$$

$\therefore$  No  $ZnS$  will precipitate at a concentration of  $H^+$  greater than  $0.1 M$

**Ex. 47.** What must be the concentration of aq.  $NH_3$ (aq.) which must be added to a solution containing  $4 \times 10^{-3} M Ag^+$  and  $0.001 M NaCl$ , to prevent the precipitation of  $AgCl$ .

Given that  $K_{sp}(AgCl) = 1.8 \times 10^{-10}$  and the formation constant of  $[Ag(NH_3)_2]^+$  is

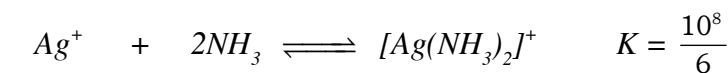
$$K_{formation} = \frac{10^8}{6}.$$

**Sol.** Calculate silver ion concentration which can be allowed to remain in the solution,

$$1.8 \times 10^{-10} = [Ag^+][Cl^-]$$

$$[Ag^+] = \frac{1.8 \times 10^{-10}}{0.001} = 1.8 \times 10^{-7} M,$$

This quantity is so small that almost all the  $Ag^+$  ion will be consumed.



$$4 \times 10^{-3} \quad b \quad 0$$

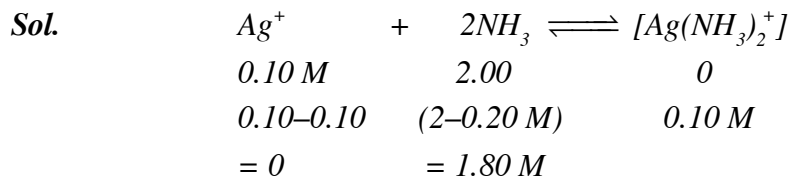
$$1.8 \times 10^{-7} \quad (b - 8 \times 10^{-3}) \quad 4 \times 10^{-3} \quad K = \frac{10^8}{6} = \frac{4 \times 10^{-3}}{1.8 \times 10^{-7} \times (b - 8 \times 10^{-3})^2}$$

$$\Rightarrow b = 0.0445$$



**Ex. 48.** 0.10 mol sample of  $\text{AgNO}_3$  is dissolved in one litre of 2.00 M  $\text{NH}_3$ . Is it possible to form  $\text{AgCl}(s)$  in the solution by adding 0.010 mol of  $\text{NaCl}$  ?

$$(K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}, K_f[\text{Ag}(\text{NH}_3)_2^+] = 1.6 \times 10^7)$$



It is assumed that all  $\text{Ag}^+$  ions have been complexed and only  $x$  amount is left

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} \Rightarrow 1.6 \times 10^7 = \frac{0.10}{x(1.80)^2}$$

$$\therefore x = 1.93 \times 10^{-9} \text{ M} = [\text{Ag}^+] \text{ undissolved}$$

$$[\text{Cl}^-] = 1.0 \times 10^{-2} \text{ M}$$

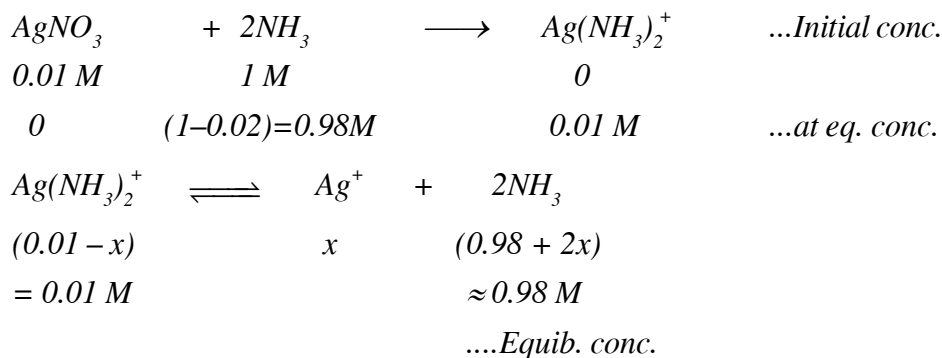
$$\therefore [\text{Ag}^+][\text{Cl}^-] = 1.93 \times 10^{-9} \times 1.0 \times 10^{-2} = 1.93 \times 10^{-11} < 1.8 \times 10^{-10} [K_{sp}(\text{AgCl})]$$

Hence,  $\text{AgCl}(s)$  will not precipitate.

**Ex. 49.** What is the concentration of  $\text{Ag}^+$  ions in  $0.01 \text{ M AgNO}_3$  that is also  $1.0 \text{ M NH}_3$ ? Will  $\text{AgCl}$  precipitate from a solution that is  $0.01 \text{ M AgNO}_3$ ,  $0.01 \text{ M NaCl}$  and  $1 \text{ M NH}_3$ ?

$$K_d(\text{Ag}[\text{NH}_3]_2^+) = 5.88 \times 10^{-8}; K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}.$$

**Sol.** Let us first assume that  $0.01 \text{ M AgNO}_3$  shall combine with  $0.02 \text{ M NH}_3$  to form  $0.01 \text{ M Ag}(\text{NH}_3)_2^+$  and then consider its dissociation.



Since  $x \ll 1$

$$K_d = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = 5.88 \times 10^{-8}$$

$$\therefore [\text{Ag}^+] = \frac{5.88 \times 10^{-8} \times 0.01}{(0.98)^2} = 6.12 \times 10^{-10} \text{ M}$$

Further, ionic product of  $\text{AgCl} = [\text{Ag}^+][\text{Cl}^-] = (6.12 \times 10^{-10})(0.01) = 6.12 \times 10^{-12}$

Because the ionic product is smaller than  $K_{sp} = 1.8 \times 10^{-10}$ , no precipitate should form.

## EXERCISE # S-I

## IONIZATION CONSTANTS AND pH

- Q.1 Calculate the number of  $H^+$  present in one ml of solution whose pH is 13. IE0001
- Q.2 (i)  $K_w$  for  $H_2O$  is  $9 \times 10^{-14}$  at  $60^\circ C$ . What is pH of water at  $60^\circ C$ . ( $\log 3 = 0.47$ ) IE0002
- (ii) What is the nature of solution at  $60^\circ C$  whose IE0003
- (a) pH = 6.7                      (b) pH = 6.35
- Q.3 The value of  $K_w$  at the physiological temperature ( $37^\circ C$ ) is  $2.56 \times 10^{-14}$ . What is the pH at the neutral point of water at this temperature? ( $\log 2 = 0.3$ ) IE0004
- Q.4 Calculate pH of following solutions :
- (a) 0.1 M HCl IE0005
- (b) 0.1 M  $CH_3COOH$  ( $K_a = 1.8 \times 10^{-5}$ ) ( $\log \sqrt{1.8} = 0.13$ ) IE0006
- (c) 0.1 M  $NH_4OH$  ( $K_b = 1.8 \times 10^{-5}$ ) IE0007
- (d)  $10^{-8}$  M HCl [ $\sqrt{401} = (20.02)$ ] [ $\log 1.051 = 0.03$ ] IE0008
- (e)  $10^{-10}$  M NaOH IE0009
- (f)  $10^{-6}$  M  $CH_3COOH$  ( $K_a = 1.8 \times 10^{-5}$ ) IE0010
- (g)  $10^{-8}$  M  $CH_3COOH$  ( $K_a = 1.8 \times 10^{-5}$ ) [ $\sqrt{401} = (20.02)$ ] [ $\log 1.051 = 0.03$ ] IE0011
- (h) Decimolar solution of Baryta ( $Ba(OH)_2$ ), diluted 100 times. ( $\log 2 = 0.3$ ) IE0012
- (i)  $10^{-3}$  mole of KOH dissolved in 100 L of water. IE0013
- (j) Equal volume of HCl solution (PH = 4) + 0.0019 N HCl solution IE0014
- Q.5 Calculate :
- (a)  $K_a$  for a monobasic acid whose 0.10 M solution has pH of 4.50.
- (b)  $K_b$  for a monoacidic base whose 0.10 M solution has a pH of 10.50. IE0015
- Q.6 Calculate the ratio of degree of dissociation ( $\alpha_2/\alpha_1$ ) when an acetic acid solution is diluted 100 times. Assume  $\alpha \ll 1$ , even on dilution. [Given  $K_a = 10^{-5}$  M] IE0016
- Q.7 Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids. [Given  $K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$ ;  $K_{a(HCN)} = 6 \times 10^{-10}$ ] IE0017
- Q.8 How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3 ? IE0018
- Q.9 pH of a dilute solution of HCl is 6.95. Calculate molarity of HCl solution.
- $$\left[ \begin{array}{l} 10^{-6.95} = 11.22 \times 10^{-8} \\ 10^{-7.05} = 8.90 \times 10^{-8} \end{array} \right]$$
- IE0205
- Q.10 The pH of aqueous solution of ammonia is 10. Find molarity of solution.  $K_b(NH_4OH) = 10^{-5}$ . IE0019

Q.11 The solution of weak monoprotic acid which is 0.01 M, has pH = 3. Calculate  $K_a$  of weak acid.

IE0020

Q.12 Boric acid is a weak monobasic acid. It ionizes in water as



Calculate pH of 0.5 M boric acid.

IE0021

### MIXTURE OF TWO OR MORE ACIDS / BASES

Q.13 The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is :-

IE0022

Q.14 Calculate pH of following solutions : [log 0.3 = -0.522]

(a) 0.1 M  $\text{H}_2\text{SO}_4$  (50 ml) + 0.4 M HCl 50 (ml)

(b) 0.1 M HA + 0.1 M HB [  $K_a$  (HA) =  $5 \times 10^{-5}$  ;  $K_a$  (HB) =  $4 \times 10^{-5}$  ]

IE0023

Q.15 Calculate pH of a solution containing 0.1M HA ( $K_a = 10^{-5}$ ) & 0.1 M HCl.

IE0024

Q.16 Calculate  $[\text{H}^+]$  and  $[\text{CHCl}_2\text{COO}^-]$  in a solution that is 0.01 M in HCl and 0.01 M in  $\text{CHCl}_2\text{COOH}$ .

Take ( $K_a = 3 \times 10^{-2}$ ) ( $\sqrt{28} = 5.3$ )

IE0206

Q.17 Calculate  $[\text{H}^+]$ ,  $[\text{CH}_3\text{COO}^-]$  and  $[\text{C}_7\text{H}_5\text{O}_2^-]$  in a solution that is 0.2 M in acetic acid and 0.1M in benzoic acid.  $K_a$ (acetic) =  $1.8 \times 10^{-5}$ ,  $K_a$ (benzoic) =  $5.4 \times 10^{-5}$ .

IE0207

### POLYPROTIC ACIDS & BASES

Q.18 What are the concentration of  $\text{H}^+$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HC}_2\text{O}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  in a 0.1 M solution of oxalic acid ?

[ $K_1 = 10^{-2}$  M and  $K_2 = 10^{-5}$  M] [ $\sqrt{41} = 6.4$ ]

IE0025

Q.19 Calculate  $[\text{H}^+]$ ,  $[\text{H}_2\text{PO}_4^-]$ ,  $[\text{HPO}_4^{2-}]$  and  $[\text{PO}_4^{3-}]$  in a 0.01M solution of  $\text{H}_3\text{PO}_4$ .

Take  $K_1 = 10^{-3}$ ,  $K_2 = 10^{-8}$ ,  $K_3 = 10^{-13}$ ,  $\sqrt{41} = 6.4$

IE0208

Q.20 Calculate pH of 0.2 M -  $\text{B(OH)}_2$  solution.

( $K_{b1} = 2 \times 10^{-5}$ ;  $K_{b2} = 4 \times 10^{-11}$ ,  $\log 2 = 0.3$ )

IE0026

### HYDROLYSIS

Q.21 What is the  $\text{OH}^-$  concentration of a 0.18 M solution of  $\text{CH}_3\text{COONa}$ . [ $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ ]

IE0027

Q.22 Calculate the pH of a 2.0 M solution of  $\text{NH}_4\text{Cl}$ . [ $K_b(\text{NH}_3) = 2 \times 10^{-5}$ ]

IE0028

Q.23 0.25 M solution of pyridinium chloride  $\text{C}_5\text{H}_6\text{N}^+\text{Cl}^-$  was found to have a pH of 2.699. What is  $K_b$  for pyridine,  $\text{C}_5\text{H}_5\text{N}$ ? ( $\log 2 = 0.3010$ )

IE0029

Q.24 Calculate the extent of hydrolysis & the pH of 0.02 M  $\text{CH}_3\text{COONH}_4$ .

[ $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$ ,  $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ ]

IE0030

- Q.25 Calculate the percent hydrolysis in a 0.06 M solution of KCN. [ $K_a(\text{HCN}) = 6 \times 10^{-10}$ ] **IE0031**
- Q.26 Calculate the extent of hydrolysis of 0.005 M  $\text{K}_2\text{CrO}_4$ . [ $K_2 = 3.2 \times 10^{-7}$  for  $\text{H}_2\text{CrO}_4$ ]  
(It is essentially strong for first ionization). **IE0209**
- Q.27 A 0.010 M solution of  $\text{PuO}_2(\text{NO}_3)_2$  was found to have a pH of 4.0. What is the hydrolysis constant,  $K_h$ ,  
for  $\text{PuO}_2^{2+}$ , and what is  $K_b$  for  $\text{PuO}_2\text{OH}^+$ ? **IE0210**
- Q.28 What is the pH of 0.1M  $\text{NaHCO}_3$ ?  $K_1 = 5 \times 10^{-7}$ ,  $K_2 = 5 \times 10^{-11}$  for carbonic acids. **IE0032**
- Q.29 Calculate pH of 0.05M potassium hydrogen phthalate,  $\text{KHC}_8\text{H}_4\text{O}_4$ .
- $$\text{H}_2\text{C}_8\text{H}_4\text{O}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HC}_8\text{H}_4\text{O}_4^- \quad \text{p}K_1 = 2.94$$
- $$\text{HC}_8\text{H}_4\text{O}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_8\text{H}_4\text{O}_4^{2-} \quad \text{p}K_2 = 5.44$$
- IE0211**
- Q.30 The acid ionization (hydrolysis) constant of  $\text{Zn}^{2+}$  is  $1.0 \times 10^{-9}$   
(a) Calculate the pH of a 0.001 M solution of  $\text{ZnCl}_2$   
(b) What is the basic dissociation constant of  $\text{Zn}(\text{OH})^+$ ? **IE0033**

### BUFFER SOLUTION

- Q.31 Calculate the pH of solution containing 0.1M - HCN and 0.1M - NaCN.  $K_a$  of HCN =  $10^{-9}$  **IE0034**
- Q.32 Calculate the pH of solution containing 0.2 M -  $\text{NH}_4\text{OH}$  and 0.1 M -  $\text{NH}_4\text{Cl}$ .  $K_b$  of  $\text{NH}_4\text{OH}$   
=  $1.8 \times 10^{-5}$ . ( $\log 2 = 0.3$ ,  $\log 1.8 = 0.26$ ) **IE0035**
- Q.33 0.4 mole  $\text{CH}_3\text{COONa}$  is added in 500 ml 0.4 M -  $\text{CH}_3\text{COOH}$  solutions. What is the pH of final solution  
?  $K_a$  of  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ . ( $\log 2 = 0.3$ ,  $\log 1.8 = 0.26$ ). **IE0036**
- Q.34 A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into  
100 mL solution. If  $\text{p}K_b$  of ammonia is 4.74, calculate value of x. **IE0037**
- Q.35 Determine  $[\text{OH}^-]$  of a 0.050 M solution of ammonia to which sufficient  $\text{NH}_4\text{Cl}$  has been added to make  
the total  $[\text{NH}_4^+]$  equal to 0.100. [ $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$ ,  $\text{p}K_b = 4.74$ ] **IE0038**
- Q.36 Calculate the pH of a solution containing 0.2 M  $\text{HCO}_3^-$  and 0.1 M  $\text{CO}_3^{2-}$   
[ $K_1(\text{H}_2\text{CO}_3) = 4 \times 10^{-7}$ ;  $K_2(\text{HCO}_3^-) = 4 \times 10^{-11}$ ] **IE0039**
- Q.37 Calculate the pH of a solution prepared by mixing 50.0 mL of 0.200 M  $\text{HC}_2\text{H}_3\text{O}_2$  and 50.0 mL of  
0.100 M NaOH. [ $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ ,  $\text{p}K_a = 4.74$ ] **IE0040**
- Q.38 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M  $\text{NH}_4\text{Cl}$  to make a basic buffer. If  $\text{p}K_a$  of  $\text{NH}_4^+$  is  
9.26, calculate pH. **IE0041**

Q.39 Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M  $\text{NH}_3$ . [ $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$ ,  $\text{p}K_b = 4.74$ ]

IE0042

Q.40 In 100 ml buffer solution of 0.1M  $\text{CH}_3\text{COOH}$  & 0.1M  $\text{CH}_3\text{COONa}$ , how many millimoles of NaOH should be added to increase its pH by 0.3.

Given ( $\log 2 = 0.3$ )

IE0043

### ACID BASE REACTIONS & TITRATIONS

Q.41 Calculate  $\text{OH}^-$  concentration at the equivalent point when a solution of 0.2 M acetic acid is titrated with a solution of 0.2 M NaOH.  $K_a$  for the acid =  $10^{-5}$ .

IE0044

Q.42 Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10M acetic acid,  $\text{CH}_3\text{COOH}$ , with 22.0 mL of 0.10 M NaOH. [ $K_a = 2 \times 10^{-5}$ ]

IE0045

Q.43 Calculate the hydronium ion concentration and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M  $\text{NH}_3$  with 0.40M HCl. [ $K_b = 2 \times 10^{-5}$ ]

IE0046

Q.44  $\text{CH}_3\text{COOH}$  (50 ml, 0.1 M) is titrated against 0.1 M NaOH solution. Calculate the pH at the addition of 0 ml, 10 ml, 20 ml, 25 ml, 40 ml, 50 ml of NaOH.  $K_a$  of  $\text{CH}_3\text{COOH}$  is  $2 \times 10^{-5}$ .  
[ $\log 2 = 0.3010$ ,  $\log 3 = 0.4771$ ]

IE0047

### INDICATORS

Q.45 For the acid indicator thymol blue, pH is 3 when half the indicator is in unionised form. Find the % of indicator in unionised form in the solution with  $[\text{H}^+] = 4 \times 10^{-3}$  M.

IE0048

Q.46 Bromophenol blue is an acid indicator with a  $K_a$  value of  $6 \times 10^{-5}$ . What % of this indicator is in its basic form at a pH of 5 ?

IE0049

Q.47 At what pH does an indicator change colour if the indicator is a weak acid with  $K_{\text{ind}} = 4 \times 10^{-4}$ . For which one(s) of the following neutralizations would the indicator be useful? Explain.

(a)  $\text{NaOH} + \text{CH}_3\text{COOH}$       (b)  $\text{HCl} + \text{NH}_3$       (c)  $\text{HCl} + \text{NaOH}$

IE0050

Q.48 An acid indicator has a  $K_a$  of  $3 \times 10^{-5}$ . The acid form of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator form 75% red to 75% blue?  
[ $\log 3 = 0.4771$ ]

IE0051

### SOLUBILITY & SOLUBILITY PRODUCT'S

Q.49 The values of  $K_{\text{sp}}$  for the slightly soluble salts MX and  $\text{QX}_2$  are each equal to  $4.0 \times 10^{-18}$ . Which salt is more soluble? Explain your answer fully.

IE0052

Q.50 The solubility of  $\text{PbSO}_4$  in water is 0.0608 g/L. Calculate the solubility product constant of  $\text{PbSO}_4$ .  
Molar mass  $\text{PbSO}_4 = 304$  g/mole

IE0053

Q.51 How many mole  $\text{CuI}$  ( $K_{\text{sp}} = 5 \times 10^{-12}$ ) will dissolve in 1.0 L of 0.10 M NaI solution ?

IE0054

Q.52 A solution of saturated  $\text{CaF}_2$  is found to contain  $4 \times 10^{-4}$  M fluoride ion. Calculate the  $K_{sp}$  of  $\text{CaF}_2$ . Neglect hydrolysis.

IE0055

Q.53 The solubility of  $\text{ML}_2$  (formula weight = 60 g/mol) in water is  $2.4 \times 10^{-5}$  g/100 mL solution. Calculate the solubility product constant for  $\text{ML}_2$ .

IE0056

Q.54 Calculate the solubility of  $\text{A}_2\text{X}_3$  in pure water, assuming that neither kind of ion reacts with water. For  $\text{A}_2\text{X}_3$ ,  $K_{sp} = 1.08 \times 10^{-23}$

IE0057

Q.55 Determine the solubility of  $\text{AgCl}$  in 0.1 M  $\text{BaCl}_2$ . [ $K_{sp}$  for  $\text{AgCl} = 1 \times 10^{-10}$ ]

IE0058

Q.56 Calculate solubility of  $\text{Ca}_3(\text{PO}_4)_2$  ( $K_{sp} = 10^{-15}$ ) in presence of 0.1 M  $\text{CaCl}_2$  solution.

IE0059

### SIMULTANEOUS SOLUBILITY

Q.57 Calculate the Simultaneous solubility of  $\text{AgSCN}$  and  $\text{AgBr}$ .  $K_{sp}$  ( $\text{AgSCN}$ ) =  $3.2 \times 10^{-12}$ ,  $K_{sp}$  ( $\text{AgBr}$ ) =  $8 \times 10^{-13}$ .

IE0060

Q.58 Calculate  $\text{F}^-$  in a solution saturated with respect of both  $\text{MgF}_2$  and  $\text{SrF}_2$ .  $K_{sp}$  ( $\text{MgF}_2$ ) =  $9.5 \times 10^{-9}$ ,  $K_{sp}$  ( $\text{SrF}_2$ ) =  $4 \times 10^{-9}$ .

IE0212

### COMPLEX FORMATION

Q.59 Calculate the solubility of  $\text{AgCl}$  in 0.2 M -  $\text{NH}_3$  solution.

Given :  $K_{sp}$  of  $\text{AgCl} = 2 \times 10^{-10}$ ,  $K_f$  of  $\text{Ag}(\text{NH}_3)_2^+ = 8 \times 10^6$ .

IE0061

Q.60 Calculate the solubility of  $\text{AgCN}$  in 0.4 M -  $\text{KCN}$  solution

(i) neglecting complex formation

(ii) considering complex formation. Given :  $K_{sp}$  of  $\text{AgCN} = 8 \times 10^{-10}$ ,  $K_d$  of  $\text{Ag}(\text{CN})_2^- = 4 \times 10^{-8}$ .

IE0213

### SOLUBILITY, CONSIDERING HYDROLYSIS

Q.61 Calculating the solubility of  $\text{MX}$  in water. Also calculate pH of solution.

Given :  $K_{sp}$  of  $\text{MX} = 4 \times 10^{-8}$ ;  $K_a$  of  $\text{HX} = 2 \times 10^{-6}$  and  $\text{MOH}$  is strong base.

IE0214

Q.62 Calculate the solubility of  $\text{AgCN}$  in a buffer solution at  $\text{pH} = 3.0$ .

Given :  $K_{sp}$  of  $\text{AgCN} = 8 \times 10^{-10}$ ,  $K_a$  of  $\text{HCN} = 5 \times 10^{-10}$ .

IE0062

### PRECIPITATION

Q.63 A solution has a  $\text{Mg}^{2+}$  concentration of 0.0010 mol/L. Will  $\text{Mg}(\text{OH})_2$  precipitate if the  $\text{OH}^-$  concentration of the solution is [ $K_{sp} = 1.2 \times 10^{-11}$ ]

(a)  $10^{-5}$  mol/L

(b)  $10^{-3}$  mol/L ?

IE0063

Q.64 200 ml of  $2 \times 10^{-4}$  M -  $\text{AgNO}_3$  solution is mixed with 400 ml of  $1.2 \times 10^{-6}$  M -  $\text{NaCl}$  solution. Predict whether precipitation of  $\text{AgCl}$  will occur or not.  $K_{sp}$  of  $\text{AgCl} = 2 \times 10^{-10}$ .

IE0064

Q.65 Calculate the minimum mass of  $\text{Na}_2\text{SO}_4$  needed to just start precipitation of  $\text{BaSO}_4$  from 500 ml of  $2 \times 10^{-5}$  M -  $\text{BaCl}_2$  solution.  $K_{sp}$  of  $\text{BaSO}_4 = 8 \times 10^{-8}$ .

IE0065

## EXERCISE # S-II

Q.1 What are the concentrations of  $H^+$ ,  $HSO_4^-$ ,  $SO_4^{2-}$  and  $H_2SO_4$  in a 0.20 M solution of sulphuric acid?

Given:  $H_2SO_4 \longrightarrow H^+ + HSO_4^-$ ; strong

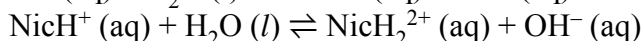
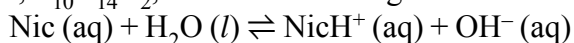


IE0066

Q.2 Calculate the pH of a 0.1M solution of  $H_2NCH_2CH_2NH_2$ ; ethylenediamine (en). Determine the  $H_2^{2+}$  concentration in the solution.  $K_{b1}$  and  $K_{b2}$  values of ethylenediamine are  $9 \times 10^{-5}$  and  $7.1 \times 10^{-8}$  respectively.

IE0215

Q.3 Nicotine,  $C_{10}H_{14}N_2$ , has two basic nitrogen atoms and both can react with water to give a basic solution



$K_{b1}$  is  $8 \times 10^{-7}$  and  $K_{b2}$  is  $10^{-10}$ . Calculate the approximate pH of a 0.20 M solution.

IE0067

Q.4 Determine the  $[S^{2-}]$  in a saturated (0.1M)  $H_2S$  solution to which enough HCl has been added to produce a  $[H^+]$  of  $2 \times 10^{-4}$ .  $K_1 = 10^{-7}$ ,  $K_2 = 10^{-14}$ .

IE0216

Q.5 An aqueous solution contains 0.01 M  $RNH_2$  ( $K_b = 2 \times 10^{-6}$ ) &  $10^{-4}$  M NaOH. The concentration of  $OH^-$  is nearly:

IE0068

Q.6 Calculate the pH of  $1.0 \times 10^{-3}$  M sodium phenoxide,  $NaOC_6H_5$ .  $K_a$  for  $HOC_6H_5$  is  $0.6 \times 10^{-10}$ .

IE0069

Q.7 Calculate the  $OH^-$  concentration and the  $H_3PO_4$  concentration of a solution prepared by dissolving 0.1 mol of  $Na_3PO_4$  in sufficient water to make 1L of solution.  $K_1 = 7.1 \times 10^{-3}$ ,  $K_2 = 6.3 \times 10^{-8}$ ,  $K_3 = 4.5 \times 10^{-13}$ .

IE0217

Q.8 Calculate the pH of 0.1 M solution of (i)  $NaHCO_3$ , (ii)  $Na_2HPO_4$  and (iii)  $NaH_2PO_4$ . Given that:



( $\log 4.2 = 0.62$ ,  $\log 4.8 = 6.8$ ,  $\log 6.2 = 0.80$ ,  $\log 7.5 = 0.88$ )

IE0070

Q.9 An ammonia-ammonium chloride buffer has a pH value of 9 with  $[NH_3] = 0.25$ . What will be the new pH if 500 ml 0.1 M KOH is added to 200 ml buffer solution ( $K_b = 2 \times 10^{-5}$ )

$[\log 2 = 0.3]$

IE0071



- Q.10 A weak base (50.0mL) was titrated with 0.1 M HCl. The pH of the solution after the addition of 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate  $K_b$  of the base and pH at the equivalence point. [ $\log 2 = 0.3$ ]  
**IE0218**
- Q.11 A weak acid (50.0mL) was titrated with 0.1 M NaOH. The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calculate  $K_a$  of the acid and pH at the equivalence point. [ $\log 2 = 0.3$ ]  
**IE0219**
- Q.12 10 ml of 0.1M weak acid  $HA$  ( $k_a = 10^{-5}$ ) is mixed with 10 ml 0.2M HCl and 10 ml 0.1M NaOH. Find the value of  $[A^-]$  in the resulting solution.  
**IE0072**
- Q.13 150 ml of 0.5 M HCN ( $K_a = 3.75 \times 10^{-9}$ ) was reacted with 1.5 M KOH for complete neutralisation. What will be molarity of HCN at equilibrium.  
**IE0073**
- Q.14 The indicator phenol red is half in the ionic form when pH is 7.2. If the ratio of the undissociated form to the ionic form is 1 : 5, find the pH of the solution. With the same pH for solution, if indicator is altered such that the ratio of undissociated form to dissociated form becomes 1 : 4, find the pH when 50 % of the new indicator is in ionic form. [ $\log 2 = 0.3$ ]  
**IE0220**
- Q.15 How much AgBr could dissolve in 1.0 L of 0.40 M  $NH_3$ ? Assume that  $Ag(NH_3)_2^+$  is the only complex formed. [ $K_f(Ag(NH_3)_2^+) = 1 \times 10^8$ ;  $K_{sp}(AgBr) = 5 \times 10^{-13}$ ]  
[ $\sqrt{50} \approx 7$ ]  
**IE0074**
- Q.16 Calculate solubility of  $PbI_2$  ( $K_{sp} = 1.4 \times 10^{-8}$ ) in water at  $25^\circ$ , which is 90% dissociated.  
$$\left( \frac{1.4}{(0.81)(3.6)} \right)^{1/3} = 0.78$$
  
**IE0075**
- Q.17 A recent investigation of the complexation of  $SCN^-$  with  $Fe^{3+}$  led to 130, 16, and 1.0 for  $K_1$ ,  $K_2$ , and  $K_3$ , respectively. What is the overall formation constant of  $Fe(SCN)_3$  from its component ions, and what is the dissociation constant of  $Fe(SCN)_3$  into its simplest ions on the basis of these data?  
**IE0221**

## EXERCISE # O-I

## Single correct

- Q.1 The conjugate acid of  $\text{NH}_2^-$  is  
 (A)  $\text{NH}_3$  (B)  $\text{NH}_2\text{OH}$  (C)  $\text{NH}_4^+$  (D)  $\text{N}_2\text{H}_4$  IE0076
- Q.2 Which of the following is not a Bronsted acid:-  
 (A)  $\text{CH}_3\text{NH}_4^+$  (B)  $\text{CH}_3\text{COO}^-$  (C)  $\text{H}_2\text{O}$  (D)  $\text{HSO}_4^-$  IE0077
- Q.3 In the reaction  
 $\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_3^-$ , the conjugate base of  $\text{HNO}_3$  is :-  
 (A)  $\text{H}_2\text{O}$  (B)  $\text{H}_3\text{O}^+$  (C)  $\text{NO}_3^-$  (D)  $\text{H}_3\text{O}^+$  and  $\text{NO}_3^-$  IE0078
- Q.4 Out of the following, amphiprotic species in aqueous medium are  
 I:  $\text{HPO}_3^{2-}$  II  $\text{OH}^-$  III  $\text{H}_2\text{PO}_4^-$  IV  $\text{HCO}_3^-$   
 (A) I, III, IV (B) I and III (C) III and IV (D) All IE0079
- Q.5 When ammonia is added to water, it decreases the concentration of which of the following ion  
 (A)  $\text{OH}^-$  (B)  $\text{H}_3\text{O}^+$  (C)  $\text{NH}_4^+$  (D)  $\text{NH}_4^+$  &  $\text{OH}^-$  IE0080
- Q.6 Which of the following pair is Lewis acid & Lewis base & Product of these is also Lewis base  
 (A)  $\text{BF}_3$ ,  $\text{NH}_3$  (B)  $\text{SiCl}_4$ ,  $2\text{Cl}^-$  (C)  $\text{CH}_3^+$ ,  $^-\text{OC}_2\text{H}_5$  (D) All of these IE0081
- Q.7 Ionic product of water will increase, if :-  
 (A) Pressure is decreased (B)  $\text{H}^+$  is added  
 (C)  $\text{OH}^-$  is increased (D) Temperature is increased IE0082
- Q.8 At  $60^\circ\text{C}$ , pure water has  $[\text{H}_3\text{O}^+] = 10^{-6.7}$  mol/lit. what is the value of  $K_w$  at  $60^\circ\text{C}$  :-  
 (A)  $10^{-6}$  (B)  $10^{-12}$  (C)  $10^{-67}$  (D)  $10^{-13.4}$  IE0083
- Q.9 Liquid  $\text{NH}_3$  ionises to a slight extent. At a certain temperature its self ionization constant  $K_{\text{SIC}(\text{NH}_3)} = 10^{-30}$ . The number of  $\text{NH}_4^+$  ions present per  $100 \text{ cm}^3$  of pure liquid are  
 (A)  $10^{-15}$  (B)  $6.022 \times 10^8$  (C)  $6.022 \times 10^7$  (D) None IE0084
- Q.10 The pH of solution is increased from 3 to 6. Its  $\text{H}^+$  ion conc. will be :-  
 (A) Reduced to half (B) Doubled  
 (C) Reduced by 1000 times (D) Increased by 1000 times IE0085
- Q.11. pOH of  $[1/200] \text{ mol/m}^3 \text{H}_2\text{SO}_4$  (aq.) solution at  $25^\circ\text{C}$  is-  
 (A) 2 (B) 5 (C) 9 (D) 12 IE0086

- Q.12 Degree of dissociation of 0.1 N  $\text{CH}_3\text{COOH}$  is :- (Dissociation constant =  $1 \times 10^{-5}$ )  
 (A)  $10^{-5}$  (B)  $10^{-4}$  (C)  $10^{-3}$  (D)  $10^{-2}$  **IE0087**
- Q.13 The pH of a 0.02 M ammonia solution which is 5% ionised will be :-  
 (A) 2 (B) 11 (C) 5 (D) 7 **IE0088**
- Q.14 The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is  
 (A) 1 (B) 2 (C) 3 (D) 11 **IE0089**
- Q.15 The concentration of  $[\text{H}^+]$  and concentration of  $[\text{OH}]^-$  of a 0.1 M aqueous solution of 2% ionised weak acid is [ionic product of water =  $1 \times 10^{-14}$ ]  
 (A)  $0.02 \times 10^{-3}$  M and  $5 \times 10^{-11}$  M (B)  $1 \times 10^{-3}$  M and  $3 \times 10^{-11}$  M  
 (C)  $2 \times 10^{-3}$  M and  $5 \times 10^{-12}$  M (D)  $3 \times 10^{-2}$  M and  $4 \times 10^{-13}$  M **IE0090**
- Q.16 What is the quantity of NaOH present in 250 cc of the solution, so that it gives a pH = 13 :-  
 (A)  $10^{-13}$  g (B)  $10^{-1}$  g (C) 1.0 g (D) 4.0 g **IE0091**
- Q.17 An aqueous solution of HCl is  $10^{-9}$  M HCl. The pH of the solution should be:-  
 (A) 9 (B) Between 6 and 7 (C) 7 (D) Unpredictable **IE0092**
- Q.18. The moles of  $\text{H}^+$  from  $\text{H}_2\text{O}$  in a 1l,  $\sqrt{5} \times 10^{-7}$  M HCl solution at  $25^\circ\text{C}$ , is  
 ( $\sqrt{5} = 2.23$ )  
 (A)  $10^{-7}$  (B)  $6.85 \times 10^{-8}$  (C)  $3.85 \times 10^{-8}$  (D)  $10^{-8}$  **IE0093**
- Q.19 Which one of the following has highest pH:-  
 (A) Distilled water (B) 1 M  $\text{NH}_3$   
 (C) 1 M NaOH (D) Water saturated with chlorine **IE0094**
- Q.20 8 gm NaOH and 4.9 gm  $\text{H}_2\text{SO}_4$  are present in one litre of the solution. What is its pH  
 (A) 1 (B) 13 (C) 12 (D) 2 **IE0095**
- Q.21 10 ml of  $\frac{M}{200}$   $\text{H}_2\text{SO}_4$  is mixed with 40 ml of  $\frac{M}{200}$   $\text{H}_2\text{SO}_4$ . The pH of the resulting solution is  
 (A) 1 (B) 2 (C) 2.3 (D) none of these **IE0096**
- Q.22 Which of the following solution will have pH close to 1.0?  
 (A) 100 ml of M/100 HCl + 100 ml of M/10 NaOH  
 (B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH  
 (C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH  
 (D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH **IE0097**

- Q.23 A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of:  
 (A) 3 (B) 4 (C) 3000 (D) 10000 **IE0098**
- Q.24 The first and second dissociation constants of an acid  $H_2A$  are  $1.0 \times 10^{-5}$  and  $5.0 \times 10^{-10}$  respectively. The overall dissociation constant of the acid will be :  
 (A)  $5.0 \times 10^{-5}$  (B)  $5.0 \times 10^{15}$  (C)  $5.0 \times 10^{-15}$  (D)  $0.2 \times 10^5$  **IE0099**
- Q.25 If  $pK_b$  for fluoride ion at  $25^\circ C$  is 10.4, the ionisation constant of hydrofluoric acid in water at this temperature is :  
 (A)  $4 \times 10^{-11}$  (B)  $3 \times 10^{-3}$  (C)  $2.5 \times 10^{-4}$  (D)  $2 \times 10^{-2}$  **IE0100**
- Q.26 pH of an aqueous solution of NaCl at  $85^\circ C$  should be  
 (A) 7 (B)  $> 7$  (C)  $< 7$  (D) 0 **IE0101**
- Q.27 1 cc of 0.1 N HCl is added to 99 cc solution of NaCl. The pH of the resulting solution will be  
 (A) 7 (B) 3 (C) 4 (D) 1 **IE0102**
- Q.28 The degree of hydrolysis of a salt of weak acid and weak base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be  
 (A) 100% (B) 50% (C) 25% (D) none of these **IE0103**
- Q.29 What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is  $2 \times 10^{-9}$  and  $K_w = 1.0 \times 10^{-14}$   
 (A) 2 (B) 5.26 (C) 8.2 (D) 9.6 **IE0104**
- Q.30 The compound whose 0.1 M solution is basic is  
 (A) Ammonium acetate (B) Ammonium chloride  
 (C) Ammonium sulphate (D) Sodium acetate **IE0105**
- Q.31 If equilibrium constant of  
 $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$   
 is  $1.8 \times 10^{-5}$ , equilibrium constant for  
 $CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$  is  
 (A)  $1.8 \times 10^{-9}$  (B)  $1.8 \times 10^9$  (C)  $5.55 \times 10^{-9}$  (D)  $5.55 \times 10^{10}$  **IE0106**
- Q.32 The  $pK_a$  of a weak acid, HA, is 4.80. The  $pK_b$  of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be :  
 (A) 8.58 (B) 4.79 (C) 7.01 (D) 9.22 **IE0107**
- Q.33 The highest pH value is of :-  
 (A) 0.1 M NaCl (B) 0.1 M  $NH_4Cl$   
 (C) 0.1 M  $CH_3COONa$  (D) 0.1 M  $CH_3COONH_4$  **IE0108**

- Q.34 pH of  $K_2S$  solution is:-  
 (A) 7 (B) Less than 7 (C) More than 7 (D) 0  
**IE0109**
- Q.35 Degree of Hydrolysis of  $\frac{N}{100}$  solution of KCN is (Given  $K_a = 1.6 \times 10^{-9}$ )  
 (A)  $2.5 \times 10^{-3}$  (B)  $2.5 \times 10^{-2}$  (C)  $2.5 \times 10^{-4}$  (D)  $2.5 \times 10^{-5}$   
**IE0110**
- Q.36 A solution of  $FeCl_3$  in water acts as acidic due to :-  
 (A) Acidic impurities (B) Ionisation (C) Hydrolysis of  $Fe^{3+}$  (D) Dissociation  
**IE0111**
- Q.37 If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [ $K_a = 2 \times 10^{-4}$ ], the pOH of the resulting solution is  
 (A) 3.4 (B) 3.7 (C) 7 (D) 10.3  
**IE0112**
- Q.38 1 M NaCl and 1M HCl are present in an aqueous solution. The solution is  
 (A) not a buffer solution and with  $pH < 7$   
 (B) not a buffer solution with  $pH > 7$   
 (C) a buffer solution with  $pH < 7$   
**IE0113**
- Q.39 The  $pK_a$  of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is :  
 (A) 4.5 (B) 2.5 (C) 9.5 (D) 7.0  
**IE0114**
- Q.40 To a 50 ml. of 0.05M formic acid, how much volume of 0.10M sodium formate must be added to get a buffer solution of  $pH = 4.0$  ?  
 ( $pK_a$  of the acid is 3.7) ( $\log 2 = 0.3$ )  
 (A) 40 ml. (B) 4 ml. (C) 50 ml. (D) 100 ml.  
**IE0115**
- Q.41 Which can act as buffer :-  
 (A)  $NH_4OH + NaOH$   
 (B)  $HCOOH + HCl$   
 (C) 40 ml. of 0.1 M NaCN + 20 ml. of 0.1 M HCl  
 (D) All of them  
**IE0116**
- Q.42 If equal volume of 0.05 M ammonium hydroxide solution is dissolved in 0.001 M ammonium chloride solution. What will be the  $OH^-$  ion concentration of this solution :  
 $K_b(NH_4OH) = 1.8 \times 10^{-5}$   
 (A)  $3.0 \times 10^{-3}$  (B)  $4.6 \times 10^{-4}$  (C)  $9.0 \times 10^{-3}$  (D)  $9.0 \times 10^{-4}$   
**IE0117**
- Q.43 Calculate the pH of a buffer prepared by mixing 600 cc of 0.6 M  $NH_3$  and 400 cc of 0.5 M  $NH_4Cl$ .  
 $K_b$  for  $NH_3 = 1.8 \times 10^{-5}$ , ( $\log 1.8 = 0.26$ )  
 (A) 11.3 (B) 9.0 (C) 9.52 (D) 5  
**IE0118**

- Q.44  $pK_b$  for  $NH_4OH$  at certain temperature is 4.74. The pH of basic buffer containing equimolar concentration of  $NH_4OH$  and  $NH_4Cl$  will be:-  
 (A) 7.74 (B) 4.74 (C) 2.37 (D) 9.26 **IE0119**
- Q.45 On addition of  $NaOH$  to  $CH_3COOH$  solution, 60% of the acid is neutralised. If  $pK_a$  of  $CH_3COOH$  is 4.7 then the pH of the resulting solution is :-  
 (A) More than 4.7 but less than 5.0 (B) Less than 4.7 but more than 4.0  
 (C) More than 5.0 (D) Remains unchanged **IE0120**
- Q.46 Henderson equation  $pH - pK_a = 5$  will be applicable to an acidic buffer when :-  
 (A)  $[Acid] = [Conjugate\ base]$  (B)  $[Acid] \times 10^5 = [Conjugate\ base]$   
 (C)  $[Acid] = [Conjugate\ base] \times 10^5$  (D)  $[acid] = 2 [conjugate\ base]$  **IE0121**
- Q.47 What amount of sodium propanoate should be added to one litre of an aqueous solution containing 0.02 mole of propanoic acid ( $K_a = 3 \times 10^{-5}$  at  $25^\circ C$ ) to obtain a buffer solution of pH 4.7  
 (A)  $4.52 \times 10^{-2}$  mol (B)  $3.52 \times 10^{-2}$  mol (C)  $2.52 \times 10^{-2}$  mol (D)  $3 \times 10^{-2}$  mol **IE0122**
- Q.48 In a buffer solution the ratio of concentration of  $NH_4Cl$  and  $NH_4OH$  is 1 : 1. When it changes in 2 : 1, what will be the value of pH of buffer ?  
 (A) Increase (B) Decrease (C) No effect (D) None **IE0123**
- Q.49 The buffer solution play an important role in :-  
 (A) Increasing the pH value (B) Decreasing the pH value  
 (C) Keeping the pH constant (D) Solution will be neutral **IE0124**
- Q.50 The total number of different kind of acidic buffers obtained during the titration of  $H_3PO_4$  with  $NaOH$  are :  
 (A) 3 (B) 1 (C) 2 (D) 0 **IE0125**
- Q.51 Which of the following solutions does not act as buffer :  
 (A)  $H_3PO_4 + NaH_2PO_4$  (B)  $NaHCO_3 + H_2CO_3$   
 (C)  $NH_4Cl + HCl$  (D)  $CH_3COOH + CH_3COONa$  **IE0126**
- Q.52 Half of the formic acid solution is neutralised on addition of a  $KOH$  solution to it. If  $K_a (HCOOH) = 2 \times 10^{-4}$  then pH of the solution is : - ( $\log 2 = 0.3010$ )  
 (A) 3.6990 (B) 10.3010 (C) 3.85 (D) 4.3010 **IE0127**
- Q.53 When 0.02 moles of  $NaOH$  are added to a litre of buffer solution, its pH changes from 5.75 to 5.80. What is its buffer capacity :-  
 (A) 0.4 (B) 0.05 (C) - 0.05 (D) 2.5 **IE0128**
- Q.54 Calculate pH when 100 ml of 0.2M  $NaOH$  is reacted with 100 ml of 0.2 M  $CH_3COOH$  ( $K_a = 10^{-5}$ )  
 (A) 9 (B) 7 (C) 5 (D) 2 **IE0129**
- Q.55 At  $90^\circ C$ , pure water has  $[H^+] = 10^{-6} M$ , if 100 ml of 0.2 M  $HNO_3$  is added to 20 ml of 1 M  $NaOH$  at  $90^\circ C$  then pH of the resulting solution will be  
 (A) 5 (B) 6 (C) 7 (D) None of these **IE0130**

- Q.56 When 20 ml of  $\frac{M}{20}$  NaOH are added to 10 ml of  $\frac{M}{10}$  HCl, the resulting solution will:-  
 (A) Turn blue litmus red  
 (B) Turn phenolphthalein solution pink colour  
 (C) Turn methyl orange red  
 (D) Will have no effect on either red or blue litmus  
**IE0131**
- Q.57 The rapid change of pH near the stoichiometric point of an acid–base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base ( $\text{In}^-$ ) forms of the indicator by the expression :-  
 (A)  $\log \frac{[\text{HIn}]}{[\text{In}^-]} = \text{pK}_{\text{In}} - \text{pH}$  (B)  $\log \frac{[\text{HIn}]}{[\text{In}^-]} = \text{pH} - \text{pK}_{\text{In}}$   
 (C)  $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pH} + \text{pK}_{\text{In}}$  (D)  $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pK}_{\text{In}} - \text{pH}$   
**IE0132**
- Q.58 Calculate the pH range in which an acid indicator with  $K_{\text{acid}}(\text{indicator}) = 1.0 \times 10^{-5}$  changes colour when the concentration of the indicator is  $1 \times 10^{-3}\text{M}$ .  
 (A)  $5 \pm 1$  (B)  $11 \pm 1$  (C)  $3 \pm 1$  (D)  $8 \pm 1$   
**IE0133**
- Q.59 In what pH range will a  $1 \times 10^{-4}\text{M}$  solution of an indicator with  $K_{\text{b}}(\text{indicator}) = 1 \times 10^{-11}$  change colour?  
 (A)  $7.0 \pm 1$  (B)  $3.0 \pm 1$  (C)  $5.5 \pm 1$  (D)  $11.0 \pm 1$   
**IE0134**
- Q.60 Indicator which is used in the titration of  $\text{CH}_3\text{COOH}$  & NaOH :-  
 (A) Methyl orange (B) Methyl red (C) Phenolphthalein (D) Litmus  
**IE0135**
- Q.61 Phenolphthalein is a :-  
 (A) Strong acid (B) Strong base (C) Weak base (D) Weak acid  
**IE0136**
- Q.62 pH–range of Methyl red indicator is :-  
 (A) 4.2–6.2 (B) 6.8–10.8 (C) 8 – 9.6 (D) 6.8 – 8.2  
**IE0137**
- Q.63 In the volumetric estimation of HCl, if we make use of phenolphthalein as an indicator, which base is unsuitable for the titration :-  
 (A) NaOH (B) RbOH (C) KOH (D)  $\text{NH}_4\text{OH}$   
**IE0138**
- Q.64 Phenolphthalein does not act as an indicator for the titration between :-  
 (A) KOH and  $\text{H}_2\text{SO}_4$  (B) NaOH and  $\text{CH}_3\text{COOH}$   
 (C) Oxalic acid and  $\text{KMnO}_4$  (D)  $\text{Ba}(\text{OH})_2$  and HCl  
**IE0139**
- Q.65 For weak acid and strong base titration, the indicator used is :-  
 (A) Potassium di-chromate (B) Methyl orange  
 (C) Litmus (D) Phenolphthalein  
**IE0140**
- Q.66 The solubility of  $\text{A}_2\text{X}_3$  is  $y \text{ mol dm}^{-3}$ . Its solubility product is  
 (A)  $6y^2$  (B)  $64y^4$  (C)  $36y^5$  (D)  $108y^5$   
**IE0141**

- Q.67 If  $K_{sp}$  for  $HgSO_4$  is  $6.4 \times 10^{-5}$ , then solubility of this substance in mole per  $m^3$  is  
 (A)  $8 \times 10^{-3}$  (B)  $6.4 \times 10^{-5}$  (C)  $8 \times 10^{-6}$  (D) 8  
**IE0142**
- Q.68 If the solubility of  $AgCl$  (formula mass=143) in water at  $25^\circ C$  is  $1.43 \times 10^{-4}$  gm/100 ml of solution then the value of  $K_{sp}$  will be :-  
 (A)  $1 \times 10^{-5}$  (B)  $2 \times 10^{-5}$  (C)  $1 \times 10^{-10}$  (D)  $2 \times 10^{-10}$   
**IE0143**
- Q.69 One litre of saturated solution of  $CaCO_3$  is evaporated to dryness, 7.0 g of residue is left. The solubility product for  $CaCO_3$  is:-  
 (A)  $4.9 \times 10^{-3}$  (B)  $4.9 \times 10^{-5}$  (C)  $4.9 \times 10^{-9}$  (D)  $4.9 \times 10^{-7}$   
**IE0144**
- Q.70  $A_3B_2$  is a sparingly soluble salt of molar mass  $M$  ( $g\ mol^{-1}$ ) and solubility  $x\ g\ lit^{-1}$ . The ratio of the molar concentration of  $B^{3-}$  to the solubility product of the salt is  
 (A)  $108 \frac{x^5}{M^5}$  (B)  $\frac{1}{108} \frac{M^4}{x^4}$  (C)  $\frac{1}{54} \frac{M^4}{x^4}$  (D) None  
**IE0145**
- Q.71. Solubility of  $Ag_2CrO_4$  ( $K_{sp} = 4 \times 10^{-13}$ ) in  $0.1\ M\ K_2CrO_4$  solution will be :-  
 (A)  $10^{-3}\ M$  (B)  $10^{-6}\ M$  (C)  $4 \times 10^{-6}\ M$  (D)  $5 \times 10^{-7}\ M$   
**IE0146**
- Q.72. How many times solubility of  $CaF_2$  is decreased in  $4 \times 10^{-3}\ M\ KF$  (aq.) solution as compare to pure water at  $25^\circ C$ . Given  $K_{sp}(CaF_2) = 3.2 \times 10^{-11}$   
 (A) 50 (B) 100 (C) 500 (D) 1000  
**IE0147**
- Q.73 At  $30^\circ C$ , In which of the one litre solution, the solubility of  $Ag_2CO_3$  (solubility product =  $8 \times 10^{-12}$ ) will be maximum :-  
 (A)  $0.05\ M\ Na_2CO_3$  (B) Pure water  
 (C)  $0.05\ M\ AgNO_3$  (D)  $0.05\ M\ NH_3$   
**IE0148**
- Q.74 What will happen if the pH of the solution of  $0.001\ M\ Mg(NO_3)_2$  solution is adjusted to  $pH = 9$  ( $K_{sp}$  of  $Mg(OH)_2 = 8.9 \times 10^{-12}$ )  
 (A) ppt will take place  
 (B) ppt will not take place  
 (C) Solution will be saturated  
 (D) None of these  
**IE0149**
- Q.75  $Na_3PO_4$  which should be added in  $10\ L$  of  $1.0 \times 10^{-5}\ M - BaCl_2$  solution without any precipitation of  $Ba_3(PO_4)_2$  is [ $K_{sp}$  of  $Ba_3(PO_4)_2 = 4 \times 10^{-23}$ ]  
 (A)  $2 \times 10^{-4}\ gm$  (B)  $0.328\ gm$  (C)  $0.164\ gm$  (D)  $0.82\ gm$   
**IE0150**



## EXERCISE # O-II

## Single correct :

- Q.1 The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is :-  
(A) 3.3 (B) 3.5 (C) 4.5 (D) 4.0 IE0151
- Q.2 How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3 :-  
(A) 1 (B) 0.02 (C) 0.009 (D) 0.01 IE0152
- Q.3 Which of the following is most soluble in water?  
(A) MnS ( $K_{sp} = 8 \times 10^{-37}$ ) (B) ZnS ( $K_{sp} = 7 \times 10^{-16}$ )  
(C) Bi<sub>2</sub>S<sub>3</sub> ( $K_{sp} = 1 \times 10^{-72}$ ) (D) Ag<sub>3</sub>(PO<sub>4</sub>) ( $K_{sp} = 1.8 \times 10^{-18}$ ) IE0153
- Q.4 Solubility of AgBr will be minimum in :-  
(A) Pure water (B) 0.1 M CaBr<sub>2</sub> (C) 0.1 M NaBr (D) 0.1 M AgNO<sub>3</sub> IE0154
- Q.5 pH of solution at first 1/4<sup>th</sup> equivalence point of Na<sub>2</sub>CO<sub>3</sub> when titrated with HCl will be (for H<sub>2</sub>CO<sub>3</sub>  $K_{a1} = 10^{-7}$ ;  $K_{a2} = 10^{-11}$ )  
(A)  $7 + \log 3$  (B)  $7 - \log 3$  (C)  $11 + \log 3$  (D)  $11 - \log 3$  IE0155
- Q.6 An acid-base indicator has a  $K_a = 1.0 \times 10^{-5}$ . The acid form of the indicator is red and the basic form is blue. Calculate the pH change required to change the colour of the indicator from 80% red to 80% blue.  
(A) 1.20 (B) 0.80 (C) 0.20 (D) 1.40 IE0156

## Assertion /Reason :

- Q.7 **Statement-1** pH of  $10^{-7}$  M NaOH solution is exist between 7 to 7.3 at 25°C.  
**Statement-2** Due to common ion effect ionization of water is reduced.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true. IE0157
- Q.8 **Statement-1** In general phenolphthalein is used as an indicator for the titration of weak acid (HA) against strong base (NaOH)  
**Statement-2** At equivalent point solution is basic.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true. IE0222

- Q.9 **Statement-1** : Moles of  $\text{Sr}^{2+}$  furnished by sparingly soluble substance  $\text{Sr}(\text{OH})_2$  decreases due to dilution.  
**Statement-2** : Solubility product constant of  $\text{Sr}(\text{OH})_2$  is not affected by dilution.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

IE0223

- Q.10 **Statement-1** : On dilution of a concentrated solution of  $\text{CH}_3\text{COOH}$ , the concentration of  $[\text{H}^+]$  decreases.  
**Statement-2** : Increase in volume is more than the increase in degree of ionisation.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

IE0158

**Multiple correct :**

- Q.11 Which of the following is correct for 0.1 M BOH solution ( $K_b = 10^{-5}$ )  
 (A) pH of solution is 11  
 (B)  $\text{OH}^-$  concentration is  $10^{-3}$  mol/L  
 (C) it's salt with HCl (i.e. BCl) form the acidic solution in water  
 (D) Phenolphthalein indicator can be used during the titration of BOH with HCl

IE0159

- Q.12 For weak monobasic acid, HA, the dissociation constant is  $2 \times 10^{-6}$ , at  $25^\circ\text{C}$ . Which of the following is/are correct regarding this acid? [ $\log 2 = 0.3$ ]  
 (A)  $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$ ;  $K_{\text{eq}} = 5 \times 10^{-9}$   
 (B) The equilibrium constant for the reaction of HA with aq. NaOH is  $2 \times 10^8$   
 (C) The pH of 0.1 M, HA solution is 3.35  
 (D) solution of  $\text{A}^-$  is basic

IE0160

- Q.13 Select correct statement for 50ml 0.1M  $\text{H}_2\text{A}(\text{aq.})$  solution ;  $K_{a_1} = 10^{-5}$  ;  $K_{a_2} = 10^{-8}$   
 (A)  $[\text{H}^+] = 2[\text{A}^{2-}]$   
 (B) pH of 0.1M  $\text{H}_2\text{A}$  solution is 3  
 (C) In above  $\text{H}_2\text{A}$  solution when 5 milimoles of NaHA are added then pH increases by 2 units  
 (D) 50 ml of 0.1M NaOH required to neutralised completely 50 ml of 0.1M  $\text{H}_2\text{A}$  solution

IE0224

Q.14 A solution containing 0.01M each of  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$  &  $\text{Cr}^{3+}$  ion. If solid  $\text{Na}_2\text{S}$  is added slowly to the solution then correct statement is based on given data -

Precipitate	PbS	Ag <sub>2</sub> S	ZnS	Cr <sub>2</sub> S <sub>3</sub>
K <sub>sp</sub>	10 <sup>-11</sup>	10 <sup>-12</sup>	10 <sup>-8</sup>	10 <sup>-10</sup>

- (A)  $\text{Pb}^{2+}$  will start precipitating first  
 (B)  $\text{Cr}^{3+}$  will start precipitating last  
 (C)  $\text{Zn}^{2+}$  will start precipitating before  $\text{Ag}^+$   
 (D) When  $\text{Zn}^{2+}$  just starts precipitating then  $\text{Pb}^{2+}$  ion gets 99.9% precipitated

IE0225

Q.15 If  $K_1$  &  $K_2$  be first and second ionisation constant of  $\text{H}_3\text{PO}_4$  and  $K_1 \gg K_2$  which is/are incorrect.

- (A)  $[\text{H}^+] = [\text{H}_2\text{PO}_4^-]$  (B)  $[\text{H}^+] = \sqrt{K_1[\text{H}_3\text{PO}_4]}$   
 (C)  $K_2 = [\text{HPO}_4^{2-}]$  (D)  $[\text{H}^+] = 3[\text{PO}_4^{3-}]$

IE0161

Q.16 10 ml. of a solution contains 0.1 M  $\text{NH}_4\text{Cl}$  + 0.01M  $\text{NH}_4\text{OH}$ . Which addition would not change the pH of solution :-

- (A) Adding 1 ml. water  
 (B) Adding 5 ml. of 0.1 M  $\text{NH}_4\text{Cl}$   
 (C) Adding 5 ml. of 0.1 M  $\text{NH}_4\text{OH}$   
 (D) Adding 10 ml. of 0.1 M  $\text{NH}_4\text{Cl}$

IE0162

Q.17 When equal volumes of the following solutions are mixed, precipitation of  $\text{AgCl}$  ( $K_{sp} = 1.8 \times 10^{-10}$ ) will occur only with:

- (A)  $10^{-4}$  M ( $\text{Ag}^+$ ) and  $10^{-4}$  M ( $\text{Cl}^-$ )  
 (B)  $10^{-5}$  M ( $\text{Ag}^+$ ) and  $10^{-5}$  M ( $\text{Cl}^-$ )  
 (C)  $10^{-6}$  M ( $\text{Ag}^+$ ) and  $10^{-6}$  M ( $\text{Cl}^-$ )  
 (D)  $10^{-10}$  M ( $\text{Ag}^+$ ) and  $10^{-10}$  M ( $\text{Cl}^-$ )

IE0163

### Paragraph for Q.18 to Q.20

8 gm weak acid HX (molecular mass = 80) is dissolved in 100 ml water. ( $K_a = 10^{-4}$ )

Q.18 Find pH of solution-

- (A) 3.3 (B) 2 (C) 2.3 (D) 3

IE0164

Q.19 If it is titrated with 0.25 M NaOH find pH at equivalence point ( $\log 5 = 0.7$ )

- (A) 9.15 (B) 8.65 (C) 4.65 (D) 4.85

IE0165

Q.20 Find  $[\text{H}^+]$  if  $10^{-3}$  mol HCl is added to 100 ml original solution ( $\sqrt{41} = 6.4$  ;  $\sqrt{5} = 2.24$ )

- (A)  $0.62 \times 10^{-2}$  (B)  $1.62 \times 10^{-2}$  (C)  $2.7 \times 10^{-2}$  (D)  $0.27 \times 10^{-2}$

IE0166

**Paragraph for Question 21 & 22**

A solution contains one mole each of HA & HB (both are weak acids) in one litre solution. Now one mole of NaOH is added to this solution so that both the acids are partially neutralised. Heat of neutralisation of HA & HB are  $-11.8$  and  $-12.4$  kcal per mole respectively and heat produced during partial neutralisation of HA & HB is  $-12.25$  kcal.

Q.21 Mole ratio of neutralisation of HA & HB is -

- (A) 1 : 4                      (B) 1 : 2                      (C) 1 : 3                      (D) 1 : 5

**IE0226**

Q.22 pH of solution containing mixture of 1 mol of HA & 1 mole of HB in 1 litre solution is

$$K_a(\text{HA}) = 1 \times 10^{-5}, K_a(\text{HB}) = 9 \times 10^{-5}$$

- (A) 2                      (B) 3                      (C) 4                      (D) 5

**IE0227**

**MATCH THE COLUMN :**

Q.23 Match the effect of addition of 1 M NaOH to 100 mL 1 M  $\text{CH}_3\text{COOH}$  (in Column I) with pH (in Column II):

**Column-I**

- (A) 25 mL of NaOH  
(B) 50 mL of NaOH  
(C) 75 mL of NaOH  
(D) 100 mL of NaOH

**Column-II**

- (P)  $\text{p}K_a$   
(Q)  $\text{p}K_a + \log 3$   
(R)  $\text{p}K_a - \log 3$   
(S)  $\frac{1}{2} [\text{p}K_w + \text{p}K_a - \log 2]$

**IE0167**

Q.24 **Column-I**

**pH**

- (A) 3  
(B) 5  
(C) 8  
(D) 9

**Column-II**

**Solution**

- (P) When equal volumes of 0.2M  $\text{NH}_4\text{OH}$  ( $K_b = 10^{-5}$ ) & 0.2M HCl are mixed  
(Q) When equal volumes of 0.2M  $\text{CH}_3\text{COONa}$  & 0.2M HCl are mixed ( $K_{a(\text{CH}_3\text{COOH})} = 10^{-5}$ )  
(R) 0.1M  $\text{Na}_2\text{HPO}_4$   
(for  $\text{H}_3\text{PO}_4$ ;  $K_{a_1} = 10^{-4}$ ;  $K_{a_2} = 10^{-6}$ ;  $K_{a_3} = 10^{-10}$ )  
(S) At 1<sup>st</sup> half equivalence point of  $\text{H}_2\text{CO}_3$  when titrated against 0.1M NaOH,  $K_{a_1} = 10^{-5}$ ,  $K_{a_2} = 10^{-9}$   
(T)  $\text{Mg}(\text{OH})_2$ ;  $K_{sp} = 5 \times 10^{-16}$

**IE0228**

## TABLE TYPE QUESTION :

Column-I (solution)	Column-II (pH of solution)	Column-III (Introduction about solution)
(A) $\text{CH}_3\text{COOH}(0.2\text{M}, 1\text{L}) + \text{NaOH}(0.1\text{M}, 1\text{L})$	(P) 1.3	(1) pH is determined by strong acid
(B) $\text{CH}_3\text{COOH}(0.1\text{M}, 1\text{L}) + \text{HCl}(0.1\text{M}, 1\text{L})$	(Q) 7	(2) Buffer solution at its maximum buffer capacity
(C) $\text{CH}_3\text{COOH}(0.1\text{M}, 1\text{L}) + \text{NH}_4\text{OH}(0.1\text{M}, 1\text{L})$	(R) 9	(3) pH is determined by salt hydrolysis.
(D) $\text{NH}_4\text{Cl}(200\text{ml}, 0.1\text{M}) + \text{NaOH}(100\text{ml}, 0.1\text{M})$	(S) 5	(4) pH is determined by buffer solution

(Given :  $(K_a)_{\text{CH}_3\text{COOH}} = 10^{-5}$  ,  $(K_b)_{\text{NH}_4\text{OH}} = 10^{-5}$ )

Q.25 Which of the following is incorrectly matched

- (A) A - S - 4                      (B) B - P - 1                      (C) D - R - 2                      (D) C - Q - 1

IE0168

Q.26 If 0.15 mole NaOH is added in solution (B) of column-I then which of the following is correct

- (A) S - 3                      (B) S - 4                      (C) R - 1                      (D) P - 3

IE0169

Q.27 If 0.1mole HCl is added in solution (A) of column-I then pH of the resulting solution will be

- (A) 7                      (B) 13                      (C) 3.0                      (D) 1

IE0170

## EXERCISE # J-MAIN

- Q.1 The solubility in water of a sparingly soluble salt  $AB_2$  is  $1.0 \times 10^{-5} \text{ mol L}^{-1}$ . Its solubility product will be  
[AIEEE-2003]  
(1)  $1 \times 10^{-15}$  (2)  $1 \times 10^{-10}$  (3)  $4 \times 10^{-15}$  (4)  $4 \times 10^{-10}$   
IE0229
- Q.2 The solubility of  $Mg(OH)_2$  is  $x$  mole/lit. then its solubility product is- [AIEEE-2002]  
(1)  $x^3$  (2)  $5x^3$  (3)  $4x^3$  (4)  $2x^2$   
IE0230
- Q.3 The molar solubility in  $\text{mol L}^{-1}$  of a sparingly soluble salt  $MX_4$  is 's'. The corresponding solubility product is  $K_{SP}$ . 's' is given in terms of  $K_{SP}$  by relation : [AIEEE-2004]  
(1)  $s = (K_{SP} / 128)^{1/4}$  (2)  $s = (128K_{SP})^{1/4}$   
(3)  $s = (256K_{SP})^{1/5}$  (4)  $s = (K_{SP}/256)^{1/5}$   
IE0231
- Q.4 The solubility product of a salt having general formula  $MX_2$ , in water is :  $4 \times 10^{-12}$ . The concentration of  $M^{2+}$  ions in the aqueous solution of the salt is - [AIEEE-2005]  
(1)  $1.0 \times 10^{-4} \text{ M}$  (2)  $2.0 \times 10^{-6} \text{ M}$  (3)  $4.0 \times 10^{-10} \text{ M}$  (4)  $1.6 \times 10^{-4} \text{ M}$   
IE0232
- Q.5 Hydrogen ion concentration in mol/L in a solution of  $\text{pH} = 5.4$  will be - [AIEEE-2005]  
(1)  $3.88 \times 10^6$  (2)  $3.98 \times 10^8$  (3)  $3.98 \times 10^{-6}$  (4)  $3.68 \times 10^{-6}$   
IE0233
- Q.6 In a saturated solution of the sparingly soluble strong electrolyte  $AgIO_3$  (molecular mass = 283) the equilibrium which sets in is - [AIEEE-2007]  
$$AgIO_3 \rightleftharpoons Ag^+_{(aq)} + IO^-_{3(aq)}$$
  
If the solubility product constant  $K_{sp}$  of  $AgIO_3$  at a given temperature is  $1.0 \times 10^{-8}$ , what is the mass of  $AgIO_3$  contained in 100 ml of its saturated solution ?  
(1)  $28.3 \times 10^{-2} \text{ g}$  (2)  $2.83 \times 10^{-3} \text{ g}$  (3)  $1.0 \times 10^{-7} \text{ g}$  (4)  $1.0 \times 10^{-4} \text{ g}$   
IE0234
- Q.7 The  $\text{pK}_a$  of a weak acid, HA, is 4.80. The  $\text{pK}_b$  of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be - [AIEEE-2008]  
(1) 9.58 (2) 4.79 (3) 7.01 (4) 9.22  
IE0235
- Q.8 Solid  $Ba(NO_3)_2$  is gradually dissolved in a  $1.0 \times 10^{-4} \text{ M Na}_2\text{CO}_3$  solution. At what concentration of  $Ba^{2+}$  will a precipitate begin to form? ( $K_{SP}$  for  $BaCO_3 = 5.1 \times 10^{-9}$ ) [AIEEE-2009]  
(1)  $8.1 \times 10^{-8} \text{ M}$  (2)  $8.1 \times 10^{-7} \text{ M}$  (3)  $4.1 \times 10^{-5} \text{ M}$  (4)  $5.1 \times 10^{-5} \text{ M}$   
IE0236
- Q.9 Solubility product of silver bromide is  $5.0 \times 10^{-13}$ . The quantity of potassium bromide (molar mass taken as  $120 \text{ g mol}^{-1}$ ) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is :- [AIEEE-2010]  
(1)  $5.0 \times 10^{-8} \text{ g}$  (2)  $1.2 \times 10^{-10} \text{ g}$  (3)  $1.2 \times 10^{-9} \text{ g}$  (4)  $6.2 \times 10^{-5} \text{ g}$   
IE0237

Q.10 In aqueous solution the ionization constants for carbonic acid are

$$K_1 = 4.2 \times 10^{-7} \text{ and } K_2 = 4.8 \times 10^{-11}$$

[AIEEE-2010]

Select the correct statement for a saturated 0.034 M solution of the carbonic acid :-

- (1) The concentration of  $H^+$  is double that of  $CO_3^{2-}$
- (2) The concentration of  $CO_3^{2-}$  is 0.034 M
- (3) The concentration of  $CO_3^{2-}$  is greater than that of  $HCO_3^-$
- (4) The concentrations of  $H^+$  and  $HCO_3^-$  are approximately equal

IE0238

Q.11 At  $25^\circ C$ , the solubility product of  $Mg(OH)_2$  is  $1.0 \times 10^{-11}$ . At which pH, will  $Mg^{2+}$  ions start precipitating in the form of  $Mg(OH)_2$  from a solution of 0.001 M  $Mg^{2+}$  ions ?

[AIEEE-2010]

- (1) 8
- (2) 9
- (3) 10
- (4) 11

IE0239

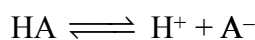
Q.12 The  $K_{sp}$  for  $Cr(OH)_3$  is  $1.6 \times 10^{-30}$ . The molar solubility of this compound in water is :-

[AIEEE-2011]

- (1)  $\sqrt[3]{1.6 \times 10^{-30}}$
- (2)  $\sqrt[4]{1.6 \times 10^{-30}}$
- (3)  $\sqrt[4]{1.6 \times 10^{-30} / 27}$
- (4)  $1.6 \times 10^{-30} / 27$

IE0171

Q.13 An acid HA ionises as



The pH of 1.0 M solution is 5. Its dissociation constant would be :-

[AIEEE-2011]

- (1)  $1 \times 10^{-10}$
- (2) 5
- (3)  $5 \times 10^{-8}$
- (4)  $1 \times 10^{-5}$

IE0172

Q.14 If  $K_{sp}$  of  $CaF_2$  at  $25^\circ C$  is  $1.7 \times 10^{-10}$ , the combination amongst the following which gives a precipitate of  $CaF_2$  is :-

[JEE-MAIN(online)-2012]

- (1)  $1 \times 10^{-2}$  M  $Ca^{2+}$  and  $1 \times 10^{-5}$  M  $F^-$
- (2)  $1 \times 10^{-4}$  M  $Ca^{2+}$  and  $1 \times 10^{-4}$  M  $F^-$
- (3)  $1 \times 10^{-3}$  M  $Ca^{2+}$  and  $1 \times 10^{-5}$  M  $F^-$
- (4)  $1 \times 10^{-2}$  M  $Ca^{2+}$  and  $1 \times 10^{-3}$  M  $F^-$

IE0173

Q.15 The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant,  $K_a$  of this acid is :-

[AIEEE-2012]

- (1)  $1 \times 10^{-7}$
- (2)  $3 \times 10^{-7}$
- (3)  $1 \times 10^{-3}$
- (4)  $1 \times 10^{-5}$

IE0174

Q.16 How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ?

[AIEEE-2013]

- (1) 0.1 L
- (2) 0.9 L
- (3) 2.0 L
- (4) 9.0 L

IE0175

Q.17 Solid  $Ba(NO_3)_2$  is gradually dissolved in a  $1.0 \times 10^{-4}$  M  $Na_2CO_3$  solution. At which concentration of  $Ba^{2+}$ , precipitate of  $BaCO_3$  begins to form ? ( $K_{sp}$  for  $BaCO_3 = 5.1 \times 10^{-9}$ )

- (1)  $5.1 \times 10^{-5}$  M
- (2)  $8.1 \times 10^{-7}$  M

[JEE-MAIN(Online)-2013]

- (3)  $4.1 \times 10^{-5}$  M
- (4)  $7.1 \times 10^{-8}$  M

IE0176

Q.18 NaOH is a strong base. What will be pH of  $5.0 \times 10^{-2}$  M NaOH solution ? ( $\log 2 = 0.3$ )

[JEE-MAIN(Online)-2013]

- (1) 13.70      (2) 13.00      (3) 14.00      (4) 12.70

IE0177

Q.19 Which one of the following arrangements represents the correct order of solubilities of sparingly soluble salts  $\text{Hg}_2\text{Cl}_2$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{BaSO}_4$  and  $\text{CrCl}_3$  respectively ?

[JEE-MAIN(Online)-2013]

- (1)  $\left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$ ,  $\left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$ ,  $(K_{sp})^{\frac{1}{2}}$ ,  $\left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$       (2)  $(K_{sp})^{\frac{1}{2}}$ ,  $\left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$ ,  $\left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$ ,  $\left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$   
 (3)  $(K_{sp})^{\frac{1}{2}}$ ,  $\left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$ ,  $\left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$ ,  $\left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$       (4)  $\left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$ ,  $\left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$ ,  $(K_{sp})^{\frac{1}{2}}$ ,  $\left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$

IE0178

Q.20 What would be the pH of a solution obtained by mixing 5 g of acetic acid and 7.5 g of sodium acetate and making the volume equal to 500 mL?

[JEE-MAIN(Online)-2013]

( $K_a = 1.75 \times 10^{-5}$ ,  $pK_a = 4.76$ )

- (1)  $4.76 < \text{pH} < 5.0$       (2)  $\text{pH} < 4.70$   
 (3) pH of solution will be equal to pH of acetic acid      (4)  $\text{pH} = 4.70$

IE0179

Q.21 In some solutions, the concentration of  $\text{H}_3\text{O}^+$  remains constant even when small amounts of strong acid or strong base are added to them. These solutions are known as :-

[JEE-MAIN(Online)-2014]

- (1) Colloidal solutions      (2) True solutions  
 (3) Ideal solutions      (4) Buffer solutions

IE0180

Q.22 Zirconium phosphate  $[\text{Zr}_3(\text{PO}_4)_4]$  dissociates into three zirconium cations of charge +4 and four phosphate anions of charge -3. If molar solubility of zirconium phosphate is denoted by S and its solubility product by  $K_{sp}$  then which of the following relationship between S and  $K_{sp}$  is correct ?

- (1)  $S = \{K_{sp}/144\}^{1/7}$       (2)  $S = \{K_{sp}/(6912)^{1/7}\}$  [JEE-MAIN(Online)-2014]  
 (3)  $S = (K_{sp}/6912)^{1/7}$       (4)  $S = \{K_{sp}/6912\}^7$

IE0181

Q.23  $pK_a$  of a weak acid (HA) and  $pK_b$  of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is

[JEE-MAIN(Offline)-2017]

- (1) 7.2      (2) 6.9      (3) 7.0      (4) 1.0

IE0182

Q.24 Addition of sodium hydroxide solution to a weak acid (HA) results in a buffer of pH 6. If ionisation constant of HA is  $10^{-5}$ , the ratio of salt to acid concentration in the buffer solution will be :

[JEE-MAIN(Online)-2017]

- (1) 4 : 5      (2) 1 : 10      (3) 10 : 1      (4) 5 : 4

IE0183



Q.25 50 mL of 0.2 M ammonia solution is treated with 25 mL of 0.2 M HCl. If  $pK_b$  of ammonia solution is 4.75, the pH of the mixture will be:- [JEE-MAIN(Online)-2017]

- (1) 8.25            (2) 4.75            (3) 9.25            (4) 3.75

IE0184

Q.26 Which of the following salts is the most basic in aqueous solution ? [JEE-MAIN(Offline)-2018]

- (1)  $\text{CH}_3\text{COOK}$     (2)  $\text{FeCl}_3$             (3)  $\text{Pb}(\text{CH}_3\text{COO})_2$     (4)  $\text{Al}(\text{CN})_3$

IE0185

Q.27 An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination ?

Base	Acid	End point	[JEE-MAIN(Offline)-2018]
(1) Strong	Strong	Pinkish red to yellow	
(2) Weak	Strong	Yellow to pinkish red	
(3) Strong	Strong	Pink to colourless	
(4) Weak	Strong	Colourless to pink	

IE0186

Q.28 An aqueous solution contains 0.10 M  $\text{H}_2\text{S}$  and 0.20 M HCl. If the equilibrium constants for the formation of  $\text{HS}^-$  from  $\text{H}_2\text{S}$  is  $1.0 \times 10^{-7}$  and that of  $\text{S}^{2-}$  from  $\text{HS}^-$  ions is  $1.2 \times 10^{-13}$  then the concentration of  $\text{S}^{2-}$  ions in aqueous solution is :

- (1)  $3 \times 10^{-20}$             (2)  $6 \times 10^{-21}$             (3)  $5 \times 10^{-19}$             (4)  $5 \times 10^{-8}$

[JEE-MAIN(Offline)-2018]

IE0187

Q.29 A aqueous solution contains an unknown concentration of  $\text{Ba}^{2+}$ . When 50 mL of a 1 M solution of  $\text{Na}_2\text{SO}_4$  is added,  $\text{BaSO}_4$  just begins to precipitate. The final volume is 500 mL. The solubility product of  $\text{BaSO}_4$  is  $1 \times 10^{-10}$ . What is the original concentration of  $\text{Ba}^{2+}$  ? [JEE-MAIN(Offline)-2018]

- (1)  $2 \times 10^{-9}$  M            (2)  $1.1 \times 10^{-9}$  M            (3)  $1.0 \times 10^{-10}$  M            (4)  $5 \times 10^{-9}$  M

IE0188

Q.30 Following four solutions are prepared by mixing different volumes of NaOH and HCl of different concentrations, pH of which one of them will be equal to 1 ? [JEE-MAIN(Online)-2018]

- (1)  $75\text{mL} \frac{M}{5} \text{HCl} + 25\text{mL} \frac{M}{5} \text{NaOH}$             (2)  $100\text{mL} \frac{M}{10} \text{HCl} + 100\text{mL} \frac{M}{10} \text{NaOH}$   
 (3)  $55\text{mL} \frac{M}{10} \text{HCl} + 45\text{mL} \frac{M}{10} \text{NaOH}$             (4)  $60\text{mL} \frac{M}{10} \text{HCl} + 40\text{mL} \frac{M}{10} \text{NaOH}$

IE0189

Q.31 The minimum volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution ( $K_{sp}$  of  $\text{PbCl}_2 = 3.2 \times 10^{-8}$ ; atomic mass of Pb = 207 u) is : [JEE-MAIN(Online)-2018]

- (1) 0.36 L            (2) 0.18 L            (3) 17.98 L            (4) 1.798 L

IE0190

Q.32 If  $K_{sp}$  of  $Ag_2CO_3$  is  $8 \times 10^{-12}$ , the molar solubility of  $Ag_2CO_3$  in 0.1 M  $AgNO_3$  is :

- (1)  $8 \times 10^{-12}$  M (2)  $8 \times 10^{-10}$  M [JEE-MAIN(Online)-2019]  
 (3)  $8 \times 10^{-11}$  M (4)  $8 \times 10^{-13}$  M

IE0240

Q.33 25 ml of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution?

- (1) 25 mL (2) 50 mL [JEE-MAIN(Online)-2019]  
 (3) 12.5 mL (4) 75 mL

IE0241

Q.34 A mixture of 100 m mol of  $Ca(OH)_2$  and 2g of sodium sulphate was dissolved in water and the volume was made up to 100 mL. The mass of calcium sulphate formed and the concentration of  $OH^-$  in resulting solution, respectively, are : (Molar mass of  $Ca(OH)_2$ ,  $Na_2SO_4$  and  $CaSO_4$  are 74, 143 and  $136 \text{ g mol}^{-1}$ , respectively;  $K_{sp}$  of  $Ca(OH)_2$  is  $5.5 \times 10^{-6}$ )

- (1) 1.9 g,  $0.14 \text{ mol L}^{-1}$  (2) 13.6 g,  $0.14 \text{ mol L}^{-1}$  [JEE-MAIN(Online)-2019]  
 (3) 1.9 g,  $0.28 \text{ mol L}^{-1}$  (4) 13.6 g,  $0.28 \text{ mol L}^{-1}$

IE0242

Q.35 The pH of rain water, is approximately :

[JEE-MAIN(Online)-2019]

- (1) 6.5 (2) 7.5 (3) 5.6 (4) 7.0

IE0243

Q.36 20 mL of 0.1 M  $H_2SO_4$  solution is added to 30 mL of 0.2 M  $NH_4OH$  solution. The pH of the resultant mixture is : [ $pK_b$  of  $NH_4OH = 4.7$ ].

[JEE-MAIN(Online)-2019]

- (1) 9.4 (2) 5.0 (3) 9.0 (4) 5.2

IE0244

Q.37 If solubility product of  $Zr_3(PO_4)_4$  is denoted by  $K_{sp}$  and its molar solubility is denoted by S, then which of the following relation between S and  $K_{sp}$  is correct

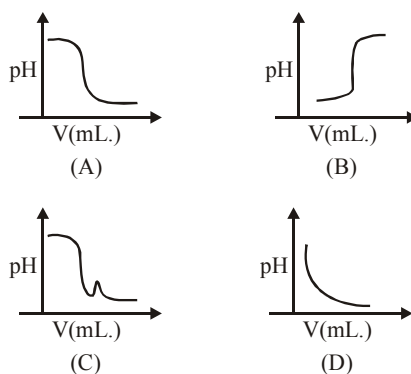
[JEE-MAIN(Online)-2019]

- (1)  $S = \left(\frac{K_{sp}}{929}\right)^{1/9}$  (2)  $S = \left(\frac{K_{sp}}{216}\right)^{1/7}$  (3)  $S = \left(\frac{K_{sp}}{144}\right)^{1/6}$  (4)  $S = \left(\frac{K_{sp}}{6912}\right)^{1/7}$

IE0245

Q.38 In an acid-base titration, 0.1 M HCl solution was added to the NaOH solution of unknown strength. Which of the following correctly shows the change of pH of the titration mixture in this experiment?

[JEE-MAIN(Online)-2019]



- (1) (A) (2) (C) (3) (D) (4) (B)

IE0246

- Q.39 The pH of a 0.02M  $\text{NH}_4\text{Cl}$  solution will be [JEE-MAIN(Online)-2019]  
 [given  $K_b(\text{NH}_4\text{OH})=10^{-5}$  and  $\log 2=0.301$ ]  
 (1) 4.65 (2) 5.35 (3) 4.35 (4) 2.65

IE0247

- Q.40 The molar solubility of  $\text{Cd}(\text{OH})_2$  is  $1.84 \times 10^{-5}$  M in water. The expected solubility of  $\text{Cd}(\text{OH})_2$  in a buffer solution of pH = 12 is : [JEE-MAIN(Online)-2019]  
 (1)  $6.23 \times 10^{-11}$  M (2)  $1.84 \times 10^{-9}$  M (3)  $\frac{2.49}{1.84} \times 10^{-9}$  M (4)  $2.49 \times 10^{-10}$  M

IE0248

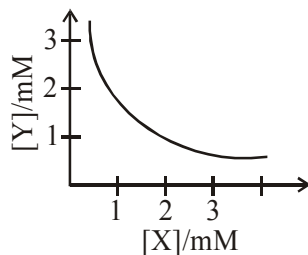
- Q.41 Two solutions A and B, each of 100 L was made by dissolving 4g of NaOH and 9.8 g of  $\text{H}_2\text{SO}_4$  in water, respectively. The pH of the resultant solution obtained from mixing 40 L of solution A and 10 L of solution B is \_\_\_\_\_. [JEE-MAIN(Online)-2020]

IE0249

- Q.42 3g of acetic acid is added to 250 mL of 0.1 M HCl and the solution made up to 500 mL. To 20 mL of this solution  $\frac{1}{2}$  mL of 5 M NaOH is added. The pH of the solution is [JEE-MAIN(Online)-2020]  
 [Given :  $\text{p}K_a$  of acetic acid = 4.75, molar mass of acetic acid = 60 g/mol,  $\log 3 = 0.4771$ ]  
 Neglect any changes in volume

IE0250

- Q.43 The stoichiometry and solubility product of a salt with the solubility curve given below is, respectively : [JEE-MAIN(Online)-2020]



- (1)  $\text{X}_2\text{Y}$ ,  $2 \times 10^{-9}\text{M}^3$  (2)  $\text{XY}_2$ ,  $1 \times 10^{-9}\text{M}^3$   
 (3)  $\text{XY}_2$ ,  $4 \times 10^{-9}\text{M}^3$  (4)  $\text{XY}$ ,  $2 \times 10^{-6}\text{M}^3$

IE0251

- Q.44 For the following Assertion and Reason, the correct option is : [JEE-MAIN(Online)-2020]

Assertion : The pH of water increases with increase in temperature.

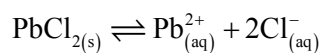
Reason : The dissociation of water into  $\text{H}^+$  and  $\text{OH}^-$  is an exothermic reaction.

- (1) Both assertion and reason are true, but the reason is not the correct explanation for the assertion.  
 (2) Both assertion and reason are false.  
 (3) Assertion is not true, but reason is true.  
 (4) Both assertion and reason are true, and the reason is the correct explanation for the assertion.

IE0252

Q.45 The  $K_{sp}$  for the following dissociation is  $1.6 \times 10^{-5}$

[JEE-MAIN(Online)-2020]



Which of the following choices is correct for a mixture of 300 mL 0.134 M  $\text{Pb}(\text{NO}_3)_2$  and 100 mL 0.4 M NaCl ?

- (1)  $Q < K_{sp}$                       (2)  $Q > K_{sp}$                       (3)  $Q = K_{sp}$                       (4) Not enough data provided

IE0253

Q.46 The solubility product of  $\text{Cr}(\text{OH})_3$  at 298 K is  $6.0 \times 10^{-31}$ . The concentration of hydroxide ions in a saturated solution of  $\text{Cr}(\text{OH})_3$  will be :

- (1)  $(18 \times 10^{-31})^{1/4}$                       (2)  $(2.22 \times 10^{-31})^{1/4}$   
(3)  $(4.86 \times 10^{-29})^{1/4}$                       (4)  $(18 \times 10^{-31})^{1/2}$

[JEE-MAIN(Online)-2020]

IE0254

## EXERCISE # J-ADVANCE

- Q.1 What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12.0) ? [JEE '1998]  
IE0255
- Q.2 The pH of 0.1 M solution of the following salts increases in the order [JEE 1999]  
(A) NaCl < NH<sub>4</sub>Cl < NaCN < HCl (B) HCl < NH<sub>4</sub>Cl < NaCl < NaCN  
(C) NaCN < NH<sub>4</sub>Cl < NaCl < HCl (D) HCl < NaCl < NaCN < NH<sub>4</sub>Cl  
IE0256
- Q.3 A buffer solution can be prepared from a mixture of [JEE 1999]  
(A) sodium acetate and acetic acid in water  
(B) sodium acetate and hydrochloric acid in water  
(C) ammonia and ammonium chloride in water  
(D) ammonia and sodium hydroxide in water.  
IE0257
- Q.4 The solubility of Pb(OH)<sub>2</sub> in water is  $6.7 \times 10^{-6}$  M. Calculate the solubility of Pb(OH)<sub>2</sub> in a buffer solution of pH = 8. [JEE '1999]  
IE0258
- Q.5 The average concentration of SO<sub>2</sub> in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO<sub>2</sub> in water at 298 K is 1.3653 moles litre<sup>-1</sup> and the pK<sub>a</sub> of H<sub>2</sub>SO<sub>3</sub> is 1.92, estimate the pH of rain on that day. [JEE 2000]  
[Given :  $10^{-1.92} = 1.2 \times 10^{-2}$ ,  $\sqrt{5.5678} = 2.5627$ ,  $\log(1.2213) = 0.0868$ ]  
IE0259
- Q.6 For sparingly soluble salt ApBq, the relationship of its solubility product (L<sub>s</sub>) with its solubility (S) is - [JEE 2001]  
(A) L<sub>s</sub> = S<sup>p+q</sup>. p<sup>p</sup>. q<sup>q</sup> (B) L<sub>s</sub> = S<sup>p+q</sup>. p<sup>p</sup>. q<sup>p</sup> (C) L<sub>s</sub> = S<sup>pq</sup>. p<sup>p</sup>. q<sup>q</sup> (D) L<sub>s</sub> = S<sup>pq</sup>. (p.q)<sup>p+q</sup>  
IE0260
- Q.7 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.  
(a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.  
(b) If 6 g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing. K<sub>a</sub> of acetic acid is  $1.75 \times 10^{-5}$  M. [JEE 2002]  
IE0261
- Q.8 A solution which is 10<sup>-3</sup> M each in Mn<sup>2+</sup>, Fe<sup>2+</sup>, Zn<sup>2+</sup> and Hg<sup>2+</sup> is treated with 10<sup>-16</sup> M sulphide ion. If K<sub>sp</sub>, MnS, FeS, ZnS and HgS are 10<sup>-15</sup>, 10<sup>-23</sup>, 10<sup>-20</sup> and 10<sup>-54</sup> respectively, which one will precipitate first ? [JEE 2003]  
(A) FeS (B) MnS (C) HgS (D) ZnS  
IE0262
- Q.9 Will the pH of water be same at 4°C and 25°C ? Explain. [JEE 2003]  
IE0263

- Q.10 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point. Given  $K_a(\text{HA}) = 5 \times 10^{-6}$  and  $\alpha \ll 1$ .  
[JEE 2004] IE0264
- Q.11 HX is a weak acid ( $K_a = 10^{-5}$ ). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is  
(A) 0.01% (B) 0.0001% (C) 0.1% (D) 0.5% [JEE 2004] IE0265
- Q.12  $\text{CH}_3\text{NH}_2$  (0.1 mole,  $K_b = 5 \times 10^{-4}$ ) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is  
(A)  $1.6 \times 10^{-11}$  (B)  $8 \times 10^{-11}$  (C)  $5 \times 10^{-5}$  (D)  $2 \times 10^{-2}$  [JEE 2005] IE0266
- Q.13 If  $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)]^+$ ;  $K_1 = 1.6 \times 10^3$  and  $[\text{Ag}(\text{NH}_3)]^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$ ;  $K_2 = 6.8 \times 10^3$ .  
The formation constant of  $[\text{Ag}(\text{NH}_3)_2]^+$  is :  
(A)  $6.08 \times 10^{-6}$  (B)  $6.8 \times 10^{-6}$  (C)  $1.6 \times 10^3$  (D)  $1.088 \times 10^7$  [JEE 2006] IE0267
- Q.14 The species present in solution when  $\text{CO}_2$  is dissolved in water :  
(A)  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  (B)  $\text{H}_2\text{CO}_3$ ,  $\text{CO}_3^{2-}$  [JEE 2006] IE0268  
(C)  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  (D)  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$
- Q.15 2.5 mL of  $\frac{2}{5}$  M weak monoacidic base ( $K_b = 1 \times 10^{-12}$  at  $25^\circ\text{C}$ ) is titrated with  $\frac{2}{15}$  M HCl in water at  $25^\circ\text{C}$ . The concentration of  $\text{H}^+$  at equivalence point is  
( $K_w = 1 \times 10^{-14}$  at  $25^\circ\text{C}$ ) [JEE 2008] IE0269  
(A)  $3.7 \times 10^{-13}$  M (B)  $3.2 \times 10^{-7}$  M (C)  $3.2 \times 10^{-2}$  M (D)  $2.7 \times 10^{-2}$  M
- Q.16 Solubility product constants ( $K_{sp}$ ) of salts of types MX,  $\text{MX}_2$  and  $\text{M}_3\text{X}$  at temperature 'T' are  $4.0 \times 10^{-8}$ ,  $3.2 \times 10^{-14}$  and  $2.7 \times 10^{-15}$ , respectively. Solubilities ( $\text{mol dm}^{-3}$ ) of the salts at temperature 'T' are in the order :  
(A)  $\text{MX} > \text{MX}_2 > \text{M}_3\text{X}$  (B)  $\text{M}_3\text{X} > \text{MX}_2 > \text{MX}$  [JEE 2008] IE0270  
(C)  $\text{MX}_2 > \text{M}_3\text{X} > \text{MX}$  (D)  $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$
- Q.17 The dissociation constant of a substituted benzoic acid at  $25^\circ\text{C}$  is  $1.0 \times 10^{-4}$ . The pH of a 0.01 M solution of its sodium salt is [JEE 2009] IE0271
- Q.18 Aqueous solutions of  $\text{HNO}_3$ , KOH,  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$  of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are) –  
(A)  $\text{HNO}_3$  and  $\text{CH}_3\text{COOH}$  (B) KOH and  $\text{CH}_3\text{COONa}$  IE0272  
(C)  $\text{HNO}_3$  and  $\text{CH}_3\text{COONa}$  (D)  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$

- Q.19 In 1 L saturated solution of AgCl [ $K_{sp}(\text{AgCl}) = 1.6 \times 10^{-10}$ ], 0.1 mol of CuCl [ $K_{sp}(\text{CuCl}) = 1.0 \times 10^{-6}$ ] is added. The resultant concentration of  $\text{Ag}^+$  in the solution is  $1.6 \times 10^{-x}$ . The value of 'x' is. [JEE -2011]  
IE0196
- Q.20 The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is  $1/100^{\text{th}}$  of that of a strong acid (HX, 1M), at  $25^\circ\text{C}$ . The  $K_a$  of HA is [JEE 2013]  
(A)  $1 \times 10^{-4}$  (B)  $1 \times 10^{-5}$  (C)  $1 \times 10^{-6}$  (D)  $1 \times 10^{-3}$   
IE0197
- Q.21 The  $K_{sp}$  of  $\text{Ag}_2\text{CrO}_4$  is  $1.1 \times 10^{-12}$  at 298 K. The solubility (in mol/L) of  $\text{Ag}_2\text{CrO}_4$  in a 0.1 M  $\text{AgNO}_3$  solution is [JEE 2013]  
(A)  $1.1 \times 10^{-11}$  (B)  $1.1 \times 10^{-10}$  (C)  $1.1 \times 10^{-12}$  (D)  $1.1 \times 10^{-9}$   
IE0198

### Paragraph For Questions 22 and 23

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of  $5.7^\circ\text{C}$  was measured for the beaker and its contents. (**Expt-1**). Because the enthalpy of neutralisation of a strong acid with a strong base is a constant ( $-57.0 \text{ kJ mol}^{-1}$ ), this experiment could be used to measure the calorimeter constant. In a second experiment (**Expt-2**), 100 mL of 2.0 M acetic acid ( $K_a = 2.0 \times 10^{-5}$ ) was mixed with 100 mL of 1.0M NaOH (under identical conditions to (**Expt-1**)) where a temperature rise of  $5.6^\circ\text{C}$  was measured.

(Consider heat capacity of all solutions as  $4.2 \text{ J g}^{-1}\text{K}^{-1}$  and density of all solutions as  $1.0 \text{ g mL}^{-1}$ )

- Q.22 Enthalpy of dissociation (in  $\text{kJ mol}^{-1}$ ) of acetic acid obtained from the **Expt-2** is [JEE 2015]  
(A) 1.0 (B) 10.0 (C) 24.5 (D) 51.4  
IE0199
- Q.23 The pH of the solution after **Expt-2**  
(A) 2.8 (B) 4.7 (C) 5.0 (D) 7.0  
IE0200
- Q.24 The solubility of a salt of weak acid (AB) at pH 3 is  $Y \times 10^{-3} \text{ mol L}^{-1}$ . The value of Y is \_\_\_\_.  
(Given that the value of solubility product of AB ( $K_{sp}$ ) =  $2 \times 10^{-10}$  and the value of ionization constant of HB ( $K_a$ ) =  $1 \times 10^{-8}$ ) [JEE 2018]  
IE0201





Q.58 Ans.  $[F^-] = 3 \times 10^{-3}M$ Q.59 Ans.  $8 \times 10^{-3} M$ Q.60 Ans. (i)  $2 \times 10^{-9}$  , (ii)  $8 \times 10^{-3}$ Q.61 Ans.  $S = 2 \times 10^{-4} M$ , pH = 8.0Q.62 Ans.  $4 \times 10^{-2}M$ 

Q.63 Ans. (a) no precipitation will occur, (b) a precipitate will form

Q.64 Ans. No.

Q.65 Ans. 0.284 gm

**EXERCISE # S-II**Q.1 Ans. 0.209 M, 0.191 M,  $9.13 \times 10^{-3} M$ , 0Q.2 Ans. pH = 11.48 ,  $[enH_2^{2+}] = 7.1 \times 10^{-8} M$ 

Q.3 Ans. 10.6

Q.4 Ans.  $[S^{2-}] = 2.5 \times 10^{-15}M$ Q.5 Ans. ( $2 \times 10^{-4}M$ )

Q.6 Ans. pH = 10.52

Q.7 Ans.  $[OH^-] = 3.73 \times 10^{-2}M$ ,  $[H_3PO_4] = 6 \times 10^{-18}M$ 

Q.8 Ans. 8.35, 9.60, 4.66

Q.9 Ans.(9.6)

Q.10 Ans.  $K_b \approx 1.73 \times 10^{-5}$ , 5.27Q.11 Ans.  $K_a \approx 1.73 \times 10^{-5}$ , 8.73Q.12 Ans. ( $10^{-5}M$ )Q.13. Ans. ( $10^{-3}M$ )

Q.14 Ans. pH = 7.9 , pH = 7.3

Q.15 Ans.  $2.8 \times 10^{-3}$  moleQ.16 Ans.  $1.6 \times 10^{-3}$ Q.17 Ans.  $K_d = 1/K_f = 4.8 \times 10^{-4}$ **EXERCISE # O-I**

Q.1 Ans.(A)

Q.2 Ans.(B)

Q.3 Ans.(C)

Q.4 Ans.(C)

Q.5 Ans.(B)

Q.6 Ans.(C)

Q.7 Ans.(D)

Q.8 Ans.(D)

Q.9 Ans.(C)

Q.10 Ans.(C)

Q.11. Ans (C)

Q.12 Ans.(D)

Q.13 Ans.(B)

Q.14 Ans.(B)

Q.15 Ans.(C)

Q.16 Ans.(C)

Q.17 Ans.(B)

Q.18. Ans.(C)

Q.19 Ans.(C)

Q.20 Ans.(B)

Q.21 Ans.(B)

Q.22 Ans.(D)

Q.23 Ans.(D)

Q.24 Ans.(C)

Q.25 Ans.(C)

Q.26 Ans.(C)

Q.27 Ans.(B)

Q.28 Ans.(B)

Q.29 Ans.(A)

Q.30 Ans.(D)

Q.31 Ans.(B)

Q.32 Ans.(C)

Q.33 Ans.(C)

Q.34 Ans.(C)

Q.35 Ans.(B)

Q.36 Ans.(C)

Q.37 Ans.(D)

Q.38 Ans.(A)

Q.39 Ans.(C)

Q.40 Ans.(C)

Q.41 Ans.(C)

Q.42 Ans.(B)

Q.43 Ans.(C)

Q.44 Ans.(D)

Q.45 Ans.(A)

Q.46 Ans.(B)

Q.47 Ans.(D)

Q.48 Ans.(B)

Q.49 Ans.(C)

Q.50 Ans.(A)

Q.51 Ans.(C)

Q.52 Ans.(A)

Q.53 Ans.(A)

Q.54. Ans.(A)

Q.55. Ans.(B)

Q.56 Ans.(D)

Q.57 Ans.(A)

Q.58 Ans.(A)	Q.59 Ans.(B)	Q.60 Ans.(C)
Q.61 Ans.(D)	Q.62 Ans.(A)	Q.63 Ans.(D)
Q.64 Ans.(C)	Q.65 Ans.(D)	Q.66 Ans.(D)
Q.67 Ans.(D)	Q.68 Ans.(C)	Q.69 Ans.(A)
Q.70.Sol.(C)	Q.71. Ans.(B)	Q.72. Ans.(B)
Q.73 Ans.(D)	Q.74 Ans.(B)	Q.75 Ans.(B)

### EXERCISE # O-II

Q.1 Ans.(A)	Q.2 Ans.(C)	Q.3 Ans.(D)
Q.4 Ans.(B)	Q.5 Ans (C)	Q.6 Ans.(A)
Q.7 Ans.(A)	Q.8 Ans.(B)	Q.9 Ans.(D)
Q.10 Ans.(A)	Q.11 Ans. (A,B,C)	Q.12 Ans.(A,B,C,D)
Q.13 Ans.(B,C)	Q.14 Ans. (A, B, D)	Q.15 Ans. (D)
Q.16 Ans.(A)	Q.17 Ans. (A)	Q.18 Ans (B)
Q.19 Ans (B)	Q.20 Ans (B)	Q.21 Ans. (C)
Q.22 Ans. (A)		
Q.23 Ans. A - (R), B - (P), C - (Q), D - (S)		
Q.24 Ans (A) - Q; (B) - P, S; (C) - R; (D) -T		
Q.25 Ans.(D)	Q.26 Ans.(B)	Q.27 Ans.(C)

### EXERCISE # J-MAIN

Q.1 Ans.(3)	Q.2 Ans.(3)	Q.3 Ans.(4)
Q.4 Ans.(1)	Q.5 Ans.(3)	Q.6 Ans.(2)
Q.7 Ans.(3)	Q.8 Ans.(4)	Q.9 Ans.(3)
Q.10 Ans.(4)	Q.11 Ans.(3)	Q.12 Ans.(3)
Q.13 Ans.(1)	Q.14 Ans.(4)	Q.15 Ans.(4)
Q.16 Ans.(4)	Q.17 Ans.(1)	Q.18 Ans.(4)
Q.19 Ans.(1)	Q.20 Ans.(1)	Q.21 Ans.(4)
Q.22 Ans.(3)	Q.23 Ans. (2)	Q.24 Ans.(3)
Q.25 Ans.(3)	Q.26 Ans.(1)	Q.27 Ans.(2)
Q.28 Ans.(1)	Q.29 Ans.(2)	Q.30 Ans.(1)
Q.31 Ans.(2)	Q.32 Ans.(2)	Q.33 Ans.(1)
Q.34 Ans.(3)	Q.35 Ans.(3)	Q.36 Ans.(3)
Q.37 Ans.(4)	Q.38 Ans.(1)	Q.39 Ans.(2)
Q.40 Ans.(4)	Q.41 Ans.(10.60)	Q.42 Ans. (5.22 to 5.24)
Q.43 Ans.(3)	Q.44 Ans(2)	Q.45 Ans.(2)
Q.46 Ans.(1)		

**EXERCISE # J-ADVANCED**

- Q.1 Ans. pH = 11.3010      Q.2 Ans.(B)      Q.3 Ans.(A, B, C)  
Q.4 Ans.  $s = 1.203 \times 10^{-3} \text{M}$       Q.5 Ans. pH = 0.91325      Q.6 Ans.(A)  
Q.7 Ans.(a) 0.0175% , (b) 4.757      Q.8 Ans.(C)  
Q.9 Ans.No, it will be  $> 7$  at  $0^\circ\text{C}$ .      Q.10 Ans.pH = 9      Q.11 Ans.(A)  
Q.12 Ans.(B)      Q.13 Ans.(D)      Q.14 Ans.(A)  
Q.15 Ans.(D)      Q.16 Ans.(D)      Q.17 Ans.(8)  
Q.18 Ans.(C), (D)      Q.19 Ans.(7)      Q.20 Ans.(A)  
Q.21 Ans.(B)      Q.22 Ans.(A)      Q.23 Ans.(B)  
Q.24 Ans. (4.47)

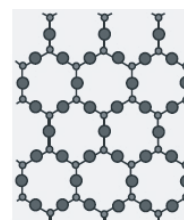
## SOLID STATE

### 1. THE SOLID STATE :

The solids are characterised by incompressibility, rigidity and mechanical strength. The molecules, atoms or ions in solids are closely packed i.e. they are held together by strong forces and can not move about at random. Thus solids have definite volume, shape, slow diffusion, low vapour pressure and possess the unique property of being rigid.

### 2. AMORPHOUS AND CRYSTALLINE SOLIDS

Solids can be classified as *crystalline* or *amorphous* on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered. It has **long range order** which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids. An amorphous solid (Greek *amorphos* = no form) consists of particles of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only **short range order**. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only.



(a)



(b)

Fig. 1.1 : Two dimensional structure of (a) quartz and (b) quartz glass

Such portions are scattered and in between, the arrangement is disordered. The structures of quartz (crystalline) and quartz glass (amorphous) are shown in Fig. 1.1 (a) and (b) respectively. While the two structures are almost identical, yet in the case of amorphous quartz glass there is no **long range order**. The structure of amorphous solids is similar to that of liquids. Glass, rubber and plastics are typical examples of amorphous solids. Due to the differences in the arrangement of the constituent particles, the two types of solids differ in their properties.

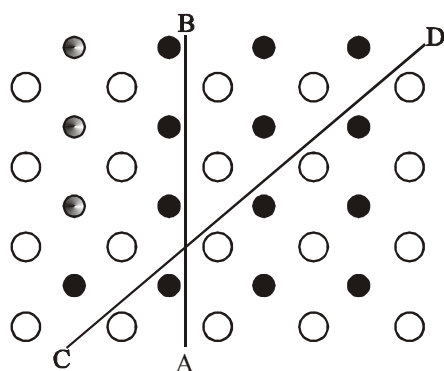


Fig. 1.2 : Anisotropy in crystals is due to different arrangement of particles along different directions.

Crystalline solids have a sharp melting point. On the other hand, amorphous solids soften over a range of temperature and can be moulded and blown into various shapes. On heating they may become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation. Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called **pseudo solids** or **super cooled liquids**. Glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

Crystalline solids are *anisotropic* in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arises from different arrangement of particles in different directions. This is illustrated in Fig. 1.2. Since the arrangement of particles is different along different directions, the value of same physical property is found to be different along each direction. Amorphous solids on the other hand are *isotropic* in nature. It is because there is no *long range* order in them and arrangement is irregular along all the directions. Therefore, value of any physical property would be same along any direction. These differences are summarised in Table below :

**Distinction between Crystalline and Amorphous Solids**

Property	Crystalline Solids	Amorphous Solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plane and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic heat of fusion	They do not have definite heat of fusion
Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Only short range order.

**Ex.1** Classify the following as amorphous or crystalline solids :

- |                        |                 |
|------------------------|-----------------|
| (a) Polyurethane       | (b) Napthalene  |
| (c) Benzoic acid       | (d) Teflon      |
| (e) Potassium nitrate  | (f) Cellophane  |
| (g) Polyvinyl chloride | (h) Fibre glass |
| (i) Copper             |                 |

**Sol.** Crystalline : (b) , (c) , (e) , (i)

Amorphous : (a) , (d) , (f) , (g) , (h)

**Note :** Polymeric substances are generally amorphous.

3. TYPES OF THE CRYSTALLINE SOLID

Types of Solid	Constituent Particles	Bonding/ Attractive forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
(1) Molecular Solids (i) Non polar	Molecules	Dispersion or London forces	Ar, CCl <sub>4</sub> , H <sub>2</sub> , I <sub>2</sub> CO <sub>2</sub>	Soft	Insulator	Very low
		Dipole-dipole	HCl, SO <sub>2</sub>	Soft	Insulator	Low
		Hydrogen bonding	H <sub>2</sub> O (ice)	Hard	Insulator	Low
(2) Ionic Solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF <sub>2</sub>	Hard but brittle	Insulator in solid state but conductors in molten state and in aqueous solutions	High
(3) Metallic Solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
(4) Covalent or network Solids	Atoms	Covalent bonding	SiO <sub>2</sub> (quartz) SiC, C (diamond) AlN,	Hard	Insulators	Very high
			C(graphite)	Soft	Conductor	

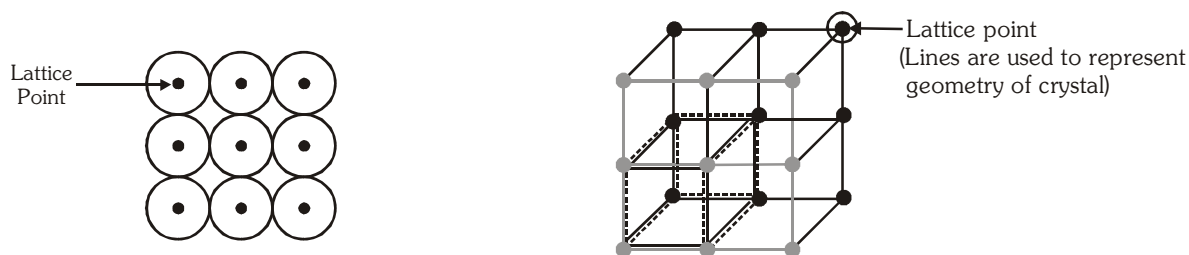
Ex.2 Classify the following solids in different categories based on the nature of intermolecular forces operating in them :

- (a) Potassium sulphate (K<sub>2</sub>SO<sub>4</sub>)
- (b) Tin (Sn)
- (c) Benzene (C<sub>6</sub>H<sub>6</sub>)
- (d) Urea (NH<sub>2</sub>CONH<sub>2</sub>)
- (e) Ammonia (NH<sub>3</sub>)
- (f) Water (H<sub>2</sub>O)
- (g) Zinc sulphide (ZnS)
- (h) Graphite (C)
- (i) Rubidium (Rb)
- (j) Argon (Ar)
- (k) Silicon carbide (SiC)
- (l) Bronze

Sol. Ionic solids : (a), (g)  
 Metallic solids : (b), (i), (l)  
 Molecular solids : (c), (d), (e), (f), (j)  
 Covalent network solids.: (h), (k)

## 4.0 SOME BASIC DEFINITION :

### 4.1 SPACE LATTICE (CRYSTAL LATTICE) :



The main characteristic of crystalline solids is a regular and repeating pattern of constituent particles. If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called crystal lattice. Thus, **a regular three dimensional arrangement of points in space is called a crystal lattice**. A portion of a crystal lattice is shown in Fig. The following are the characteristics of a crystal lattice:

- Each point in a lattice is called **lattice point** or **lattice site**.
- Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.
- Lattice points are joined by straight lines to bring out the geometry of the lattice.

### 4.2. UNIT CELL :

Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

A unit cell is characterized by the edge lengths  $a$ ,  $b$  and  $c$  along the three edges of the unit cell and the angles  $\alpha$ ,  $\beta$  and  $\gamma$  between the pair of edges :  $bc$ ,  $ca$  and  $ab$ , respectively.

#### TYPE OF UNIT CELLS -

##### 4.2.1 Primitive and Centred Unit cells

Unit cells can be broadly divided into two categories, primitive and centred unit cells.

###### (a) Primitive Unit Cells (P)

When constituent particles are present only on the corner positions of a unit cell, it is called as **primitive unit cell**.

###### (b) Centred Unit Cells

When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a centred unit cell. **Centred unit cells** are of three types:

- Body-Centred Unit Cells (I)** : Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.
- Face-Centred Unit Cells (F)** : Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.
- End-Centred Unit Cells (E)** : In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.

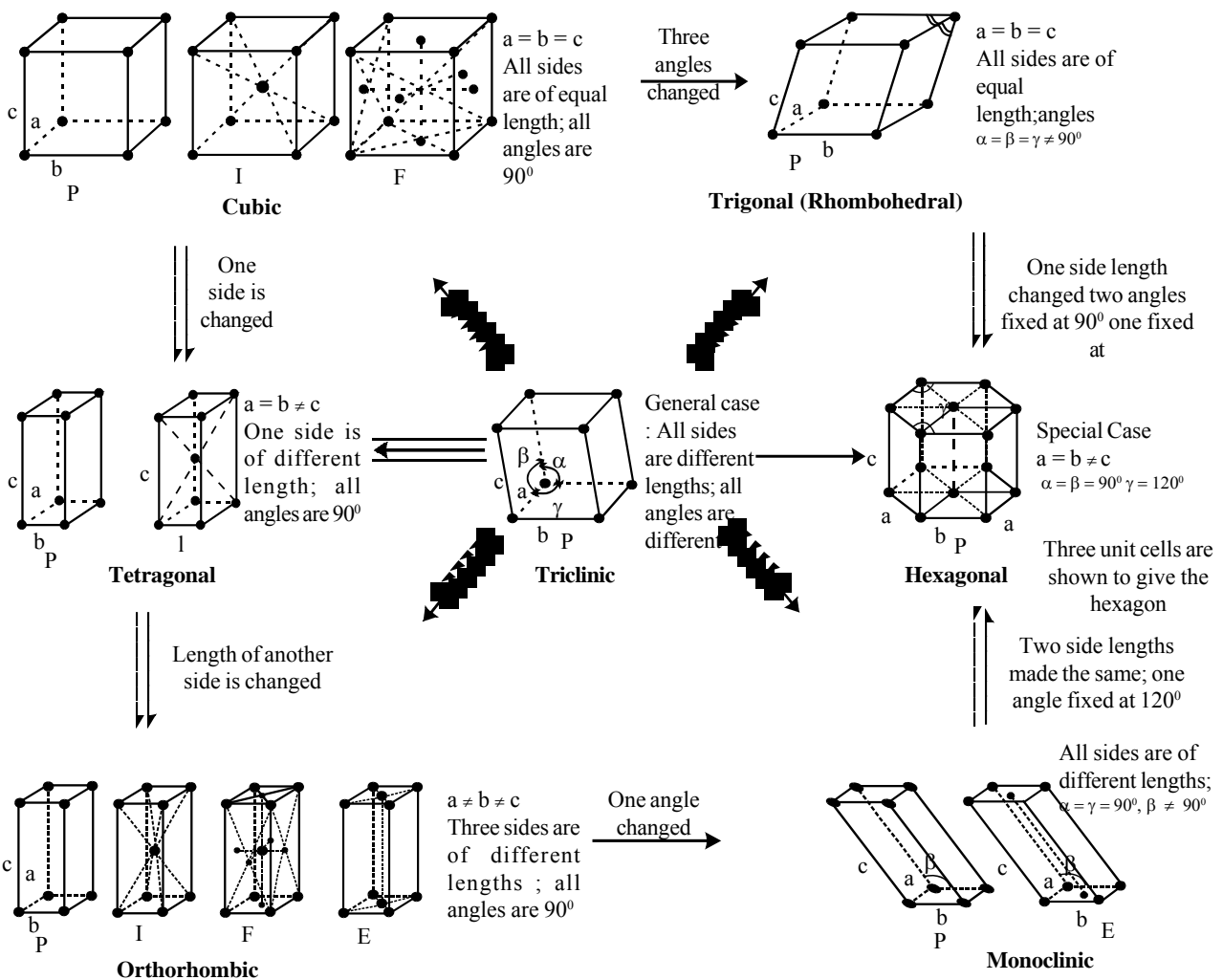
### 4.3. THE SEVEN CRYSTAL SYSTEMS

On the basis of the classification of symmetry, the lattice have been divided into seven systems. These can be grouped into 7 crystal systems. These seven systems with the characteristics of their axes (angles and intercepts) along with some examples of each are given in the following table :

Seven Primitive Unit cells and their Possible Variations as Centred Unit Cells

Crystal system	Possible Variations	Axial distance or edge lengths	Axial angles	Examples
Cubic	Primitive, body-centred, Face centre	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, $\text{SnO}_2$ , $\text{TiO}_2$ , $\text{CaSO}_4$
Orthorhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, $\text{KNO}_3$ , $\text{BaSO}_4$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Graphite, ZnO, CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite ( $\text{CaCO}_3$ ), HgS (Cinnabar)
Monoclinic	Primitive, End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$ , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , $\text{H}_3\text{BO}_3$

### 4.4. BRAVAIS LATTICES : There are 14 Bravais lattices :





**4.5. CO-ORDINATION NUMBER :**

The number of nearest particles around a specific particle in a given crystalline substance is called *co-ordination* number.

**4.6. PACKING EFFICIENCY OR PACKING DENSITY (P.E.) :**

Packing efficiency is defined as the ratio of volume occupied by the constituent particles to the total volume of the crystalline substance.

$$\text{P.E.} = \frac{\text{Volume occupied by particles present in a crystal}}{\text{Volume of crystal}}$$

$$\text{P.E.} = \frac{\text{Volume occupied by particles present in unit cell}}{\text{Volume of Unit Cell}}$$

$$\text{P.E.} = \frac{Z \times (4/3)\pi r^3}{V}, \text{ where } Z = \text{number of atoms present in unit cell}$$

**4.7. DENSITY OF THE CRYSTAL :**

$$\text{Density of crystal} = \text{Density of an unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\text{Mass of the unit cell} = \text{Number of particles present in a unit cell} \times \text{Mass of one particles} = Z \times m$$

$$\text{But mass of one particles (m)} = \frac{\text{Particle mass}}{\text{Avogadro Number}} = \frac{M}{N_A}$$

$$\text{Mass of an unit cell} = Z \times \frac{M}{N_A}$$

$$\text{Density of an unit cell} = \frac{Z \times \frac{M}{N_A}}{V}$$

$$\therefore \text{Density of Crystal, } d = \text{Density of an unit cell} = \frac{Z \times M}{V \times N_A} \text{ g cm}^{-3}$$

**5.0 ANALYSIS OF CUBIC CRYSTAL :****5.1. GEOMETRY OF A CUBE**

Number of corners = 8

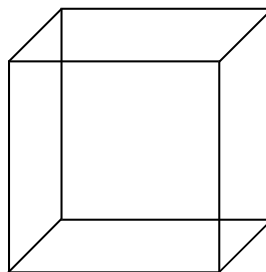
Number of faces = 6

Number of edges = 12

Number of cube centre = 1

Number of cube diagonals = 4

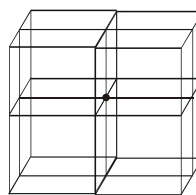
Number of face diagonals = 12



**5.2 CONTRIBUTION OF A CONSTITUENT PARTICLE AT DIFFERENT SITES OF CUBE :**

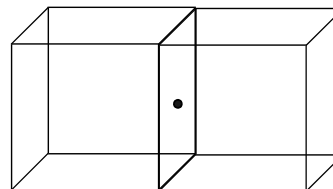
**5.2.1** A corner of a cube is common in 8 cubes.

So  $\frac{1}{8}$  th part of a particle is present at this corner of cube.



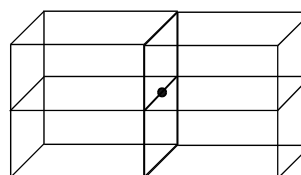
**5.2.2** A face of a cube is common in 2 cubes.

So  $\frac{1}{2}$  th part of a particle is present at the face of a cube.



**5.2.3** An edge of a cube is common in four cubes,

so  $\frac{1}{4}$  th part of particle is present at the edge of a cube

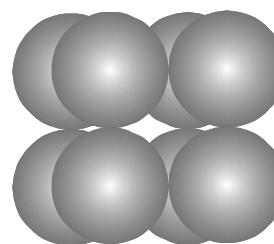
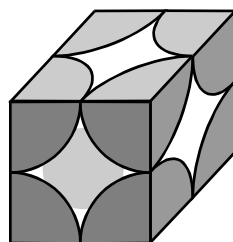
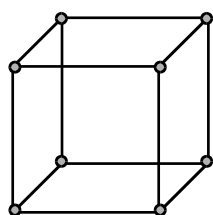


**5.3 TYPE OF CUBIC UNIT CELL :**

**5.3.1 Simple/Primitive/Basic Unit cell (Simple cubic, SC) ;**

A unit cell having lattice point only at corners called as primitive or simple unit cell. In this case there is one particle at each of the eight corners of the unit cell.

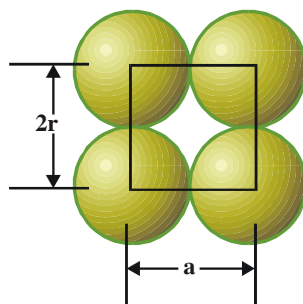
Considering a particles at one corner as the centre, it will be found that this atom is surrounded by six equidistant neighbours (particles) and thus the co-ordination number will be six. If 'a' is the side of the unit cell, then the distance between the nearest neighbours shall be equal to 'a'.



**(a) Relationship between Edge length 'a' and Particle radius 'r' :-**

i.e., 
$$a = 2r$$
  

$$r = \frac{a}{2}$$



(One face of SC)

(b) **Number of particles present in unit cell (Z) :** In this case one particle lies at each corner. Hence simple cubic unit cell contains a total of  $\frac{1}{8} \times 8 = 1$  particle /unit cell.

(c) **Packing efficiency (P. E.) :**

$$\text{P.E.} = \frac{\text{Volume occupied by particles present in unit cell}}{\text{Volume of unit cell}} = \frac{Z \times \frac{4}{3} \pi r^3}{V} \quad \left[ \text{Volume of atom} = \frac{4}{3} \pi r^3 \right]$$

$$\text{P.E.} = \frac{1 \times \frac{4}{3} \times \pi \times \left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 0.52 \text{ or } 52\% \quad \left[ r = \frac{a}{2} \text{ and } V = a^3, Z = 1 \right]$$

In SC, 52% of total volume is occupied by particles.

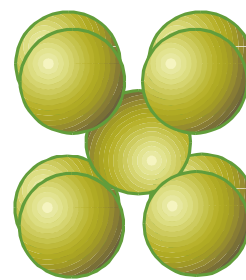
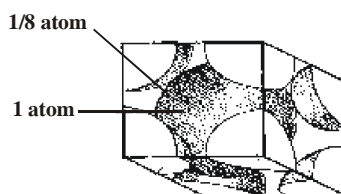
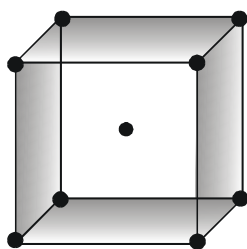
$\therefore$  Void space  $\approx (100 - 52) = 48\%$

(d) **Coordination number (CN)**

Nearest neighbour	Distance	Number
1	a	6
2	$\sqrt{2}a$	12
3	$\sqrt{3}a$	8

### 5.3.2. Body Centred Cubic unit cell (BCC):

A unit cell having lattice point at the body centre in addition to the lattice points at every corner is called as body centered unit cell. Here the central particle is surrounded by eight equidistant particles and hence the co-ordination number is eight. The nearest distance between two particles will be  $\frac{a\sqrt{3}}{2}$

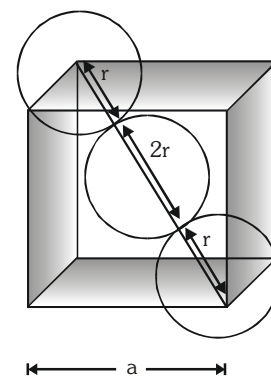


(a) **Relationship between edge length 'a' and particle radius 'r' :**

In BCC, along cube diagonal all particles touches each other and the length of cube diagonal is  $\sqrt{3}a$ .

$$\text{So, } \sqrt{3}a = 4r$$

$$\text{i.e. } r = \frac{\sqrt{3}a}{4}$$



(b) Number of particle present in unit cell (Z):

$$Z = \left(\frac{1}{8} \times 8\right) + (1 \times 1) = 1 + 1 = 2 \text{ particles/unit cell.}$$

(Corner)                      (Body centre)

In this case one particle lies at the each corner of the cube. Thus contribution of the 8 corners is  $\left(\frac{1}{8} \times 8\right) = 1$ , while that of the body centred is 1 in the unit cell. Hence total number of particles per unit cell is  $1 + 1 = 2$

(c) Packing efficiency :

$$\text{P.E.} = \frac{Z \times \frac{4}{3} \pi r^3}{V} = \frac{2 \times \frac{4}{3} \times \pi \left(\frac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68 \text{ or } 68\% \quad \left[ Z = 2, r = \frac{\sqrt{3}a}{4}, V = a^3 \right]$$

In BCC, 68% of total volume is occupied by particles.

$\therefore$  Void space =  $100 - 68 = 32\%$

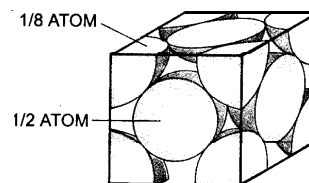
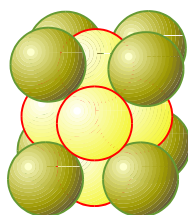
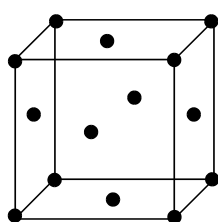
(d) Coordination number (CN)

Nearest neighbour	Distance	Number
1	$\sqrt{3} \frac{a}{2}$	8
2	a	6
3	$\sqrt{2} a$	12

5.3.3 Face Centred Cubic unit cell (FCC):

A unit cell having lattice point at every face centre in addition to the lattice point at every corner called as face centred unit cell.

In this case there are eight particles at the eight corners of the unit cell and six particles at the centre of six faces. Considering a particle at the face centre as origin, it will be found that this face is common to two cubes and there are twelve points surrounding it situated at a distance which is equal to half the face diagonal of the unit cell. Thus the co-ordination number will be twelve and the distance between the two nearest particles will be  $\frac{a}{\sqrt{2}}$ .

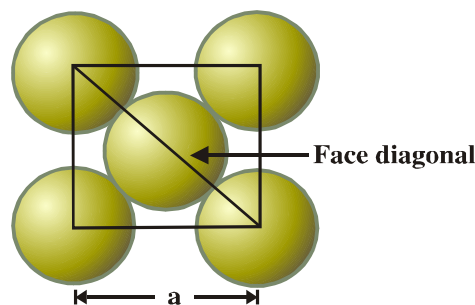


**(a) Relationship between edge length 'a' and atomic radius 'r' :**

In FCC, along the face diagonal all atoms touches each other and the length of face diagonal is  $\sqrt{2}a$ .

$$\text{So } 4r = \sqrt{2}a$$

$$\text{i.e. } r = \frac{a}{2\sqrt{2}}$$

**(b) Number of particles per unit cell : (Z)**

$$Z = \left(\frac{1}{8} \times 8\right) + \left(6 \times \frac{1}{2}\right) = 1 + 3 = 4 \text{ particles/unit cell}$$

Corner faces

In this case, one particle lies at the each corner of the cube and one particle lies at the centre of each face of the cube. It may noted that only 1/2 of each face sphere lie within the unit cell and there are six such faces. The total contribution of 8 corners is  $\left(\frac{1}{8} \times 8\right) = 1$ , while that of 6 face centred particles is  $\left(\frac{1}{2} \times 6\right) = 3$  in the unit cell.

Hence, total number of particles per unit cell is  $1 + 3 = 4$

**(c) Packing efficiency :**

$$\text{P.E.} = \frac{Z \times \frac{4}{3} \pi r^3}{V} \quad [Z = 4, r = \frac{a}{2\sqrt{2}}, V = a^3]$$

$$= \frac{4 \times \frac{4}{3} \pi \times \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

In FCC, 74% of total volume is occupied by particles. This is maximum for crystals having identical particles.

$$\therefore \text{Void space} = 100 - 74 = 26 \%$$

**(d) Coordination number (CN)**

Nearest neighbour	Distance	Number
1	$\frac{a}{\sqrt{2}}$	12
2	a	6
3	$\frac{\sqrt{3}}{2}a$	24

5.4 SUMMARY OF CUBIC CRYSTAL :

Unit cell	No. of particles per unit cell (Z)	2r =	CN	Volume occupied by particles (%)
Simple cube(SC)	1	a	6	52
Body centred cube(BCC)	2	$\frac{a\sqrt{3}}{2}$	8	68
Face centred cube(FCC)	4	$\frac{a}{\sqrt{2}}$	12	74

**Ex.3.** An element (atomic mass = 60) having face centred cubic crystal has a density of  $6.23 \text{ g cm}^{-3}$ . What is the edge length of the unit cell ? (Avogadro constant,  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ )

**Sol.** Since element has fcc structure hence there are 4 atoms in a unit cell ( $Z = 4$ ), Atomic mass is 60 ( $M = 60$ ),  $N_A = 6.02 \times 10^{23}$  and  $d = 6.23 \text{ g cm}^{-3}$ .

$$\therefore d = \frac{Z \times M}{V \times N_A}$$

$$\text{or } V = \frac{Z \times M}{d \times N_A} = \frac{(4) (60 \text{ g mol}^{-1})}{(6.23 \text{ g cm}^{-3})(6.02 \times 10^{23} \text{ mol}^{-1})}$$

$$= 64 \times 10^{-24} \text{ cm}^3$$

Let  $\ell$  be the length of the edge of the unit cell.

$$\therefore \ell^3 = V = 64 \times 10^{-24} \text{ cm}^3 \quad \text{or} \quad \ell = 4.0 \times 10^{-8} \text{ cm}$$

**Ex.4.** The density of Al is  $5.4 \text{ g/cm}^3$ . If it crystallise in fcc lattice, determine its atomic radius.

**Sol.**  $d = \frac{ZM}{N_A \cdot V} \Rightarrow 5.4 = \frac{4 \times 27}{N_A \times (2\sqrt{2}r)^3}$

$$\therefore r = 1.136 \times 10^{-8} \text{ cm} = 1.136 \text{ \AA}$$

**Ex.5.** A solid crystallises in cubic crystal in which 'X' atoms occupy all the corners and body centres and 'Y' atoms occupy all the face-centres. What is the simplest formula of solid?

**Sol.**  $Z_X = 8 \times \frac{1}{8} + 1 = 2$

$$Z_Y = 6 \times \frac{1}{2} = 3$$

$$\therefore \text{Simplest formula of solid} = X_2Y_3$$

## 6. CLOSE PACKING OF IDENTICAL SOLID SPHERES

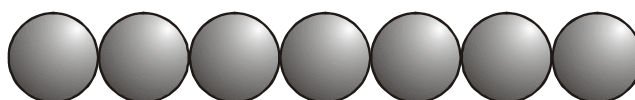
The solids which have non-directional bonding, their structures are determined on the basis of geometrical consideration. For such solids, it is found that the lowest energy structure is that in which each particle is surrounded by the greatest possible number of neighbours. In order to understand the structure of such solids, let us consider the particles as hard sphere of equal size in three directions. Although there are many ways to arrange the hard spheres but the one in which maximum available space is occupied will be economical which is known as **closed packing**.

To clearly understand the packing of these spheres, the packing can be categorised as :

- (i) Close packing in one dimension.
- (ii) Close packing in two dimension.
- (iii) Close packing in three dimension.

### 6.1 CLOSE PACKING IN ONE DIMENSION :

In one dimension , only one arrangement of spheres is possible as shown in fig.



Close packing of spheres in one dimension

Each sphere is touched by other two spheres, hence coordination numbers of packing is two.

### 6.2 CLOSE PACKING IN TWO DIMENSION :

Two possible types of two dimensional packing are

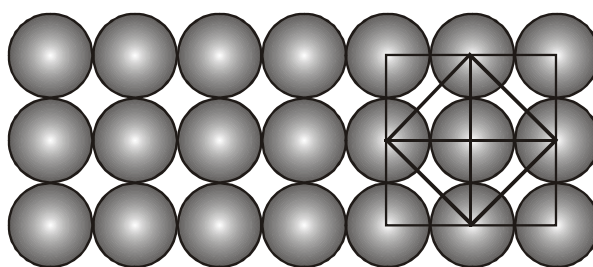
- (i) Square close packing in two dimension.
- (ii) Hexagonal close packing in two dimension.

#### (i) Square close packing in two dimension :

When two rows are placed in such a manner, that spheres of one row are placed immediately below of the other, the resulting packing is called two dimensional square close packing.

- (i) Since all the rows are identical, the packing is called AAA ..... type packing.
- (ii) Each sphere is touched by four other, hence coordination number is four.
- (iii) If centres of spheres are connected, square cells are formed , hence it also called two dimensional square packing.
- (iv) This type of packing is not very effective in terms of utilisation of space.

$$(v) \text{ Packing efficiency} = \frac{1 \times \pi r^2}{a^2} = \frac{1 \times \pi (a/2)^2}{a^2} = \frac{\pi}{4} = 0.78 \text{ or } 78\%$$

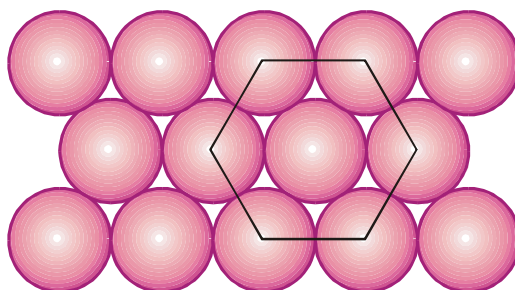


**(ii) Hexagonal close packing in two dimension :**

If various one dimensional close pack rows are placed in such a way that spheres of top row fits in depression of bottom row spheres, the resulting packing is called two dimensional hexagonal close packing.

- (i) Every third row sphere comes exactly at top of first row sphere, hence the packing is called ABABAB ..... packing.
- (ii) If centres are joined, hexagonal unit cells are formed. Hence this is called two dimensional hexagonal close packing.
- (iii) This packing is most efficient in utilising space in two dimensional arrangement.
- (iv) Each sphere is touched by six other, hence coordination number is six.

$$(v) \text{ Packing efficiency} = \frac{3 \times \pi \left(\frac{a}{2}\right)^2}{\frac{a^2 \sqrt{3}}{4} \times 6} = \frac{\pi}{2\sqrt{3}} = 0.90 \text{ or } 90\%$$

**6.3 CLOSE PACKING IN THREE DIMENSIONS :**

When two dimensional packing structure are arranged one above the other, depending upon type of two dimensional arrangement in a layer, and the relative positions of spheres in above or below layer, various types of three dimensional packing results. To define 3-D lattice, six lattice parameters are required - 3 edge lengths & 3 angles.

- (i) Simple cubic packing (A A A A .....)
- (ii) Hexagonal close packing (AB AB AB .....)
- (iii) Cubic close packing or face centred cubic (ABC ABC...)



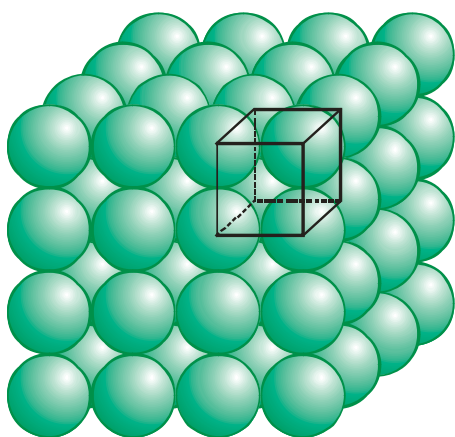
### 6.3.1 Three dimensional close packing from square two dimensional packing

#### (Simple cubic packing in three dimension)

The two dimensional square close packed layer are placed, in such a manner that spheres in each layer comes immediately on top of below layer, simple cubic packing results. Important points :

- (i) Spheres all aligned vertically and horizontally in all directions.
- (ii) The unit cell for this packing is simple cubic unit cell.
- (iii) In this packing, only 52% of available space is occupied by spheres.
- (iv) Each sphere is in contact with six spheres and hence coordination number is 6.

(v) Packing efficiency =  $\frac{1 \times \frac{4}{3} \pi r^3}{(2r)^3} = \frac{\pi}{6} \approx 0.52$



Simple cubic lattice formed by  
A A A ... arrangement

Coordination number = 6

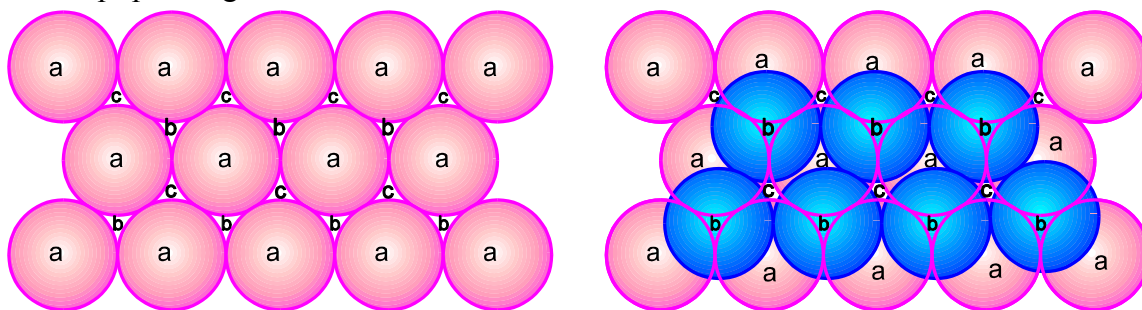
First neighbour = 6 at a distance = a

Second neighbour = 12 at  $(\sqrt{2}a)$  distance

Third neighbour = 8 at  $(\sqrt{3}a)$  distance

### 6.3.2 Three dimensional close packing from hexagonal two dimensional packing :

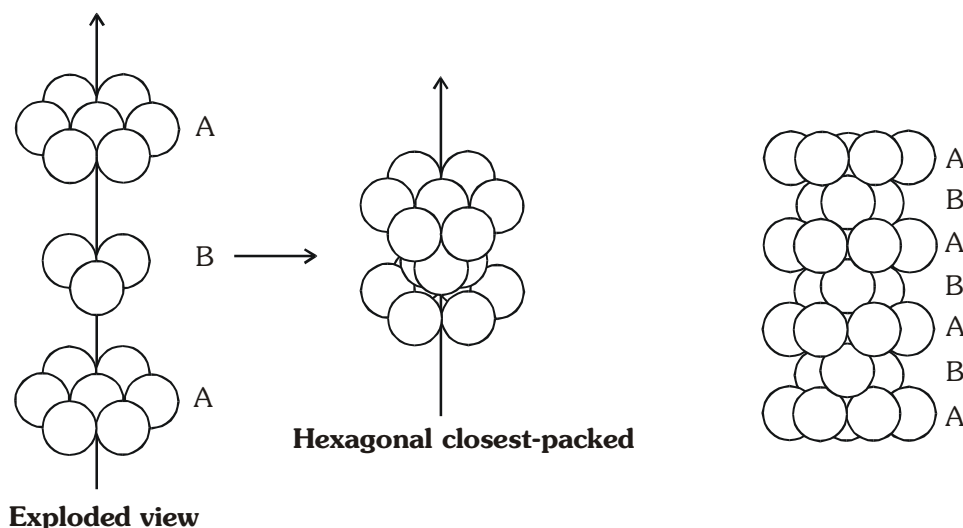
In hexagonal close packing, there are two types of the voids (open space or space left) which are divided into two sets 'b' and 'c' for convenience. The spaces marked 'c' are curved triangular spaces with tips pointing upwards whereas spaces marked 'b' are curved triangular spaces with tips pointing downwards.



Now we extend the arrangement of spheres in three dimensions by placing second close packed layer (hexagonal close packing) (B) on the first layer (A). The spheres of second layer may placed either on space denoted by 'b' or 'c'. It may be noted that it is not possible to place spheres on both types of voids (i.e. b and c). Thus half of the voids remain unoccupied by the second layer. The second layer also have voids of the types 'b' and in order to build up the third layer, there are following ways :

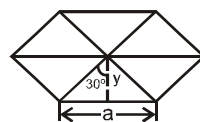
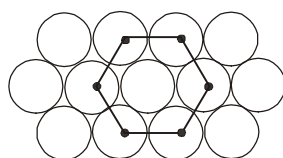
**(I) Hexagonal close packing (HCP)**

- (i) In one way, the spheres of the third layer lie on the spaces of second layer (B) in such a way that they lie directly above those in the first layer(A). In other words we can say that the third layer becomes identical to the first layer. Such arrangement is called AB AB AB ....type packing or hexagonal close packing (hcp).
- (ii) Maximum possible space is occupied by spheres.
- (iii) Each sphere is touched by 12 other spheres in 3D (6 is one layer, 3 in top layer and 3 in bottom) and hence the coordination number is 12.



**(iv) Packing efficiency of HCP units**  
**Relation between a, b, c and R :**

$$a = b = 2R$$



$$\tan 30^\circ = \frac{a}{2 \times y}$$

So

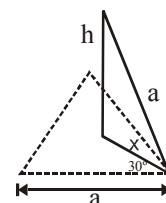
$$y = \frac{a \times \sqrt{3}}{2 \times 1} = \frac{\sqrt{3}}{2} a.$$

$$\text{Base Area} = 6 \left[ \frac{1}{2} a \times \frac{\sqrt{3}}{2} a \right] = \frac{6\sqrt{3}a^2}{4}$$

**Calculation of c :**

$$\cos 30^\circ = \frac{a}{2 \times x}$$

$$x = \frac{2a}{2 \times \sqrt{3}} = \frac{a}{\sqrt{3}}$$



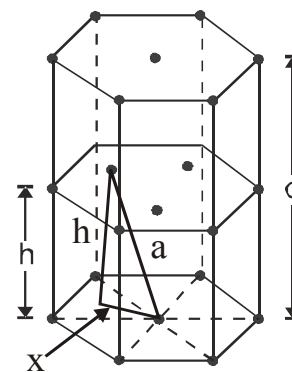
Applying pythagoras theorem :  $x^2 + h^2 = a^2$

$$\text{So } h^2 = a^2 - x^2 = a^2 - \frac{a^2}{3} = \frac{2}{3} a^2$$

$$h = \sqrt{\frac{2}{3}} a \quad \text{so} \quad c = 2h = 2\sqrt{\frac{2}{3}} a$$

So volume of hexagon = area of base  $\times$  height

$$= \frac{6\sqrt{3}}{4} \times a^2 \times 2\sqrt{\frac{2}{3}} a = \frac{6\sqrt{3}}{4} \times (2R)^2 + 2\sqrt{\frac{2}{3}} \times (2R) = 24\sqrt{2} R^3$$



(v) **Effective no. of particles (Z)**

$$Z = 3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6} = 3 + 1 + 2 = 6.$$

It must be noted that all three spheres of 'B' layer are not exactly inside the unit cell. But the contribution of three spheres are taken because the same volume of other spheres in that layer is also inside the unit cell.

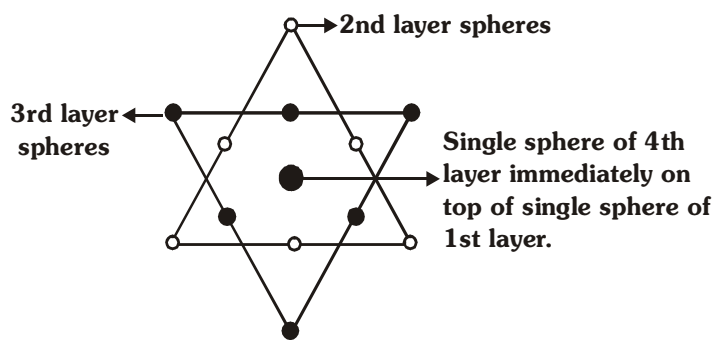
(vi) **Packing efficiency** =  $\frac{6 \times \frac{4}{3} \pi R^3}{24\sqrt{2} R^3} = \frac{\pi}{3\sqrt{2}} = 0.74$  or 74%.

(vii) **Density (d)** =  $\frac{\text{mass}}{\text{volume}} = \left[ \frac{Z \times M}{N_A \times \text{volume}} \right]$

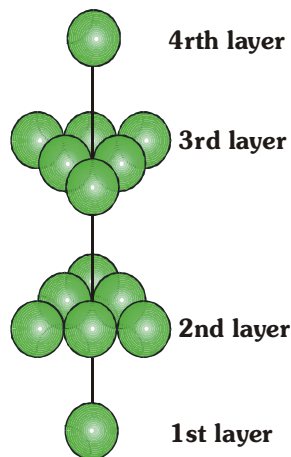
(II) **Cubic close packing (CCP) or face centered cubic (FCC)**

In second way, the spheres of the third layer (C) lie on the second layer (B) in such a way that they lie over the unoccupied spaces 'C' of the first layer(A). If this arrangement is continued in the same order every fourth layer becomes identical to the first. Such arrangement of particle is called ABC ABC ABC.... or cubic close packing (ccp) or face centered cubic (fcc).

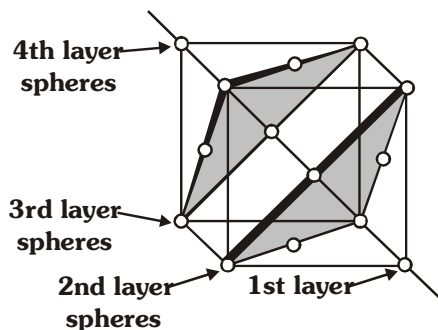
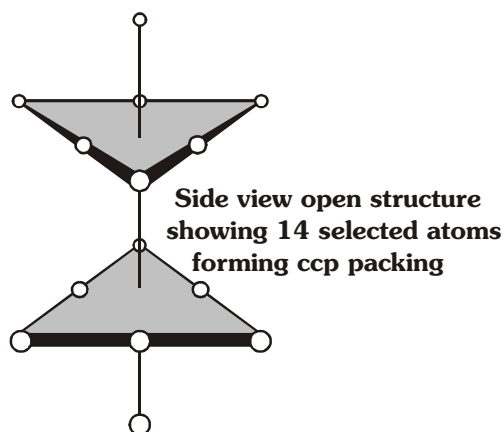
It may be noted that in ccp (or fcc) structures, each sphere is surrounded by 12 spheres hence the coordination number of each sphere is 12. The spheres occupy 74% of the total volume and 26% of is the empty space in both (hcp and ccp) structures.



Open structure show top view of 14 spheres forming ccp packing.



Side view exploded space filling diagram showing 14 selected atom forming ccp packing



fcc unit cell showing 14 spheres

(i) Relation between 'a' and 'R' :

$$a \neq 2R$$

$$\sqrt{2}a = 4R \quad (\text{sphere are touching along the face diagonal})$$

(ii) Effective no. of particles per unit cell (Z)

$$Z = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$$

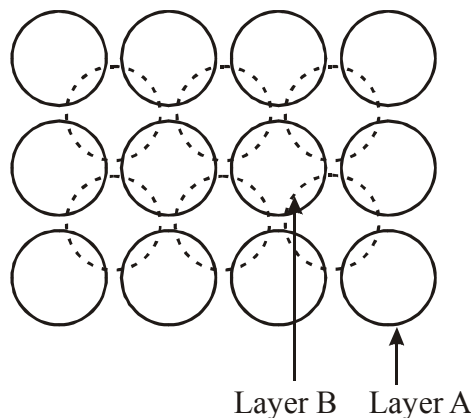
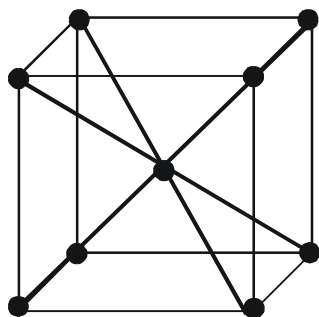
(iii) Packing fraction :

$$\text{P.F.} = \frac{4 \times \frac{4}{3} \pi R^3}{4 \times 4 \times 4 R^3} \times \sqrt{2} \times 2 = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

(iv) Density (d) =  $\frac{Z \times M}{N_A \times a^3}$

### 6.3.3 Body centred cubic (bcc):

There is another possible arrangement of packing of spheres known as body centred cubic (bcc) arrangement. This arrangement is observed in square close packing in which there is suitable space between the spheres in each layer. In bcc arrangement, the spheres of the second layer lie at the space (hollows or voids) in the first layer.



Thus each sphere of the second layer touches four spheres of the first layer. Now spheres of the third layer are placed exactly about the spheres of first layer. In this way each sphere of the second layer touches eight spheres (four of 1st layer and four of 3rd layer). Therefore coordination number of each sphere is 8 in bcc structure. The spheres occupy 68% of the total volume 32% of the volume is the empty space.

## 7. STRUCTURES OF VARIOUS ELEMENTS

Li	Be											
Na	Mg	Al										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au		

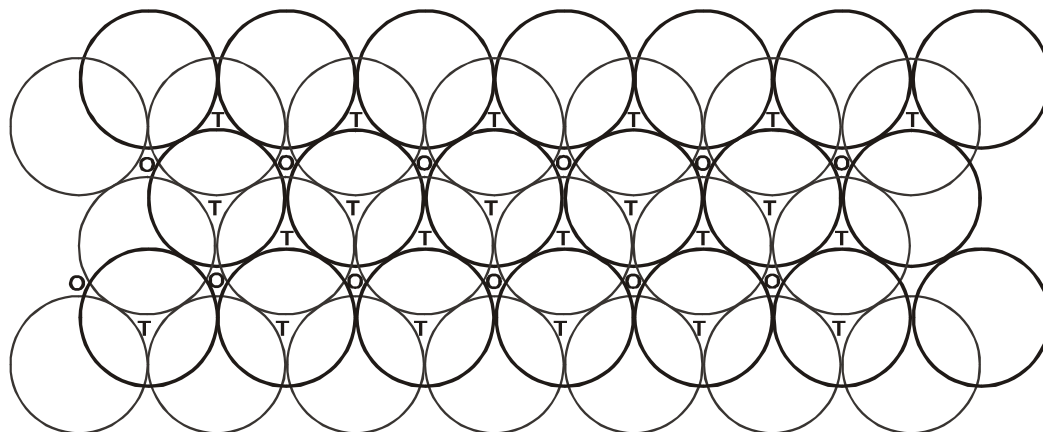
Body-centre Cubic [bcc]  
 Face central cubic [fcc]  
 Simple Cubic [sc]

Hexagonal Closed packed [hcp]

## 8. INTERSTICES OR VOIDS OR HOLES IN CRYSTALS

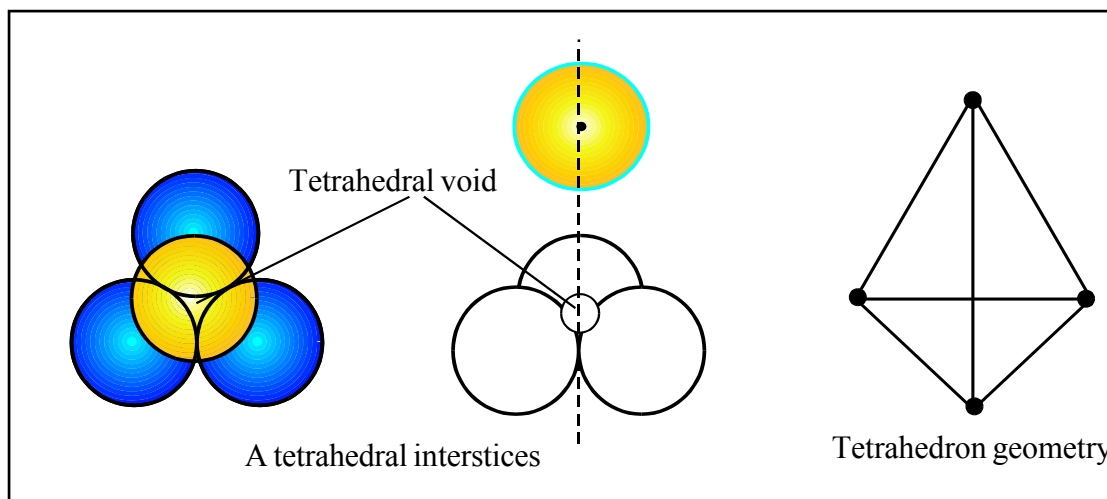
It has been shown that the particles are closely packed in the crystals even than there is some empty space left in between the spheres. This is known as interstices (or interstitial site or hole or empty space or voids). In three dimensional close packing (CCP & HCP) the interstices are of two types :

(i) tetrahedral voids and (ii) octahedral voids.

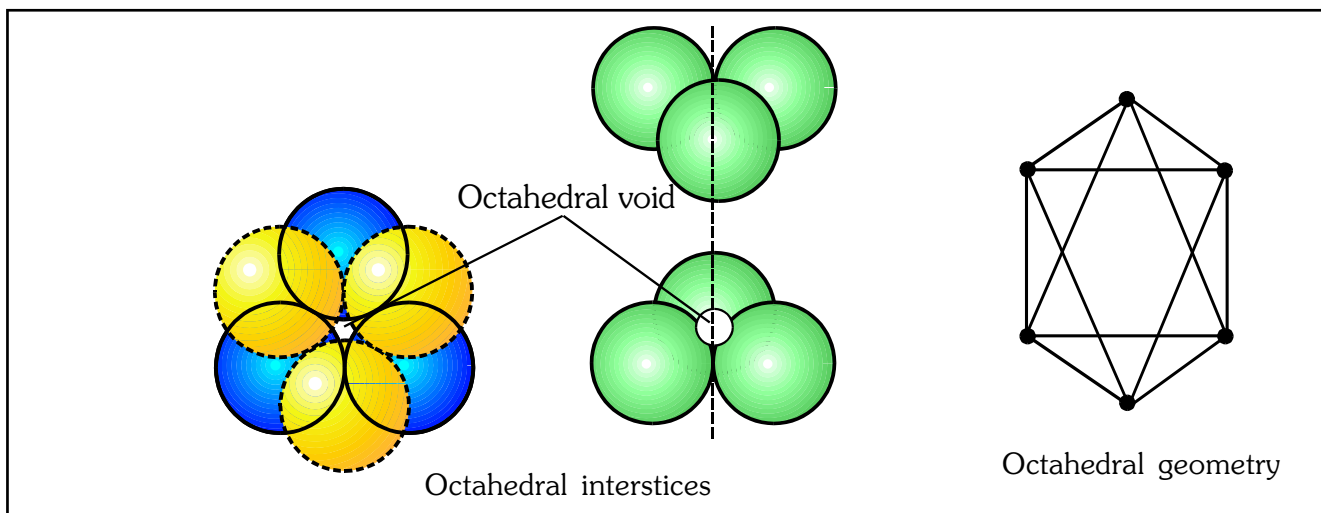


A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void

- (i) **Tetrahedral voids :** We have seen that in hexagonal close packing (hcp) and cubic close packing (ccp), each sphere of second layer touches with three spheres of first layer. Thus, they leave a small space in between which is known as **tetrahedral site or interstices**. In another words, the vacant space between 4 touching spheres is called as tetrahedral void. Since a sphere touches three spheres in the below layer and three spheres in the above layer hence there are two tetrahedral sites associated with one sphere. It may be noted that a tetrahedral site does not mean that the site is tetrahedral in geometry but it means that this site is surrounded by four spheres and the centres of these four spheres lie at the apices of a regular tetrahedron.



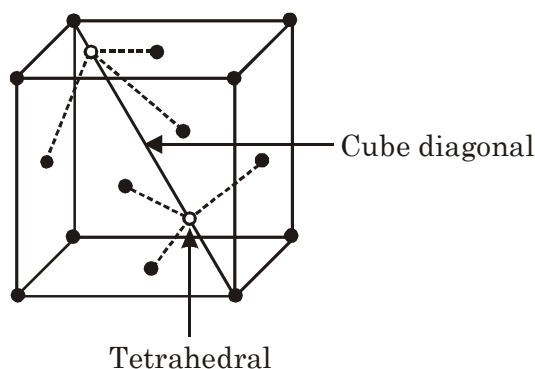
- (ii) **Octahedral voids :** Hexagonal close packing (hcp) and cubic close packing (ccp) also form another type of interstices (or site), which is called octahedral site (or interstices). In another words, the vacant space between 6 touching spheres is called as octahedral void. In the figure two layers of close packed spheres are shown. The spheres of first layer are shown by full circles while that of second layer by dotted circles. Two triangles are drawn by joining the centres of three touching spheres of both the layers.



The apices of these triangles point are in opposite directions. On super imposing these triangles on one another, an octahedral site is created. It may be noted that an octahedral site does not mean that the hole is octahedral in shape but it means that this site is surrounded by six nearest neighbour lattice points arranged octahedrally.

### 8.1 POSITIONS OF TETRAHEDRAL VOIDS IN AN FCC UNIT CELL :

In FCC, one corner and its three face centred atom of faces meeting at that corner form a tetrahedral void. In FCC, two tetrahedral voids are obtained along one cube diagonal. So in FCC 8 tetrahedral voids are present.



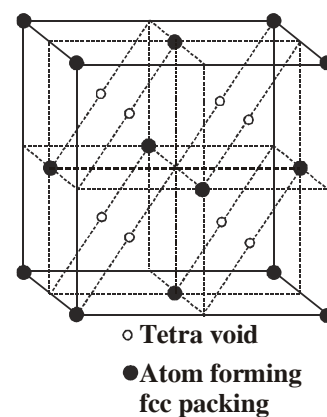
Alternatively, the centre of tetrahedral void is located on the centre

of body diagonal of each small cube of volume  $\left(\frac{a^3}{8}\right)$ .

$$\text{Total number of particles per unit cell} = \frac{1}{2} \times 6 + 8 \times \frac{1}{8} = 4$$

Total number of tetrahedral void = 8

$\therefore$  Effective number of tetrahedral void per particle = 2.



### 8.2 POSITION OF OCTAHEDRAL VOID IN FCC UNIT CELL :

Position of octahedral void is at mid-point of each edge

(total 12 edges in a cube) and at the centre of cube.

Each octahedral void located at mid point of edge contributes  $\frac{1}{4}$  to the unit cell. The octahedral void situated at the centre contributes 1.

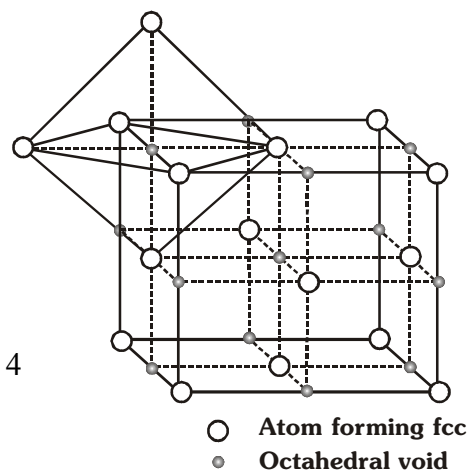
In FCC, total number of octahedral voids are

$$(1 \times 1) + (12 \times \frac{1}{4}) = 1 + 3 = 4$$

(Cube centre)                      (edge)

In FCC, number of particles = 4

$\therefore$  Effective number of octahedral voids per particle = 1



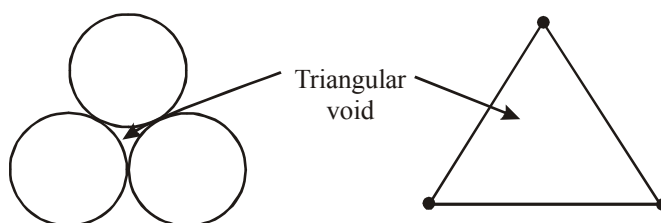
### 8.3 POSITION OF TETRAHEDRAL AND OCTAHEDRAL VOID IN HCP:

- (i) Above & below each sphere, there is a tetrahedral void, hence number of tetrahedral void per unit cell = 12
- (ii) Other than TV, all voids are OV & number of OV per unit cell =  $2 \times 3 = 6$

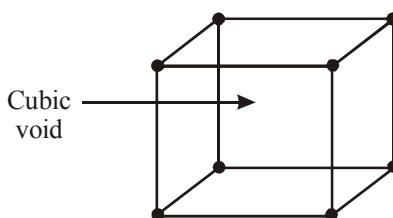
**Note :** In any closed packing of maximum efficiency, there are two TV & one OV per particle

### 8.4 Triangular and cubic voids :

- (i) **Triangular void :** It is formed by three spheres in a plane.



- (ii) **Cubic void :** It is formed in simple cubic unit cell by eight spheres at the corners of cube.





### 9. CRYSTAL OF DIAMOND

The crystal is FCC for C atom & alternate tetrahedral voids are also occupied by carbon atoms.

$$* Z = \frac{1}{8} \times 8 + 6 \times \frac{1}{2} + 4 = 8$$

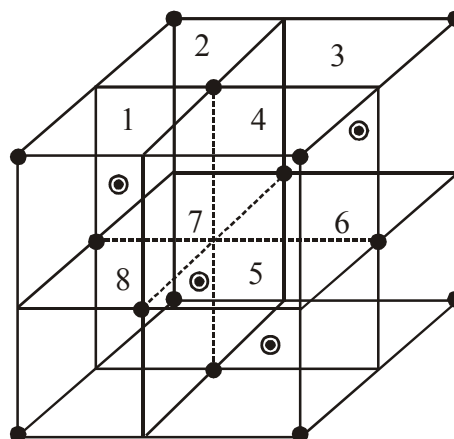
$$* CN = 4$$

$$* \frac{\sqrt{3}a}{4} = 2r = d_{C-C}$$

$$* \text{Number of C-C bonds/unit cell} = 4 \times 4 = 16$$

$$* \text{Number of C-C bonds/C-atom} = \frac{16}{8} = 2$$

$$* PE = \frac{8 \times \frac{4}{3} \pi r^2}{\left(\frac{8r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}\pi}{16} \approx 0.34 \text{ or } 34\%$$



### CLASS ILLUSTRATION

**Ex.6** A solid crystallises in close packing for 'P' atoms and 25% of tetrahedral voids are occupied by 'Q' atoms. What is the simplest formula of solid ?

**Sol.**  $Z_p = 1$  (say)

$$Z_Q = \frac{25}{100} \times 2 = \frac{1}{2}$$

$$\therefore \text{Simplest formula of solid} = PQ_{1/2} = P_2Q$$

**Ex.7** Calculate the radius ( $r$ ) of largest sphere which may be fitted in the (i) triangular voids (ii) tetrahedral voids (iii) octahedral voids (iv) cubic voids made by identical spheres of radius, ' $R$ ', without disturbing the crystal.

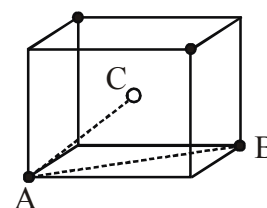
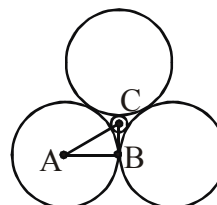
**Sol.** (i)  $AB = R$   
 $AC = R + r$   
 $\angle BAC = 30^\circ$

$$\text{Now, } \cos 30^\circ = \frac{AB}{AC} \Rightarrow \frac{\sqrt{3}}{2} = \frac{R}{R+r}$$

$$r = \left( \frac{2}{\sqrt{3}} - 1 \right) R = 0.155R$$

(ii)  $AB = \sqrt{2}a = 2R$

$$AC = \frac{\sqrt{3}a}{2} = R + r$$



$$\text{Now, } \frac{R+r}{R} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$\therefore r = \left( \sqrt{\frac{3}{2}} - 1 \right) R = 0.225R$$

(iii)  $AB = R$

$$AC = R + r$$

$$\angle BAC = 45^\circ$$

$$\text{Now, } \cos 45^\circ = \frac{AB}{AC} \Rightarrow \frac{1}{\sqrt{2}} = \frac{R}{R+r}$$

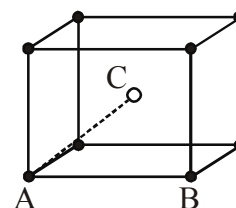
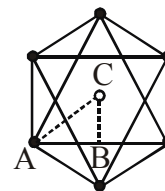
$$\therefore r = (\sqrt{2} - 1)R = 0.414R$$

(iv)  $AB = a = 2R$

$$AC = \frac{\sqrt{3}a}{2} = R + r$$

$$\text{Now, } \frac{R+r}{R} = \sqrt{3}$$

$$\therefore r = (\sqrt{3} - 1)R = 0.732R$$



**Ex.8** An element (molar mass = 60 gm/mole) crystallises in CCP lattice. If density is 6.25 gm/cm<sup>3</sup> and the distance between next nearest neighbour is  $d\text{\AA}$ , then the value of 'd' is ( $N_A = 6 \times 10^{23}$ ).

**Ex.8 Ans.(4)**

$$d = \frac{ZM}{N_A \cdot a^3}$$

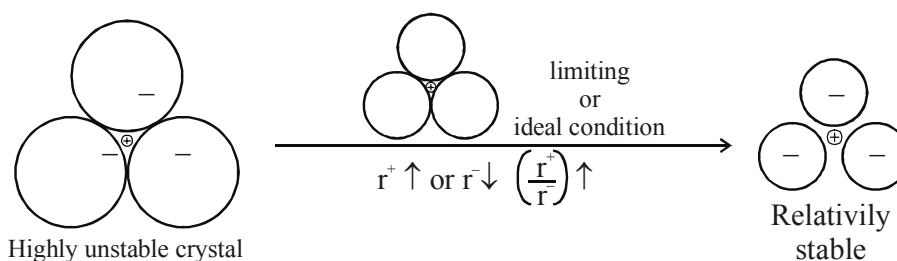
$$6.25 = \frac{4 \times 60}{6 \times 10^{23} \times a^3} \Rightarrow a = 4 \times 10^{-8} \text{cm} = 4\text{\AA}$$

## 10 PACKING IN IONIC SOLID

- (i) Normally anions are bigger than cations, hence ionic solids are considered as the packing of anions and cations are supposed to occupy the voids.
- (ii) Oppositely charged particles should lie closer and similarly charged particles should lie away from each other.
- (iii) Each ion tends to maximise its coordination number (Number of oppositely charged ions around it).

Point (ii) and (iii) contradict each other because on increase the CN, the repulsion between like charges will also increase. Hence, in all the ionic solids, there must be a balance with the help of relative size of ions to ensure maximum CN and minimum repulsion between like charges.

### 10.1 LIMITING OR IDEAL RADIUS RATIO $\left(\frac{r^+}{r^-}\right)$ :



The minimum  $\frac{r^+}{r^-}$  values for the existence of a cation in a particular void is called **limiting radius ratio** for that void.

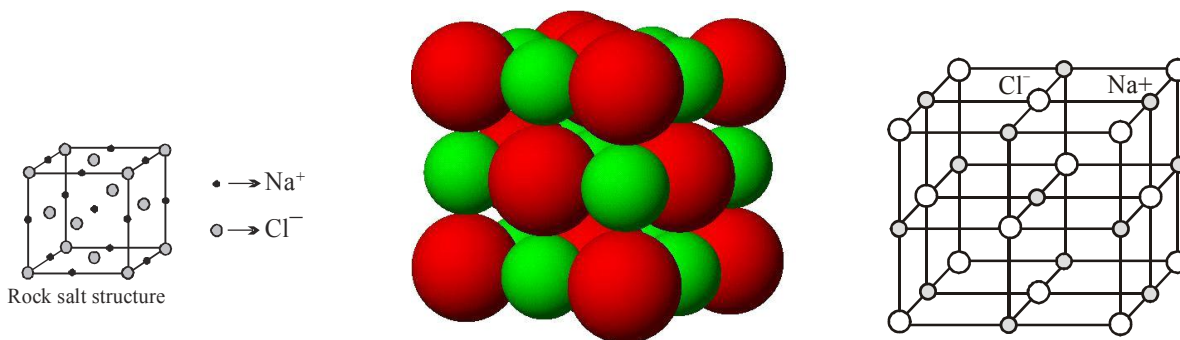
With the increase in radius ratio, space between anions will increase & hence the cation may tend for higher coordination number.

Voids	CN	Limiting $r^+/r^-$	Range of $r^+/r^-$
Triangular	3	0.155	0.155 – 0.225
Tetrahedral	4	0.225	0.225 – 0.414
Octahedral	6	0.414	0.414 – 0.732
Cubic	8	0.732	0.732 – 1.000

\* For values lesser than 0.155, crystal will not exist.

10.2 TYPES OF IONIC STRUCTURES:

10.2.1 Rock salt structure (NaCl) :



The bigger  $\text{Cl}^-$  forms cubic close packing and small  $\text{Na}^+$  occupy positions of all octahedral voids. The radius ratio  $\frac{r^+}{r^-}$  lie in the range 0.414 – 0.732.

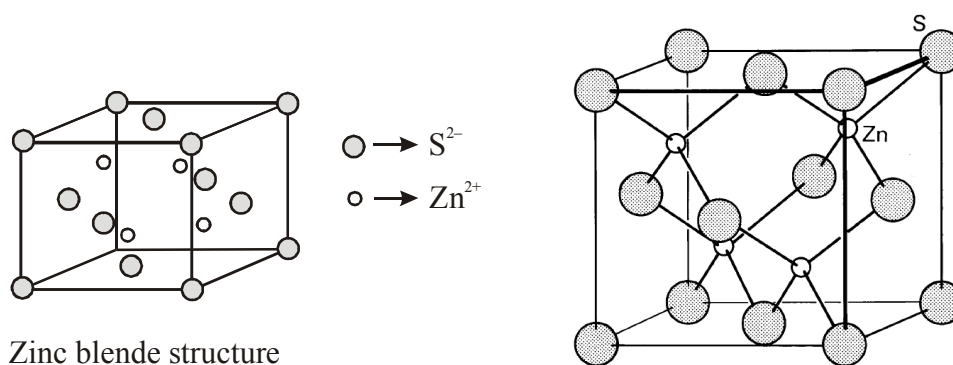
- (i) Each  $\text{Na}^+$  is surrounded by six  $\text{Cl}^-$  and each  $\text{Cl}^-$  is surrounded by six  $\text{Na}^+$  ion. [6:6 coordination]
- (ii) No. of  $\text{Na}^+$  and  $\text{Cl}^-$  in each unit cell is 4.
- (iii) Number of formula units of NaCl per unit cell is equal to 4.

(iv) The density of NaCl crystal is given by  $d = \left( \frac{4 \times M_{\text{NaCl}}}{N_A \times a^3} \right)$

(v) The edge length of NaCl unit cell is given by  $(2r^+ + 2r^-) \Rightarrow \frac{a}{2} = r^+ + r^-$

10.2.2 Zinc blende (sphalerite) structure (ZnS) :

Larger ion ( $\text{S}^{2-}$ ) forming ccp arrangement and smaller ion ( $\text{Zn}^{2+}$ ) filling half or alternate tetrahedral voids



(i) C.N. of  $\text{Zn}^{2+} = 4$  ; C.N. of  $\text{S}^{2-} = 4$  [4 : 4 coordination]

(ii) Formula units of ZnS per unit cell = 4. (iii)  $d_{\text{ZnS}} = \frac{4 \times M_{\text{ZnS}}}{N_A \times a^3}$  (iv)  $r_{\text{Zn}^{2+}} + r_{\text{S}^{2-}} = \frac{a\sqrt{3}}{4}$

### 10.2.3 Cesium chloride structure (CsCl) :

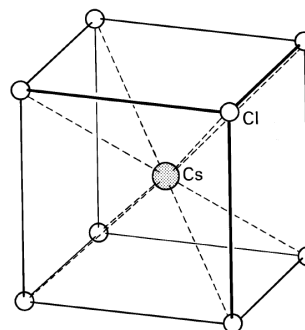
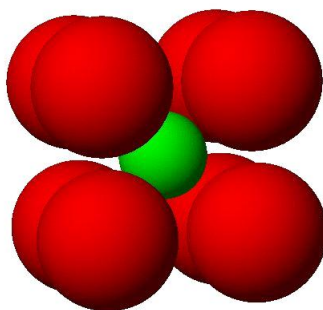
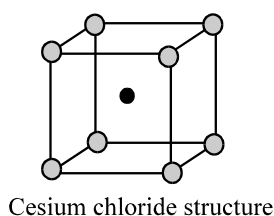
$\text{Cl}^-$  at the corners of cube and  $\text{Cs}^+$  in the center (cubic void).

(i) C.N. of  $\text{Cs}^+ = 8$  ; C.N. of  $\text{Cl}^- = 8$  [8 : 8 coordination]

(ii) Formula units of CsCl per unit cell = 1

(iii)  $d_{\text{CsCl}} = \frac{M_{\text{CsCl}}}{N_A \times a^3}$

(iv)  $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{a\sqrt{3}}{2} \Rightarrow \boxed{r^+ + r^- = \frac{a\sqrt{3}}{2}}$



### 10.2.4 Fluorite structure ( $\text{CaF}_2$ ) :

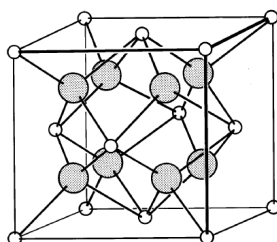
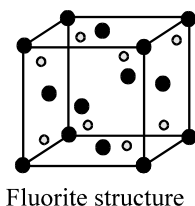
$\text{Ca}^{2+}$  forming ccp arrangement and  $\text{F}^-$  filling all tetrahedral voids.

(i) C.N. of  $\text{F}^- = 4$  ; C.N. of  $\text{Ca}^{2+} = 8$  [8 : 4 coordination]

(ii) Formula units of  $\text{CaF}_2$  per unit cell = 4

(iii)  $d_{\text{CaF}_2} = \frac{4 \times M_{\text{CaF}_2}}{N_A \times a^3}$

(iv)  $r_{\text{Ca}^{2+}} + r_{\text{F}^-} = \frac{a\sqrt{3}}{4}$



### 10.2.5 Antifluorite structure ( $\text{Li}_2\text{O}$ ) :

$\text{O}^{2-}$  ion forming ccp and  $\text{Li}^+$  taking all tetrahedral voids.

(i) C.N. of  $\text{Li}^+ = 4$   
C.N. of  $\text{O}^{2-} = 8$

(ii) Formula units of  $\text{Li}_2\text{O}$  ; per unit cell = 4

(iii)  $d_{\text{Li}_2\text{O}} = \frac{4 \times M_{\text{Li}_2\text{O}}}{N_A \times a^3}$

(iv)  $r_{\text{Li}^+} + r_{\text{O}^{2-}} = \frac{a\sqrt{3}}{4}$

### 10.2.6 Corundum Structure ( $\text{Al}_2\text{O}_3$ ) :

$\text{O}^{2-}$  forming hcp and  $\text{Al}^{3+}$  filling 2/3 octahedral voids.

**10.2.7 Rutile structure (TiO<sub>2</sub>) :**

O<sup>2-</sup> forming hcp while Ti<sup>4+</sup> ions occupy half of the octahedral voids.

**10.2.8 Pervoskite structure (CaTiO<sub>3</sub>) :**

Ca<sup>2+</sup> in the corner of cube, O<sup>2-</sup> at the face center and Ti<sup>4+</sup> at the centre of cube.

**10.2.9 Spinel and inverse spinel structure (MgAl<sub>2</sub>O<sub>4</sub>) :**

O<sup>2-</sup> forming fcc, Mg<sup>2+</sup> filling 1/8 of tetrahedral voids and Al<sup>3+</sup> taking half of octahedral voids.

In an inverse spinel structure, O<sup>2-</sup> ion form FCC lattice, A<sup>2+</sup> ions occupy 1/4 of the octahedral voids and trivalent cation occupies 1/8 of the tetrahedral voids and 1/4 of the octahedral voids.

**Ex.9** A solid A<sup>+</sup>B<sup>-</sup> has NaCl type close packed structure. If the anion has a radius of 250 pm, what should be the ideal radius for the cation ? Can a cation C<sup>+</sup> having a radius of 180 pm be slipped into the tetrahedral site of the crystal A<sup>+</sup>B<sup>-</sup> ? Give reason for your answer.

**Sol.** In Na<sup>+</sup>Cl<sup>-</sup> crystal each Na<sup>+</sup> ion is surrounded by 6 Cl<sup>-</sup> ions and vice versa. Thus Na<sup>+</sup> ion is placed in octahedral hole.

The limiting radius ratio for octahedral site = 0.414

$$\text{or } \frac{A^+}{B^-} = \frac{r}{R} = 0.414$$

Given that radius of anion (B<sup>-</sup>) R = 250 pm

$$\text{i.e. radius of cation (A}^+) \quad r = 0.414 R = 0.414 \times 250 \text{ pm}$$

$$\text{or } \quad r = 103.5 \text{ pm}$$

Thus ideal radius for cation (A<sup>+</sup>) is r = 103.5 pm.

We know that (r/R) for tetrahedral hole is 0.225.

$$\therefore \frac{r}{R} = 0.225$$

$$\text{or } \quad r = 0.225 R = 0.225 \times 250 = 56.25 \text{ pm}$$

Thus ideal radius for cation is 56.25 pm for tetrahedral hole. But the radius of C<sup>+</sup> is 180 pm. It is much larger than ideal radius i.e. 56.25 pm. Therefore we can not slip cation C<sup>+</sup> into the tetrahedral site.

**Ex.10** A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mole of it? How many of these are tetrahedral voids?

**Sol.** Since, for every atom forming hcp structure there are two tetrahedral voids and one octahedral void.

$$\text{Total voids} = 3 \times 0.5 = 1.5 \text{ mol and total tetrahedral void} = 2 \times 0.5 = 1 \text{ mol.}$$

**Ex.11** A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

**Sol.** In one unit cell of ccp, no. of N = 4 ; total no. of tetrahedral void = 8 ; occupied tetrahedral void by M = 8/3 ; Empirical formula : N<sub>4</sub>M<sub>8/3</sub> = N<sub>3</sub>M<sub>2</sub>.

## 11. IMPERFECTIONS IN SOLIDS

Although crystalline solids have short range as well as long range order in the arrangement of their constituent particles, yet crystals are not perfect. Usually a solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallisation process occurs at fast or moderate rate. Single crystals are formed when the process of crystallisation occurs at extremely slow rate. Even these crystals are not free of defects.

The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, **point defects** and **line defects**. Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects. We shall confine our discussion to point defects only.

### 11.1 Types of Point Defects

Point defect can be classified into three types:

- (i) Stoichiometric defects
- (ii) Non-stoichiometric defects
- (iii) Impurity added defect

#### (i) Stoichiometric Defect

These are the point defect that do not disturb the stoichiometry of the solid. They are also called **intrinsic** or **thermodynamic defects**. Basically these are of two types; vacancy defects and interstitial defect.

##### (a) Vacancy Defect :

When some of the lattice sites are vacant, the crystal is said to have vacancy defect. This results in decrease in density of the substance. This defect can also develop when a substance is heated.

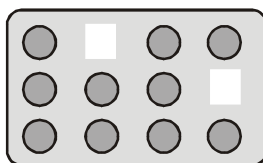


Fig. : Vacancy defects

**(b) Interstitial Defect :** When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect. This defect increases the density of the substance.

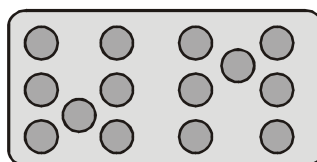


Fig. : Interstitial defects

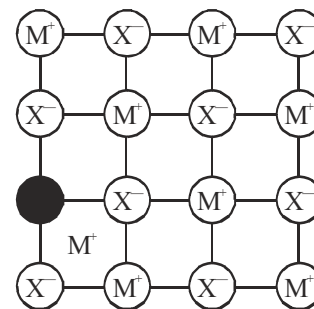
Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as **Frenkel and Schottky defects**.

(c) **Frenkel Defect** : This defect is shown by ionic solids.

The smaller ion (usually cation) is delocalised from its normal site to an interstitial site. It creates a vacancy defect at its original site and an interstitial defect at its new location.

Frenkel defect is also called **dislocation defect**. It does not change the density of the solid.

Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of  $Zn^{2+}$  and  $Ag^+$  ions.



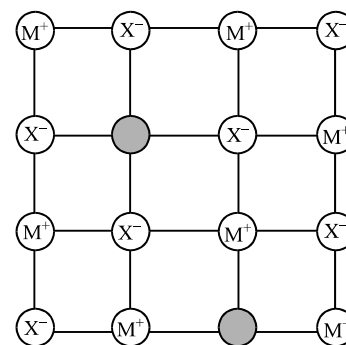
Frenkel Defect

**Influences** : Makes solid crystals good conductor. In Frenkel defect, ions in interstitial sites increase the dielectric constant.

(d) **Schottky Defect** : It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (in stoichiometric ratio)

Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately,

$10^6$  Schottky pairs per  $cm^3$  at room temperature. In  $1\text{ cm}^3$  there are about  $10^{22}$  ions. Thus, there is one Schottky defect per  $10^{16}$  ions. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.



Schottky Defect

**Influence** : The presence of large number of schottky defects in crystal results in significant decrease in its density.

(ii) **Non-Stoichiometric Defects**

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types:

- (a) Metal excess defect.
- (b) Metal deficiency defect.

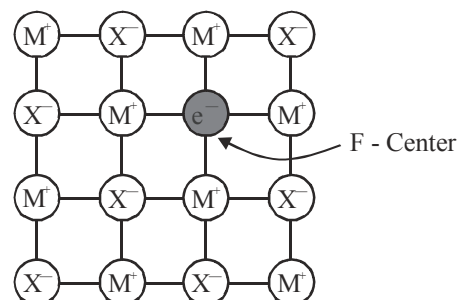


**(a) Metal Excess Defect****(I) Metal excess defect due to anionic vacancies :**

Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl<sup>-</sup> ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na<sup>+</sup> ions.

The released electrons diffuse into the crystal and occupy anionic sites. As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called **F-centres** (from the German word **Farbenzenter** for colour centre).

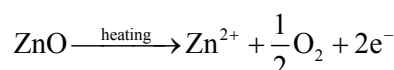
They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).



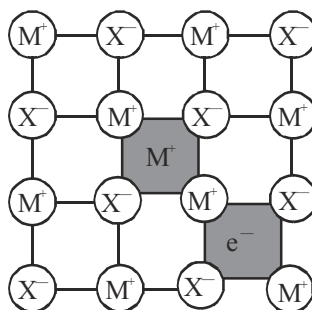
Metal excess defects  
due to anion vacancies

**(II) Metal excess defect due to the presence of extra cations at interstitial sites :**

Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.



Now there is excess of zinc in the crystal and its formula becomes Zn<sub>1+x</sub>O. The excess Zn<sup>2+</sup> ions move to interstitial sites and the electrons to neighbouring interstitial sites.



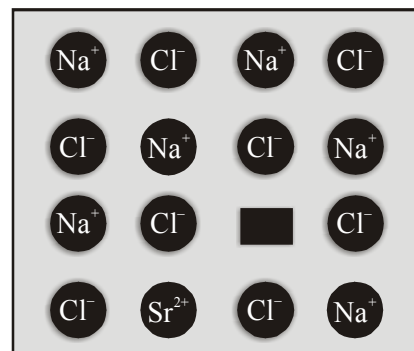
Metal excess defects  
due to interstitial cation

**(b) Metal Deficiency Defect**

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of Fe<sub>0.95</sub>O. It may actually range from FeO<sub>0.93</sub>O to Fe<sub>0.96</sub>O. In crystals of FeO, some Fe<sup>2+</sup> cations are missing and the loss of positive charge is made up by the presence of required number of Fe<sup>3+</sup> ions.

**(iii) Impurity Defects**

If molten NaCl containing a little amount of  $\text{SrCl}_2$  is crystallised, some of the sites of  $\text{Na}^+$  ions are occupied by  $\text{Sr}^{2+}$ . Each  $\text{Sr}^{2+}$  replaces two  $\text{Na}^+$  ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of  $\text{Sr}^{2+}$  ions. Another similar example is the solid solution of  $\text{CdCl}_2$  and  $\text{AgCl}$ .



Introduction of cation vacancy in NaCl by substitution of  $\text{Na}^+$  by  $\text{Sr}^{2+}$

- Note:** (i) As temperature increases, no. of defects increases exponentially.
- (ii) For defect formation :  $\Delta H > 0$  ,  $\Delta S > 0$   
 $\therefore$  More spontaneous at higher temperatures.
- (iii) No matter how many imperfections are present in a crystal, it is always electrically neutral (no net charge).

**12. ELECTRICAL PROPERTIES**

Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from  $10^{-20}$  to  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$ . Solids can be classified into three types on the basis of their conductivities.

- (i) **Conductors** : The solids with conductivities ranging between  $10^4$  to  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$  are called conductors. Metals having conductivities in the order of  $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$  are good conductors.
- (ii) **Insulators** : These are the solids with very low conductivities ranging between  $10^{-20}$  to  $10^{-10} \text{ ohm}^{-1} \text{ m}^{-1}$ .
- (iii) **Semiconductors** : These are the solids with conductivities in the intermediate range from  $10^{-6}$  to  $10^4 \text{ Ohm}^{-1} \text{ m}^{-1}$ .

**12.1 : Conduction of Electricity in Metals**

A conductor may conduct electricity through movement of electrons or ions. Metallic conductors belong to the former category and electrolytes to the latter.

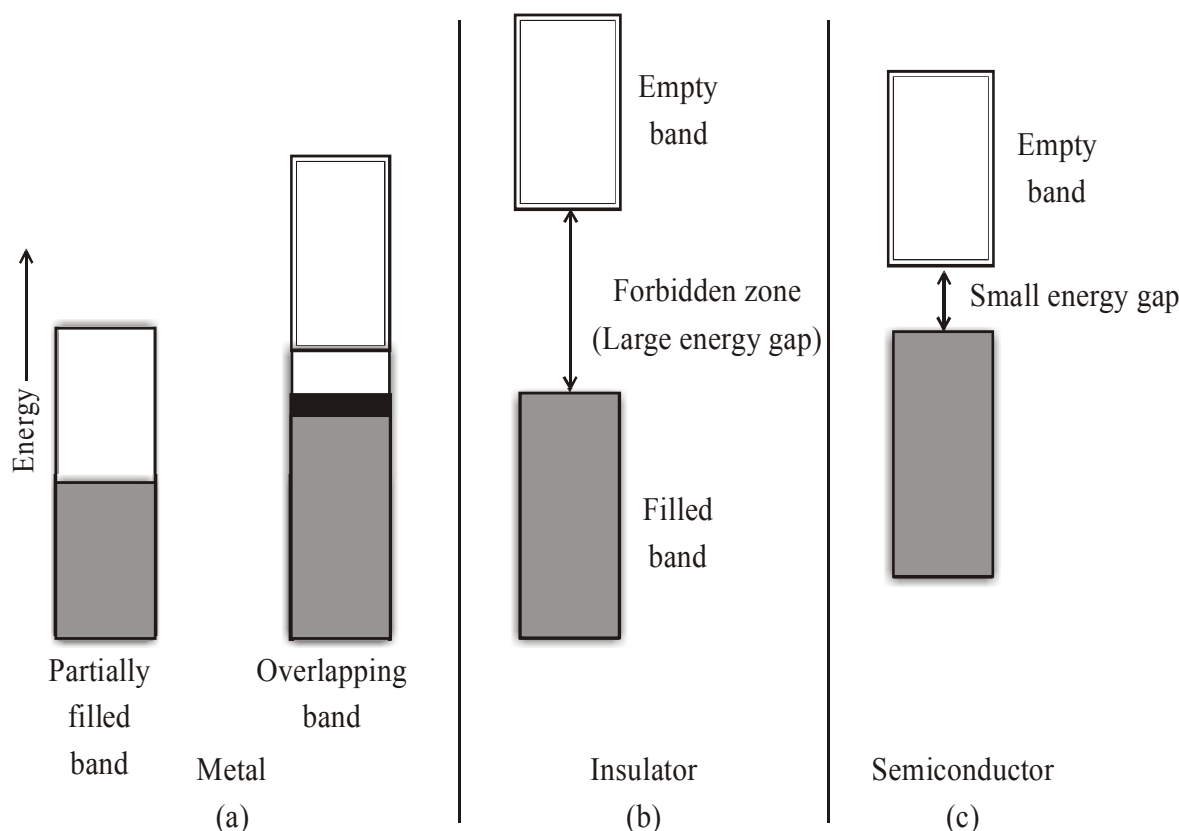
Metals conduct electricity in solid as well as molten state. The conductivity of metals depend upon the number of valence electrons available per atom. The atomic orbitals of metal atoms from molecular orbitals which are so close in energy to each other as to form a band. If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows conductivity.

### 12.2 : Insulator :

If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electron cannot jump to it and such a substance has very small conductivity and it behaves as an insulator.

### 12.3 : Conduction of Electricity in Semi-conductor

In case of semiconductors, the gap between the valence band and conduction band is small. Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band. Substances like silicon and germanium show this type of behaviour and are called **intrinsic semiconductors**.



**Distinction among (a) metals (b) insulators and (c) semiconductors.**

**In each case, an unshaded area represents a conduction band.**

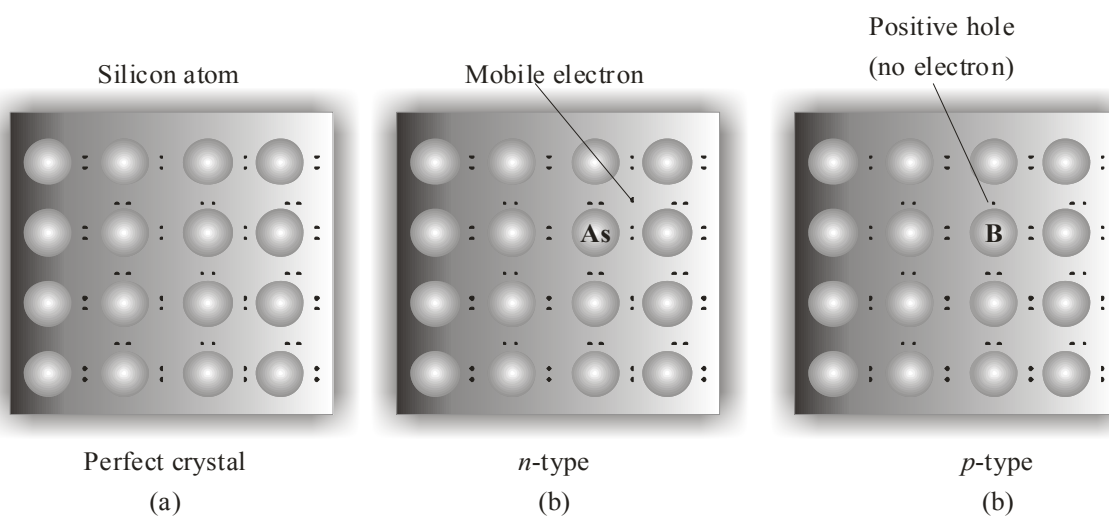
The conductivity of these intrinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called **doping**. Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce *electrical defect* in them.

(a) **Electron – rich impurities**

Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours. When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron is extra and becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or germanium). Here the increase in conductivity is due to the negatively charged electron, hence silicon doped with electron-rich impurity is called ***n-type semiconductor***.

(b) **Electron – deficit impurities**

Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called ***electron hole or electron vacancy***. An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semi conductors are called ***p-type semiconductors***.



***Creation of n-type and p-type semi conductors by doping groups 13 and 15 elements***

**(c) Applications of n-type and p-type semiconductors**

Various combinations of *n*-type and *p*-type semiconductors are used for making electronic components. Diode is a combination of *n*-type and *p*-type semiconductor and is used as a rectifier. Transistors are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. *npn* and *pnp* type of transistors are used to detect or amplify radio or audio signals. The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.

Germanium and Silicon are group 14 elements and therefore, have a characteristic valency of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of group 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of groups 13-15 are InSb, AlP and GaAs. Gallium arsenide (GaAs) semiconductor have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of groups 12-16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO<sub>2</sub> and ReO<sub>3</sub> behave like metals. Rhenium oxide, ReO<sub>3</sub> is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO<sub>2</sub>, VO<sub>3</sub> and TiO<sub>3</sub> show metallic or insulating properties depending on temperature.

**13. MAGNETIC PROPERTIES :**

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis. Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton,  $\mu_B$ . It is equal to  $9.27 \times 10^{-24} \text{ A m}^2$ .

On the basis of their magnetic properties, substances can be classified into five categories: (i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic and (v) ferrimagnetic.

**(i) Paramagnetism :**

Paramagnetic substances are weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. O<sub>2</sub>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> are some examples of such substances.

**(ii) Diamagnetism :**

Diamagnetic substances are weakly repelled by a magnetic field. H<sub>2</sub>O, NaCl and C<sub>6</sub>H<sub>6</sub> are some examples of such substances. They are weakly magnetised in a magnetic field in opposite direction. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

(iii) **Ferromagnetism :**

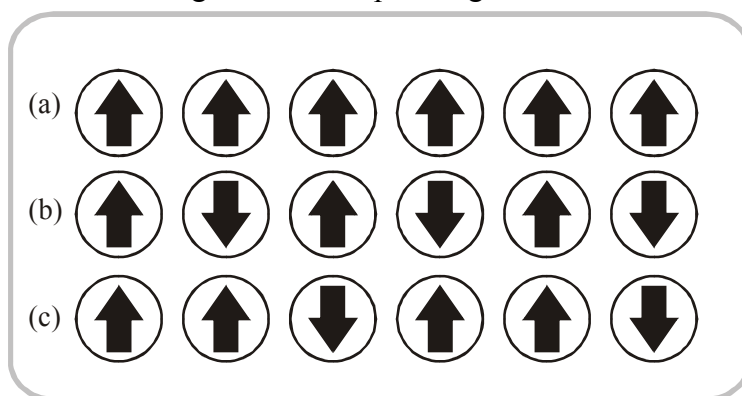
A few substances like iron, cobalt, nickel, gadolinium and  $\text{CrO}_2$  are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called **domains**. Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

(iv) **Antiferromagnetism :**

Substances like  $\text{MnO}$  showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment

(v) **Ferrimagnetism :**

Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers. They are weakly attracted by magnetic field as compared to ferromagnetic substances.  $\text{Fe}_3\text{O}_4$  (magnetite) and ferrites like  $\text{MgFe}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.



Schematic alignment of magnetic moments in (a) ferromagnetic  
(b) antiferromagnetic and (c) ferrimagnetic

## PREVIOUS YEARS SOLVED QUESTION

1. A metal crystallises into two cubic phases, FCC and BCC whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of FCC and BCC. [JEE-1999]

Ans. 1.259

$$\text{Sol. } \rho_{\text{Fcc}} = \frac{4 \times M}{N_A \times (3.5 \times 10^{-10})^3}$$

$$\rho_{\text{Bcc}} = \frac{2 \times M}{N_A \times (3 \times 10^{-10})^3}$$

$$\frac{\rho_{\text{Fcc}}}{\rho_{\text{Bcc}}} = \frac{4}{2} \times \left(\frac{3}{3.5}\right)^3$$

$$= 1.259$$

2. The coordination number of a metal crystallising in a hcp structure is [JEE-2000]  
(A) 12 (B) 4 (C) 8 (D) 6

Ans. (A)

Sol. Theory Based

3. In any ionic solid [MX] with schottky defects, the number of positive and negative ions are same. [T/F] [JEE-2000]

Ans. True

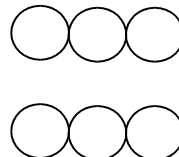
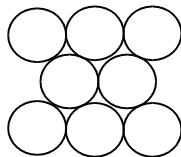
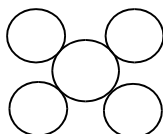
Sol. Theory Based

4. In a solid "AB" having NaCl structure "A" atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is

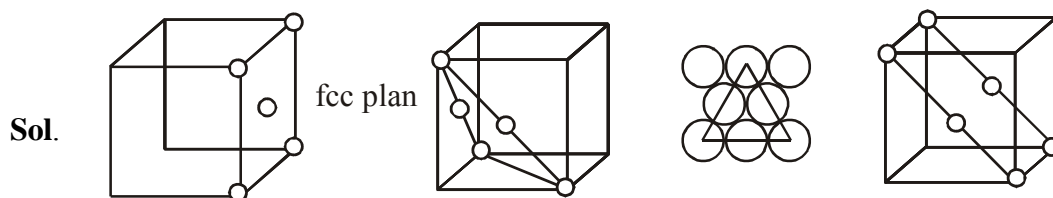
(A) AB<sub>2</sub> (B) A<sub>2</sub>B (C) A<sub>4</sub>B<sub>3</sub> (D) A<sub>3</sub>B<sub>4</sub> [JEE-2000]

$$\text{Sol. } \left. \begin{array}{l} Z_A = 8 \times \frac{1}{8} + 4 \times \frac{1}{2} = 3 \\ Z_B = 1 + 12 \times \frac{1}{4} = 4 \end{array} \right\} \Rightarrow A_3B_4$$

5. The figures given below show the location of atoms in three crystallographic planes in FCC lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. [JEE-2000]



Ans.



6. A substance  $A_xB_y$  crystallises in a FCC lattice in which atoms “A” occupy each corner of the cube and atoms “B” occupy the centres of each face of the cube. Identify the correct composition of the substance  $A_xB_y$ .
- (A)  $AB_3$  (B)  $A_4B_3$   
 (C)  $A_3B$  (D) composition cannot be specified [JEE-2002]

Ans. (A)

Sol.  $AB_3$

7. Marbles of diameter 10 mm each are to be arranged on a flat surface so that their centres lie within the area enclosed by four lines of length each 40 mm. Sketch the arrangement that will give the maximum number of marbles per unit area, that can be enclosed in this manner and deduce the expression to calculate it.

[JEE 2003]

Ans. 18

Sol. 
$$\frac{n \times \pi r^2}{a^2} = \frac{\pi}{2\sqrt{3}}$$

$$\frac{n \times \pi 5^2}{40 \times 40} = \frac{\pi}{2\sqrt{3}}$$

$$n = 18.475$$

$$n \approx 18$$

8. (i) AB crystallizes in a rock salt structure with  $A : B = 1 : 1$ . The shortest distance between A and B is  $Y^{1/3}$  nm. The formula mass of AB is  $6.023 Y$  amu where Y is any arbitrary constant. Find the density in  $\text{kg m}^{-3}$ .
- (ii) If measured density is  $20 \text{ kg m}^{-3}$ . Identify the type of point defect. [JEE-2004]

Sol. (i) shortest distance b/w A & B =  $Y^{1/3}$  nm

$$a = 2Y^{1/3}$$

$$\rho = \frac{4 \times 6.023 Y \times 10^{-3}}{6.023 \times 10^{23} \times [2Y^{1/3} \times 10^{-9}]^3}$$

$$\rho = \frac{4 \times 10^{-3}}{8 \times 10^{-4}}$$

$$= 5 \text{ kgm}^{-3}$$

- (ii) copy statement for answer Key



9. Which of the following FCC structure contains cations in alternate tetrahedral voids?

- (A) NaCl                      (B) ZnS                      (C) Na<sub>2</sub>O                      (D) CaF<sub>2</sub>                      [JEE 2005]

Ans. (B)

10. An element crystallises in FCC lattice having edge length 400 pm. Calculate the maximum diameter which can be placed in interstitial sites without disturbing the structure. [JEE 2005]

Ans. 117.1 pm

Sol.  $\sqrt{2} a = 4r$

$$r = \frac{\sqrt{2}a}{4}$$

for octahedral void

$$r^1 = .414 \times 141.4$$

$$d = 2r^1$$

$$= 117.07$$

11. The edge length of unit cell of a metal having atomic weight 75 g/mol is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ( $N_A = 6 \times 10^{23}$ ). Give the answer in pm. [JEE 2006]

Ans. 216.5 pm

Sol.  $a = 5 \text{ \AA}$

$$M = 75 \text{ gram/mol}$$

$$d = 2 \text{ gram/cm}$$

r

$$2 = \frac{Z \times 75}{(6.02 \times 10^{23})(5 \times 10^{-8})^3}$$

$$Z = 2 \text{ (Bcc)}$$

$$\sqrt{3} a = 4r$$

$$r = \frac{\sqrt{3}a}{4} = 2.165 \text{ \AA}$$

12. Match the crystal system / unit cells mentioned in Column I with their characteristic features mentioned in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the OMR.

**Column I**

- (A) simple cubic and face-centred cubic  
 (B) cubic and rhombohedral  
 (C) cubic and tetragonal  
 (D) hexagonal and monoclinic

**Column II**

- (P) have these cell parameters  $a = b = c$   
 and  $\alpha = \beta = \gamma$   
 (Q) are two crystal systems  
 (R) have only two crystallographic angles of  $90^\circ$   
 (S) belong to same crystal system.

[JEE 2007]

Ans. (A) P, S ; (B) -P,Q ; (C) - Q ; (D) - Q,R

## Paragraph for Question No. 13 to 15

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

13. The number of atoms in this HCP unit cells is [JEE 2008]

- (A) 4 (B) 6 (C) 12 (D) 17

Ans. (B)

Sol.  $12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 \times 1 = 6$  atoms

14. The volume of this HCP unit cell is [JEE 2008]

- (A)  $24\sqrt{2}r^3$  (B)  $16\sqrt{2}r^3$  (C)  $12\sqrt{2}r^3$  (D)  $\frac{64}{3\sqrt{3}}r^3$

Ans. (A)

Sol.  $V = \frac{6\sqrt{3}a^3}{4} \times C$

$$a = 2r$$

$$C = \frac{4\sqrt{2}r}{\sqrt{3}}$$

$$V = 24\sqrt{2}r^3$$

15. The empty space in this HCP unit cell is [JEE 2008]

- (A) 74% (B) 47.6% (C) 32% (D) 26%

Ans. (D)

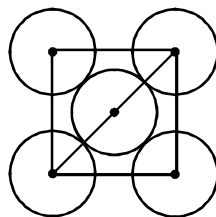
16. The correct statement(s) regarding defects in solid is (are) [JEE 2009]

- (A) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion.  
 (B) Frenkel defect is a dislocation defect  
 (C) Trapping of an electron in the lattice leads to the formation of F-center.  
 (D) Schottky defects have no effect on the physical properties of solids.

Ans. (B,C)

17. The packing efficiency of the two-dimensional square unit cell shown below is

[JEE-2010]



(A) 39.27%

(B) 68.02%

(C) 74.05%

(D) 78.54%

Ans. (D)

Sol. 
$$PF = \frac{2\pi r^2}{\left(\frac{4r}{\sqrt{2}}\right)^2} = .785$$

$$\% PF = 78.5\%$$

**EXERCISE : S-I****METALLIC CRYSTALS****Cubic crystals**

- A closed packed structure of uniform spheres has the edge length of 600 pm. Calculate the radius of sphere, if it exist in ( $\sqrt{2} = 1.4, \sqrt{3} = 1.7$ )

(a) simple cubic lattice      (b) BCC lattice      (c) FCC lattice

**SS0001**
- Xenon crystallises in the face-centred cubic lattice and the edge length of the unit cell is  $438\sqrt{2}$  pm. What is the nearest neighbour distance and what is the radius of xenon atom?

**SS0002**
- The effective radius of the iron atom is  $\sqrt{2}$  Å. It has FCC structure. Calculate its density (Fe = 56 amu,  $N_A = 6 \times 10^{23}$ )

**SS0003**
- Calculate the ratio of densities if same element undergoes fcc as well as simple cubic packing. Assume same atomic radius in both crystals.

**SS0004**
- Potassium has body-centred cubic structure with the nearest neighbour distance  $260\sqrt{3}$  pm. Its density would be ( $\frac{1}{(5.2)^3} = 0.007, N_A = 6 \times 10^{23}, K = 39$ )

**SS0005**
- A cubic solid is made up of two elements 'A' and 'B'. Atoms 'B' are at the corners of the cube and 'A' at the body centre. What is the simplest formula of compound?

**SS0006**
- An element 'X' crystallizes in bcc. Find volume of unit cell in (Å)<sup>3</sup>, if atomic radius is  $\sqrt{3}$  Å.

**SS0007**
- A lattice has simple cube unit cell then number of faces which meets at a corner of a cube in this lattice is.

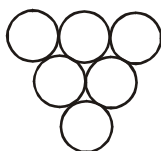
**SS0008**
- How many next nearest neighbours does potassium have in bcc lattice?

**SS0009**
- Number of crystal systems having, only 2 types of Bravais lattices = x,  
Number of crystal systems having, atleast 2 interfacial angles equal = y,  
all the three interfacial angles and all the three axes lengths equal = z  
Then find  $y - (x + z)$ .

**SS0010**

## PACKING IN SOLIDS

11. A cubic solid is made by atoms 'A' forming close pack arrangement, 'B' occupying one-fourth of tetrahedral void and C occupying half of the octahedral voids. What is the formula of compound ?  
SS0011
12. If number of nearest neighbours, next nearest ( $2^{\text{nd}}$  nearest) neighbour and next to next nearest ( $3^{\text{rd}}$  nearest) neighbours are x, y and z respectively for body centred cubic unit cell, then calculate value of  $\frac{xy}{z}$  is.  
SS0012
13. In FCC unit cell, what fraction of edge is not covered by atoms ?  
SS0013
14. Element A crystallizes in hcp. Calculate total number of tetrahedral voids in 24 micrograms of A ( $N_A = 6 \times 10^{23}$ , Atomic mass of A = 48)  
SS0014
15. For ABC ABC ABC ... packing, distance between two successive tetrahedral void is X and distance between two successive octahedral void is y in an unit cell, then  $\frac{y\sqrt{2}}{X}$  is  
SS0015
16. An element 'M' crystallizes in ABAB....type packing. If adjacent layer A & B are  $10\frac{\sqrt{2}}{\sqrt{3}}$  pm apart, then calculate radius of largest sphere which can be fitted in the void without disturbing the lattice arrangement (Given :  $\sqrt{2} = 1.414$ )  
SS0016
17. A 3d unit cell is such that one of its planes has the following arrangement of atoms.



What will be the number of next nearest neighbour in such unit cell?

- SS0017
18. The density of solid Argon is 1.6 gm/ml at  $-233^\circ\text{C}$ . If the atomic volume of Argon is assumed to be  $\frac{5}{3} \times 10^{-23}$   $\text{cm}^3$  then what % of solid Argon is apparently empty space ? (Ar = 40,  $N_A = 6 \times 10^{23}$ )  
SS0018
19. An element crystallizes in a structure having FCC unit cell of an edge 200 pm. Calculate the density, if 200 g of this element contains  $2.4 \times 10^{24}$  atoms. ( $N_A = 6 \times 10^{23}$ )  
SS0019

20. Find packing fraction of three dimensional unit cell of AAAAA.....type hypothetical arrangement in which hexagonal packing is taken in layer.

SS0020

**IONIC CRYSTALS**

21. If the radius of  $\text{Mg}^{2+}$  ion,  $\text{Cs}^+$  ion,  $\text{O}^{2-}$  ion,  $\text{S}^{2-}$  ion and  $\text{Cl}^-$  ion are  $0.65 \text{ \AA}$ ,  $1.69 \text{ \AA}$ ,  $1.40 \text{ \AA}$ ,  $1.84 \text{ \AA}$ , and  $1.81 \text{ \AA}$  respectively, calculate the co-ordination numbers of the cations in the crystals of  $\text{MgS}$ ,  $\text{MgO}$  and  $\text{CsCl}$ .

SS0021

22. The two ions  $\text{A}^+$  and  $\text{B}^-$  have radii  $88 \text{ pm}$  and  $200 \text{ pm}$  respectively. In the closed packed crystal of compound  $\text{AB}$ , predict the co-ordination number of  $\text{A}^+$ .

SS0022

23. Spinel is a important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one-eighth of the tetrahedral holes occupied by one type of metal ion and one half of the octahedral hole occupied by another type of metal ion. Such a spinel is formed by  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{O}^{2-}$ , with  $\text{Zn}^{2+}$  in the tetrahedral holes. Give the formula of spinel.

SS0023

24.  $\text{KF}$  crystallizes in the  $\text{NaCl}$  type structure. If the radius of  $\text{K}^+$  ion is  $132 \text{ pm}$  and that of  $\text{F}^-$  ion is  $135 \text{ pm}$ , what is the shortest  $\text{K}-\text{F}$  distance? What is the edge length of the unit cell? What is the closet  $\text{K}^+-\text{K}^+$  distance?

SS0024

25.  $\text{CsCl}$  has bcc unit cell with edge length  $400 \text{ pm}$ . Calculate the interionic distance in  $\text{CsCl}$ .

SS0025

26. The density of  $\text{KBr}$  is  $2.38 \text{ g cm}^{-3}$ . The length of the edge of the unit cell is  $700 \text{ pm}$ . Find the number of formula unit of  $\text{KBr}$  present in the single unit cell.

$$(N_A = 6 \times 10^{23} \text{ mol}^{-1}, \text{ At. mass : K} = 39, \text{ Br} = 80)$$

SS0026

27. A crystal of lead(II) sulphide has  $\text{NaCl}$  structure. In this crystal the shortest distance between  $\text{Pb}^{+2}$  ion and  $\text{S}^{2-}$  ion is  $300 \text{ pm}$ . What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.

SS0027

28. If the length of the body diagonal for  $\text{CsCl}$  which crystallises into a cubic structure with  $\text{Cl}^-$  ions at the corners and  $\text{Cs}^+$  ions at the centre of the unit cell, is  $7 \text{ \AA}$  and the radius of the  $\text{Cs}^+$  ion is  $1.69 \text{ \AA}$ , what is the radius of  $\text{Cl}^-$  ion?

SS0028

29.  $\text{RbI}$  crystallizes in  $(8 : 8)$  structure in which each  $\text{Rb}^+$  is surrounded by eight iodide ions each of radius  $2.17 \text{ \AA}$ . Find the length of one side of  $\text{RbI}$  unit cell, assuming anion, anion contact.

SS0029

30. Solid AB has NaCl type structure. If the radius of  $A^+$  and  $B^-$  are  $0.8 \text{ \AA}$  and  $1.2 \text{ \AA}$  respectively and formula mass of AB is  $48 \text{ g/mole}$ , what is the density of AB solid.

Take : Avogadro's number =  $6 \times 10^{23}$

SS0030

**PROBLEMS RELATED WITH DEFECTS IN SOLID**

31. The composition of a sample of wustite is  $Fe_{0.93}O_{1.0}$ . What percentage of iron is present in the form of Fe(III)?

SS0031

32. If NaCl is doped with  $10^{-3} \text{ mol \% SrCl}_2$ , what is the number of cation vacancies per mole of NaCl? ( $N_A = 6 \times 10^{23}$ )

SS0032

33. AgCl has the same structure as that of NaCl. The edge length of unit cell of AgCl is found to be  $523.5 \text{ pm}$  and the density of AgCl is  $6.0 \text{ g cm}^{-3}$ . Find the percentage of sites that are unoccupied.

[ $Ag = 108$ ,  $(5.235)^3 = 143.5$ ]

SS0033

34. A non stoichiometric compound  $Fe_7S_8$  consist of iron in both  $Fe^{+2}$  and  $Fe^{+3}$  form and sulphur is present as sulphide ions. Calculate cation vacancies as a percentage of  $Fe^{+2}$  initially present in the ideal crystal.

SS0034

35. The density of ZnS crystal (Zinc blende structure) having 10% Frenkel defect is

[  $r_{Zn^{2+}} = 40\sqrt{3} \text{ pm}$ ,  $r_{S^{2-}} = 110\sqrt{3} \text{ pm}$ ,  $Zn = 65.2$ ,  $S = 32$  ] [ $6^4 = 1296$ ]

SS0035

EXERCISE : S-II

1. An element (atomic weight = 125) crystallises in simple cubic structure. Diameter of the largest atom which can be placed without disturbing unit cell is 366 pm. If the density of element 'x' gm/cm<sup>3</sup>, the value of

$$\left(\frac{6x}{5}\right) \text{ is -}$$

[Given :  $\sqrt{3} = 1.732$  ,  $N_A = 6 \times 10^{23}$  ]

SS0036

2. The density of diamond from the fact that it has face centred cubic structure with two atoms per lattice point and unit cell edge length of 3.6 Å, is 'x' gm / cm<sup>3</sup>, then the value of (1.458x) is ( $N_A = 6 \times 10^{23}$ )

SS0037

3. Iron crystallizes in several modifications. At about 910°C, the body-centred cubic 'α' form undergoes a transition to the face-centred cubic 'γ' form. Assuming that the distance between nearest neighbours is the same in the two forms at the transition temperature, the ratio of the density of γ iron to that of α iron at the transition temperature, x : 1, then the value of (3√6x) is.

SS0038

4. What is the percent by mass of titanium in rutile, a mineral that contain titanium and oxygen, if structure can be described as a closest packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium? (Ti = 48)

SS0039

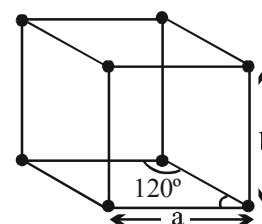
5. An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two extra atoms on one of its body diagonal. If the volume of this unit cell is  $2.4 \times 10^{-23}$  cm<sup>3</sup> and density of element is 7.2 g cm<sup>-3</sup>, calculate the number of atoms present in 288 g of element.

SS0040

6. What will be packing fraction of solid in which atoms are present at corners and cubic void is occupied. The insertion of the sphere into void does not disturb simple cubic lattice.

SS0041

7. Ice crystallizes in a hexagonal lattice. At the low temperature at which the structure was determined, the lattice constants where  $a = 5$  Å, and  $b = 3.5\sqrt{3}$  Å  
How many molecules are contained in the given unit cell?



$$[\text{density (ice)} = \frac{16}{17.5} \text{ gm/cm}^3]$$

SS0042



8. The mineral hawleyite, one form of CdS, crystallizes in one of the cubic lattices, with edge length  $5.87 \text{ \AA}$ . The density of hawleyite is  $4.63 \text{ g cm}^{-3}$ . (Cd = 112)
- (i) In which cubic lattice does hawleyite crystallize?
- (ii) Find the Schottky defect in  $\text{g cm}^{-3}$ .

SS0043

9. KCl crystallizes in the same type of lattice as does NaCl. Given that  $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.5$  and  $\frac{r_{\text{Na}^+}}{r_{\text{K}^+}} = 0.7$
- Calculate:
- (a) The ratio of the sides of unit cell for KCl to that for NaCl and
- (b) The ratio of densities of NaCl to that for KCl.

$$\left( \left( \frac{8}{7} \right)^3 = 1.5, \frac{74.5}{58.5} = 1.25 \right)$$

SS0044

10. A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.
- (a) What is the empirical formula of the compound?
- (b) What is the co-ordination number of the Mn ion?
- (c) Calculate the edge length of the unit cell, if the radius of Mn ion is  $0.65 \text{ \AA}$  and that of  $\text{F}^-$  ion is  $1.36 \text{ \AA}$ .

SS0045

11. Potassium crystallizes in a body-centred cubic lattice with edge length,  $a = 5.2 \text{ \AA}$ .
- (a) What is the distance between nearest neighbours?
- (b) What is the distance between next-nearest neighbours?
- (c) How many nearest neighbours does each K atom have?
- (d) How many next-nearest neighbours does each K atom have?
- (e) What is the density of crystalline potassium?
- (Given : K = 39,  $(5.2)^3 = 140$ )

SS0046

12. An element X (atomic weight =  $24 \text{ gm/mole}$ ) forms a face centred cubic lattice. If the edge length of the lattice is  $4 \times 10^{-8} \text{ cm}$  and the observed density is  $2.40 \times 10^3 \text{ kg/m}^3$ , calculate the percentage occupancy of lattice points by X element. (Given :  $N_A = 6 \times 10^{23}$ )

SS0047

13. Calculate the density (in  $\text{gm/cm}^3$ ) of NaCl type ionic solid (MW =  $75 \text{ gm/mol}$ ) if distance between two nearest cations is  $250\sqrt{2} \text{ pm}$  (avogadro number =  $6 \times 10^{23}$ )

SS0048



## EXERCISE : O-I

## SINGLE CORRECT :

1. Which of the following are the correct axial distances and axial angles for rhombohedral system ?  
 (A)  $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$  (B)  $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$   
 (C)  $a \neq b = c, \alpha = \beta = \gamma = 90^\circ$  (D)  $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$  SS0050
2.  $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$  represents  
 (A) tetragonal system (B) orthorhombic system  
 (C) monoclinic system (D) triclinic system SS0051
3. Diamond belongs to the crystal system :  
 (A) Cubic (B) triclinic (C) tetragonal (D) hexagonal SS0052
4. A match box exhibits -  
 (A) Cubic geometry (B) Monoclinic geometry  
 (C) Tetragonal geometry (D) Orthorhombic geometry SS0053
5. Which of the following solids substances will have same refractive index when measured in different directions?  
 (A) NaCl (B) Monoclinic sulphur (C) Rubber (D) Graphite SS0054
6. In the body-centred cubic unit cell & face centred cubic unit cell, the radius of atom in terms of edge length(a) of the unit cell is respectively:  
 (A)  $\frac{a}{2}, \frac{a}{2\sqrt{2}}$  (B)  $\frac{a}{2\sqrt{2}}, \frac{\sqrt{3}a}{4}$  (C)  $\frac{\sqrt{3}a}{4}, \frac{a}{2\sqrt{2}}$  (D)  $\frac{\sqrt{3}a}{2}, \frac{a}{2\sqrt{2}}$  SS0055
7. Crystal system in which maximum number of Bravais lattices are possible is  
 (A) Cubic (B) Triclinic (C) Orthorhombic (D) Rhombohedral SS0056
8. Number of atoms at second nearest position from a given atom in a BCC structure is  
 (A) 8 (B) 6 (C) 12 (D) 4 SS0057
9. Percentage area of each face covered by atoms in a FCC unit cell is -  
 (A) 60.4% (B) 68% (C) 74% (D) 78.5% SS0058
10. Correct sequence of the coordination number in SC, FCC & BCC is-  
 (A) 6, 8, 12 (B) 6, 12, 8 (C) 8, 12, 6 (D) 8, 6, 12 SS0059

11. If 'Z' is the number of atoms in the unit cell that represents the closest packing sequence ---A B C A B C ---, the number of tetrahedral voids in the unit cell is equal to  
 (A) Z (B) 2Z (C) Z/2 (D) Z/4 SS0060
12. The interstitial hole is called tetrahedral because  
 (A) It is formed by four spheres.  
 (B) Partly same and partly different.  
 (C) It is formed by four spheres the centres of which form a regular tetrahedron.  
 (D) None of the above three. SS0061
13. The size of an octahedral void formed in a closest packed lattice as compared to tetrahedral void is  
 (A) Equal (B) Smaller (C) Larger (D) Not definite SS0062
14. If the anions (A) form hexagonal closest packing and cations (C) occupy only 2/3 octahedral voids in it, then the general formula of the compound is  
 (A) CA (B) CA<sub>2</sub> (C) C<sub>2</sub>A<sub>3</sub> (D) C<sub>3</sub>A<sub>2</sub> SS0063
15. Which one of the following schemes of ordering closest packed sheets of equal sized spheres do not generate close packed lattice.  
 (A) ABCABC (B) ABACABAC (C) ABBAABBA (D) ABCBCABCBC SS0064
16. Copper metal crystallizes in FCC lattice. Edge length of unit cell is 362 pm. The radius of largest atom that can fit into the voids of copper lattice without disturbing it is  
 (A) 53 pm (B) 45 pm (C) 93 pm (D) 87 pm SS0065
17. Packing fraction in 2-D hexagonal arrangement -  
 (A)  $\frac{\pi}{3\sqrt{2}}$  (B)  $\frac{\pi}{3\sqrt{3}}$  (C)  $\frac{\pi}{2\sqrt{3}}$  (D)  $\pi/6$  SS0066
18. In fcc unit cell smallest distance between octahedral void & tetrahedral void is -  
 (a = edge length of unit cell )  
 (A)  $\frac{a}{\sqrt{2}}$  (B)  $\frac{\sqrt{3}a}{2}$  (C) a (D)  $\frac{\sqrt{3}a}{4}$  SS0067

19. What is not true regarding hexagonal close packing (hcp)  
 (A) packing fraction is 0.74  
 (B) coordination number is 12  
 (C) ABC ABC.....type packing  
 (D) Containing both tetrahedral and octahedral voids  
**SS0068**
20. In which of the following arrangement distance between two nearest neighbours is maximum, considering identical sized atoms in all arrangements?  
 (A) Simple cubic (B) bcc (C) fcc (D) equal in all  
**SS0069**
21. How many unit cell are there in 1 gram cubic crystal of NaCl?  
 (A)  $\frac{4 \times N_A}{58.5}$  (B)  $\frac{N_A}{58.5}$  (C)  $\frac{N_A}{58.5 \times 4}$  (D)  $\frac{N_A}{58.5 \times 8}$   
**SS0070**
22. The density of  $\text{CaF}_2$  (fluorite structure) is  $3.18 \text{ g/cm}^3$ . The length of the side of the unit cell is (Ca = 40, F = 19)  
 (A) 253 pm (B) 344 pm (C) 546 pm (D) 273 pm  
**SS0071**
23. The coordination number of cation and anion in Fluorite  $\text{CaF}_2$  and CsCl are respectively  
 (A) 8:4 and 6:3 (B) 6:3 and 4:4 (C) 8:4 and 8:8 (D) 4:2 and 2:4  
**SS0072**
24. A compound XY crystallizes in 8 : 8 lattice with unit cell edge length of 480 pm. If the radius of  $\text{Y}^-$  is 225 pm, then the radius of  $\text{X}^+$  is  
 (A) 127.5 pm (B) 190.68 pm (C) 225 pm (D) 255 pm  
**SS0073**
25. The mass of a unit cell of CsCl corresponds to  
 (A) 1  $\text{Cs}^+$  and 1  $\text{Cl}^-$  (B) 1  $\text{Cs}^+$  and 6  $\text{Cl}^-$  (C) 4  $\text{Cs}^+$  and 4  $\text{Cl}^-$  (D) 8  $\text{Cs}^+$  and 1  $\text{Cl}^-$   
**SS0074**
26. An ionic compound AB has ZnS type structure. If the radius  $\text{A}^+$  is 22.5 pm, then the ideal radius of  $\text{B}^-$  would be  
 (A) 54.35 pm (B) 100 pm (C) 145.16 pm (D) none of these  
**SS0075**
27. Edge length of  $\text{M}^+\text{X}^-$  (NaCl structure) is  $7.2 \text{ \AA}$ . Assuming  $\text{M}^+ - \text{X}^-$  contact along the cell edge, radius of  $\text{X}^-$  ion is ( $r_{\text{M}^+} = 1.6 \text{ \AA}$ ):  
 (A)  $2.0 \text{ \AA}$  (B)  $5.6 \text{ \AA}$  (C)  $2.8 \text{ \AA}$  (D)  $38 \text{ \AA}$   
**SS0076**



## EXERCISE : O-II

## SINGLE CORRECT :

- The only incorrect statement for the packing of identical spheres in two dimension is :
  - For square close packing , coordination number is 4.
  - For hexagonal close packing, coordination number is 6.
  - There is only one void per atom in both, square and hexagonal close packing.
  - Hexagonal close packing is more efficiently packed than square close packing. **SS0085**
- Correct statement for ccp is :
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 4 octahedral voids
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 6 octahedral voids
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 8 octahedral voids
  - Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 12 octahedral voids **SS0086**
- Which of the following statements is correct in the rock-salt structure of an ionic compounds?
  - coordination number of cation is four whereas that of anion is six.
  - coordination number of cation is six whereas that of anion is four.
  - coordination number of each cation and anion is four.
  - coordination number of each cation and anion is six. **SS0087**

## MORE THAN ONE MAY BE CORRECT :

- Which of the following statements is/are correct :
  - In an anti-fluorite structure, anions form FCC lattice and cations occupy all tetrahedral voids.
  - If the radius of cations and anions are  $0.2 \text{ \AA}$  and  $0.95 \text{ \AA}$ , then coordination number of cation in the crystal is 4.
  - Each sphere is surrounded by six voids in two dimensional hexagonal close packed layer.
  - 8  $\text{Cs}^+$  ions occupy the second nearest neighbour locations of a  $\text{Cs}^+$  ion in CsCl crystals.
- Select correct statement(s) **SS0088**
  - Density of crystal always increases due to substitutional impurity defect.
  - An ion is transferred from a lattice site to an interstitial position in Frenkel defect.
  - In AgCl, the silver ion is displaced from its lattice position to an interstitial position. Such a defect is called a frenkel defect **SS0089**
  - None
- Lead metal has a density of  $11.34 \text{ g/cm}^3$  and crystallizes in a face-centred lattice. Choose the correct alternatives ( $\text{Pb} = 208$ ,  $N_A = 6 \times 10^{23}$ )
  - the volume of one unit cell is  $1.22 \times 10^{-22} \text{ cm}^3$ .
  - the volume of one unit cell is  $1.22 \times 10^{-19} \text{ cm}^3$ .
  - the atomic radius of lead is 175 pm.
  - the atomic radius of lead is 155.1 pm. **SS0090**

7. Which of the following statement(s) is/are correct ?
- (A) NaCl is a 'AB' crystal lattice that can be interpreted to be made up of two individual fcc unit cells of  $A^+$  and  $B^-$  fused together in such a manner that the corner of one unit cell becomes the edge centre of the other.
- (B) In a face centred cubic unit cell, the body centre is an octahedral void.
- (C) In fcc unit cell, octahedral and tetrahedral voids are equal in number.
- (D) Tetrahedral voids =  $2 \times$  octahedral voids, is valid for ccp and hcp. SS0091
8. Select the correct statement (s) :
- (A) CsCl mainly shows Schottky defect      (B) ZnS mainly shows Frenkel defect
- (C) NaCl unit cell contain  $4Na^+$  and  $4Cl^-$       (D) Truncated octahedron have 24 corners. SS0092
9. Select the correct statement(s) –
- (A) The ionic crystal of AgBr has Schottky defect.
- (B) The unit cell having crystal parameters,  $a = b \neq c$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$  is hexagonal
- (C) Ionic compounds having Frenkel defect has high  $r^+/r^-$  ratio.
- (D) The co-ordination number of  $Na^+$  ion in NaCl is 6 SS0093
10. Which of the following is/are true ?
- (A) Ratio of nearest neighbours in simple cubic cell to next nearest neighbours in face centred is cubic cell is 1.
- (B) Packing efficiency of a unit cell in which atoms are present at each corner and each edge centre is about 26 % in metallic crystal.
- (C) Distance between two planes in FCC or HCP arrangement is same for a metal existing in both forms, with same atomic radius.
- (D) If number of unit cell along one edge are 'x', then total number of unit cell in cube =  $x^3$  SS0094

#### ASSERTION / REASON :

11. **Statement-1** : In Antifluorite structure ( $Li_2O$ ), the oxide ions occupy c.c.p. (cubic close packing) and  $Li^+$  ions, 100% tetrahedral voids.

**Statement-2** : The distance of the nearest neighbours in antifluorite structure is  $\frac{\sqrt{3}a}{4}$ , where 'a' is the edge length of the cube

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true. SS0095



- 12. Statement-1 :** In FCC unit cell, packing efficiency is more when all tetrahedral voids are filled with spheres of maximum possible size as compared with packing efficiency when all octahedral voids are filled in similar way.  
**Statement-2 :** Tetrahedral voids are more in the number than octahedral voids in FCC.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true. SS0096
- 13. Statement-1 :** In diamond, carbon atoms occupy alternate tetrahedral voids in the FCC lattice formed by the carbon atoms.  
**Statement-2 :** In diamond, packing fraction is more than 74%.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true. SS0097
- 14. Statement-1 :** Due to Frenkel defect, there is no effect on the density of the crystalline solid.  
**Statement-2 :** In Frenkel defect, no cation or anion leaves the crystal.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true. SS0098
- 15. Statement-1 :** Conductivity of silicon increased by doping it with group 15 element.  
**Statement-2 :** Doping means introduction of small amount of impurities like P or As into pure silicon crystal.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true. SS0099

**COMPREHENSION :****Paragraph for Q.16 & Q.17**

Solid balls of radius 17.32 cm crystallises in bcc pattern. During one such crystallisation, some oxygen gas is trapped. This trapped oxygen at 640K creates pressure of 5 atm.

**Assume :**

- (i) BCC arrangement is not disturbed due to trapping of gas.  
 (ii) Gas is uniformly distributed inside unit cell

[Take  $R = 0.08 \text{ atm-litre/mole-K}$  ,  $N_A = 6 \times 10^{23}$  , Mass of a solid ball = 64 gms]

- 16.** Number of oxygen molecules present in an unit cell is -  
 (A)  $2.4 \times 10^{24}$       (B)  $1.2 \times 10^{24}$       (C)  $6 \times 10^{23}$       (D)  $3 \times 10^{23}$  SS0100
- 17.** Calculate percentage increase in density due to trapping of gas  
 (A) 16.67 %      (B) 33.33 %      (C) 100%      (D) 50% SS0101

**Paragraph for (Que. 18 to 21)**

Calcium crystallizes in a cubic unit cell with density 3.2 g/cc. Edge-length of the unit cell is 437 pm.

18. The type of unit cell is  
 (A) Simple cubic      (B) BCC      (C) FCC      (D) Edge-centred      **SS0102**
19. The nearest neighbour distance is  
 (A) 154.5 pm      (B) 309 pm      (C) 218.5 pm      (D) 260 pm      **SS0103**
20. The number of nearest neighbours of a Ca atom are  
 (A) 4      (B) 6      (C) 8      (D) 12      **SS0104**
21. If the metal is melted, density of the molten metal was found to be 3 g/cc. What will be the percentage of empty space in the molten metal?  
 (A) 31%      (B) 36%      (C) 28%      (D) 49%      **SS0105**

**TABLE TYPE COMPREHENSION :**

- | Column-I                                  | Column-II                                      | Column-III                                   |
|---|--|--|
| (A) NaCl (Rock salt) structure            | (i) Cation - FCC<br>Anion - Tetrahedral void   | (I) All tetrahedral voids are occupied       |
| (B) CsCl structure                        | (ii) Anion - FCC<br>Cation - Tetrahedral voids | (II) All octahedral voids are occupied       |
| (C) ZnS (zinc blende) structure           | (iii) Anion - SC<br>Cation - Cubic voids       | (III) 50 % of tetrahedral voids are occupied |
| (D) CaF <sub>2</sub> (fluorite) structure | (iv) Anion - FCC<br>Cation - Octahedral void   | (IV) All octahedral voids are empty          |
22. Which of the following is correct match ?  
 (A) A, i, I      (B) A, ii, IV      (C) A, iv, II      (D) A, iv, IV      **SS0106**
23. Which of the following is incorrect match ?  
 (A) B, iii, I      (B) C, ii, III      (C) D, i, I      (D) D, i, IV      **SS0107**
24. Which of the following is correct match ?  
 (A) D, ii, I      (B) B, iv, IV      (C) D, iii, I      (D) C, ii, IV      **SS0108**

**MATCH THE COLUMN :**

25. Match the column

**Column I**

- (A) Tetragonal and Hexagonal  
 (B) Cubic and Rhombohedral  
 (C) Monoclinic and Triclinic  
 (D) Cubic and Hexagonal

**Column II**

- (P) are two crystal systems  
 (Q)  $a = b \neq c$   
 (R)  $a \neq b \neq c$   
 (S)  $a = b = c$

SS0109

26. Match the column:

**Column I**

- (A) Rock salt structure  
 (B) Zinc Blend structure  
 (C) Fluorite structure

**Column II**

- (P) Co-ordination number of cation is 4  
 (Q)  $\frac{\sqrt{3}a}{4} = r_+ + r_-$   
 (R) Co-ordination number of cation and anion are same  
 (S) Distance between two nearest anion is  $\frac{a}{\sqrt{2}}$

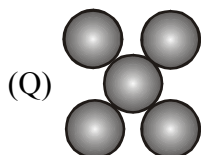
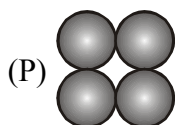
SS0110

**MATCHING LIST TYPE :**

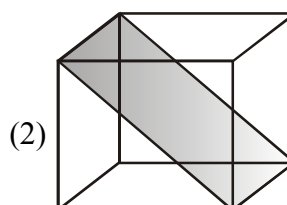
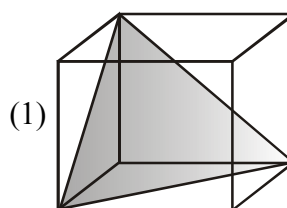
27. Match the column

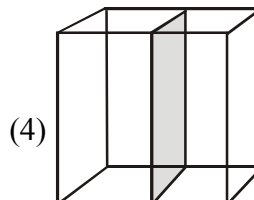
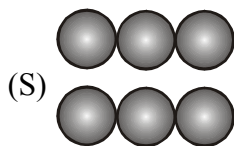
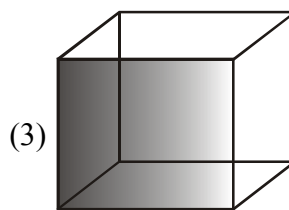
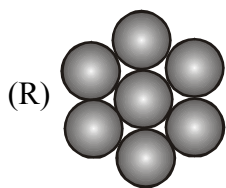
**Column I**

(Arrangement of the atoms/ions)

**Column II**

(Planes in fcc lattice)





Code:

	P	Q	R	S
(A)	4	3	1	2
(B)	4	3	2	1
(C)	3	2	1	4
(D)	1	2	4	3

SS0111

28. Column I

Column II

[Distance in terms of edge length of cube (a)]

(P) 0.866 a

(1) Shortest distance between cation & anion in CsCl structure.

(Q) 0.707 a

(2) Shortest distance between two cation in CaF<sub>2</sub> structure.

(R) 0.433 a

(3) Shortest distance between carbon atoms in diamond.

(S) a

(4) shortest distance between next nearest cations in rock salt structure.

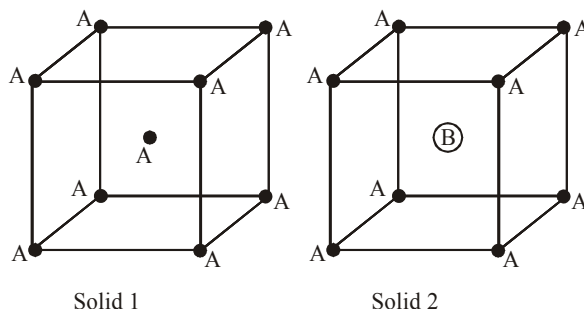
Code:

	P	Q	R	S
(A)	4	3	1	2
(B)	1	2	3	4
(C)	3	2	1	4
(D)	1	2	4	3

SS0112

## EXERCISE : J-MAIN

1. Consider the bcc unit cells of the solids 1 and 2 with the position of atoms as shown below. The radius of atom B is twice that of atom A. The unit cell edge length is 50% more in solid 2 than in 1. What is the approximate packing efficiency in solid 2? [Jee-Main (online)Jan-19]



- (1) 45%                      (2) 65%                      (3) 90%                      (4) 75%                      **SS0113**
2. The ratio of number of atoms present in a simple cubic, body centered cubic and face centered cubic structure are, respectively : [Jee-Main (online)Jan-19]
- (1) 1 : 2 : 4                      (2) 8 : 1 : 6                      (3) 4 : 2 : 1                      (4) 4 : 2 : 3                      **SS0114**
3. An element has a face-centred cubic (fcc) structure with a cell edge of  $a$ . The distance between the centres of two nearest tetrahedral voids in the lattice is : [Jee-Main (online)Jan-19]
- (1)  $\frac{a}{2}$                       (2)  $a$                       (3)  $\frac{3}{2}a$                       (4)  $\sqrt{2}a$                       **SS0115**
4. At  $100^\circ\text{C}$ , copper (Cu) has FCC unit cell structure with cell edge length of  $x \text{ \AA}$ . What is the approximate density of Cu (in  $\text{g cm}^{-3}$ ) at this temperature ? [Jee-Main (online)April-19]  
[Atomic Mass of Cu = 63.55u]
- (1)  $\frac{105}{x^3}$                       (2)  $\frac{211}{x^3}$                       (3)  $\frac{205}{x^3}$                       (4)  $\frac{422}{x^3}$                       **SS0116**
4. Which primitive unit cell has unequal edge lengths ( $a \neq b \neq c$ ) and all axial angles different from  $90^\circ$  [Jee-Main (online)April-19]
- (1) Tetragonal                      (2) Hexagonal                      (3) Monoclinic                      (4) Triclinic                      **SS0116**
5. The radius of the largest sphere which fits properly at the centre of the edge of body centred cubic unit cell is : (Edge length is represented by 'a') :- [Jee-Main (online)April-19]
- (1)  $0.134a$                       (2)  $0.027a$                       (3)  $0.067a$                       (4)  $0.047a$                       **SS0117**
6. A solid having density of  $9 \times 10^3 \text{ kg m}^{-3}$  forms face centred cubic crystals of edge length  $200\sqrt{2} \text{ pm}$ . What is the molar mass of the solid ? [Jee-Main (online)April-19]  
(Avogadro constant  $\cong 6 \times 10^{23} \text{ mol}^{-1}$ ,  $\pi \cong 3$ )
- (1)  $0.0216 \text{ kg mol}^{-1}$                       (2)  $0.0305 \text{ kg mol}^{-1}$                       (3)  $0.4320 \text{ kg mol}^{-1}$                       (4)  $0.0432 \text{ kg mol}^{-1}$

**SS0118**

7. Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be :-  
[Jee-Main (offline)-12]
- (1) 152 pm                      (2) 75 pm                      (3) 300 pm                      (4) 240 pm                      **SS0119**
8. In a face centred cubic lattice, atoms of A form the corner points and atoms of B form the face centred points. If two atoms of A are missing from the corner points, the formula of the ionic compound is  
[Jee-Main (online)-13]
- (1)  $AB_2$                       (2)  $AB_3$                       (3)  $AB_4$                       (4)  $A_2B_5$                       **SS0120**
9. Which one of the following statements about packing in solids is **incorrect** ?  
[Jee-Main (online)-13]
- (1) Void space in ccp mode of packing is 26%  
(2) Coordination number in hcp mode of packing is 12  
(3) Void space in hcp mode of packing is 32%  
(4) Coordination number in bcc mode of packing is 8                      **SS0121**
10. An element having an atomic radius of 0.14 nm crystallizes in an fcc unit cell. What is the length of a side of the cell ?  
[Jee-Main (online)-13]
- (1) 0.96 nm                      (2) 0.4 nm                      (3) 0.24 nm                      (4) 0.56 nm                      **SS0122**
11. Experimentally it was found that a metal oxide has formula  $M_{0.98}O$ . Metal M, is present as  $M^{2+}$  and  $M^{3+}$  in its oxide. Fraction of the metal which exists as  $M^{3+}$  would be :- [Jee-Main (offline)-13]
- (1) 7.01%                      (2) 4.08%                      (3) 6.05%                      (4) 5.08                      **SS0123**
12. The total number of octahedral void(s) per atom present in a cubic close packed structure is :-  
[Jee-Main (online)-14]
- (1) 1                      (2) 2                      (3) 3                      (4) 4                      **SS0124**
13. In a monoclinic unit cell, the relation of sides and angles are respectively [Jee-Main (online)-14]
- (1)  $a \neq b \neq c$  and  $\alpha \neq \beta \neq \gamma \neq 90^\circ$                       (2)  $a \neq b \neq c$  and  $\beta = \gamma = 90^\circ \neq \alpha$   
(3)  $a = b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$                       (4)  $a \neq b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$                       **SS0125**
14. The appearance of colour in solid alkali metal halides is generally due to :  
[Jee-Main (online)-14]
- (1) Frenkel defect                      (2) F-centres                      (3) Schottky defect                      (4) Interstitial position  
**SS0126**
15. In a face centred cubic lattice atoms A are at the corner points and atoms B at the face centred points. If atom B is missing from one of the face centred points, the formula of the ionic compound is :  
[AIEEE-2011, Jee-Main (online)-14]
- (1)  $AB_2$                       (2)  $A_2B_3$                       (3)  $A_5B_2$                       (4)  $A_2B_5$                       **SS0127**

16. CsCl crystallises in body centred cubic lattice. if 'a' is its edge length then which of the following expression is correct : [Jee-Main (offline)-14]

(1)  $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{\sqrt{3}}{2} a$     (2)  $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \sqrt{3} a$     (3)  $r_{\text{Cs}^+} + r_{\text{Cl}^-} = 3a$     (4)  $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{3a}{2}$

SS0128

17. Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately :- [Jee-Main (offline)-15]

(1) 5.72 Å                      (2) 0.93 Å                      (3) 1.86 Å                      (4) 3.022 Å                      SS0129

18. Which of the following compounds is metallic and ferromagnetic ? [Jee-Main (offline)-16]

(1) MnO<sub>2</sub>                      (2) TiO<sub>2</sub>                      (3) CrO<sub>2</sub>                      (4) VO<sub>2</sub>                      SS0130

19. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be :- [Jee-Main (offline)-17]

(1) 2a                      (2)  $2\sqrt{2} a$                       (3)  $\sqrt{2} a$                       (4)  $\frac{a}{\sqrt{2}}$                       SS0131

20. Which type of defect has the presence of cations in the interstitial sites -

(1) Vacancy defect                      (2) Frenkel defect                      [Jee-Main (offline)-18]  
(3) Metal deficiency defect                      (4) Schottky defect                      SS0132

21. All of the following share the same crystal structure except :- [Jee-Main (online)-18]

(1) RbCl                      (2) CsCl                      (3) LiCl                      (4) NaCl                      SS0133

22. Which of the following arrangements shows the schematic alignment of magnetic moments of antiferromagnetic substance ? [Jee-Main (online)-18]

(1)  $\uparrow \downarrow \downarrow \downarrow \downarrow \uparrow$                       (2)  $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$

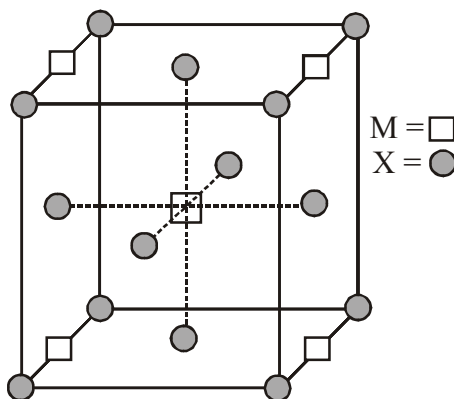
(3)  $\uparrow \uparrow \downarrow \uparrow \uparrow \downarrow$                       (4)  $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$                       SS0134

EXERCISE : J-ADVANCED

1. The number of hexagonal faces that present in a truncated octahedron is. [JEE-2011]

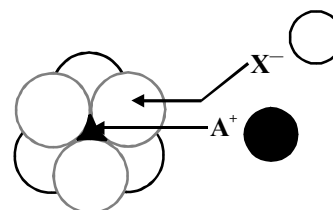
SS0135

2. A compound  $M_pX_q$  has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is : [JEE-2012]



- (A) MX                      (B)  $MX_2$                       (C)  $M_2X$                       (D)  $M_5X_{14}$                       SS0136

3. The arrangement of  $X^-$  ions around  $A^+$  ion in solid AX is given in the figure (not drawn to scale). If the radius of  $X^-$  is 250 pm, the radius of  $A^+$  is - [JEE-2013]



- (A) 104 pm                      (B) 125 pm                      (C) 183 pm                      (D) 57 pm                      SS0137

4. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions m and n respectively, are - [JEE-2015]

- (A)  $\frac{1}{2}, \frac{1}{8}$                       (B)  $1, \frac{1}{4}$                       (C)  $\frac{1}{2}, \frac{1}{2}$                       (D)  $\frac{1}{4}, \frac{1}{8}$                       SS0138

5. The **CORRECT** statement(s) for cubic close packed (ccp) three dimensional structure is (are)

- (A) The number of the nearest neighbours of an atom present in the topmost layer is 12  
 (B) The efficiency of atom packing is 74% [JEE-2016]  
 (C) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively

- (D) The unit cell edge length is  $2\sqrt{2}$  times the radius of the atom                      SS0139



6. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is  $8 \text{ g cm}^{-3}$ , then the number of atoms present in 256g of the crystal is  $N \times 10^{24}$ . The value of N is **[JEE-2017]**

SS0140

7. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instructions given below. Neglect the charge balance.

**[JEE-2018]**

- (i) Remove all the anions (X) except the central one
- (ii) Replace all the face centered cations (M) by anions (X)
- (iii) Remove all the corner cations (M)
- (iv) Replace the central anion (X) with cation (M)

The value of  $\left( \frac{\text{number of anions}}{\text{number of cations}} \right)$  in Z is \_\_\_\_\_.

SS0141

## ANSWER KEY

## EXERCISE : S-I

- |   |                                   |
|---|-----------------------------------|
| 1. Ans. (a) 300 pm, (b) 255 pm, (c) 210 pm                        | 2. Ans. 438 pm, 219 pm            |
| 3. Ans. 5.83 g cm <sup>-3</sup>                                   | 4. Ans. ( $\sqrt{2} : 1$ )        |
| 5. Ans. (0.9 gm/cm <sup>-3</sup> )                                | 6. Ans. A, B                      |
| 7. Ans. (64)  | 8. Ans. (12)                      |
| 9. Ans. (6)   | 10. Ans. (2)                      |
| 11. Ans. A <sub>2</sub> BC  | 12. Ans. (4)                      |
| 13. Ans. (0.293)  | 14. Ans. ( $6 \times 10^{17}$ )   |
| 15. Ans. (2) $\frac{\frac{a}{\sqrt{2}} \times \sqrt{2}}{a/2} = 2$ | 16. Ans. (2.07 pm)                |
| 17. Ans. (6)  | 18. Ans. (60%)                    |
| 19. Ans. 41.67 g cm <sup>-3</sup>                                 | 20. Ans. 0.60                     |
| 21. Ans. 4, 6, 8  | 22. Ans. (6)                      |
| 23. Ans. ZnAl <sub>2</sub> O <sub>4</sub>                         | 24. Ans. 267 pm, 534 pm, 377.6 pm |
| 25. Ans. 346.4 pm   | 26. Ans. 4                        |
| 27. Ans. a = 600 pm, V = $2.16 \times 10^{-22}$ cm <sup>3</sup>   | 28. Ans. 1.81 Å                   |
| 29. Ans. 4.34 Å   | 30. Ans. (5 gm/cm <sup>3</sup> )  |
| 31. Ans. 15.05 %  | 32. Ans. $6.0 \times 10^{18}$     |
| 33. Ans. 10   | 34. Ans. 12.5 %                   |
| 35. Ans. 3.0 gm/cm <sup>3</sup>                                   |                                   |

## EXERCISE : S-II

- |  |                            |
|--|----------------------------|
| 1. Ans. (2)  | 2. Ans. (5)                |
| 3. Ans. Ans. 8   | 4. Ans. 60%, +4            |
| 5. Ans. $5 \times 10^{24}$   | 6. Ans. 0.72               |
| 7. Ans. 4  |                            |
| 8. Ans. (i) FCC (ii) 0.116 g/cc  | 9. Ans. (a) 1.143, (b) 1.2 |
| 10. Ans. (a) MnF <sub>3</sub> , (b) 6, (c) 4.02 Å                                      |                            |
| 11. Ans. (a) 4.5 Å, (b) 5.2 Å, (c) 8, (d) 6, (e) 0.929 g/cm <sup>3</sup>               |                            |
| 12. Ans. 96 %  | 13. Ans. (4)               |
| 14. Ans. Mg <sub>2</sub> SiO <sub>4</sub> , Fe <sub>2</sub> SiO <sub>4</sub> , 57.14 % |                            |

**EXERCISE : O-I**

- |             |             |             |
|-------------|-------------|-------------|
| 1. Ans.(A)  | 2. Ans.(D)  | 3. Ans.(A)  |
| 4. Ans.(D)  | 5. Ans.(C)  | 6. Ans.(C)  |
| 7. Ans. (C) | 8. Ans (B)  | 9. Ans (D)  |
| 10. Ans (B) | 11. Ans.(B) | 12. Ans.(C) |
| 13. Ans.(C) | 14. Ans.(C) | 15. Ans.(C) |
| 16. Ans.(A) | 17. Ans.(C) | 18. Ans (D) |
| 19. Ans (C) | 20. Ans (D) | 21. Ans.(C) |
| 22. Ans.(C) | 23. Ans.(C) | 24. Ans.(B) |
| 25. Ans.(A) | 26. Ans.(B) | 27. Ans.(A) |
| 28. Ans.(A) | 29. Ans.(D) | 30. Ans.(D) |
| 31. Ans.(D) | 32. Ans.(B) | 33. Ans(C)  |
| 34. Ans (C) | 35. Ans.(D) |             |

**EXERCISE : O-II**

- |  |                  |                |
|--|------------------|----------------|
| 1. Ans. (C)  | 2. Ans.(B)       | 3. Ans.(D)     |
| 4. Ans.(A,C)   | 5. Ans.(B,C)     | 6. Ans.(A,C)   |
| 7. Ans.(A,B,D)                                       | 8. Ans.(A,B,C,D) | 9. Ans.(A,B,D) |
| 10. Ans.(A,B,C,D)                                    | 11. Ans.(B)      | 12. Ans.(D)    |
| 13. Ans.(C)  | 14. Ans.(A)      | 15. Ans.(A)    |
| 16. Ans.(B)  | 17. Ans.(D)      | 18. Ans.(C)    |
| 19. Ans.(B)  | 20. Ans.(D)      | 21. Ans.(A)    |
| 22. Ans.(C)  | 23. Ans.(A)      | 24. Ans.(D)    |
| 25. Ans.(A) → P, Q ; (B) → P,S ; (C) → P,R ; (D) → P |                  |                |
| 26. Ans.(A) → R,S ; (B) → P,Q,R,S ; (C) → Q          |                  |                |
| 27. Ans.Ans.(A)                                      | 28. Ans.(B)      |                |

**EXERCISE : J-MAIN**

- 
- |             |             |             |             |
|-------------|-------------|-------------|-------------|
| 1. Ans.(3)  | 2. Ans.(1)  | 3. Ans.(1)  | 4. Ans.(4)  |
| 5. Ans.(3)  | 6. Ans.(2)  | 7. Ans.(1)  | 8. Ans.(3)  |
| 9. Ans.(3)  | 10. Ans.(2) | 11. Ans.(2) | 12. Ans.(1) |
| 13. Ans.(2) | 14. Ans.(2) | 15. Ans.(4) | 16. Ans.(1) |
| 17. Ans.(3) | 18. Ans.(3) | 19. Ans.(4) | 20. Ans.(2) |
| 21. Ans.(2) | 22. Ans.(4) |             |             |

**EXERCISE : J-ADVANCED**

- 
- |             |                |             |
|-------------|----------------|-------------|
| 1. Ans. (8) | 2. Ans.(B)     | 3. Ans. (A) |
| 4. Ans. (A) | 5. Ans.(B,C,D) | 6. Ans.(2)  |
| 7. Ans.(3)  |                |             |



## SURFACE CHEMISTRY

### 1. INTRODUCTION

पृष्ठ रसायन सतह या अंतरापृष्ठ पर होने वाली परिघटनाओं से संबंधित क्षेत्र है। अंतरापृष्ठ या सतह को स्थूल प्रावस्थाओं से अलग दर्शाने के लिए एक हाइपफन (–) या स्लैश (/) का उपयोग किया जाता है। उदाहरणार्थ, एक ठोस एवं गैस के बीच अंतरापृष्ठ को, ठोस – गैस या ठोस/गैस द्वारा दर्शाया जाता है। पूर्ण मिश्रणीयता के कारण गैसों के मध्य कोई अंतरापृष्ठ नहीं होता। पृष्ठ रसायन में हम जिन स्थूल प्रावस्थाओं के सम्पर्क में आते हैं वे शुद्ध यौगिक या विलयन हो सकते हैं। अंतरापृष्ठ की मोटाई बहुधा कुछ अणुओं तक सीमित रहती है, परंतु इसका क्षेत्रफल स्थूल प्रावस्थाओं के कणों के आकार पर निर्भर करता है। बहुत-सी ध्यान देने योग्य महत्वपूर्ण परिघटनाएं जैसे, संक्षारण, इलेक्ट्रोड प्रक्रम, विषमांगी उत्प्रेरण, विलिनीकरण एवं क्रिस्टलीकरण, अंतरापृष्ठ पर परिलक्षित होती हैं।

### 2. ADSORPTION

अणुक स्पीशीज का किसी ठोस (या द्रव)के स्थूल (bulk) की अपेक्षा पृष्ठ पर संचित होने की प्रवृत्ति अधिशोषण कहलाती है। अणुक स्पीशीज या पदार्थ जो कि पृष्ठ पर सांद्रित या संचित होता है **अधिशोष्य** (adsorbate) कहलाता है एवं पदार्थ जिसके पृष्ठ पर अधिशोषण होता है, **अधिशोषक** कहलाता है।

#### 2.1 DISTINCTION BETWEEN ADSORPTION AND ABSORPTION :

अधिशोषण में, अधिशोष्य की सान्द्रता केवल अधिशोषक की सतह पर बढ़ती है, जबकि अवशोषण में पदार्थ की सान्द्रता, ठोस के सम्पूर्ण निकाय या स्थूल में समान रूप से वितरित हो जाती है।



ऐसे अनेक उदाहरण हैं जो यह प्रदर्शित करते हैं कि किसी ठोस के पृष्ठ की प्रवृत्ति, संपर्क में आने वाली प्रावस्था के अणुओं को आकर्षित कर धारित करने की होती है। यह अणु केवल पृष्ठ पर ही रहते हैं एवं स्थूल में गहराई पर नहीं जाते। अणुक स्पीशीज का किसी ठोस या द्रव के स्थूल की अपेक्षा पृष्ठ पर संचित होना अधिशोषण कहलाता है। अधिशोषण निश्चित रूप से पृष्ठीय परिघटना है। विशेष रूप से बारीक चूर्ण अवस्था में ठोस, जो अधिक पृष्ठ क्षेत्रफल के होते हैं, जैसे चारकोल, सिलिका जेल, ऐलुमिना जेल, मिट्टी, कोलाइड सूक्ष्म विभाजित धातुएं इत्यादि अच्छे अवशोषक का कार्य करते हैं।

- (i) अधिशोषण में सतह तथा स्थूल पर अन्तिम नमूने के संगठन में अधिक अन्तर होगा जबकि अवशोषण में संगठन लगभग समान होगा
- (ii) अधिशोषण की दर समय के साथ घटती है जबकि अवशोषण लगभग नियत दर दर होता है
- (iii) अधिशोषण हमेशा ऊष्माक्षेपी होता है परन्तु अवशोषण ऊष्माशोषी या उष्माक्षेपी हो सकता है।

#### क्रियाविधियों में अधिशोषण

- (i) यदि चूर्णित चारकोल वाले बंद पात्र में  $O_2$ ,  $H_2$ ,  $CO$ ,  $Cl_2$ ,  $NH_3$  या  $SO_2$  जैसी गैसों ली जाएं, तो ऐसा देखा जाता है कि पात्र में गैस का दाब घट जाता है। गैस के अणु चारकोल की सतह पर सांद्रित हो जाते हैं अर्थात् गैसों सतह पर अधिशोषित हो जाती हैं।
- (ii) एक कार्बनिक रंजक जैसे मेथिलीन ब्लू के विलयन में जब जांतव चारकोल मिलाकर विलयन को अच्छी प्रकार हिलाया जाता है, तो **निस्स्यंद** (छनित्र) रंगहीन हो जाता है क्योंकि रंजक के अणु चारकोल की सतह पर एकत्रित हो जाते हैं अर्थात् अधिशोषित हो जाते हैं।

- (iii) अपरिष्कृत शर्करा के जलीय विलयन को जब जांतव चारकोल की परतों पर से प्रवाहित किया जाता है तो यह रंगहीन हो जाता है क्योंकि रंगीन पदार्थ चारकोल द्वारा अधिशोषित कर लिए जाते हैं।
- (iv) सिलिका जेल की उपस्थिति में वायु शुष्क हो जाती है, क्योंकि जल के अणु जेल की सतह पर अधिशोषित हो जाते हैं।

**Ex. 1.** 8.21 L क्षमता के एक पात्र में 1.5 atm तथा 27°C पर NH<sub>3</sub> गैस उपस्थित है। अब 5 gm चारकोल को मिलाया गया है तथा पर्याप्त समय के लिए छोड़ दिया गया है कुछ समय पश्चात् गैस का दाब 1.2 atm घट जाता है। प्रति ग्राम चारकोल द्वारा अधिशोषित NH<sub>3</sub> गैस के द्रव्यमान की गणना कीजिए? चारकोल का आयतन नगण्य है।

**Sol.** 
$$\text{Mass of NH}_3 \text{ gas adsorbed} = \frac{\Delta P \cdot V \cdot M}{RT} = \frac{0.3 \times 8.21 \times 17}{0.0821 \times 300} = 1.7 \text{ gm}$$

$$\therefore \text{Mass of NH}_3 \text{ gas adsorbed per gm of charcoal} = \frac{17}{5} = 0.34 \text{ gm}$$

**2.2 अधिशोषण की क्रियाविधि/ कारण :** अधिशोषण की उत्पत्ति इस तथ्य से होती है कि अधिशोषक के पृष्ठीय कण जैसे वातावरण में नहीं होते जिसमें स्थूल के अंदर के कण होते हैं।

- (i) अधिशोषक के अंदर के कणों पर लगने वाले सभी बल आपस में संतुलित होते हैं परंतु पृष्ठीय कण सभी दिशाओं में अपनी प्रकार के परमाणुओं या अणुओं से घिरे नहीं होते, अतः उन पर असंतुलित या अधिशोष आकर्षण बल होते हैं। अधिशोषक के ये बल ही अधिशोष्य कणों को आकर्षित करने के लिए उत्तरदायी होते हैं।
- (ii) दूसरा महत्वपूर्ण कारक जो अधिशोषण की विशेषता चित्रित करता है, वह है अधिशोषण ऊष्मा। अधिशोषण होने पर पृष्ठ के अवशिष्ट बलों में सदैव कमी आती है अर्थात् पृष्ठ ऊर्जा में कमी आती है जो कि ऊष्मा के रूप में प्रकट होती है। अतः अधिशोषण सदा एक ऊष्माक्षेपी प्रक्रम होता है। दूसरे शब्दों में, अधिशोषण का  $\Delta H$  हमेशा ऋणात्मक होता है। जब एक गैस अधिशोषित होती है, तो इस के अणुओं का संचलन (movement) सीमित हो जाता है। इससे अधिशोषण के पश्चात् गैस की एन्ट्रॉपी घट जाती है। अर्थात्  $\Delta S$  ऋणात्मक होता है। इस प्रकार अधिशोषण होने पर निकाय की एन्थैल्पी एवं एन्ट्रॉपी घटती हैं। किसी प्रक्रम के स्वतः प्रवर्तित होने के लिए, ऊष्मागतिकीय आवश्यकता यह है कि स्थिर ताप एवं दाब पर  $\Delta G$  ऋणात्मक होना चाहिए अर्थात् गिब्स ऊर्जा में कमी होनी चाहिए। समीकरण  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta G$  के आधार पर  $\Delta G$  तभी ऋणात्मक हो सकता है जब  $\Delta H$  का मान पर्याप्त ऋणात्मक हो, क्योंकि  $-T\Delta S$  का मान धनात्मक है। अतः अधिशोषण प्रक्रम में, जो कि स्वतः प्रवर्तित होता है, इन दोनों गुणकों का संयोजन  $\Delta G$  को ऋणात्मक बनाता है। जैसे-जैसे अधिशोषण बढ़ता है  $\Delta H$  कम ऋणात्मक होता जाता है एवं अंत में  $\Delta H$ ,  $T\Delta S$  के तुल्य हो जाता है एवं  $\Delta G$  का मान शून्य हो जाता है। इस अवस्था पर साम्य स्थापित हो जाता है।

अधिशोष्य (adsorbate) कणों की निम्न गतिविधियाँ हो सकती हैं

- (i) यदि प्रकृति तथा परिस्थिति अनुकूल हो तो अवशोषण में स्थूल (bulk) में विसरित हो जायेगी :
- (ii) वह सतह पर गति कर सकते हैं।
- (iii) वह सतह के बाहर आ सकते हैं जिसका परिणाम विशोषण होता है।

सामान्यतया विशोषण प्रथम कोटि गतिकी का अनुसरण करता है तथा आरहीनीयस समीकरण का पालन करता है।

**Ex.2.** उस समय की गणना कीजिये जिस पर हाइड्रोजन अणु 500 K पर Pt सतह पर अवशोषित हो सकते हैं। ( $A = 14 \times 10^{15} \text{ sec}^{-1}$ ,  $E_a = 10 \text{ kcal/mole}$ )

**Sol.** 
$$T_{av} = \frac{1}{1.4 \times 10^{15} e^{-10}} = \frac{e^{10}}{1.4 \times 10^{15}}$$

**2.3 अधिशोषण के प्रकार (Types of adsorption) :**

ठोसो पर गैसों के अधिशोषण दो प्रकार के होते हैं।

- (i) **भौतिक अधिशोषण :** यदि किसी ठोस के पृष्ठ पर गैस का संचयन दुर्बल वाण्डरवाल बलों के कारण होता है तो अधिशोषण को भौतिक अधिशोषण (physical adsorption or physisorption) कहते हैं।
- (ii) **रसायनिक अधिशोषण या रसोवशोषण :** जब गैस के अणु या परमाणु ठोस पृष्ठ पर रासायनिक बंधों से जुड़ते हैं, तो अधिशोषण, रसायनिक अधिशोषण या रसोवशोषण (chemical adsorption or chemisorption) कहलाता है, रसायनिक बंध प्रकृति में सहसंयोजक या आयनिक हो सकते हैं। रसोवशोषण में उच्च सक्रियण ऊर्जा सम्मिलित होती है, अतः इसे सामान्यतः सक्रियत अधिशोषण संदर्भित किया जाता है। कभी-कभी ये दोनों प्रक्रम साथ-साथ होते हैं एवं अधिशोषण का प्रकार निश्चित करना आसान नहीं होता।

**Note :**

निम्न ताप पर होने वाला भौतिक अधिशोषण ताप बढ़ाने पर रसोवशोषण में बदल जाता है। उदाहरण वेफ लिए, हाइड्रोजन पहले निकेल की सतह पर वाण्डरवालस बलों के द्वारा अधिशोषित होती है। तत्पश्चात् हाइड्रोजन के अणु, परमाणुओं में वियोजित होते हैं जो कि रसोवशोषण द्वारा निकेल की सतह पर बंधे रहते हैं।

□ **भौतिक और रसायनिक अधिशोषण में तुलना : (Comparison of physisorption and chemisorption)**

भौतिक अधिशोषण	रसायनिक अधिशोषण
1. यह अन्तः अणुक वाण्डरवाल बलों के कारण होता है।	रसायनिक बंध बनने के कारण होता है।
2. यह विशिष्ट नहीं होता	यह विशिष्ट होता है।
3. यह उत्क्रमणीय होता है।	यह अनुत्क्रमणीय होता है।
4. यह गैस की प्रकृति पर निर्भर करता है अधिक सरलता से द्रवणीय गैसों तेजी से अधिशोषित होती है	यह भी गैस की प्रकृति पर निर्भर करता है। वे गैसों जो अधिशोषक से क्रिया करती हैं, रसोवशोषण दर्शाती हैं।
5. अधिशोषण की उष्मा कम होती है। (20-40 kJ mol <sup>-1</sup> )	अधिशोषण की उष्मा अधिक होती है। (80-240 kJ mol <sup>-1</sup> )
6. अधिशोषण के लिए निम्न ताप सहायक होता है। यह ताप बढ़ने पर घटता है।	अधिशोषण के लिए उच्च ताप सहायक होता है। यह ताप बढ़ने पर बढ़ता है।
7. कोई योग्य सक्रियण ऊर्जा आवश्यक नहीं होती है	उच्च सक्रियण ऊर्जा चाहिए।
8. अधिशोषण के लिए उच्च दाब सहायक होता है। दाब में कमी से विशोषण (desorption) होता है।	अधिशोषण के लिए उच्च दाब भी सहायक होता है। परन्तु दाब में कमी से विशोषण नहीं होता है।
9. यह पृष्ठीय क्षेत्रफल पर निर्भर करता है। यह पृष्ठीय क्षेत्रफल के बढ़ने पर बढ़ता है	यह भी पृष्ठीय क्षेत्रफल पर निर्भर करता है। यह भी पृष्ठीय क्षेत्रफल के बढ़ने पर बढ़ता है।

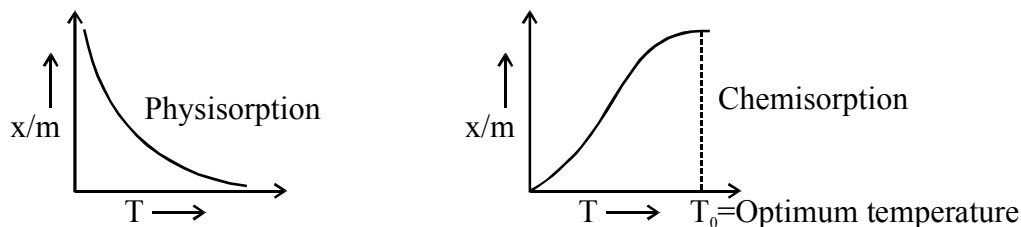
**नोट :**

- (i) रासायनिक अधिशोषण अनुत्क्रमणीय है।
- (ii) रासायनिक अधिशोषण अधिक ऊष्माक्षेपी होता है इसलिये इसकी E<sub>a</sub> नगण्य होनी चाहिये, लेकिन वास्तविकता में यह उच्च होती है क्योंकि अधिशोषण के पहले अधिशोष्य अणु में बंध विदलन की आवश्यकता होती है। उच्च E<sub>a</sub> के कारण यह सक्रियत अधिशोषण कहलाता है।





(iv) ताप बढ़ाने पर भौतिक अधिशोषण का मात्रा घटती है लेकिन रासायनिक अधिशोषण बढ़ता है।

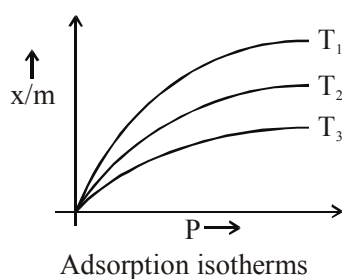


$x$  : अधिशोष्य का द्रव्यमान

तथा  $m$  : अधिशोषक का द्रव्यमान

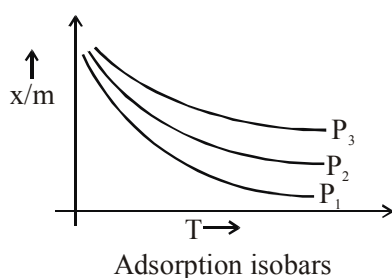
## 2.4 ठोस पर गैसों के अधिशोषण को प्रभावित करने वाले कारक :

- (i) **गैस की प्रकृति :** आसानी से द्रवणीय गैस (उच्च क्रांतिक तापों वाली) अधिक मात्रा में अधिशोषित हो जाती है।
- (ii) **अधिशोषक की प्रकृति :** विशिष्ट पृष्ठ क्षेत्रफल प्रति इकाई द्रव्यमान अधिशोषक के पृष्ठ क्षेत्रफल को बताता है जितना विशिष्ट पृष्ठ क्षेत्रफल अधिक होगा अधिशोषण उतना अधिक होगा। चारकोल, सिलिका जैल ऐल्युमिना जैल, कोलोइड अच्छे अधिशोषक हैं।
- (iii) **पृष्ठ क्षेत्रफल :** पृष्ठ क्षेत्रफल बढ़ाने पर अधिशोषण बढ़ता है।
- (iv) **दाब :** तंत्र के आयतन में कमी के कारण ठोस सतह पर गैस का अधिशोषण बढ़ता है तथा इसलिये दाब बढ़ाने पर अधिशोषण की मात्रा बढ़ती है।



$$T_1 < T_2 < T_3$$

- (v) **ताप :**  $T \uparrow$  भौतिक अधिशोषण  $\downarrow$  रासायनिक अधिशोषक  $\uparrow$



$$P_1 < P_2 < P_3$$

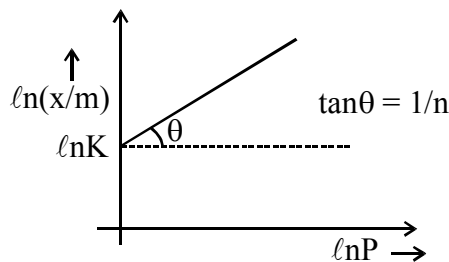
2.4.1 Freundlich adsorption isotherm :

फ्रॉयडल्लिच, ने 1909 में ठोस अधिशोषक के इकाई द्रव्यमान द्वारा एक निश्चित ताप पर अधिशोषित गैस की मात्रा एवं दाब के मध्य एक प्रयोगाश्रित (empirical) संबंध दिया। संबंध को निम्न समीकरण द्वारा व्यक्त किया जा सकता है।

$$\frac{x}{m} = K \cdot P^{1/n} \quad (n \geq 1)$$

जहाँ 'x' अधिशोषक के 'm' द्रव्यमान द्वारा P दाब पर अधिशोषित गैस का द्रव्यमान है। k एवं n स्थिरांक हैं जो कि किसी निश्चित ताप पर अधिशोषक एवं गैस की प्रकृति पर निर्भर करते हैं।

$$\ln\left(\frac{x}{m}\right) = \ln K + \frac{1}{n} \ln P$$

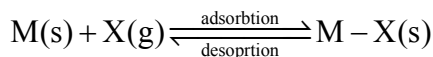


परिणामों से समर्थन होता है। फ्रॉयडल्लिच समताप एक सीधी रेखा है। इस प्रकार यह उच्च दाब पर असफल हो जाता है।

2.4.2 लेग्यूमर अधिशोषण समताप :

इसने सैद्धान्तिक रूप से साम्य की स्थिति को व्युत्पन्न किया। माना कि अधिशोषण है।

- (a) एकल परतीय
- (b) ठोस सतह पर समरूप (uniform)
- (c) अधिशोष्य कण सतह पर एक दूसरे से क्रिया नहीं करते हैं।



किसी सतह पर :

अधिशोषण की दर,  $r_a \propto P$

$$\propto (1 - \theta)$$

$$\therefore r_a = K_a P(1 - \theta)$$

जहाँ,  $\theta$  = अधिशोषक कणों द्वारा पहले से घेरे गये पृष्ठ क्षेत्रफल का प्रभाज

तथा विशोषण की दर,  $r_d \propto \theta \Rightarrow r_d = K_d \cdot \theta$

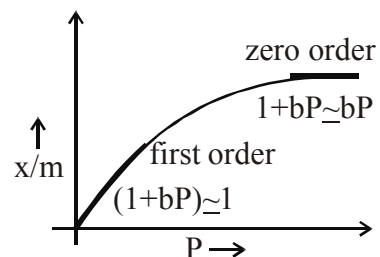
साम्य पर  $r_a = r_d$

$$\theta = \frac{K_a P}{K_d + K_a P} = \frac{\frac{K_a}{K_d} P}{1 + \frac{K_a}{K_d} P} = \frac{K_{eq} P}{1 + K_{eq} P}$$

अब,  $\frac{x}{m} \propto \theta$

$$\frac{x}{m} = K\theta = K \frac{K_{eq} P}{1 + K_{eq} P} = \frac{aP}{1 + bP}$$

a, b = constant



## 2.5 ADSORPTION FROM SOLUTION PHASE :

ठोस, विलयनों से भी घुले हुए पदार्थों का अधिशोषण कर सकते हैं। जब ऐसीटिक अम्ल के जलीय विलयन को चारकोल के साथ हिलाया जाता है तो अम्ल का एक अंश चारकोल के द्वारा अधिशोषित हो जाता है एवं विलयन में अम्ल की सांद्रता घट जाती है। इसी प्रकार से लिटमस का विलयन चारकोल के साथ हिलाने पर रंगहीन हो जाता है। जब  $Mg(OH)_2$  को मैग्नेसॉन अभिकर्मक की उपस्थिति में अवक्षेपित किया जाता है तो यह नीला रंग ग्रहण कर लेता है। यह रंग मैग्नेसॉन के अधिशोषण के कारण होता है। विलयन प्रावस्था से अधिशोषण में निम्नलिखित प्रेक्षण प्राप्त किए गए हैं।

- अधिशोषण की सीमा ताप के बढ़ने पर घटती है।
- अधिशोषण की सीमा, अधिशोषक का पृष्ठीय क्षेत्रापफल बढ़ने पर बढ़ती है।
- अधिशोषण की सीमा, विलयन में विलेय की सांद्रता पर निर्भर करती है।
- अधिशोषण की सीमा अधिशोषण एवं अधिशोष्य की प्रकृति पर निर्भर करती है।

विलयनों से अधिशोषण की परिशुद्ध क्रियाविधि ज्ञात नहीं है। फॉयन्डलिक समीकरण विलयनों से अधिशोषण के व्यवहार का इस अंतर के साथ सन्निकट वर्णन करती है कि दाब के स्थान पर विलयन की सांद्रता पर विचार किया जाता है। अर्थात्,

$$\frac{x}{m} = kC^{1/n}$$

((यहाँ  $C$  साम्यसांद्रता है, अर्थात् अधिशोषण पूर्ण होने पर सांद्रता))

उपरोक्त समीकरण का लघुगणक लेने पर हम पाते हैं

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

$\log \frac{x}{m}$  को  $\log C$  के विपरीत आलेखित करने पर एक सीधी रेखा प्राप्त होती है जो कि फॉयन्डलिक समतापी के सत्यापन को दर्शाती है। इसको प्रायोगिक तौर पर ऐसीटिक अम्ल की विभिन्न सांद्रताओं के विलयन लेकर परखा जा सकता है। विलयनों के समान आयतन, चारकोल की समान मात्राओं में अलग-अलग फ्लास्कों में मिलाये जाते हैं। अधिशोषण के पश्चात् प्रत्येक फ्लास्क में ऐसीटिक अम्ल की अंतिम सांद्रता ज्ञात की जाती है। प्रारंभिक एवं अंतिम सांद्रताओं में अंतर, 'x' का मान देता है। उपरोक्त समीकरण का उपयोग करते हुए फॉयन्डलिक समतापी की सत्यता स्थापित की जा सकती है।

## 2.6 अधिशोषण के अनुप्रयोग :

अधिशोषण की परिघटना के अनेक अनुप्रयोग हैं। कुछ महत्वपूर्ण अनुप्रयोग यहाँ सूचीबद्ध किए गए हैं-

### (i) उच्च निर्वात उत्पन्न करने में :

अत्यधिक उच्च निर्वात उत्पन्न करने के लिए, निर्वात पंप द्वारा निर्वातित पात्र से लेशमात्र वायु, चारकोल पर अधिशोषित करके निकाली जा सकती है।

### (ii) गैस मास्क :

गैस मास्क (एक युक्ति, जिसमें साक्रियित चारकोल या अधिशोषकों का मिश्रण होता है) का उपयोग कोयले की खानों में साँस लेते समय, विषैली गैसों को अधिशोषित करने के लिए किया जाता है।

**(iii) आद्रता पर नियंत्रण :**

सिलिका जेल एवं ऐलुमिनियम जेल का उपयोग नमी को दूर करने एवं आद्रता को नियंत्रित करने के लिए किया जाता है।

**(iv) विलयनों से रंगीन पदार्थों को हटाना**

जांतव चारवफोल विलयनों की रंगीन अशुद्धियों को अधिशोषित कर रंग हटा देता है।

**(v) विषमांगी उत्प्रेरण :**

उत्प्रेरक की ठोस सतह पर अभिक्रियाओं का अधिशोषण अभिक्रिया की दर बढ़ा देता है। औद्योगिक महत्व की ऐसी कई गैसीय अभिक्रियाएं हैं, जिनमें ठोस उत्प्रेरकों का होना आवश्यक है। अमोनिया के उत्पादन में लोहे का उत्प्रेरक की तरह उपयोग  $H_2SO_4$  का संपर्क प्रक्रम से उत्पादन, एवं तेलों के हाइड्रोजनीकरण में सूक्ष्मविभाजित निकैल का उपयोग, विषमांगी उत्प्रेरण के उत्कृष्ट उदाहरण हैं।

**(vi) अक्रिय गैसों का पृथक्करण :**

गैसों के चारकोल द्वारा अधिशोषण की मात्रा में भिन्नता होने के कारण मिश्रण में से अक्रिय गैसों को नारियल चारकोल पर, विभिन्न तापों पर अधिशोषित करके पृथक् किया जा सकता है।

**(vii) व्याधियों के उपचार में :**

अनेक औषध कीटाणुओं को अधिशोषण द्वारा मारने में प्रयुक्त होते हैं।

**(viii) झाग प्लवन प्रक्रम :**

चीड़ के तेल एवं झाग कारक का उपयोग करके एक निम्न श्रेणी के सल्फाइड अयस्क को सिलिका जेल एवं अन्य मृदा पदार्थों से पृथक् कर सांद्रित किया जा सकता है।

**(ix) अधिशोषण सूचक :**

कुछ अवक्षेपों की सतहें, जैसे- सिल्वर हैलाइड, इओसिन, फ्लुओरेसाइन आदि जैसे कुछ रंजकों को अवशोषित कर सकती हैं एवं इस प्रकार अंतिम बिंदु पर अभिलाक्षणिक रंग प्रदान करती हैं।

**(x) वर्णलेखिकीय विश्लेषण :**

अधिशोषण की परिघटना पर आधारित वर्णलेखिकीय विश्लेषण के विश्लेषिक एवं औद्योगिक क्षेत्रों में अनेक उपयोग हैं।

**3. उत्प्रेरण (Catalysis)**

विभिन्न बाहरी पदार्थों के विभिन्न रासायनिक अभिक्रियाओं पर प्रभाव का व्यवस्थित अध्ययन सर्वप्रथम 1835 में बर्जीलियस ने किया। उसने ऐसे पदार्थों के लिए उत्प्रेरक पद का सुझाव दिया। वे पदार्थ जो रासायनिक अभिक्रिया के पश्चात् रासायनिक एवं मात्रात्मक रूप से अपरिवर्तित रहते हुए, रासायनिक अभिक्रिया की दर में वृद्धि कर देते हैं, उत्प्रेरक कहलाते हैं एवं इस परिघटना को उत्प्रेरण कहते हैं।

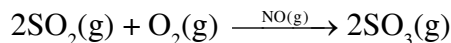
**3.1 समांगी एवं विषमांगी उत्प्रेरण (Homogeneous and Heterogeneous Catalysis) :**

उत्प्रेरण मुख्यतः दो समूहों में विभाजित किया जा सकता है।

**(a) समांगी उत्प्रेरण (Homogeneous catalysis) :**

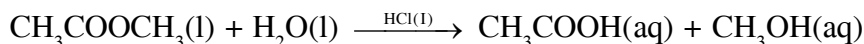
जब अभिक्रियक एवं उत्प्रेरक समान प्रावस्था (अर्थात् द्रव या गैस) में हों तो प्रक्रम समांगी उत्प्रेरण कहलाता है। समांगी उत्प्रेरण के कुछ उदाहरण निम्नलिखित हैं।

- (i) सीसा कक्ष विधि (लेड चेंबर प्रक्रम) में नाइट्रोजन के ऑक्साइडों की उत्प्रेरक की तरह उपस्थिति में, सल्फर डाइऑक्साइड का डाइऑक्सीजन के साथ अभिक्रिया द्वारा सल्फर डाइऑक्साइड में ऑक्सीकरण।



अभिक्रियक, सल्फर डाइऑक्साइड तथा ऑक्सीजन एवं उत्प्रेरक नाइट्रिक ऑक्साइड सभी समान प्रावस्था में हैं।

- (ii) हाइड्रोक्लोरिक अम्ल द्वारा प्रदत्त  $\text{H}^+$  आयनों से मेथिल ऐसीटेट का जल अपघटन उत्प्रेरित होता है।

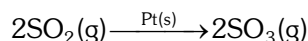


अभिक्रियक एवं उत्प्रेरक दोनों ही समान प्रावस्था में हैं।

### 3.2 विषमांगी उत्प्रेरण (Heterogeneous catalysis) :

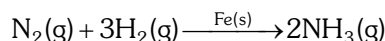
उत्प्रेरकी प्रक्रम जिसमें अभिक्रियक एवं उत्प्रेरक भिन्न प्रावस्थाओं में होते हैं, विषमांगी उत्प्रेरण कहलाता है। विषमांगी उत्प्रेरण के कुछ उदाहरण निम्नलिखित हैं

- (i) Pt की उपस्थिति में सल्फर डाइऑक्साइड का सल्फर ट्राइऑक्साइड में ऑक्सीकरण



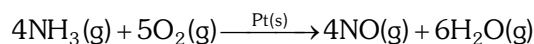
अभिक्रियक गैसीय प्रावस्था में हैं जबकि उत्प्रेरक ठोस अवस्था में हैं।

- (ii) हैबर प्रक्रम में सूक्ष्म विभाजित लोहे की उपस्थिति में अमोनिया बनने में डाइनाइट्रोजन एवं डाइहाइड्रोजन के मध्य संयोजन



अभिक्रियक गैसीय प्रावस्था में हैं जबकि उत्प्रेरक ठोस प्रावस्था में हैं।

- (iii) ओस्टवाल्ड प्रक्रम में, प्लेटिनम गेज की उपस्थिति में, अमोनिया का नाइट्रिक ऑक्साइड में ऑक्सीकरण



अभिक्रियक गैसीय प्रावस्था में हैं जबकि उत्प्रेरक ठोस प्रावस्था में हैं।

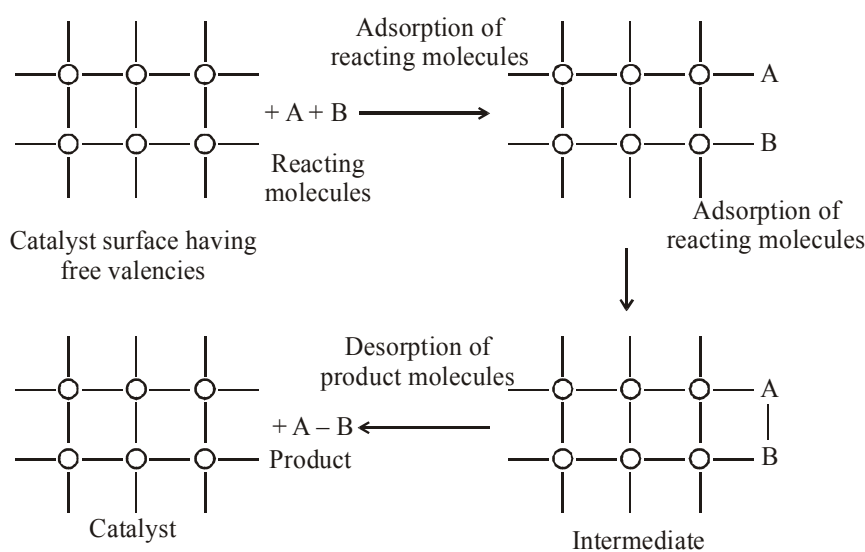
### विषमांगी उत्प्रेरण का अधिशोषण सिद्धांत (Adsorption Theory of Heterogeneous Catalysis) :

यह सिद्धांत विषमांगी उत्प्रेरण की क्रियाविधि को स्पष्ट करता है। प्राचीन सिद्धान्त जो कि उत्प्रेरण का अधिशोषण सिद्धान्त कहलाता था, के अनुसार गैसीय प्रावस्था या विलयन में अभिक्रियक, ठोस उत्प्रेरक के पृष्ठ पर अधिशोषित हो जाते हैं। पृष्ठ पर अभिक्रियकों की सांद्रता में वृद्धि अभिक्रिया की दर को बढ़ा देती है। अधिशोषण एक ऊष्माक्षेपी अभिक्रिया है अतः अधिशोषण की ऊष्मा, अभिक्रिया की दर बढ़ाने में प्रयुक्त हो जाती है।

उत्प्रेरण क्रिया को मध्यवर्ती यौगिक के बनने के पदों में वर्णित किया जा सकता है। आधुनिक अधिशोषण सिद्धांत मध्यवर्ती यौगिक निर्माण सिद्धांत एवं प्राचीन अधिशोषण सिद्धांत का संयोजन है। उत्प्रेरण क्रिया उत्प्रेरक की सतह पर केंद्रित होती है। क्रियाविधि में पाँच पद सम्मिलित होते हैं।

- उत्प्रेरक की सतह पर अभिक्रियकों का विसरण
- उत्प्रेरक की सतह पर अभिक्रियक अणुओं का अधिशोषण
- एक मध्यवर्ती निर्माण द्वारा उत्प्रेरक की सतह पर रासायनिक अभिक्रिया का होना।
- उत्प्रेरक सतह से अभिक्रिया उत्पादों का विशोषण होने के बाद सतह का दोबारा अधिक अभिक्रिया होने के लिए उपलब्ध कराना।

- (v) अभिक्रिया उत्पादों का उत्प्रेरक की सतह से दूर विसरण उत्प्रेरक की सतह पर मुक्त संयोजकताएं होती हैं, जैसा स्थूल के आंतरिक भाग में नहीं है। यह संयोजकताएं रासायनिक आकर्षण बलों के लिए स्थान उपलब्ध करवाती हैं। जब कोई गैस एक ऐसी सतह के संपर्क में आती है तो इसके अणु शिथिल रासायनिक संयोजन के कारण वहाँ बँध जाते हैं। यदि अलग प्रकार के अणु पास-पास अधिशोषित हो जाएं तो एक दूसरे से अभिक्रिया कर सकते हैं जिससे नए अणु बन जाते हैं। इस प्रकार बने अणु सतह को नए अभिक्रियक अणुओं के लिए छोड़ते हुए वाष्पीकृत हो जाते हैं। यह सिद्धांत समझाता है कि अभिक्रिया के अंत में उत्प्रेरक का द्रव्यमान एवं रासायनिक संघटन क्यों अपरिवर्तित रहता है तथा यह कम मात्रा में भी कैसे प्रभावी होता है। तथापि, यह उत्प्रेरक वर्धक एवं उत्प्रेरक विष की क्रिया को स्पष्ट नहीं करता।।

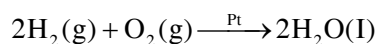


**Adsorption of reacting molecules, formation of intermediate and desorption of products**

### 3.3 Important features of solid catalysts :

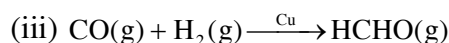
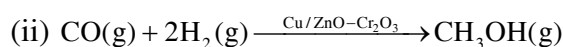
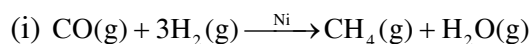
(a) **सक्रियता (Activity) :**

बहुत सीमा तक का उत्प्रेरक की सक्रियता रसोवशोषण की प्रबलता पर निर्भर करती है। सक्रिय होने के लिए अभिक्रियक, उत्प्रेरक पर पर्याप्त प्रबलता से अधिशोषित होने चाहिए। तथापि वे इतनी प्रबलता से अधिशोषित नहीं होने चाहिए कि वे गतिहीन हो जाएं एवं अन्य अभिक्रियकों के लिए उत्प्रेरक की सतह पर कोई स्थान रिक्त न रहे। हाइड्रोजनन अभिक्रियाओं के लिए यह पाया गया है कि उत्प्रेरकी सक्रियता आवर्तसारणी में वर्ग 5 से वर्ग 11 के तत्वों तक बढ़ती है, जिनमें वर्ग 7 से 9 के तत्व अधिकतम सक्रियता दर्शाते हैं।



(b) **Selectivity :**

किसी उत्प्रेरक की वरणात्मकता उसकी किसी अभिक्रिया को दिशा देकर एक विशेष उत्पाद बनाने की क्षमता है। उदाहरणार्थ  $\text{H}_2$  एवं  $\text{CO}$  से प्रारंभ करके एवं भिन्न उत्प्रेरकों के प्रयोग से हम भिन्न-भिन्न उत्पाद प्राप्त कर सकते हैं।



अतः यह निष्कर्ष निकाला जा सकता है कि, उत्प्रेरक के कार्य की प्रकृति अत्यधिक विशिष्ट होती है, अर्थात् कोई पदार्थ एक विशेष अभिक्रिया के लिए ही उत्प्रेरक हो सकता है, सभी अभिक्रियाओं के लिए नहीं।



- (vi) आमाशय में पेप्सिन एन्जाइम प्रोटीनों को पेप्टाइडों में परिवर्तित करता है जबकि आँत में अग्नाशय ट्रिप्सिन प्रोटीनों को जल अपघटन द्वारा एमीनो अम्लों में परिवर्तित करता है।
- (vii) दुग्ध का दही में परिवर्तन : यह एक एन्जाइमिक अभिक्रिया है जो कि दही में उपस्थित लेक्टोबैसिलस एन्जाइम द्वारा होती है।

### 3.5.1 एन्जाइम उत्प्रेरण के अभिलक्षण

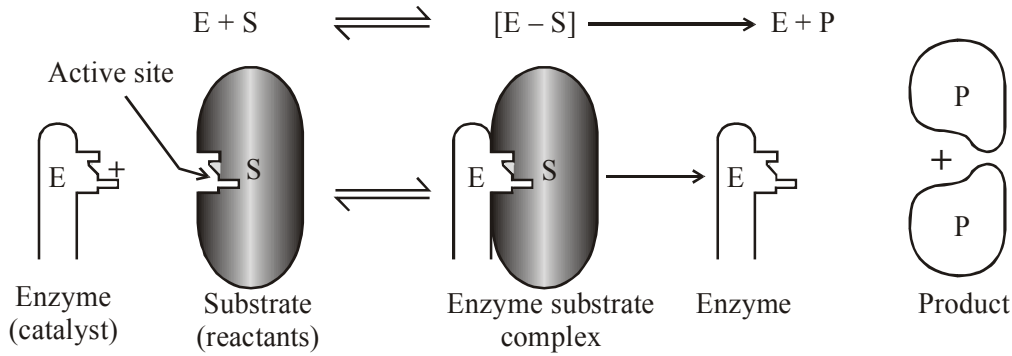
एन्जाइम उत्प्रेरण दक्षता एवं उच्च कोटि की विशिष्टता में अनूठा है। एन्जाइम उत्प्रेरण के द्वारा निम्न अभिलक्षण दर्शाए जाते हैं

- सर्वोत्तम दक्षता : एन्जाइम का एक अणु अभिक्रियक के दस लाख अणुओं को प्रति मिनट परिवर्तित कर सकता है।
- उच्च विशिष्ट प्रकृति- प्रत्येक एन्जाइम की विशिष्टता किसी एक अभिक्रिया के लिए होती है अर्थात् एक उत्प्रेरक एक से अधिक अभिक्रियाओं को उत्प्रेरित नहीं कर सकता। उदाहरणार्थ एन्जाइम यूरिया, केवल यूरिया के जल अपघटन को उत्प्रेरित करता है। यह किसी अन्य एमाइड के जल अपघटन को उत्प्रेरित नहीं करता।
- इष्टतम ताप (Optimum temperature) पर सर्वाधिक सक्रिय - एन्जाइम उत्प्रेरित अभिक्रिया की दर एक निश्चित ताप पर जिसे इष्टतम ताप कहते हैं, अधिकतम हो जाती है। अनुकूल इष्टतम ताप के किसी भी ओर एन्जाइम की सक्रियता घट जाती है। एन्जाइम सक्रियता का इष्टतम ताप परास 298-210K है। मानव शरीर का ताप 310K होने के कारण यह एन्जाइम-उत्प्रेरित अभिक्रियाओं के लिए उपयुक्त होता है।
- सर्वाधिक सक्रिय- एन्जाइम उत्प्रेरित अभिक्रिया की दर एक निश्चित pH पर जिसे इष्टतम pH कहते हैं, अधिकतम होती है इसका मान 5-7 के मध्य होता है।
- सक्रियक एवं सहएन्जाइमों की उपस्थिति में वर्धमान सक्रियता - एन्जाइम की सक्रियता कुछ पदार्थों की उपस्थिति में, जिन्हें सहएन्जाइम कहते हैं, बढ़ जाती है। यह देखा गया है कि जब थोड़ा सा अप्रोटीन (जैसे विटामिन), एन्जाइम के साथ उपस्थित होता है तो, एन्जाइमी की उत्प्रेरकी महत्वपूर्ण रूप से बढ़ जाती है। सक्रियक साधारणतया धात्विक आयन जैसे  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{CO}^{2+}$ ,  $\text{Cu}^{2+}$ , आदि हाते हैं। ये धात्विक आयन एन्जाइम अणुओं से दुर्बल रूप से आबंधित होने पर उत्प्रेरकी सक्रियता बढ़ा देते हैं। एमिलेज सोडियम क्लोराइड की उपस्थिति में अर्थात्  $\text{Na}^+$  आयनों की उपस्थिति उत्प्रेरकीय रूप में बहुत सक्रिय होता है।
- संदमक एवं विष का प्रभाव- सामान्य उत्प्रेरकों के समान एन्जाइम भी कुछ पदार्थों की उपस्थिति में संदमित एवं विषाक्त हो जाते हैं। संदमक अथवा विष, एन्जाइम की सतह पर उपस्थित सक्रिय क्रियात्मक समूहों से अन्योन्यक्रिया करके एन्जाइमों की सारणी कुछ एन्जाइमी अभिक्रियाएँ उत्प्रेरकी सक्रियता को प्रायः कम या पूरी तरह समाप्त कर देते हैं। शरीर में कई औषधों का प्रयोग उनके एन्जाइम को संदमित करने के गुण से संबन्धित होता है। शरीर में कई औषधों की क्रिया एन्जाइम संदमक से संबन्धित होती है।

### 3.5.2 Mechanism of enzyme catalysis :

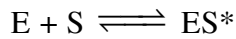
एन्जाइम के कोलाॅइडी कणों की सतहों पर बहुत सारे कोटर होते हैं। ये कोटर अभिलक्षणिक आकृति के होते हैं एवं इनमें सक्रिय समूह जैसे  $-\text{NH}_2$ ,  $-\text{COOH}$ ,  $-\text{SH}$ ,  $-\text{OH}$ , etc. आदि होते हैं। वास्तव में यह सतह पर उपस्थित सक्रिय केंद्र होते हैं। अभिक्रियक के अणु जिनकी परिपूरक आकृति होती है, इन कोटरों में एक ताले में चाबी के समान फिट हो जाते हैं। सक्रिय समूहों की उपस्थिति के कारण एक सक्रियत संकुल बनता है जो विघटित होकर उत्पाद देता है। इस प्रकार, एन्जाइम उत्प्रेरित अभिक्रियाओं का दो पदों में सम्पन्न होना माना जा सकता है।



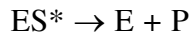


### 3.5.3 एंजाइम उत्प्रेरित अभिक्रिया की क्रियाविधि :

**पद 1:** एंजाइम के क्रियाधार से बंध बनाकर एक सक्रिय संकुल का निर्माण करना।

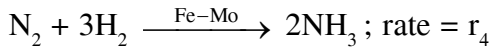
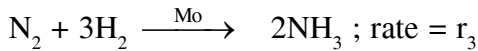
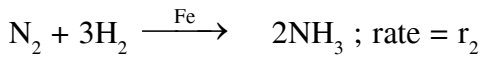
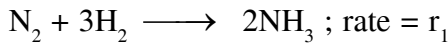


**पद 2:** सक्रिय संकुल का विघटन होकर उत्पाद बनाना।



### 3.6 उत्प्रेरकीय वर्धक :

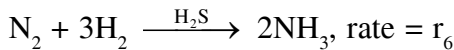
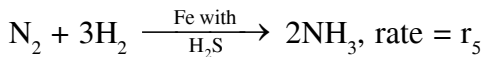
यह वे पदार्थ हैं जो उस अभिक्रिया के उत्प्रेरक नहीं हैं, लेकिन उत्प्रेरक की सक्रियता को बढ़ाते हैं



प्रायोगिक रूप से,  $r_1 = r_3 < r_2 < r_4$  यह बताता है कि Mo इस अभिक्रिया का उत्प्रेरक नहीं है लेकिन जब यह आयरन के साथ मिलाया जाता है, यह आयरन की उत्प्रेरकीय सक्रियता को बढ़ाता है, इसलिये Mo इस अभिक्रिया का उत्प्रेरक वर्धक है।

### 3.7 उत्प्रेरक विधि :

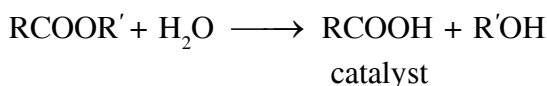
यह वे पदार्थ हैं जो उस अभिक्रिया के उत्प्रेरक नहीं हैं, लेकिन उत्प्रेरक की सक्रियता को घटाते हैं।



प्रायोगिक रूप से,  $r_1 = r_6 < r_5 < r_2$  यह बताता है कि  $H_2S$  अभिक्रिया का उत्प्रेरक नहीं है, परन्तु यह Fe उत्प्रेरक की सक्रियता को घटाता है। इसलिये  $H_2S$  इस अभिक्रिया में उत्प्रेरक विष है।

### 3.8 स्वतः उत्प्रेरक :

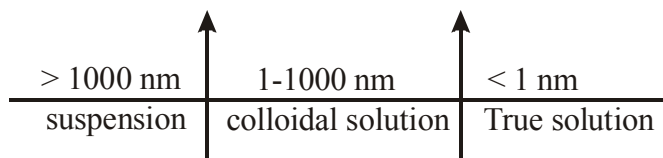
यह ऐसी अभिक्रिया है जिनमें अभिक्रिया का कुछ उत्पाद अभिक्रिया को उत्प्रेरित करता है।



#### 4. COLLOIDS

कोलॉइड एक विषमांगी तंत्र होता है जिसमें एक पदार्थ बहुत बारीक कणों के रूप में (परिक्षिप्त प्रावस्था) एक दूसरे पदार्थ में परिक्षेपित रहता है जिसे **परिक्षेपित माध्यम** कहते हैं।

##### 4.1 कण का आकार (Particle size) :



##### 4.2 कोलाइडो की प्रावस्था (Phase of colloids) :

कोलॉइडी तंत्र में विषमांगी अभिलक्षण होता है। इसमें दो प्रावस्थाएँ परिक्षिप्त प्रावस्था और परिक्षेपण माध्यम, उपस्थित होती है।

(a) **परिक्षिप्त प्रावस्था (Dispersed Phase) :** यह एक कम अनुपात में उपस्थित अवयव (component) है और यह वास्तविक विलयन में विलेय जैसा होता है। उदाहरण के लिए जल में सल्फर की कोलॉइडी अवस्था में, सल्फर परिक्षिप्त प्रावस्था की भांति व्यवहार करता है।

(b) **परिक्षेपण माध्यम (Dispersion Medium) :** इसमें सामान्यतः उपस्थित अवयवों की मात्रा आधिक्य में होती है और यह विलयन में विलायक के जैसा होता है।

कोलॉइडी तंत्र के परिक्षेपण माध्यम में परिक्षिप्त प्रावस्था के कण प्रकीर्णित या छितराये हुए (scattered) रहते हैं।

##### 4.3 कोलाइडों का वर्गीकरण (Classification of colloids) :

कोलाइडो को उनके कुछ महत्वपूर्ण लक्षणों के आधार पर कई प्रकारों से वर्गीकृत किया जा सकता है।

##### 4.3.1 परिक्षिप्त प्रावस्था और परिक्षेपण माध्यम की भौतिक अवस्था :

यह इस बात पर निर्भर करता है कि परिक्षिप्त प्रावस्था और परिक्षेपण माध्यम ठोस, द्रव या गैस है, आठ प्रकार के कोलॉइडी तंत्र सम्भव है।

एक गैस का अन्य गैस के साथ मिश्रण संमागी होता है और यह एक कोलॉइडी तंत्र नहीं होता। विभिन्न प्रकार के कोलाइडों के उदाहरण को उनके अभिलाक्षणिक नामों के साथ नीचे तालिका में दिया गया है।

कोलॉइडी तंत्रों के प्रकार

परिक्षिप्त प्रावस्था	परिक्षेपण माध्यम	कोलॉइड का प्रकार	उदाहरण
ठोस	ठोस	ठोस सॉल	कुछ रंगीन काँच एवं रत्न पत्थर
ठोस	द्रव	सॉल	प्रलेप (पेंट), कोशिका तरल
ठोस	गैस	एरोसॉल	धुआँ, धूल
द्रव	ठोस	जेल	पनीर, मक्खन, जेली
द्रव	द्रव	पायस (Emulsion)	दूध, बालों की क्रीम
द्रव	गैस	एरोसॉल	धुंध, कोहरा, बादल, कीटनाशक स्प्रे
गैस	ठोस	ठोस सॉल	प्यूमिक पत्थर, फोम रबर
गैस	द्रव	झाग	फेन, फैंटी गई क्रीम साबुन के झाग

- \* एक कोलॉइडी तंत्र जिसमें परिक्षेपण माध्यम द्रव या गैस है 'सॉल' (sols) कहलाता है। यदि परिक्षेपण माध्यम जल है तो ये हाइड्रोसॉल या एक्वासॉल या जलीय सॉल कहलाता है और जब परिक्षेपण माध्यम एल्कोहॉल या बेंजीन हो, तब इसके अनुसार इन्हें ऐल्कोसॉल या बेंजोसॉल कहा जाता है।
- \* कोलॉइडी तंत्र जिसमें परिक्षेपण माध्यम गैस है, ऐरोसॉल (aerosols) कहलाता है।
- \* कोलॉइडी तंत्र जिसमें परिक्षेपण माध्यम ठोस है, जेल (gels) कहलाता है। जैसे पनीर आदि, ये अधिक दृढ़ (rigid) संरचना वाले होते हैं। कुछ कोलाइड जैसे जिलेटिन, दोनों प्रकार का, सॉल और जैल, जैसा व्यवहार करते हैं। उच्च ताप और निम्न सान्द्रता पर जिलेटिन का कोलाइड एक हाइड्रोसॉल होता है परन्तु निम्न ताप और जिलेटिन की उच्च सान्द्रता पर हाइड्रोसॉल को जैल में परिवर्तित किया जा सकता है।

#### 4.3.2 प्रावस्थाओं की परस्पर अन्योन्य क्रिया या स्नेहता के आधार पर :

कोलाइडो को उनके कुछ महत्वपूर्ण लक्षणों के आधार पर कई प्रकार से वर्गीकृत किया जा सकता है परिक्षिप्त प्रावस्था और परिक्षेपण माध्यम के मध्य स्नेहता या परस्पर अन्योन्य क्रिया के आधार पर कोलाइडों को दो प्रकारों में वर्गीकृत किया जा सकता है।

##### (i) द्रव स्नेही कोलॉइड (Lyophilic Colloids) :

कोलॉइडी तंत्र जिसमें परिक्षिप्त प्रावस्था के कणों की परिक्षेपण माध्यम के लिये अधिक स्नेहता (great affinity) होती है, द्रव स्नेही (विलायक-स्नेही) कोलॉइड कहलाता है। इस प्रकार के कोलाइडों में परिक्षिप्त प्रावस्था आसानी से अवक्षेपित नहीं होती है और सॉल अधिक स्थायी होता है। इस प्रकार के कोलॉइडी तंत्रों में, यदि (even if) अवक्षेपण हो भी जाता है तो भी इसे परिक्षेपण माध्यम के साथ सरलता से हिलाने (agitating) पर कोलॉइडी अवस्था में पुनः रूपान्तरित किया जा सकता है। अतः इस प्रकार द्रव स्नेही कोलाइड उत्क्रमणीय होते हैं। जब परिक्षेपण माध्यम जल होता है तब ये जल स्नेही या हाइड्रोफिलिक कोलाइड कहलाते हैं। द्रव स्नेही कोलाइडों के कुछ सामान्य उदाहरणों में, गोंद, जिलेटिन, स्टार्च, रबर, प्रोटीन आदि हैं।

##### (ii) द्रव विरोधी कोलॉइड (Lyophobic colloids) :

कोलॉइडी तंत्र जिसमें परिक्षिप्त प्रावस्था के कणों की परिक्षेपण माध्यम से कोई स्नेहता (affinity) नहीं होती, द्रव विरोधी (विलायक विरोधी) कोलाइड कहलाते हैं। यह, विद्युत अपघट्य की कुछ मात्रा को मिलाकर हिलाने पर या गर्म करने पर आसानी से अवक्षेपित (या स्कन्दीत) हो जाते हैं। ये कम स्थायी और अनुत्क्रमणीय होते हैं। जब परिक्षेपण माध्यम जल होता है तब ये जल विरोधी (hydrophobic) कोलाइड कहलाते हैं। द्रव विरोधी कोलॉइडो के उदाहरणों में धातुओं के सॉल और इनके अघुलनशील यौगिकों जैसे सल्फाइड और ऑक्साइड हैं।

द्रव स्नेही और द्रव विरोधी कोलॉइडो के मध्य आवश्यक अन्तरो को निम्न तालिका में संक्षिप्त किया गया है।

## द्रवस्नेही और द्रव विरोधी सॉल के मध्य अन्तर

गुण	द्रव स्नेही सॉल	द्रवविरोधी सॉल
1. प्रकृति	उत्क्रमणीय	अनुत्क्रमणीय
2. निर्माण	इन्हे परिक्षेपण माध्यम के साथ पदार्थ को हिलाकर या गर्म करके आसानी से बनाया जा सकता है। इन्हे स्थायीत्व के लिए किसी प्रकार के विद्युतअपघट्य की आवश्यकता नहीं होती है।	इन्हें बनाना कठिन है इनके लिए विशेष विधियों का उपयोग किया जाता है। इनके स्थायीत्व के लिए स्थायीकारक (stabiliser) को मिलाना आवश्यक है।
3. स्थायित्व	ये अधिक स्थायी होते हैं और विद्युत अपघट्य द्वारा आसानी से स्कंदित नहीं होते।	ये सामान्यतः अस्थायी होते हैं और विद्युतअपघट्य मिलाने पर सरलता से स्कंदित हो जाते हैं।
4. आवेश	कणों पर बहुत कम आवेश या कोई आवेश नहीं होता है। यह माध्यम की pH पर निर्भर करता है	कोलॉइडी कणों पर अभिलाक्षणिक आवेश (धनात्मक या ऋणात्मक) होता है।
5. श्यानता	माध्यम की तुलना में श्यानता अत्यधिक श्यानता, उच्च होती है।	माध्यम के लगभग बराबर होती है।
6. विद्युत क्षेत्र में गमन	कण विद्युत क्षेत्र में गमन कर भी सकते और नहीं भी।	कोलॉइडी कणों का विद्युत क्षेत्र में गमन धनाग्र (cathode) या ऋणाग्र (anode) की ओर होता है।
7. विलायकीकरण (Solvation)	कणों का विलायकीकरण अत्यधिक होता है।	कणों का विलायकीकरण नहीं होता।
8. विद्युत अपघट्यों का प्रभाव	स्कंदन के लिये विद्युत अपघट्य की उच्च मात्रा आवश्यक होती है।	स्कन्दन के लिये विद्युत अपघट्य की कम मात्रा ही पर्याप्त होती है।
9. उदाहरण	अधिकांशतः कार्बनिक पदार्थ होते हैं जैसे स्टार्च, गोंद, प्रोटीन, जिलेटिन आदि। gelatin etc.	सामान्यतः अकार्बनिक पदार्थ होते हैं जैसे धातु सॉल, सल्फाइड और ऑक्साइड सॉल।

### 4.3.3 परिक्षित प्रावस्था के कणों के प्रकार पर आधारित वर्गीकरण:

परिक्षित प्रावस्था के कणों के प्रकार के आधार पर कोलॉइडों को बहुआण्विक, बृहदाण्विक तथा सहचारी कोलॉइडों में वर्गीकृत किया जाता है।

#### (i) बहुआण्विक कोलॉइड :

विलीन करने पर किसी पदार्थ के बहुत से परमाणु या लघु अणु एकत्रित होकर पुंज जैसी ऐसी स्पीशीज बनाते हैं जिनका आकार (साइज) कोलॉइडी सीमा (व्यास  $< 1\text{nm}$ ) में होता है। इस प्रकार प्राप्त स्पीशीज बहुआण्विक कोलॉइड कहलाती है। उदाहरण के लिए एक गोल्ड सॉल में अनेक परमाणु युक्त भिन्न-भिन्न आकारों के कण हो सकते हैं। सल्फर सॉल में एक हजार या उससे भी अधिक  $\text{S}_8$  सल्फर अणु वाले कण उपस्थित रहते हैं।

#### (ii) बृहदाण्विक कोलॉइड :

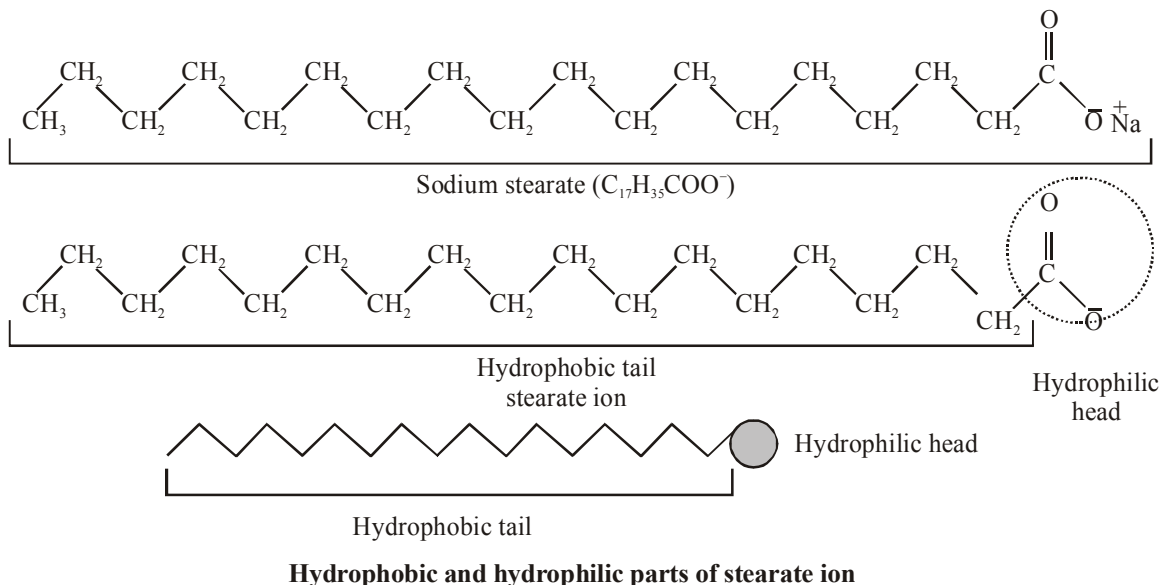
बृहदाणु (एकक 15) उचित विलायकों में ऐसे विलयन बनाते हैं जिनमें बृहदाणुओं का आकार कोलॉइडी सीमा में होता है ऐसे निकाय बृहदाण्विक कोलॉइड कहलाते हैं। ये कोलॉइड बहुत स्थायी होते हैं और अनेक अर्थों में यथार्थ विलयनों के समान होते हैं। प्राकृतिक रूप से पाए जाने वाले बृहदाण्विक कोलॉइडों के उदाहरण हैं- स्टार्च, सेलुलोज प्रोटीन और एन्जाइम एवं मानव निर्मित बृहदाणु हैं- पॉलीथीन, नायलोन, पॉली स्टायरीन, संश्लेषित रबर आदि।

#### (iii) सहचारी कोलॉइड (मिसेल) :

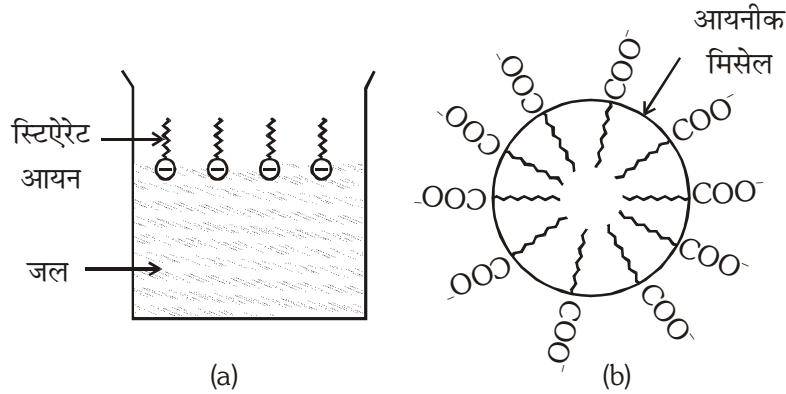
कुछ पदार्थ ऐसे हैं जो कम सांद्रताओं पर सामान्य प्रबल वैद्युतअपघट्य के समान व्यवहार करते हैं परन्तु उच्च सांद्रताओं पर कणों का पुंज बनने के कारण कोलॉइड के समान व्यवहार करते हैं। इस प्रकार पुंजित कण मिसेल कहलाते हैं। ये सहचारी कोलॉइड भी कहलाते हैं। मिसेल केवल एक निश्चित ताप से अधिक ताप पर बनते हैं जिसे **क्राफ्ट ताप** कहते हैं, एवं सांद्रता एक निश्चित सांद्रता से अधिक होती है, जिसे **क्रांतिक मिसेल सांद्रता (CMC)** कहते हैं। तनु करने पर ये कोलॉइड पुनः अलग-अलग आयनों में टूट जाते हैं। पृष्ठ सक्रिय अभिकर्मक जैसे साबुन एवं संश्लेषित परिमार्जक इसी वर्ग में आते हैं। इन कोलॉइडों में द्रवविरोधी एवं द्रवस्नेही दोनों ही भाग होते हैं। मिसेल में 100 या उससे अधिक अणु हो सकते हैं।

#### मिसेल निर्माण की क्रियाविधि :

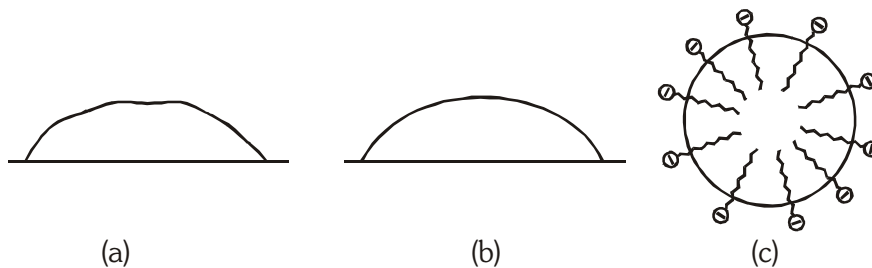
आइए, हम साबुन के विलयन का उदाहरण लेते हैं। पानी में घुलनशील साबुन उच्च वसा अम्लों के सोडियम अथवा पोटैशियम लवण होते हैं जिन्हें  $\text{RCOO}^- \text{M}^+$  द्वारा व्यक्त किया जा सकता है। उदाहरणार्थ, सोडियम स्टेरेट (जो कि अनेक बट्टी वाले साबुनों का प्रमुख घटक है।) जल में विलीन करने पर  $\text{RCOO}^-$  एवं  $\text{Na}^+$  आयनों में विघटित हो जाता है। किंतु  $\text{RCOO}^-$  आयन के दो भाग होते हैं- एक लंबी हाइड्रोकार्बन श्रृंखला (जिसे 'अध्रुवीय पुच्छ' भी कहते हैं), जो जलविरागी (जल प्रतिकर्षी) होती है तथा ध्रुवीय समूह  $\text{COO}^-$  (जिसे 'ध्रुवीय आयनिक शीर्ष' भी कहते हैं।) जो जलरागी (जल को स्नेह करने वाला) या जलस्नेही होता है।



$\text{RCOO}^-$  आयन पृष्ठ पर इस प्रकार उपस्थित रहते हैं कि उनका  $\text{COO}^-$  समूह जल में तथा हाइड्रोकार्बन श्रृंखला R, पृष्ठ से दूर रहती है। परंतु क्रांतिक मिसेल सांद्रता पर ऋणायन विलयन के स्थूल में खिंच आते हैं एवं गोलीय आकार में इस प्रकार एकत्रित हो जाते हैं कि इनकी हाइड्रोकार्बन श्रृंखलाएं गोले के केन्द्र की ओर इंगित होती है तथा  $\text{COO}^-$  भाग गोले के पृष्ठ पर रहता है। ध्रुवीय समूह है, इस प्रकार बना पुंज **आयनिक मिसेल** कहलाता है। इन मिसेलों में इस प्रकार के 100 तक आयन हो सकते हैं। इसी प्रकार अपमार्जकों जैसे सोडियम लॉरिल सल्फेट,  $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^- \text{Na}^+$  में लंबी हाइड्रोकार्बन श्रृंखला सहित- $\text{SO}_4^-$  अतः मिसेल बनने की क्रियाविधि साबुनों के समान ही है।

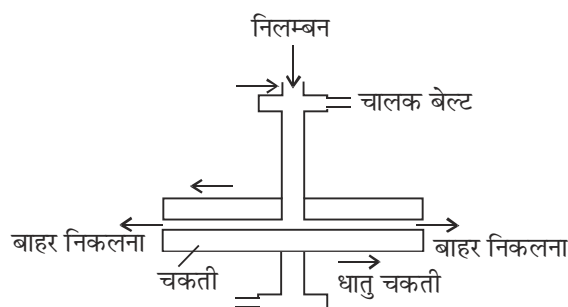


**साबुनों की शोधन-क्रिया :** यह पहले बताया जा चुका है कि मिसेल में एक जल विरोधी हाइड्रोकार्बन का केंद्रीय क्रोड होता है। साबुन की शोधन-क्रिया इस यथार्थ के कारण है कि साबुन के अणु तेल की बूंदों के चारों ओर इस प्रकार से मिसेल बनाते हैं कि स्टीरेट आयन का जलविरागी भाग बूंदों के अंदर होता है एवं जलरागी भाग चिकनाई की बूंदों के बाहर काँटों की तरह निकला रहता है। चूँकि ध्रुवीय समूह जल से अन्योन्यक्रिया कर सकते हैं, अतः स्टीरेट आयनों से घिरी हुई तेल की बूंदें जल में खिंच जाती हैं एवं गंदी सतह से हट जाती है। इस प्रकार साबुन तेलों तथा वसाओं का पायसीकरण (Emulsification) करके धुलाई में सहायता करता है। छोटी गोलियों के चारों ओर का ऋण आवेशित आवरण उन्हें एक साथ आकर पुंज बनाने से रोकता है।

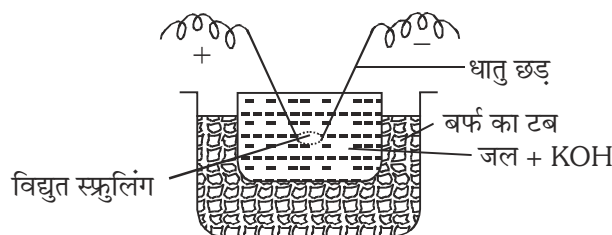




कण कोलॉइडी आकार में नीचे बैठ जाते हैं और फिर द्रव में परिक्षिप्त हो जाते हैं। कोलॉइडी विलयन को स्थिरता (stabilize) देने के लिये सामान्यतः एक स्थायीकारक (stabilizer) मिलाया जाता है। इस विधि द्वारा कोलॉइडी ग्रेफाइट [एक स्नेहक (lubricant)] और प्रिंटिंग स्याही (printing ink) को बनाया जाता है। कोलॉइडी ग्रेफाइट के निर्माण में टैनिन (Tannin) को स्थायीकारक (stabilizer) के रूप में प्रयोग किया जाता है और काजल (lampblack) के कोलॉइडी विलयन (भारतीय स्याही) में गमअरेबीक (gum arabic) का प्रयोग किया जाता है।



- (B) **वैद्युत परिक्षेपण (ब्रेडिंग की आर्क विधि) :** यह विधि स्वर्ण, चाँदी एवं प्लेटिनम आदि के समान, धातुओं के कोलॉइडी विलयनों को बनाने में प्रयुक्त होती हैं। धातु के इलेक्ट्रोड को जल में उपयुक्त स्थाई कारक जैसे KOH को मिला कर, विद्युत स्फुरलिंग पैदा की जाती है। जल को ठंडा रखने के लिए पात्र को बर्फ में रखा जाता है। अत्यधिक उष्मा धातु के कुछ भाग को वाष्पित कर देती है जो कि ठंडे जल में संघनित हो कोलॉइडी कण देते हैं।

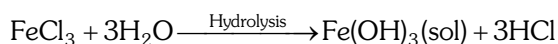
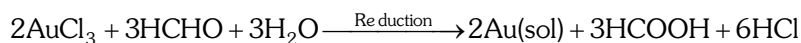
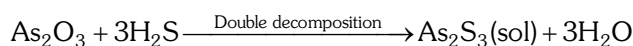


- (C) **पराश्रव्य परिक्षेपण (Ultrasonic dispersion) :** उच्च आवृत्ति की ध्वनि तरंगों को सामान्यतः पराश्रव्य तरंगे कहते हैं। जब क्वार्ट्ज क्रिस्टल (quartz crystal) के चक्को (discs) को उच्च आवृत्ती जनित्र (generator) के साथ जोड़ा जाता है, तब इन तरंगों को बनाया जा सकता है। कोलॉइडी विलयन को बनाने के लिये पराश्रव्य तरंगों का उपयोग सर्वप्रथम वुड और लुमीस (wood and Loomis) द्वारा 1927 में किया गया था कई सारे पदार्थों जैसे तेल, पारा (mercury), सल्फर, सल्फाइड और धातुओं के ऑक्साइड को पराश्रव्य तरंगों की सहायता से बहुत सरलता से कोलॉइडी अवस्था में परिक्षिप्त किया जा सकता है।
- (D) **पेप्टीकरण (Peptization) :** (यह स्कंदन के विपरीत क्रिया है)
- पेप्टीकरण को इस प्रकार परिभाषित किया जा सकता है कि किसी अवक्षेप को वैद्युतअपघट्य की थोड़ी सी मात्रा की उपस्थिति में परिक्षेपण माध्यम के साथ हिलाकर कोलॉइडी सॉल में परिवर्तित करने वाला प्रक्रम पेप्टीकरण कहलाता है। इस प्रक्रम में प्रयुक्त वैद्युतअपघट्य पेप्टीकारक कहलाता है। यह विधि सामान्यतः ताजे बने अवक्षेप को कोलॉइडी सॉल में परिवर्तित करने में प्रयुक्त की जाती है। पेप्टीकरण के दौरान अवक्षेप, वैद्युत अपघट्य के किसी एक प्रकार के आयनों को अपनी सतह पर अवशोषित कर लेता है जिससे अवक्षेप पर ऋणात्मक अथवा धनात्मक आवेश उत्पन्न हो जाता है जो अंततः कोलॉइडी आकार के छोटे कणों में विभक्त हो जाता है।
- ताजा अवक्षेपित फ़ैरिक हाइड्रोक्साइड को कम मात्रा में फ़ैरिक क्लोराइड विलयन से अभिकृत करने पर तुरंत गहरे लाल-भूरे रंग का विलयन प्राप्त होता है। इस प्रक्रिया में फ़ैरिक क्लोराइड पेप्टीकारक है।
  - ताजा तैयार किया गया सिल्वर क्लोराइड का अवक्षेप तनु हाइड्रोक्लोरिक अम्ल की बहुत कम मात्रा द्वारा कोलॉइडी विलयन में परिवर्तित हो जाता है।
  - कैडमियम सल्फाइड को हाइड्रोजन सल्फाइड द्वारा पेप्टीकृत किया जा सकता है।



## (ii) संघनन विधियाँ (Condensation Methods)

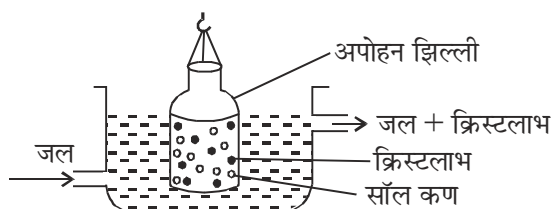
- (A) **विलायकों के विनिमय से (By exchange of solvents)** : यदि एल्कोहॉल में बनाये गये सल्फर या फॉस्फोरस के विलयन को जल में डाला जाता है, तो सल्फर या फॉस्फोरस की निम्न घुलनशीलता (low solubility) के कारण सल्फर या फॉस्फोरस का कोलॉइडी विलयन प्राप्त होता है। इस प्रकार कई सारे पदार्थों जिनके कोलॉइडी विलयनों को एक विलायक (solvent) में पदार्थ के विलयन को लेकर तथा इसके विलायक में, जिसमें यह कम विलेय होते हैं, में डालकर बनाया जा सकता है।
- (B) **भौतिक अवस्था में परिवर्तन द्वारा (By change of physical state)** : निश्चित मात्रा के तत्वों जैसे पारा (mercury) और सल्फर के कोलॉइडी विलयनों को एक स्थायीकारक (stabilizer) (अमोनियम लवण या सिट्रेट) वाले ठण्डे जल में से इनकी वाष्प को गुजारने से प्राप्त किया जाता है।
- (C) **रासायनिक विधियाँ (Chemical methods)** : रासायनिक विधि में रासायनिक अभिक्रिया ऐसे माध्यम में की जाती है जिसमें कि परिक्षिप्त प्रावस्था आंशिक विलेय होती है। अतिसंतृप्तता की परिस्थिति उत्पन्न की जाती है परन्तु वास्तविक अवक्षेपण को रोक दिया जाता है कुछ महत्वपूर्ण अभिक्रियाएँ निम्न हैं-



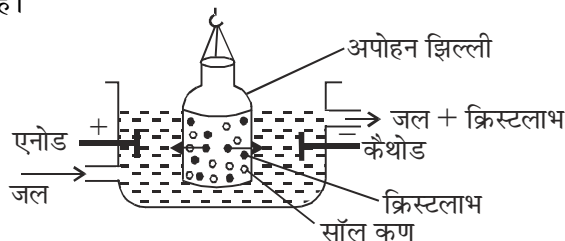
## 4.5 कोलॉइडी विलयनों का शुद्धिकरण (Purification of colloidal solutions)

उपरोक्त विधियों द्वारा बनाये गये कोलॉइडी विलयनों में सामान्यतः विद्युत अपघट्यों की अत्यधिक मात्रा और कुछ अन्य विलेय अशुद्धियाँ होती हैं। कोलॉइडी विलयनों के स्थायित्व के लिये विद्युत अपघट्यों की आंशिक मात्रा में उपस्थिति आवश्यक है परन्तु इनकी अधिक मात्रा, कोलॉइडी विलयन को स्कंदित कर देती है। अतः इसके लिये इन विलेय अशुद्धियों की सान्द्रता को आपेक्षित सीमा तक कम करना आवश्यक है। अशुद्धियों को आवश्यक सीमा तक कम करने के लिए उपयोग की गयी विधियों को कोलॉइडी विलयनों का शुद्धिकरण कहते हैं। कोलॉइडी विलयनों का शुद्धिकरण निम्न विधियों द्वारा किया जाता है।

- (i) **अपोहन (Dialysis)** : यह एक उपयुक्त झिल्ली (membrane) द्वारा विसरण करके कोलॉइडी विलयन में घुले हुए पदार्थों को पृथक करने का प्रक्रम है। चूंकि वास्तविक विलयन के कण (आयन या छोटे अणु) जन्तु झिल्ली (ब्लैंडर) या पार्चमेन्ट पत्र या सेलोफेन शीट में से पारगमित (passthroug) हो सकते हैं परन्तु कोलॉइडी कण नहीं, अतः झिल्ली को अपोहन में प्रयुक्त किया जा सकता है। इस उद्देश्य के लिये प्रयुक्त उपकरण **अपोहक (Dialyser)** कहलाता है। कोलॉइडी विलयन से भरा एक उपयुक्त झिल्ली का बेग एक पात्र में लटकाया जाता है जिसमें से होकर जल, निम्न चित्रानुसार निरंतर बहता रहता है। अणु एवं आयन झिल्ली में से विसरित होकर बाहरी जल में आ जाते हैं एवं शुद्ध कोलॉइडी विलयन शेष रह जाता है।



- (ii) **विद्युत अपोहन (Electro-dialysis) :** साधारणतया अपोहन का प्रक्रम बहुत मन्द होता है। यदि अशुद्ध कोलॉइडी विलयन में विलेय पदार्थ केवल वैद्युत अपघट्य हो तो इसे विद्युत क्षेत्र लगाकर तीव्र किया जा सकता है तब इस प्रक्रम को वैद्युत अपोहन नाम दिया जाता है। कोलॉइडी विलयन को एक उपयुक्त झिल्ली के बेग में लेकर दोनों इलेक्ट्रोडों में मध्य रखा जाता है जबकि शुद्ध जल को पात्र में प्रत्येक ओर (side) भरा जाता है चित्र में दर्शाये अनुसार इलेक्ट्रोड लगाये जाते हैं। कोलॉइडी विलयन में उपस्थित आयन विपरीत आवेश वाले इलेक्ट्रोडों की ओर झिल्ली से बाहर गमन कर जाते हैं।



- (iii) **अतिसूक्ष्म फिल्टरन या निस्यंदन (Ultrafiltration) :** अतिसूक्ष्म फिल्टरन, वह प्रक्रम है जिसमें विशेष रूप से बनाये गए फिल्टर (निस्यंदक), जो कि कोलॉइडी कणों के अतिरिक्त अन्य सभी पदार्थों के लिए पारगम्य होता है, द्वारा कोलॉइडी विलयन में उपस्थित घुलनशील विलयों और विलायकों से कोलॉइडी कणों को पृथक किया जाता है। कोलॉइडी कण सामान्य फिल्टर पत्र में से गुजर सकते हैं क्योंकि इनके रंध्र (pores) बहुत बड़े होते हैं, किन्तु कोलॉइडी कणों को निकलने से रोकने के लिए फिल्टर पेपर के रंध्रों का आकार कोलोडीयन विलयन के साथ संसेचन (impregnating) द्वारा हटाया (reduced) जा सकता है और इसके बाद फार्मैल्डिहाइड में भिगोकर कठोर किया जाता है। सामान्य कोलोडीयन एल्कोहॉल एवं ईथर के मिश्रण में नाइट्रोसेलुलोज का 4% विलयन होता है। एक अतिसूक्ष्म फिल्टर पत्र को एक कोलोडीयन विलयन में भिगोकर, फार्मैल्डिहाइड में कठोर बनाकर एवं अंत में सुखाकर बनाया जाता है। इस प्रकार के अतिसूक्ष्म फिल्टर पत्र का प्रयोग कर कोलॉइडी कणों को अन्य पदार्थों से पृथक किया जा सकता है। अतिसूक्ष्म फिल्टरन एक धीमा प्रक्रम है। प्रक्रम की गति बढ़ाने के लिए दाब या चूषण (suction) का प्रयोग किया जाता है।

शुद्ध कोलॉइडी विलयन प्राप्त करने के लिए अतिसूक्ष्म फिल्टर पत्र पर शेष बचे कोलॉइडी कणों को ताजे परिक्षेपण माध्यम (विलायक) के साथ हिलाया (stirred) जाता है।

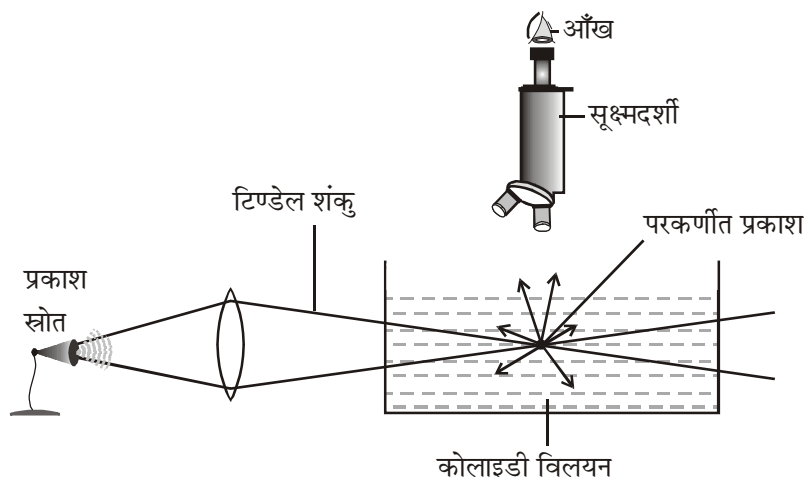
## 4.6 Properties of Colloidal Solutions :

### 4.6.1 Colligative properties:

जब प्रकाश की एक प्रबल और पुंजीत किरण (converging beam) को कोलॉइडी विलयन से गुजारा जाता है, तो (चित्रानुसार) इसका पथ दृश्यमान (नीले प्रकाश) हो जाता है जब इसे प्रकाश पुंज के समकोण पर देखा जाता है। इस प्रभाव को टिण्डेल प्रभाव कहते हैं। यह प्रकाश नीले शंकु जैसा प्रेक्षित होता है जिसे टिण्डेल शंकु कहाँ जाता है।

### 4.6.2 Optical Properties :

- (I) टिण्डेल प्रभाव, कोलॉइडी कणों द्वारा प्रकाश के प्रकीर्णन के कारण होता है। प्रकाश का प्रकीर्णन सामान्य परावर्तन के कारण नहीं हो सकता क्योंकि कणों की आकृति, दृश्य प्रकाश के तरंगदैर्घ्य की तुलना में बहुत कम या लघु (smaller) होती है और ये प्रकाश तरंग को परावर्तित करने में अक्षम (unable) होती है। निश्चित ही कोलॉइडी कण सर्वप्रथम दृश्य प्रकाश को अवशोषित करते हैं और फिर अवशोषित प्रकाश का एक भाग कोलॉइडी कणों की सतह से छोटी तरंगदैर्घ्य के प्रकाश के रूप में प्रकीर्णित (scattering) होता है। चूंकि अधिकतम प्रकाश का प्रकीर्णन आपतित प्रकाश के स्थान से समकोण पर होता है यह तब दिखाई देता है जब इसे इसी दिशा में देखा जाए।



### टिण्डेल प्रभाव

टिण्डेल प्रभाव को निम्न स्थितियों में प्रेक्षित किया जाता है :

- परिक्षिप्त कणों का व्यास प्रयुक्त प्रकाश के तरंगदैर्घ्य से बहुत कम नहीं होना चाहिए।
- परिक्षिप्त प्रावस्था और परिक्षेपण माध्यम के अपवर्तनांक परिमाण में बहुत अधिक अंतर होना चाहिए। यह अवस्था द्रव विरोधी कोलॉइडों द्वारा सन्तुष्ट होती है।

यह महत्वपूर्ण है कि टिण्डेल प्रभाव को वास्तविक विलयन में नहीं देखा जा सकता क्योंकि इनके कण प्रकीर्णन के लिये बहुत छोटे होते हैं।

टिण्डेल प्रभाव का उपयोग अतिसूक्ष्मदर्शी या परासूक्ष्मदर्शी से किया जाता है और कोलॉइडी विलयनों में कोलॉइडी कणों की संख्या ज्ञात करने में किया जाता है।

### नोट :

टिण्डेल प्रभाव का उपयोग कोलॉइडी एवं वास्तविक विलयन में विभेद करने में किया जाता है। जिगमोन्डी ने 1903 में एक उपकरण, जिसे अतिसूक्ष्मदर्शी कहा जाता है, को बनाने में टिण्डेल प्रभाव का उपयोग किया। एक काँच के पात्र में उपस्थित कोलॉइडी विलयन पर तीव्र प्रकाश किरण पुंज संकेंद्रित (Focus) किया जाता है। फिर इस संकेंद्रित प्रकाश के किरण पुंज को लंबवत् दिशा में अतिसूक्ष्मदर्शी द्वारा देखा जाता है। पृथक-पृथक कोलॉइडी कण अंधेरी पृष्ठभूमि में चमकदार तारों के समान प्रतीत होते हैं। अतिसूक्ष्मदर्शी वास्तविक कोलॉइडी कणों को प्रदर्शित नहीं करता, बल्कि उन के द्वारा प्रकीर्णित प्रकाश का अवलोकन कराता है। अतः अतिसूक्ष्मदर्शी कोलॉइडी कणों के आकार एवं आकृति के बारे में कोई सूचना नहीं देता।

**(II) रंग (Colour) :** कोलॉइडी विलयन का रंग, कण के आकार व आकृति के रंग के समान हमेशा एक जैसा नहीं होता है। कोलॉइडी विलयनों का रंग निम्न कारको (factors) पर निर्भर करता है :

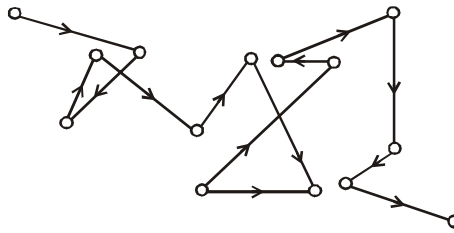
- कोलॉइडी कणों की आकृति और आकार पर
- प्रकाश स्रोत के तरंगदैर्घ्य पर
- वह तरिका जिस पर प्रेक्षक परावर्तन या पारगमन द्वारा प्रकाश ग्रहण करता है।

### उदाहरण :

- परिशुद्ध सोना (Finest gold) लाल रंग में होता है जैसे-जैसे इसके कणों की आकृति बढ़ती है यह बैंगनी हो जाता है और फिर नीला तथा अंत में सुनहरी (golden) हो जाता है।
- परावर्तित प्रकाश में देखने पर दूध का तनु विलयन नीला एवं संचरित (transmitted) प्रकाश में देखने पर लाल दिखाई देता है।

4.6.3 यांत्रिकी गुण (Mechanical Properties) :

- (a) **ब्राउनियन गति (Brownian movement) :** कोलॉइडी कण अनियमित और टेढ़ी-मेढ़ी गति की अवस्था में होते हैं। द्रव में निलम्बित (Suspended) कणों की यह गतिकीय क्रिया, ब्राउनीयन गति कहलाती है। रॉबर्ट ब्राउन ने पानी में निलम्बित पराग कणों के साथ इस गति को सर्वप्रथम प्रेक्षित किया था।
- (b) **गति का कारण (Cause of movement) :** ब्राउनीयन गति को परिक्षेपण माध्यम के अणुओं द्वारा कोलॉइडी कणों से असमान टक्कर के द्वारा समझाया गया है। ब्राउनीयन गति बिलोडन प्रभाव डालती है जो कणों को स्थिर नहीं होने देता तथा इस प्रकार कोलॉइडी सॉल के स्थायित्व के लिए उत्तरदायी होता है।  
यह याद रखना चाहिए कि ब्राउनीयन गति समय के साथ परिवर्तित नहीं होती परन्तु ताप के साथ परिवर्तित हो जाती है।



Brownian movement

(c) महत्व :

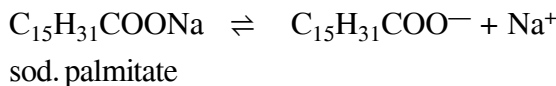
ब्राउनीयन गति में कोलॉइडी कण गुरुत्वाकर्षण के कारण नीचे नहीं बैठते हैं और इस प्रकार यह इनके स्थायित्व के लिये उत्तरदायी होता है।

4.6.4 Electrical Properties :

(I) कोलाइडी कणों पर आवेश (Charge of colloidal particles)

**आवेश की उत्पत्ति (Origin of charge) :** कोलॉइडी कणों पर आवेश की उत्पत्ति के सन्दर्भ में कई प्रकार के कारणों को दिया जाता है जो नीचे दिये गये हैं :

- (i) **घर्षण विद्युतीकरण (Frictional electrification) :** यह माना जाता है कि घर्षण, माध्यम के अणुओं के साथ परिक्षिप्त प्रावस्था के कणों की रगड़ (rubbing) के कारण होता है।
- (ii) **पृष्ठ अणुओं का वियोजन (Dissociation of the surface molecules) :**  
यह कोलॉइडी कणों पर विद्युत आवेश को बताता है। उदाहरण के लिये साबुन (सोडियम पॉमीटेट)(sodium palmitate) के जलीय विलयन का उनके आयनों में वियोजन होता है।



Na<sup>+</sup> आयन विलयन में निकल जाते हैं जबकि C<sub>15</sub>H<sub>31</sub>COO<sup>-</sup> आयनों की प्रवृत्ति हाइड्रोकार्बन श्रृंखला में उपस्थित दुर्बल आकर्षण बल के कारण समूहबद्ध (aggregates) होने की होती है। इस प्रकार ऋण आयन जो कोलॉइडी आकार के होते हैं, ऋणावेश रखते हैं।

(iii) विलयन से आयनों का प्राथमिक अधिशोषण (Preferential adsorption of ions from solution) :

कोलॉइडी कणों पर आवेश को सामान्यतः विद्युत अपघट्य के धनात्मक या ऋणात्मक आयनों को प्राथमिक अधिशोषण द्वारा ग्रहण किया जाता है। इस प्रकार AgCl के कण क्लोराइड विलयन से Cl<sup>-</sup> आयनों का अधिशोषण कर सकते हैं और Ag<sup>+</sup> आयनों को Ag<sup>+</sup> के आधिक्य वाले विलयन से अधिशोषण कर सकते हैं। प्रथम स्थिति में सॉल ऋणआवेशित होगा और द्वितीय स्थिति में धनावेशित होगा।

## (iv) इलेक्ट्रॉन का प्रग्रहण (Capture of electron) :

यह ब्रीडिंग आर्क विधि (Bredig's arc method) द्वारा सॉल के अवक्षेपण के दौरान वायु से होता है।

## (v) कणों की सतह पर आण्विक विद्युत अपघट्यों का वियोजन :

अवक्षेपण के दौरान सल्फाइडो पर  $H_2S$  अणुओं का अधिशोषण होता है।  $H_2S$  के वियोजन से,  $H^+$  आयनों की कमी हो जाती है और कोलॉइडी कण ऋणात्मक आवेशित हो जाते हैं।

कोलॉइडी कणों पर हमेशा विद्युत आवेश रहता है। विलयन के सभी कोलॉइडी कणों पर आवेश की प्रकृति समान होती है जो कि धनात्मक या ऋणात्मक हो सकती है। कुछ सामान्य सॉल की सूची उनके कणों पर आवेश की प्रकृति के साथ नीचे दी गई है।

धनात्मक आवेशित सॉल	ऋणात्मक आवेशित सॉल
जलयोजित धात्विक ऑक्साइड जैसे- e.g. $Al_2O_3 \cdot xH_2O$ , $CrO_3 \cdot xH_2O$ तथा $Fe_2O_3 \cdot xH_2O$ , etc.	धातुएं, जैसे- कॉपर, सिल्वर, गोल्ड सॉल
क्षारकीय रंजक पदार्थ जैसे- मेथिलीन नील (methylene blue) सॉल	धात्विक सल्फाइड, जैसे, $As_2S_3$ , $Sb_2S_3$ , $CdS$ सॉल
हिमोग्लोबिन (रक्त)	अम्लीय रंजक पदार्थ, जैसे - इओसिन, कॉगो रेड सॉल
ऑक्साइड, जैसे $TiO_2$ सॉल	स्टार्च, गोंद, जिलेटिन, मट्टी (clay), चारकोल इत्यादि के सॉल

सॉल कणों पर आवेश एक या अधिक कारणों से होता है यथा धातुओं के वैद्युतपरिक्षेपण के समय सॉल कणों के द्वारा इलेक्ट्रॉन प्रग्रहण (Capture), विलयन से आयनों का अधिमन्य अधिशोषण एवं/ या विद्युतीय दोहरी परत बनने के कारण। आयनों का अधिमन्य अधिशोषण सर्वाधिक मान्य कारण है। सॉल कण धनात्मक या ऋणात्मक आयनों के अधिमन्य अधिशोषण द्वारा धनात्मक या ऋणात्मक आवेश ग्रहण कर लेते हैं। परिक्षेपण माध्यम में दो या अधिक आयन उपस्थित होने पर कोलॉइडी कणों द्वारा उस आयन का अधिमन्य अधिशोषण होता है जो कोलॉइड में भी उपस्थित होता है। इसे निम्नलिखित उदाहरण द्वारा समझा जा सकता है।

- (a) जब सिल्वर नाइट्रेट विलयन को पोटैशियम आयोडाइड विलयन में मिलाया जाता है, तब अवक्षेपित सिल्वर आयोडाइड परिक्षेपण माध्यम में से आयोडाइड आयनों को अधिशोषित करके ऋण-आवेशित कोलॉइडी विलयन देता है। किंतु जब  $KI$  विलयन को  $AgNO_3$  विलयन में मिलाया जाता है तो परिक्षेपण माध्यम से  $Ag^+$  आयनों के अधिशोषण के कारण धन-आवेशित सॉल बनता है।

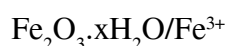


ऋण-आवेशित

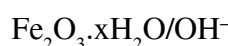


धन-आवेशित

- (b) यदि गर्म जल के आधिक्य में  $FeCl_3$  मिलाया जाये तो  $Fe^{3+}$  आयनों के अधिशोषण से धन आवेशित जलयोजित फेरिक ऑक्साइड का सॉल बनता है। किंतु यदि फेरिक क्लोराइड को  $NaOH$  में मिलाया जाये तो  $OH^-$  आयनों के अधिशोषण के साथ एक ऋण-आवेशित सॉल प्राप्त होता है।

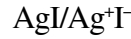
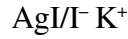


धन-आवेशित



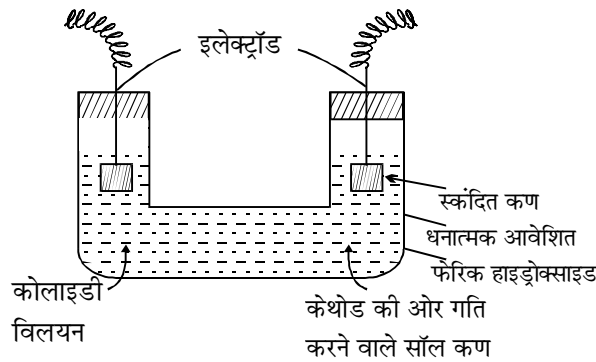
ऋण-आवेशित

उपरोक्त अधिमन्य अधिशोषण द्वारा पृष्ठ पर धन या ऋण आवेश ग्रहण कर लेने के पश्चात् कोलॉइडी कणों की सतह माध्यम में से प्रतिआयनों को आकर्षित करती है जिससे आयनों की दूसरी परत बनती है जैसा कि नीचे दर्शाया गया है।



**(II) विद्युत कण संचलन या धन कण संचलन (Electrophoresis or Cataphoresis) :**

एक कोलॉइडी विलयन में, कोलॉइडी कण विद्युत आवेशित होते हैं और परिक्षेपण माध्यम समान परन्तु विपरित आवेश वाला होता है इस प्रकार कोलॉइडी विलयन सम्पूर्ण रूप से वैद्युत उदासीन होता है जब विद्युत धारा को कोलॉइडी विलयन में से गुजारा जाता है। तो आवेशित कण विपरित आवेशित इलेक्ट्रोडों जहाँ आवेश की हानि के कारण स्कन्दन होता है, कि ओर गति करते हैं।



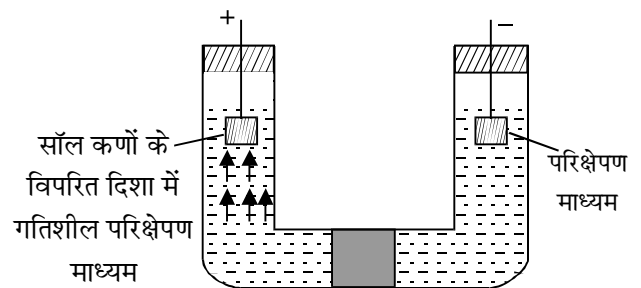
प्रक्रम जिसमें विद्युत क्षेत्र की उपस्थिति में कोलॉइडी कणों का गमन विपरित आवेशित इलेक्ट्रोड की ओर होता है वैद्युत कण संचलन या धन कण संचलन कहलाता है।

इस प्रक्रम का उपयोग कोलॉइडी कणों पर उपस्थित आवेश को ज्ञात करने के लिये किया जाता है उदाहरण के लिये, जब फेरिक हाइड्रोक्साइड के सॉल को एक U-नली में लिया जाए और इसमें वैद्युत क्षेत्र लगाया जाये तब फेरिक हाइड्रोक्साइड (सॉल) के कण चित्रानुसार ऋणाग्र (cathode) के पास संचयित (accumulated) हो जाते हैं। यह प्रदर्शित करता है कि फेरिक हाइड्रोक्साइड सॉल के कण धनात्मक आवेशित होते हैं।

**(III) विद्युत परासरण (Electro-osmosis) :**

प्रक्रम जिसमें, विद्युत क्षेत्र की उपस्थिति में परिक्षेपण

माध्यम का गमन सम्मिलित है न की कोलॉइडी कणों का, विद्युत परासरण कहलाता है। U-नलिका के दोनों भागों में शुद्ध विलायक (परिक्षेपण माध्यम) लिजिए। U-नलिका के निम्नतम मध्य भाग में, रन्ध्र युक्त (porous) डायफ्रॉम जिसमें कोलॉइडी विलयन उपस्थित है जो U-नलिका को दो भागों में विभाजित करती हैं। चित्रानुसार U-नलिका के प्रत्येक भाग में, एक इलेक्ट्रोड उपस्थित है।



जब इलेक्ट्राडों पर इलेक्ट्राड विभव लगाया जाता है, तो सॉल की ठोस प्रावस्था (कोलॉइडी तंत्र) गति नहीं कर सकती। परन्तु विलायक (परिक्षेपण माध्यम) रन्ध्रयुक्त डायफ्रॉम से होता हुआ किसी एक इलेक्ट्राड की ओर गति कर सकता है। वैद्युत परासरण के कारण परिक्षेपण माध्यम के गमन की दिशा सॉल कणों पर आवेश का निर्धारण करती है। उदाहरण के लिए यदि परिक्षेपण माध्यम कैथोड (ऋणात्मक इलेक्ट्राड) की ओर गति करता है तो सॉल के कण भी ऋणात्मक आवेशित होते हैं, क्योंकि परिक्षेपण माध्यम धनात्मक आवेशित होता है। इस प्रकार सम्पूर्ण कोलॉइडी विलयन उदासीन होता है।

(IV) **Zeta potential,  $\xi$**  : कोलॉइडी कणों के चारों ओर विपरीत आवेशों की दो परतों का संयोजन हेल्महोल्ट्स विद्युतीय दोहरी परत कहलाता है। आधुनिक विचारों के अनुसार आयनों की प्रथम परत दृढ़तापूर्वक बँधी रहती है, जिसे स्थिर परत कहते हैं, जबकि दूसरी परत गतिशील होती है। जिसे विसरित परत कहते हैं। आवेशों का पृथक्करण विभव का आधार होता है, अतः स्थिर एवं विसरित भागों पर विपरीत चिह्नक के आवेशों के कारण दोनों परतों के मध्य विभवान्तर उत्पन्न हो जाता है। विपरीत आवेशों वाली स्थिर एवं विसरित परतों के मध्य यह विभवान्तर वैद्युत गतिक विभव या जीटा विभव कहलाता है। कोलॉइडी कणों पर बराबर एवं एक जैसे आवेशों की उपस्थिति कोलॉइडी विलयनों को स्थायित्व देने के लिए मुख्य रूप से उत्तरदायी होती है क्योंकि समान आवेशों के मध्य प्रतिकर्षण बल उन्हें पास-पास आकर सहमिलन या पुंजित होने से रोकते हैं।

(V) **सम विभव बिन्दु** : यह वह pH है जिस पर कोलोइडी कणों पर कोई आवेश नहीं होता है

4.7 **स्कंदन (Coagulation)** : कोलॉइडी सॉल, कोलॉइडी कणों पर विद्युत आवेशों की उपस्थिति के कारण स्थायी (stable) होते हैं क्योंकि विद्युत प्रतिकर्षण के कारण कण एक दूसरे के पास नहीं आ पाते। किसी तरह आवेश को दूर करने से कणों का संगुणन (aggregation) होगा और इस प्रकार अवक्षेपण शीघ्रता से होगा।

यह प्रक्रिया जिसके द्वारा सॉल में परिक्षिप्त अवस्था के कण अवक्षेपित हो जाते हैं स्कन्दन (coagulation) कहलाती है। यदि स्कंदित कण पात्र के तल (bottom) पर बैठने के बदले में (Instead) परिक्षेपण माध्यम की सतह पर तेरते हैं, तो स्कंदन को ऊर्णन (flocculation) कहते हैं। अधिकांश सॉल में विपरित आवेश के विद्युतअपघट्य को मिलाने से स्कन्दन होता है ऐसा होने का कारण यह है कि कोलॉइडी कण, विद्युत अपघट्य के आयनों, जिनका आवेश कोलॉइडी कणों के विपरित होता है, को अपने ऊपर ग्रहण कर लेते हैं। इसके परिणामस्वरूप कोलॉइडी कणों पर आवेश उदासीन हो जाता है इस प्रकार स्कन्दन होता है उदाहरण के लिये, आर्सेनियस सल्फाइड ( $As_2S_3$ ) का विलयन (ऋणात्मक आवेशित), बेरीयम क्लोराइड ( $BaCl_2$ ) विलयन को मिलाने से अवक्षेपित होता है। इसका कारण यह है कि सॉल के ऋणआवेशित कण बेरीयम आयन को ग्रहण कर लेते हैं और उदासीन हो जाते हैं जो कि सॉल का स्थायित्व कम करता है इसके परिणामस्वरूप अवक्षेपण होता है।

यह प्रेक्षित किया गया है कि किसी निश्चित विलयन के स्कन्दन को प्राप्त करने के लिये भिन्न-भिन्न प्रकार के विद्युत अपघट्यों की अलग-अलग मात्रा की आवश्यकता होती है।

किसी विद्युत अपघट्य की मिली मोल प्रति लीटर में न्यूनतम सांद्रता जो किसी सॉल को दो घंटों में स्कंदित करने के लिए आवश्यक हो, **स्कंदन मान** या **ऊर्णन मान** कहलाती है। जितनी कम मात्रा की आवश्यकता होगी उतनी ही अधिक उस आयन की स्कंदन शक्ति होगी।

स्कंदन मान के व्युत्क्रम (reciprocal) को स्कन्दन क्षमता (coagulating power) के रूप में भी व्यक्त किया जाता है।

उदाहरण के लिये आर्सेनिक सल्फाइड विलयन के लिए  $NaCl$ ,  $BaCl_2$  और  $AlCl_3$  के स्कन्दन मान क्रमशः 51, 0.69 और

0.093 मिलीमोल/लीटर है। इस प्रकार इनकी स्कन्दन क्षमताएँ  $\frac{1}{51}$ ,  $\frac{1}{0.69}$  और  $\frac{1}{0.093}$  है जो कि क्रमशः 0.0196, 1.449 और 10.75 होगी।

ऋणात्मक आवेशित आर्सेनिक सल्फाइड और धनात्मक आवेशित फेरिक हाइड्रोक्साइड विलयन के लिए कुछ विद्युत अपघट्यों के स्कन्दन मानों को नीचे तालिका में दिया गया है। स्कन्दन आयनों (आयन जिनका आवेश, उनके कोलॉइडी कणों के विपरित है) की संयोजकताएँ भी दी गयी है।

#### विभिन्न विद्युत अपघट्यों के स्कन्दन मान (Coagulation values of different electrolytes)

आर्सेनिक सल्फाइड सॉल			फेरिक हाइड्रोक्साइड सॉल		
विद्युत अपघट्य	स्कंदित धनायन की संयोजकता	स्कंदन मान की संयोजकता	विद्युत अपघट्य	स्कंदित ऋणायन	स्कंदन मान
K <sub>2</sub> SO <sub>4</sub>	1	63	KBr	1	138
NaCl	1	51	KNO <sub>3</sub>	1	132
KNO <sub>3</sub>	1	50	KCl	1	103
MgSO <sub>4</sub>	2	0.81	K <sub>2</sub> CrO <sub>4</sub>	2	0.320
BaCl <sub>2</sub>	2	0.69	K <sub>2</sub> SO <sub>4</sub>	2	0.215
AlCl <sub>3</sub>	3	0.093	K <sub>3</sub> Fe(CN) <sub>6</sub>	3	0.096

उपरोक्त तालिका से यह स्पष्ट है कि आर्सेनिक सल्फाइड सॉल के अवक्षेपण में Al<sup>3+</sup> आयन की स्कन्दन क्षमता, सोडियम (Na<sup>+</sup>) या पोटेशियम (K<sup>+</sup>) आयनों की तुलना में लगभग 550 गुना अधिक है पुनः यह प्रेक्षित किया गया है कि ऋणात्मक आवेशित आर्सेनिक सल्फाइड सॉल, धनायनों द्वारा स्कन्दित होती है जबकि धनात्मक आवेशित फेरिक हाइड्रोक्साइड सॉल, ऋणायनों द्वारा स्कन्दित होती है।

**हार्डी-शुल्ज नियम (Hardy-Schulz rules) :** H. शुल्ज (1882) और W.B. हार्डी (1900) ने सॉल के स्कन्दन पर विद्युत अपघट्यों के प्रभाव को जानने के लिये निम्न नियमों को दिया।

- (1) केवल सॉल कणों पर उपस्थित आवेश से विपरित आवेश रखने वाले आयन स्कन्दन के लिये प्रभावी होते हैं। अर्थात् धनायनों द्वारा ऋणात्मक आवेशित सॉल अच्छे प्रकार से स्कंदित होता है और एक धनात्मक सॉल ऋणायनों द्वारा स्कंदित होती है।
- (2) स्कंदित आयन पर आवेश, सॉल के स्कंदन को प्रभावित करता है। सामान्य रूप में, सक्रिय आयनों की स्कंदन क्षमता सक्रिय आयनों की संयोजकता बढ़ने के साथ बढ़ती है। सक्रिय आयन के चिन्ह और संयोजकता सम्बन्धी नियमित प्रेक्षणों के बाद हार्डी और शुल्ज ने एक नियम प्रतिपादित किया। जिसे हार्डी-शुल्ज नियम कहाँ गया। जो कि निम्न प्रकार है :

"सक्रिय आयन की जितनी अधिक संयोजकता होती है, उतनी ही अधिक उसकी सॉल को अवक्षेपण करने की क्षमता होगी"

इस प्रकार, धनायनों की स्कंदन क्षमता Al<sup>3+</sup> > Ba<sup>2+</sup> or Mg<sup>2+</sup> > Na<sup>+</sup> या K<sup>+</sup> के क्रम में होती है।

इसी प्रकार, धनात्मक आवेशित सॉल के स्कंदन के लिए ऋणायनों की स्कंदन क्षमता निम्न क्रम में होती है





Ex3. 50 l कोलाईडी विलयन के पूर्ण स्कंदन के लिये 11.7 gm NaCl की आवश्यकता होती है तो वैद्युत अपघट्य का स्कंदन मान क्या है ?

$$\text{Sol. Coagulation value} = \frac{\text{millimole of electrolyte}}{\text{L of colloidal solution}} = \frac{11.7}{58.5} \times 1000 = 4$$

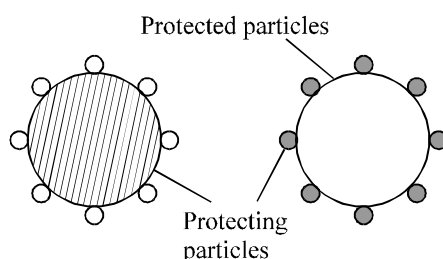
**स्कंदन की कुछ अन्य विधियाँ (Some other methods of coagulation) :**

विद्युत अपघट्यों को मिलाने से स्कन्दन को निम्न विधियों द्वारा भी प्राप्त किया जा सकता है।

- (i) **सतत् अपोहन द्वारा (By persistent dialysis) :** यह प्रेक्षित किया गया है कि विद्युत अपघट्य की सूक्ष्म मात्रा विलयन के साथ संयोजित (associate) होती है। जिसके कारण यह स्थायी होता है। यदि विलयन का लगातार अपोहन (prolonged dialysis) करवाया जाए तो विद्युत अपघट्य की सूक्ष्म मात्रा हट (remove) जाती है और स्कंदन हो जाता है।
- (ii) **कोलाइडों के परस्पर स्कन्दन द्वारा (By mutual coagulation of colloids) :** जब विपरीत आवेशो वाले दो सॉलो (Sols) को एक उपयुक्त अनुपात में आपस में मिश्रित किया जाता है, तो स्कन्दन होता है। एक के आवेश को दूसरे के द्वारा उदासीनीकृत कर दिया जाता है। उदाहरण के लिये जब ऋणात्मक आवेशित आर्सेनिक सॉल को धनात्मक आवेशित फेरिक हाइड्रोक्साइड सॉल में मिलाया जाता है, तो दोनों का एक साथ अवक्षेपण होता है।
- (iii) **विद्युत विधि द्वारा (By electrical method) :** यदि द्रव विरोधी सॉल के विद्युत आवेश को कोई भी विद्युत क्षेत्र लगाने से हटा (remove) दिया जाता है जैसा कि विद्युत कण संचलन में होता है, तो अवक्षेपण प्राप्त होता है।
- (iv) **क्वथन द्वारा :** जब एक सॉल को उबाला जाता है तो परिक्षेपण माध्यम के अणुओं के साथ संघट्ट (Collisions) बढ़ने से अधिशोषित परत विक्षुब्ध हो जाती है। इससे कणों पर उपस्थित आवेश कम हो जाता है और अंततः इसके कारण वे अवक्षेप के रूप में नीचे बैठे जाते हैं।
- (v) **वैद्युतअपघट्य मिलाकर :** जब एक वैद्युतअपघट्य प्रचुर मात्रा में मिलाया जाता है तो कोलाईडी कण अवक्षेपित हो जाते हैं। इसका कारण यह है कि कोलाईडी कण अपने से विपरीत आवेश वाले आयनों से अन्योन्यक्रिया करते हैं। इससे उदासीनीकरण होता है जिससे स्कंदन हो जाता है। कणों पर आवेश के उदासीनीकरण के लिए उत्तरदायी आयन स्कंदक आयन कहलाते हैं। एक ऋण आयन धनात्मक आवेशित सॉल का स्कंदन करता है और इसवेफ विलोमतः भी होता है।

**4.8 रक्षण कोलाइड (Protective colloids) :** द्रव स्नेही सॉल, द्रव विरोधी सॉल की तुलना में अधिक स्थायी होते हैं। इसका कारण यह है कि द्रव स्नेही कोलाइड व्यापक रूप से जलयोजित होते हैं और ये जलयोजित कण बहुत बड़े समूह के रूप में संयोजित नहीं होते हैं।

उपयुक्त वैद्युत अपघट्य को मिलाने से द्रवविरोधी (lyophobic) सॉल अधिक आसानी से स्कन्दित हो जाते हैं। वैद्युत अपघट्यों को मिलाने से द्रवविरोधी सॉल के अवक्षेपण को रोकने के लिये इसमें कुछ मात्रा द्रवस्नेही कोलाइड की मिला दी जाती है। इस प्रकार द्रवस्नेही कोलाइड को **रक्षण कोलाइड (protective colloid)** कहाँ जाता है और वैद्युत अपघट्य से द्रवस्नेही कोलाइड की क्रिया रक्षण ऋणायन के रूप में जानी जाती है। रक्षण कोलाइडों के रूप में सामान्यतः उपयोग किये जाने वाले पदार्थ, जिलेटिन (gelatin), गमअरेबीक (gum arabic), केसीन (casein) स्टार्च (starch), गोंद आदि हैं। एक गोल्ड सॉल, जिसमें रक्षण कोलाइड के रूप में जिलेटिन की कुछ मात्रा उपस्थित है, के स्कंदन के लिये सोडियम क्लोराइड की बहुत अधिक मात्रा की आवश्यकता होती है।



**स्पष्टीकरण (Explanation) :**

रक्षी कोलॉइड के कण जलविरोधी कोलॉइड के कणों पर अधिशोषित हो जाते हैं, तथा इसके चारों ओर रक्षात्मक परत बनाते हैं। (चित्रानुसार) रक्षात्मक परत अवक्षेपणकारी (Precipitating) आयनों को कोलॉइडी कणों के सम्पर्क में आने से रोकती है। वर्तमान विचारधारा के अनुसार जलविरोधी कोलॉइड के स्थायित्व में वृद्धि जलस्नेही व जलविरोधी कोलॉइडों के पारस्परिक अधिशोषण (adsorption) के कारण होती है। वास्तव में छोटे कण चाहे रक्षी कोलॉइड के हों या जलविरोधी कोलॉइड के हों, बड़े कणों पर अधिशोषित होते हैं।

एक रक्षण कोलॉइड की स्वर्ण संख्या सॉल की मिलीग्राम में वह न्यूनतम मात्रा है जिसे लाल गोल्ड के मानक कोलॉइडी सॉल के 10 ml में डालने पर गोल्ड के सॉल का स्कन्दन (अर्थात् लाल रंग से नीले रंग में परिवर्तन) नहीं हो जाता है जब सोडियम क्लोराइड के 10% विलयन के 1 ml को तेजी से इसमें मिलाया जाता है। रक्षण कोलाइड की स्वर्ण संख्या जितनी कम होगी उतनी ही अधिक उसकी रक्षात्मक क्रिया होगी।

**Ex.4** 0.02 gm द्रव स्नेही कोलोइड, 10 ml द्रव विरोधी कोलाइड में 1 ml 10 % NaCl विलयन मिलाने से उत्पन्न होने वाले स्कंदन को ठीक रोक देता है। द्रव स्नेही कोलाइड की स्वर्ण संख्या क्या है ?

**Sol.** Mg of lyophilic colloid =  $0.02 \times 1000 = 20$

**4.9 EMULSIONS :**

पायस, एक द्रव का कोलॉइडी विलयन होता है, इसे इस प्रकार से भी परिभाषित किया जा सकता है कि, पायस एक विषमांगी तंत्र होता है जिसमें एक से अधिक अमिश्रणीय द्रवों, जो कि बूंदों (droplets), के रूप में रहते हैं, जिनका व्यास सामान्यतः  $0.1 \mu$  से अधिक होता है, एक दूसरे में परिक्षिप्त रहते हैं

उदाहरण के लिए, दुध एक पायस है जिसमें द्रव वसा की छोटी-बुंदें, जलीय माध्यम में परिक्षिप्त होती हैं। कॉड लीवर तेल भी एक पायस है जिसमें जल के कण तेल में परिक्षिप्त होते हैं। इसका अर्थ है कि अधिकतम पायसों में एक द्रव तो जल और अन्य द्रव तेल होता है यहाँ पर 'तेल' शब्द का प्रयोग उन सभी कार्बनीक पदार्थों के लिये किया गया है जो जल में विलेय हैं।

पायस को निम्न प्रकार वर्गीकृत किया जाता है :

- (1) **जलीय प्रकार के पायस में तेल (O/W) :** इन पायसों में तेल परिक्षिप्त प्रावस्था तथा जल परिक्षेपण माध्यम बनाता है। इसे O/W या W में O द्वारा व्यक्त करते हैं। उदाहरण के लिए, दूध (जल में परिक्षिप्त द्रव वसा), वेनिशिंग क्रीम इत्यादि। ये जलीय पायस भी कहलाते हैं।
- (2) **तेलीय प्रकार में जल (W/O) :** इन पायसों में जल परिक्षिप्त प्रावस्था तथा तेल परिक्षेपण माध्यम होता है। इसे W/O या O में W द्वारा व्यक्त करते हैं। उदाहरण के लिए बटर, कोल्ड क्रीम इत्यादि तेल पायस (oil emulsion) भी कहलाते हैं।

दो अमिश्रणीय द्रवों को हिलाने (agitating) से प्राप्त पायस का प्रकार, दोनों अवयवी द्रवों की सापेक्ष मात्राओं पर निर्भर करता है। द्रव जो आधिक्य में है, परिक्षेपण माध्यम को बनाता है इसी प्रकार पायसों के दो प्रकारों को, किसी एक द्रव की सान्द्रता में परिवर्तन द्वारा, आपस में अन्तः रूपान्तरित (interconvert) किया जा सकता है।

**4.9.1 पायस का निर्माण, पायसीकरण (Emulsification) :**

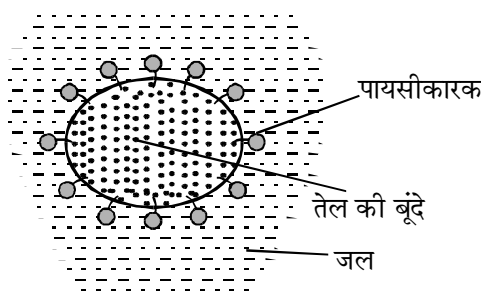
पायसीकरण एक विधि है जिसमें पायस का निर्माण होता है। सामान्यतः एक पायस का निर्माण, अमिश्रणीय (immiscible) द्रव के मिश्रण को रखने पर दो अलग-अलग परतें बनने से होता है। तेल की छोटी बूंदें (globules) ऊपर उठकर उपरी परत बनाती हैं जबकि जलीय माध्यम नीचे की परत का निर्माण करता है।

परतों को अलग होने से बचाने के लिए और स्थायी पायस प्राप्त करने के लिए, एक तृतीय पदार्थ की बहुत कम मात्रा मिलायी जाती है। इस पदार्थ को एमल्सिफायर (emulsifier) या पायसीकरण अभिकर्मक (emulsifying agent) कहलाता है। सामान्यतः उपयोग में लिये जाने वाले पायसीकारक साबुन, अपमार्जक और द्रवस्नेही कोलाइड होते हैं। दुध में उपस्थित द्रव स्नेही कोलाइड केसीन (casein) एक पायसीकारक की भांति कार्य करता है। यह जल में परिक्षिप्त वसा अणुओं के चारों ओर (around) एक रक्षण परत बनाते हैं। इस कारण दुध एक स्थायी पायस है।

**पायसीकारक की कार्यप्रणाली (Function of emulsifier) :** पायसीकारक या पायसीकरण अभिकर्मक का मुख्य कार्य, तेल और जल के मध्य अन्तः पृष्ठीय तनाव (interfacial tension) को कम करना है और इस प्रकार ये दो द्रवों को आपस में मिलाने में मदद करते हैं। उदाहरण के लिये साबुन या अपमार्जक (पायसीकारक) का एक अणु, तेल और जल के मध्य अन्तः पृष्ठों पर सान्द्रित हो जाता है। पायसीकारक का ध्रुवीय सिरा जल में और अध्रुवीय सिरा तेल में चित्रानुसार होता है। साबुन में,  $\text{RCOONa}$ , R अध्रुवीय सिरा होता है जबकि  $\text{COO}^- \text{Na}^+$  ध्रुवीय सिरा होता है।

#### 4.9.2 पायस के गुणधर्म (Properties of emulsion) :

- सॉल की तुलना में पायस के परिक्षिप्त प्रावस्था के कणों का आकार सामान्यतः बड़ा होता है।
- पायसों के गुणधर्म भी कोलॉइडी कणों के समान होते हैं जैसे कि टिण्डेल प्रभाव, ब्राउनीयन गति (दिया गया कण अत्यधिक बड़ा न हो), वैद्युत कण संचलन, स्कन्दन आदि।



**विपायसीकरण (Demulsification) :** प्रक्रम जिसमें एक पायस को दो अलग-अलग द्रव परतों के रूप में तोड़ा जाता है विपायसीकरण (demulsification) कहलाता है। विपायसीकरण प्राप्त करने के लिए निम्न विधियों का उपयोग किया जाता है :

- रसायनिक विधि (Chemical Methods) :** एक पायस को विपायसीकृत, एक रसायनिक पदार्थ मिलाकर किया जा सकता है रसायनिक पदार्थ वह होता है, जिसकी परिक्षिप्त प्रावस्था और परिक्षेपण माध्यम पर क्रिया, उस वास्तविक पायसीकारक (emulsifying agent) के विपरित होती है जिसे पायस को स्थायी बनाने के लिये उपयोग किया जाता है।
- अपकेन्द्रण (Centrifugation) :** दुध से क्रिम को अपकेन्द्रण विधि द्वारा पृथक किया जाता है।
- शीतलन (Cooling) :** दुध से वसा को हटाने के लिये इसे कुछ घण्टों तक फ्रिज में रखा जाता है।

#### 4.9.3 जल में तेल प्रकार के पायस (O/W) :

- कई औषधियाँ बनाने के लिये जैसे-दवाईयाँ, क्रिम, जैल और कई प्रकार के लोशन, पायस होते हैं यह माना जाता है कि औषधियाँ जब कोलॉइडी अवस्था जैसे पायस में होती हैं तब ये अधिक प्रभावी और शरीर उत्तकों (tissues) द्वारा सरलता से पचायी (essimilated) जा सकती हैं।
- सभी पेन्ट पायस होते हैं।
- शरीर की आंतों में वसा का, पाचन पायसीकरण द्वारा सहायक होता है। वसा का एक छोटा भाग, आंतों के क्षारीय विलयन के साथ एक माध्यम (medium) साबुन (पायसीकारक) का निर्माण करता है और यह पायसीकरण साबुन, शेष या अवशेष वसा को पाचक एन्जाइमों के लिये इनकी चयापचयी (metabolic) क्रियाओं को करने में सरल बना देता है।
- साबुन और अपमार्जक जल में तेल पायस के निर्माण द्वारा धूल (dust) और गन्दगी को कपड़ों से हटा देता है।
- दुध, जल में द्रव वसा का पायस है।

- (6) धातुकर्म की विधि में, एक महत्वपूर्ण पद, अयस्क की सान्द्रता है जो कि सामान्यतः झागप्लावन विधि द्वारा किया जाता है और जिसमें एक तेल को, जल में लिये गये अयस्क को अन्तिम रूप से अलग करने के लिये, मिलाया जाता है। अयस्क के कण झाग बनने के कारण सतह पर आ जाते हैं जबकि अन्य अशुद्धियाँ, पात्र के तल पर शेष रह जाती हैं।
- (7) जल में रेत-गिट्टी-सीमेन्ट के या आसफाल्ट (Asphalt) के पायस को इमारतों और सड़कों के निर्माण में उपयोग किया जाता है।

#### NOTE- जैल (GELS)

ऐसा कोलॉइडी तंत्र जिसमें द्रव परिक्षिप्त प्रावस्था व ठोस परिक्षिप्त माध्यम के रूप में होते हैं जैल कहलाते हैं। सामान्य उदाहरण है ; बूट पॉलिश, जैली, गम ऐरेबिक, ऐगार-ऐगार, पनीर व सिलिसिक अम्ल।

#### 4.10 कोलाइडों का उपयोग (Uses of Colloids) :

##### (1) औषधियाँ (Medicines) :

औषधियाँ जिनमें, गोल्ड, सिल्वर या कैल्शियम आदि कोलॉइडी रूप में होता है, अधिक प्रभावी होती हैं और मानव तंत्र द्वारा सरलता से पचा ली जाती हैं।

##### (2) रंजक (Dyes) :

रंजक में, परिमीत कोलॉइडी पदार्थों का उपयोग कपड़ा रंजक उद्योगों में रंगों को दृढ़ता देने के लिये किया जाता है।

##### (3) रबर उद्योगों में (Rubber industry) :

लेटेक्स, ऋणावेशित कणों का एक कोलॉइडी विलयन होता है। रबर प्लेटेड की बनी वस्तुएँ एनोड (anode) पर बनाती हैं। विद्युत क्षेत्र की उपस्थिति में रबर के कण एनोड (anode) पर जमा (deposited) हो जाते हैं और वस्तुएँ (article) रबर प्लेटेड बन जाती हैं।

##### (4) धुँएँ के आवरण (Smoke screens) :

धुँएँ का आवरण जिसमें वायु में परिक्षिप्त टाइटेनियम डाई ऑक्साइड उपस्थित होता है, का उपयोग युद्ध कार्यों (warfare) में छिपने (concealment) और चमकदार श्वेत पर्दों के लिए किया जाता है।

##### (5) डेल्टा बनाने के लिये (Formation of delta) :

नदी का जल अपने साथ मिट्टी (clay) के आवेशित कणों और कई अन्य पदार्थों को कोलॉइडी विलयन के रूप में लाता है। जब समुद्र का जल इन कणों के सम्पर्क में आता है तब नदी जल में उपस्थित कोलॉइडी कण, समुद्री जल में उपस्थित वैद्युत अपघट्यों द्वारा स्कंदित होकर डेल्टा बनाते हैं।

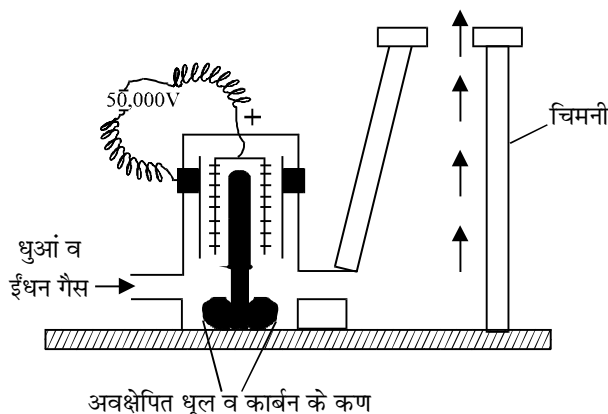
##### (6) जल शुद्धिकरण के लिए (Purification of water) :

जल में धुंधलापन (turbidity) ऋणात्मक आवेशित मिट्टी के कणों की उपस्थिति के कारण होता है। पौटाश ऐलम (potash alum) जिसमें  $Al^{3+}$  आयन होते हैं, को मिलाने पर, कोलॉइडी कणों पर उपस्थित ऋणात्मक आवेश को उदासीन कर देते हैं और इस प्रकार इनका स्कन्दन होता है स्कंदित पदार्थ नीचे बैठ जाता है और इस प्रकार यह शुद्ध हो जाता है।

##### (7) कृत्रिम वर्षा (Artificial rain) :

कृत्रिम वर्षा कराने के लिये विद्युतिकृत (electrified) धूल (sand) कणों को बादलों पर जो कि कोलाइडी विलयन या हवा में पानी के आवेशित कण होते हैं, को छिड़कर कराया जाता है।

- (8) **धूम का अवक्षेपण (Smoke precipitation) :** औद्योगिक क्षेत्रों में चिमनी से बाहर निकलने वाला धुआ, पीड़ादायक (nuisance) और हानिकारक (health hazard) होता है यह कोलॉइडी कण आवेशित कण होते हैं और इस प्रकार इन्हें वैद्युत अवक्षेपण [कॉट्रेल अवक्षेपण कारक (Cottrell Precipitator)] द्वारा गैसों से हटाया जाता है।



कॉट्रेल अवक्षेपण कारक में धूम उच्च वैद्युत आवेशित प्लेटों से बने कक्षों में से गुजारा जाता है जहाँ पर कार्बन और धूल कण अवक्षेपित हो जाते हैं और शेष गैसों चित्रानुसार चिमनी से बाहर निकल जाती है।

- (9) **सीवेज अपशिष्ट (Sewage disposal) :**

सीवेज जल में गंदगी, मिट्टी, किचड़ आदि के कण होते हैं जो कोलॉइडी आकार के होते हैं और एक विद्युत आवेश रखते हैं और इसलिए ये आसानी से तल में नहीं बैठते हैं ये कण धनकण संचलन (cataphoresis) द्वारा हटाये जा सकते हैं। इस क्रिया के लिये धातु इलेक्ट्रोडों वाले दो टैंकों के एक तंत्र का उपयोग किया जाता है जब विद्युत क्षेत्र लगाया जाता है तब धूल के कण विपरित आवेशित इलेक्ट्रोडों पर स्कंदित हो जाते हैं एकत्र पदार्थ कई रूपों में उपयोग किया जाता है।

- (10) **साबुन एवं अपमार्जकों की शोधन क्रिया :**

कपड़ों पर चिपकी धूल आदि को साबुन के विलयन से निम्न की उपस्थिति में धोया (wash off) जा सकता है।

- यदि कोलॉइडी विलयन जल में (मिश्रण) बनाया जाता है तो गंदगी, तेलीय पदार्थों के सरल अधिशोषण द्वारा हटायी जाती है और इस प्रकार कपड़ों को धोया जाता है।
- यह जल और ग्रीस (स्केहक) के मध्य अन्तः पृष्ठीय तनाव को कम करता है और यह जल में ग्रीस का पायसीकरण करता है। यांत्रिक क्रिया जैसे रगड़ना (rubbing) द्वारा केवल पदार्थों के साथ धूल कणों को भी अलग कर देते हैं।

- (11) **फोटोग्राफी में (In Photography) :**

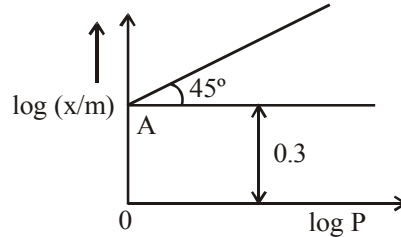
फोटोग्राफी प्रक्रमों में कई प्रकार के कोलॉइडी तंत्रों का उपयोग किया जाता है फोटोग्राफी प्लेट के निर्माण में जिलेटिन में सिल्वर ब्रोमाइड को पतली काँच की प्लेटों पर लेपित (coated) किया जाता है। निर्माण और स्थिरीकरण में कई प्रकार के कोलॉइडी पदार्थों का उपयोग होता है। भिन्न-भिन्न प्रकार की कलर प्रिंटिंग में, जिलेटिन और अन्य कोलॉइडी मिश्रणों का उपयोग किया जाता है।

- (12) **आकाश का नीला रंग :**

कोलाडी कण केवल नीले प्रकाश का प्रकीर्णन करते हैं और शेष प्रकाश को अवशोषित कर लेते हैं। आकाश में कई सारे धूल और जल के कण उपस्थित होते हैं ये नीले प्रकाश को प्रकीर्णन करते हैं, इस कारण आकाश नीला दिखाई देता है यदि किसी प्रकार का कोई भी प्रकीर्णन नहीं होता तो आकाश पूर्ण रूप से काला दिखाई देता।

EXERCISE # S-1

1.  $\log \left( \frac{x}{m} \right)$  vs  $\log P$  के मध्य वक्र धातु सतह पर  $\text{NH}_3$  गैस के अधिशोषण को बताता है। 2 atm दाब पर 50 gm धातु सतह द्वारा अधिशोषित  $\text{NH}_3$  गैस के भार की गणना कीजिए



SC0001

2. जब एक वक्र को  $\log x/m$  तथा  $\log P$  (जहाँ P atm में है) के मध्य आरेखित किया जाता है, तब यह  $45^\circ$  के कोण के साथ एक सिधी रेखा होती है तथा यह y-अक्ष को 0.3010 पर प्रतिच्छेद करती है, यदि 0.3 atm के दाब पर अधिशोषक द्वारा प्रति ग्राम अधिशोषित गैस की मात्रा क्या होगी। ( $\log 2 = 0.3010$ )

SC0002

3. 500 K पर 8.21 L के एक पात्र में  $\text{O}_2$  गैस का अधिशोषण सतह पर भौतिक अधिशोषण होता है जिससे इसका आंशिक दाब 6 atm से घटकर 'P' atm हो जाता है यदि अधिशोषण सतह पर स्थानों की कुल संख्या  $2 \times 10^{23}$  है तथा प्रत्येक स्थान तीन  $\text{O}_2$  अणुओं को प्रभावी रूप से स्थान उपलब्ध कराता है तो P(atm) ज्ञात कीजिए।

$[N_A = 6 \times 10^{23}]$

SC0003

4. 1.25 mg गम अरेबिका (Gum Arabica) (स्वर्ण संख्या = 0.25) को 50 ml मानक गोल्ड सॉल में मिलाया गया। बिना स्कन्दन हुए इस गोल्ड सॉल में 10% NaCl विलयन का कितना अधिकतम आयतन (ml में) मिलाया जा सकता है

SC0004

5. हीमोग्लोबिन की स्वर्ण संख्या 0.3 है। 100 ml गोल्ड सॉल के लिए हीमोग्लोबिन के भार (mg में) की गणना कीजिये, जिससे कि गोल्ड सॉल 10 ml, 10% NaCl विलयन द्वारा स्कन्दित नहीं हो

SC0005

6.  $1.2 \times 10^{-3}$  M की सान्द्रता पर एक साबुन ( $\text{C}_{17}\text{H}_{35}\text{COONa}$ ) का विलयन कोलाइडल सॉल बनाता है।  $1 \text{ mm}^3$  में उपस्थित कोलाइडी कणों की औसत संख्या  $2.4 \times 10^{13}$  है। एक कोलाइडी कण (मिसेल) में स्टिरेट आयनों की औसत संख्या क्या होती है। दिया है : आवोगाद्रो संख्या =  $6 \times 10^{23}$

SC0006

7. निम्न में से कितने प्रक्रम, स्कंदन प्रक्रम के कारण प्रेक्षित होते हैं

- (A) नदी तथा समुद्र के मिलन स्थल पर डेल्टा का निर्माण
- (B) आकाश का नीला रंग
- (C) चिमनी में धुँएँ से कोयला राख का अवक्षेपण
- (D) द्रवविरोधी विलयन का अनुक्रमणीय क्षय
- (E) ब्राउनियन गति
- (F) डिटर्जेंट की प्रक्षालन क्रिया
- (G) कृत्रिम वर्षा
- (H) जल को स्वच्छ करने में एलम का प्रयोग

SC0007

8. ऐसे सॉल की संख्या बताइये जो ऋणात्मक आवेशित हैं
- |   |                             |
|---|-----------------------------|
| $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ सॉल | $\text{Sb}_2\text{S}_3$ सॉल |
| Ag सॉल  | Cu सॉल                      |
| रक्त  | क्षारीय रंजक                |
| मिट्टी का सॉल   | स्टार्च का सॉल              |
| सोडियम स्टियरेट का सॉल                                | सोडियम लॉरिल सल्फेट का सॉल  |
| चारकोल का सॉल   |                             |

SC0008

9. 200 ml गोल्ड सॉल के स्कंदन के लिए 585 ml 1% w/w NaCl विलयन जिसका घनत्व 1.2 gm/ml है, की आवश्यकता होती है तो NaCl के स्कंदन का मान क्या होगा ?

[उत्तर milli-moles /litre में लिखिये]

SC0009

10. स्टार्च के अणु सूत्र को  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$  के रूप में प्रदर्शित किया जा सकता है। यदि ऐसे एक स्टार्च अणु की स्वर्ण संख्या 6.48 है तथा उपरोक्त स्टार्च के 0.01 मिलीमोल का 1 ml, 10% सोडियम क्लोराइड विलयन द्वारा स्कन्दन रोकने के लिए इसमें 10 ml गोल्ड सॉल मिलाये जाने की आवश्यकता होती है तो 'n' के मान की गणना कीजिये।

SC0010

## EXERCISE # S-2

1. एक पात्र में ठोस सतह पर  $O_2$  गैस अणु अधिशोषित हुये जिससे इसका आंशिक दाब 1 atm से घटकर 0.5 atm हो गया।

दिया है :  $N_A = 6 \times 10^{23}$

पात्र का आयतन = 2.24 L

ताप = 273 K

ठोस सतह का कुल क्षेत्रफल =  $10^2 \text{ cm}^2$

प्रति इकाई क्षेत्रफल सक्रिय स्थानों की संख्या =  $10^{24} \text{ m}^{-2}$

प्रति सक्रिय स्थान पर अधिशोषित  $O_2$  अणुओं की संख्या ज्ञात कीजिए।

SC0011

2. बैन्जीन में 0.03 M अम्ल विलयन को जल की सतह पर गिराया गया। बैन्जीन वाष्पीकृत हो जाती है तथा अम्ल ठोस प्रकार की एक एकल अणुक परत का निर्माण करता है अम्ल की एकल अणुक परत से जल की सतह के  $54000 \text{ cm}^2$  क्षेत्रफल को घेरने के लिए उपरोक्त विलयन के कितने आयतन की आवश्यकता (ml में) होती है, (अम्ल के एक अणु द्वारा घेरा गया क्षेत्रफल  $0.3 \text{ nm}^2$  है।) ( $N_A = 6 \times 10^{23}$ )

SC0012

3. एक कोलाइडी कण का व्यास  $5000 \text{ \AA}$  है। यदि निर्मित पदार्थ अर्थात् परिक्षेपित प्रावस्था का घनत्व  $4 \text{ gm/cc}$ , है तो कोलाइडी कण के प्रति इकाई द्रव्यमान के पृष्ठीय क्षेत्रफल का मान ( $\text{m}^2/\text{gm}$  में) ज्ञात कीजिए।

SC0013

4. एक पात्र में बेंजीन का ईथर में, 2M विलयन का 1 लीटर उपस्थित है। विलयन में चारकोल के एक 3 kg टुकड़े को डुबाया गया है। बेन्जीन के अणु चारकोल की सतह पर अधिशोषित होते हैं तथा एक परत बनाते हैं। परिणामी विलयन की मोलरता घटकर 1M हो जाती है। यदि चारकोल पर अधिशोषण के उपलब्ध पृष्ठीय क्षेत्रफल  $12\sqrt{3} \text{ cm}^2/\text{kgm}$  हो तो एक बेंजीन अणु में दो निकटतम कार्बन परमाणुओं के मध्य दूरी ( $\text{\AA}$  में) ज्ञात कीजिए।

(मानें कि बेंजीन की आकृति पूर्णतः षट्कोणीय है।)

[प्रयोग करें :  $N_A = 6 \times 10^{23}$ ]

अपने उत्तर को पहले 100 से गुणा कीजिए तथा अपने उत्तर के अंकों को (दशमलव स्थान को छोड़कर) तब तक योग कीजिए जब तक आपको इकाई अंक प्राप्त न हो जाए।

SC0014

5.  $273^\circ\text{C}$  तथा 2 atm पर 5 ग्राम पेल्लेडियम की सतह पर  $112 \text{ cm}^3$  हाइड्रोजन, एक समान रूप से अधिशोषित होती है। यदि हाइड्रोजन अणु का प्रभावी पृष्ठ क्षेत्रफल  $0.4 \text{ nm}^2$  है, तो पेल्लेडियम का विशिष्ट पृष्ठ क्षेत्रफल क्या होगा। :

SC0015

6. अधिशोषक सतह से गैस का विशोषण (desorption) आरहीनियस समीकरण का अनुसरण करता है। वह औसत समय जब तक एक  $N_2$ , 400K पर Pt सतह पर अधिशोषित रह सकता है, क्या है ?

[दिया गया है पूर्व चरघातांकी गुणांक,  $A = 1.25 \times 10^8 \text{ s}^{-1}$  ;

विशोषण की सक्रियण ऊर्जा =  $16 \text{ Kcal}$ ,  $e^{-20} = 5 \times 10^{-8}$ ]

SC0016



7.  $\text{AgNO}_3$  विलयन में KI को मिलाकर बनाये गए एक कोलाइड का शुद्धीकरण अपोहन (dialysis) द्वारा किया गया। उपरोक्त कोलाइड के 1 l को पूर्ण स्कन्दित करने के लिए आवश्यक एक वैद्युत अपघट्य 'AB' (GMM = 60) का न्यूनतम द्रव्यमान (ग्राम में) क्या होगा दिया है:

सक्रिय आयन जिनमें ऊर्णन होता है	ऊर्णन मान (mmole/l)
$\text{A}^+$	50
$\text{B}^-$	100

SC0017

8. 70K पर, आयरन सतह पर  $\text{N}_2$  गैस का अधिशोषण फ्रेडलिच अधिशोषण का अनुसरण करता है, प्रायोगिक आंकड़े हैं

P(bar)	4	25	64
$\frac{x}{m}$	0.2	0.5	0.8

जहाँ  $\frac{x}{m}$  P bar दाब पर प्रति ग्राम आयरन अधिशोषित  $\text{N}_2$  गैस का द्रव्यमान (gm में) है तो 36 bar तथा 70 K पर प्रतिग्राम

आयरन अधिशोषित N गैस के मोल है।

SC0018

9. 19 gm/ml घनत्व की धातु के  $1.9 \times 10^{-4}$  ग्राम को एक लीटर जल में परिक्षेपित कर एक सॉल बनाया गया है। जिसमें गोलीय धातु कणों की त्रिज्या 10 nm है। प्रति  $\text{cm}^3$  सॉल है। :

SC0019

SC0020

## EXERCISE # O-I

Select the correct alternative. (Only one is correct)

1. निम्न कौनसी गैस ठोस पर अधिक मात्रा में अधिशोषित होगी।  
 (A) वह गैस जो अध्रुवीय अणु रखती है (B) वह गैस जो उच्चतम क्रान्तिक ताप ( $T_c$ ) रखती है  
 (C) वह गैस जो न्यूनतम क्रान्तिक ताप रखती है (D) वह गैस जो उच्चतम क्रान्तिक दाब रखती है  
SC0021
2. भौतिक अधिशोषण की उष्मा की परास है  
 (A) 1 से 10 kJ mol<sup>-1</sup> (B) 20 से 40 kJ mol<sup>-1</sup> (C) 40 से 200 kJ mol<sup>-1</sup> (D) 200 से 400 kJ mol<sup>-1</sup>  
SC0022
3. कौनसा अधिशोषण बहुपरतीय होता है।  
 (A) भौतिक अधिशोषण (B) रासायनिक अधिशोषण (C) दोनों (D) इनमें से कोई नहीं  
SC0023
4. उत्क्रमणीय अधिशोषण है।  
 (A) रासायनिक अधिशोषण (B) भौतिक अधिशोषण (C) दोनों (D) कोई नहीं  
SC0024
5. पायस (emulsion) कोलाइडी तन्त्र है।  
 (A) दो ठोसों का (B) दो द्रवों का  
 (C) एक गैस व एक ठोस का (D) एक गैस व एक द्रव का  
SC0025
6. रासायनिक अधिशोषण में बंधित बलों की प्रकृति है।  
 (A) शुद्धतम भौतिक जैसा कि वाण्डर वॉल बल (B) शुद्धतम रासायनिक  
 (C) हमेशा रासायनिक व भौतिक दोनों साथ-साथ (D) इनमें से कोई नहीं  
SC0026
7. कोलाइडल कणों के साथ सम्बन्धित टिण्डल प्रभाव का कारण है  
 (A) विद्युत आवेश की उपस्थिति (B) प्रकाश का प्रकीर्णन  
 (C) प्रकाश का अवशोषण (D) प्रकाश का परावर्तन  
SC0027
8. निम्न में रासायनिक अधिशोषण के अनुरूप नहीं है-  
 (A) इसकी अधिशोषण की उष्मा उच्च होती है (B) यह उच्च ताप पर होता है  
 (C) यह उत्क्रमणीय है (D) यह एक आण्विक परत बनाता है  
SC0028
9. कोलाइडी अवस्था में कणों के आकार की परास है-  
 (A) 1 nm से कम (B) 1 nm के 100 nm के मध्य  
 (C) 100 nm से अधिक (D) उपरोक्त में से कोई नहीं  
SC0029
10. कोलाइड का निम्न द्वारा शुद्धिकरण हो सकता है।  
 (A) संघनन (B) पेप्टीकरण (C) स्कन्दन (D) अपोहन  
SC0030
11. दूध उदाहरण है।  
 (A) पायस का (B) निलम्बन का (C) झाग का (D) सॉल का  
SC0031

12. सॉल में कोलॉइडी कण स्कन्दित हो सकते हैं।  
 (A) गर्म करके (B) विद्युत अपघट्य मिलाकर  
 (C) विपरीत आवेशित सॉल मिलाकर (D) उपरोक्त में से कोई भी विधि **SC0032**
13. इमल्सीकारक एक अभिकर्मक है जो-  
 (A) परिक्षेपण को बढ़ाता है (B) इमल्सन को संमागीकृत (homogenizes) करता है  
 (C) इमल्सन को स्थायीकृत करता है (D) इमल्सन के ऊर्णन में सहायता करता है **SC0033**
14. कोहरा एक कोलॉइडी तन्त्र है।  
 (A) द्रव में गैस का (B) गैस में द्रव का (C) गैस में गैस का (D) ठोस में द्रव का **SC0034**
15. नीचे कुछ विद्युत अपघट्य दिये गए हैं, प्रदर्शित कीजिए निम्न में से कौन तेजी से व न्यूनतम सान्द्रता में स्वर्ण सॉल का स्कन्दन करेगा।  
 (A) NaCl (B) MgSO<sub>4</sub> (C) Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (D) K<sub>4</sub>[Fe(CN)<sub>6</sub>] **SC0035**
16. जब एक द्रवविरोधी कोलॉइडी विलयन को प्रेक्षित (observed) किया जाता है। तब हम देख सकते हैं।  
 (A) कोलॉइडी कण द्वारा प्रकीर्णित प्रकाश (B) कोलॉइडी कण का आकार  
 (C) कोलॉइडी कण की आकृति (D) कोलॉइडी कण का आपेक्षिक आकार **SC0036**
17. कोलॉइडी कण पर विद्युत आवेश को प्रदर्शित किया जाता है।  
 (A) ब्राउनियन गति द्वारा (B) विद्युत कण संचलन द्वारा  
 (C) अल्ट्रा सूक्ष्मदर्शी द्वारा (D) आप्त्विक चलनी (sieves) द्वारा **SC0037**
18. सॉल का स्कन्दन करने के लिए आवश्यक विद्युत अपघट्य की न्यूनतम मात्रा को कहा जाता है  
 (A) ऊर्णन मान (B) स्वर्ण संख्या (C) रक्षण मान (D) इनमें से कोई नहीं **SC0038**
19. धुओं अवक्षेपक निम्न नियम पर कार्य करता है।  
 (A) वितरण नियम (B) कोलॉइडों पर आवेश का उदासीनीकरण  
 (C) लॉ-शॉतेलिए नियम (D) विद्युत अपघट्य का योग **SC0039**
20. द्रव स्नेही सॉल के सन्दर्भ में निम्न में से कौनसा कथन सत्य नहीं है?  
 (A) परिक्षिप्त प्रावस्था व परिक्षेपण माध्यम के मध्य अन्तः क्रिया होती है  
 (B) यह अत्यधिक स्थाई होते हैं व आसानी से स्कन्दित नहीं होते हैं  
 (C) इन्हें स्थायीकारक (stabilizer) की आवश्यकता होती है  
 (D) कण जलयोजित (hydrated) होते हैं **SC0040**
21. As<sub>2</sub>S<sub>3</sub> सॉल है  
 (A) धनात्मक कोलॉइड (B) ऋणात्मक कोलॉइड (C) उदासीन कोलॉइड (D) इनमें से कोई नहीं **SC0041**
22. क्रान्तिक मिसेल सान्द्रता (CMC) पर पृष्ठ-सक्रियक अणु -  
 (A) विघटित होते हैं (B) वियोजित होते हैं (C) संगुणित होते हैं (D) पूर्ण घुलनशील होते हैं **SC0042**
23. छोटी द्रव बूंदें अन्य द्रव में परिक्षिप्त होती हैं, इसे कहा जाता है।  
 (A) निलम्बन (B) पायस (C) जैल (D) वास्तविक विलयन **SC0043**

24. प्रक्रम जो उत्पाद द्वारा उत्प्रेरित होता है, कहलाता है,  
 (A) अम्ल-क्षार उत्प्रेरण (B) स्व उत्प्रेरण (C) ऋणात्मक उत्प्रेरण (D) समांगी उत्प्रेरण **SC0044**
25. टिण्डल प्रभाव देखा जाता है।  
 (A) विलयन में (B) विलायक में (C) अवक्षेप में (D) कोलॉइडी सॉल में **SC0045**
26. एक द्रव, प्रकाश के पुंज को प्रकीर्णित कर देता है लेकिन जब फिल्टर पेपर में से गुजरता है तो कुछ शेष नहीं रहता। द्रव की निम्न रूप में व्याख्या हो सकती है।  
 (A) निलम्बन (B) तेल (C) कोलॉइडी सॉल (D) वास्तविक विलयन **SC0046**
27. दिये गए कोलॉइड को स्कन्दित करने के लिए आयन की क्षमता निर्भर करती है।  
 (A) इसके आवेश पर (B) आवेश के चिन्ह पर  
 (C) आवेश के परिमाण पर (D) परिमाण व आवेश के चिन्ह दोनों पर **SC0047**
28. आरसिनियस सल्फाइड सॉल ऋणावेशित होता है। इस सॉल की अधिकतम अवक्षेपण क्षमता निम्न द्वारा दी जाती है-  
 (A)  $K_2SO_4$  (B)  $CaCl_2$  (C)  $Na_3PO_4$  (D)  $AlCl_3$  **SC0048**
29. निम्न में से संगुणित कोलॉइड का उदाहरण है।  
 (A) प्रोटीन + जल (B) साबुन + जल (C) रबर + बन्जीन (D)  $As_2O_3 + Fe(OH)_3$  **SC0049**
30. यद्यपि कमरे के ताप पर नाइट्रोजन, सतह पर अधिशोषित नहीं होती है यह 83K पर सतह पर अधिशोषित होती है। निम्न में से कौनसा कथन सही है -  
 (A) 83K पर, एकल आण्विक सतह का निर्माण होता है।  
 (B) 83K पर, बहुआण्विक सतह का निर्माण होता है।  
 (C) 83K पर, नाइट्रोजन अणु रासायनिक बंधों द्वारा बंधो होते हैं।  
 (D) 83K पर, नाइट्रोजन परमाणुओं के रूप में अधिशोषित होती है। **SC0050**
31. द्रवविरोधी साल की स्वर्ण संख्या एक ऐसा गुण है कि-  
 (A) इसका मान अधिक तो पेप्टिकृत क्षमता भी अधिक होगी।  
 (B) इसका मान कम तो पेप्टिकृत क्षमता अधिक होगी।  
 (C) इसका मान कम तो रक्षी क्षमता अधिक होगी।  
 (D) इसका मान अधिक तो रक्षी क्षमता भी अधिक होगी। **SC0051**
32. निम्न में से कौन से कथन, भौतिक अधिशोषण के सन्दर्भ में गलत हैं -  
 (A) उच्च दाब पर इससे अधिशोषण सतह पर बहुआण्विक सतह का निर्माण होता है।  
 (B) अधिशोषण की एन्थैल्पी ( $\Delta H_{adsorption}$ ) कम तथा धनात्मक है।  
 (C) यह वान्डर वाल्स बलों के कारण होता है।  
 (D) आसानी से द्रवणीय गैसों शीघ्रता से अधिशोषित होती है। **SC0052**
33. एक कोलाइडी कण का आयतन  $V_C$ , एक सत्य विलयन में एक विलेय का आयतन  $V_t$  तथा निलम्बित कण के आयतन  $V_s$  को व्यवस्थित किया जा सकता है।  
 (A)  $V_C = V_t = V_s$  (B)  $V_s < V_C < V_t$   
 (C)  $V_s > V_C > V_t$  (D)  $V_C > V_s > V_t$  **SC0053**

34. निम्न में से कौनसा गुण, भौतिक अधिशोषण का नहीं है -  
 (A) अत्यधिक विशिष्ट प्रकृति (B) उत्क्रमणीय  
 (C) बहुसतही (D) उष्माक्षेपी **SC0054**
35.  $As_2S_3$  साल के स्कंदन के लिए निम्न विद्युत अपघट्यों को, स्कंदन क्षमता के बढ़ते क्रम में व्यवस्थित कीजिए -  
 (I)  $Na_3PO_4$  (II)  $MgCl_2$  (III)  $AlCl_3$   
 (A) I > II > III (B) I < II < III (C) I = III < II (D) III < I < II **SC0055**
36. गैस जो सक्रियत चारकोल की सतह पर सर्वाधिक तेजी से अधिशोषित होती है।  
 (A)  $N_2$  (B)  $H_2$  (C)  $O_2$  (D)  $SO_2$  **SC0056**
37. विद्युत क्षेत्र के प्रभाव में कोलाइडी कणों का अभिगमन कहलाता है-  
 (A) विद्युत परासरण (B) विद्युतकण संचलन (C) विद्युत अपोहन (D) इसमें से कोई नहीं **SC0057**
38. कौनसी अभिक्रिया विष्मांगी उत्प्रेरण को दर्शाती है  
 (A)  $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$   
 (B)  $2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$   
 (C)  $CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(aq.) + CH_3OH(aq.)$   
 (D) उपरोक्त सभी **SC0058**
39. वर्धक तथा विष रसायनिक अभिक्रिया में प्रयुक्त होने वाले वे पदार्थ है जो कि  
 (A) उत्प्रेरक की गतिविधि क्रमशः बढ़ाते है तथा घटाते है  
 (B) उत्प्रेरक की गतिविधि क्रमशः घटाते व बढ़ाते है  
 (C) उत्प्रेरक पर कोई प्रभाव नहीं डालते है  
 (D) जब जरूरत हो उत्प्रेरक के स्थान पर उपयोग किया जा सकता है **SC0059**
40. पेप्टीकरण प्रक्रम को परिभाषित किया जाता है  
 (A) दो आयनिक विलयनों को मिलाकर अवक्षेप बनाया जाता है  
 (B) कोलाइडी सॉल का अवक्षेप मे रूपान्तरण  
 (C) अवक्षेप का कोलाइडी सॉल में रूपान्तरण  
 (D) विलयन से अवक्षेप को समृद्ध करना **SC0060**

## EXERCISE # O-II

(More than one may be correct)

- निम्न में से कौनसा कथन सत्य है/हैं?  
 (A) हार्डी शुल्ज नियम स्कन्दन से सम्बन्धित है  
 (B) कोलॉइडों द्वारा ब्राउनियन गति व टिण्डल प्रभाव दर्शाये जाते हैं  
 (C) जब द्रव में द्रव परिक्षिप्त रहता है, तो इसे जैल कहते हैं  
 (D) स्वर्ण संख्या द्रवस्नेही कोलॉइड की रक्षी क्षमता का माप है SC0061
- निम्न में से कौनसा कथन सत्य है/हैं?  
 (A) भौतिक अधिशोषण बहुपरतीय अदिशात्मक व अविशिष्ट होता है  
 (B) रासायनिक अधिशोषण सामान्यतः एक परतीय व विशिष्ट होता है  
 (C) भौतिक अधिशोषण परमाणुओं की मुक्त संयोजकता के कारण होता है  
 (D) रासायनिक अधिशोषण, भौतिक अधिशोषण से प्रबल होता है SC0062
- निम्न में से कौनसा कथन सत्य है/हैं?  
 (A) एक विलयन KI विलयन में  $\text{AgNO}_3$  विलयन के आधिक्य के योग द्वारा बनाया जाता है। कोलॉइडी कणों पर उत्पन्न आवेश धनात्मक होता है  
 (B) भौतिक अधिशोषण पर दाब का प्रभाव उच्च होता है यदि तापमान कम हों  
 (C) स्वर्ण संख्या स्वर्ण परत पूर्ण होने की मात्रा का सूचकांक है  
 (D) कोई नहीं SC0063
- कोलॉइडी विलयन शुद्धिकृत हो सकता है।  
 (A) अपोहन द्वारा (B) विद्युत अपोहन द्वारा  
 (C) विद्युत कण संचलन द्वारा (D) अतिसूक्ष्म फिल्टरन द्वारा SC0064
- निम्न में से द्रव स्नेही नहीं है।  
 (A) जिलेटिन सॉल (B) सिल्वर सॉल (C) सल्फर सॉल (D)  $\text{As}_2\text{S}_3$  सॉल SC0065
- कोलॉइडी स्वर्ण निम्न द्वारा निर्मित हो सकता है।  
 (A) ब्रेडिंग आर्क विधि द्वारा (B)  $\text{AuCl}_3$  का अपचयन द्वारा  
 (C) जल अपघटन द्वारा (D) पेप्टीकरण द्वारा SC0066
- KI विलयन में  $\text{AgNO}_3$  का विलयन मिलाने पर, जिससे कोलाइडीय सॉल प्राप्त किया जा सकता है, हैं -  
 (A) 100 mL, 0.1 M  $\text{AgNO}_3$  + 100, 0.1 M KI  
 (B) 100 mL, 0.1 M  $\text{AgNO}_3$  + 100, 0.2 M KI  
 (C) 100 mL, 0.2 M  $\text{AgNO}_3$  + 100, 0.1 M KI  
 (D) 100 mL, 0.15 M  $\text{AgNO}_3$  + 100, 0.25 M KI SC0067

## Question No. 8 to 10(3 questions)

जब कभी गैसों के एक मिश्रण को समान परिस्थितियों में निश्चित अधिशोषक के सम्पर्क में रखा जाता है, तो अधिक प्रबल अधिशोष्य अधिक मात्रा में अधिशोषित होता है अर्थात्  $\text{H}_2\text{O}$ ,  $\text{N}_2$  व  $\text{O}_2$  की तुलना में सिलिका पर अधिक मात्रा में अधिशोषित होता है। यह प्रदर्शित करता है कि कुछ अधिशोष्य पूर्णतः अधिशोषित होते हैं। यह भी देखा गया है कि पूर्णतः अधिशोषणीय अधिशोषक, अधिशोषक की सतह से दुर्बल अधिशोषित पदार्थ को मुक्त कर सकता है।

- निम्न कौनसी गैस अधिकतम मात्रा में अधिशोषित होती है।  
 (A) He (B) Ne (C) Ar (D) Xe SC0068

9. निम्न कौनसी गैस शेष सभी गैसों को प्रतिस्थापित कर सकती है।  
 (A) O<sub>2</sub> (B) N<sub>2</sub> (C) CO (D) H<sub>2</sub> SC0069
10. जब ताप बढ़ता है।  
 (A) अधिशोषण की मात्रा बढ़ती है। (B) अधिशोषण की मात्रा घटती है।  
 (C) अधिशोषण पर कोई प्रभाव नहीं पड़ता। (D) अधिशोषण की मात्रा पहले घटती है, व फिर बढ़ती है।

SC0070

**Question No. 11 to 12 (2 questions)**

कोलॉइडों के वृहद् आण्विक प्रकार में, परिक्षिप्त कण स्वयं में वृहद् अणु (बहुलक) होते हैं। चूंकि यह अणु कोलॉइडी कणों की तुलना में विमा रखते हैं, अतः इनका परिक्षेपण वृहद् आण्विक कोलॉइड कहलाता है। अधिकांश द्रव स्नेही सॉल इस वर्ग से सम्बन्धित होते हैं। निश्चित कोलॉइड जो निम्न सान्द्रताओं पर सामान्य प्रबल विद्युतअपघट्य के समान व्यवहार करते हैं, लेकिन संगुणित कणों के निर्माण के कारण उच्च सान्द्रता पर कोलॉइडी गुण दर्शाते हैं इन्हें मिसेल या संगुणित कोलॉइड कहते हैं सतह सक्रिय अभिकर्मक जैसे साबुन व संश्लेषित अपमार्जक इस वर्ग से सम्बन्धित होते हैं।

CMC कुल पृष्ठ सक्रियक सान्द्रता के साथ बढ़ता है। CMC से अधिक सान्द्रता पर, यह सामान्तर परतों का निर्माण करते हैं जिसे लैमिलर मिसेल कहा जाता है जो जैविक कला से सम्बन्धित होता है, दो अणु मोटी परत में, पृथक् अणु परतों के लम्बवृत्त होता है ताकि जल स्नेही समूह जलीय विलयन में बाहर की ओर व अध्रुवीय माध्यम में अन्दर की ओर हो।

सान्द्र विलयन में, मिसेल षट्कोणीय क्रम में व्यवस्थित लम्बे सिलेण्डर का रूप ग्रहण करता है व इसे लाइटोट्रोपिक मिसोमारफ कहा जाता है।

जलीय विलयन (ध्रुवीय माध्यम) में, ध्रुवीय समूह बाहर की ओर निर्देशित होते हैं व जल विरोधी हाइड्रोकार्बन श्रृंखला केन्द्र की ओर निर्देशित होती हैं।

- ◆ यह आयनों का निर्माण करने में समर्थ होते हैं।
- ◆ साबुन व अपमार्जक के अणु में द्रव स्नेही व द्रव विरोधी भाग होते हैं जो संगुणित होकर मिसेल बनाते हैं।
- ◆ मिसेल में 100 या अधिक अणु होते हैं।

11. सही कथन(कथनों) का चयन कीजिए :
- (A) सतह सक्रिय कारक जैसे साबुन व संश्लेषित अपमार्जक मिसेल हैं  
 (B) साबुन इमल्सीकारक हैं  
 (C) स्टीरेट आयन (C<sub>17</sub>H<sub>35</sub>COO<sup>-</sup>) के C<sub>17</sub>H<sub>35</sub> (हाइड्रोकार्बन भाग) व -COO<sup>-</sup> (कार्बोक्सिलेट भाग) दोनों जलविरोधी होते हैं  
 (D) सभी असत्य कथन है SC0071

12. साबुन की प्रक्षालन क्रिया (cleansing action) होती है क्योंकि-
- (A) ऑयल व ग्रीस साबुन मिसेल के जलविरोधी केन्द्रों में अवशोषित हो सकते हैं व धूल जाते हैं  
 (B) ऑयल व ग्रीस साबुन मिसेल के जलस्नेही केन्द्रों में अवशोषित हो सकते हैं व धूल जाते हैं  
 (C) ऑयल व ग्रीस जलस्नेही व जलविरोधी केन्द्रों दोनों में अवशोषित हो सकते हैं लेकिन धूलते नहीं हैं  
 (D) प्रक्षालन क्रिया मिसेल से सम्बन्धित नहीं है SC0072

## Question No.13 to 15 (3 questions)

द्रव स्नेही कोलॉइडों की रक्षी क्षमता को स्वर्ण संख्या के पदों में दर्शाया जाता है जिसे जिंकमोण्डी ने दिया था। स्वर्ण संख्या रक्षी कोलॉइड की मिलीग्राम में वह मात्रा होती है जो 10 mL लाल स्वर्ण सॉल के स्कन्दन को रोकती है जब सोडियम क्लोराइड के 10 प्रतिशत विलयन को 1 mL इसमें मिलाया जाता है। अतः द्रव स्नेही कोलॉइड की स्वर्ण संख्या कम होने पर, रक्षी क्षमता अधिक होगी-

13. 10% NaCl के एक mL विलयन को 0.025 g स्टॉर्च की उपस्थिति में 10 mL लाल स्वर्ण सॉल में मिलाया जाता है, तो स्कन्दन रूक जाता है। स्टॉर्च की स्वर्ण संख्या है :  
 (A) 0.025 (B) 0.25 (C) 2.5 (D) 25 **SC0073**
14. निम्न कौनसा कथन सही है/हैं  
 (A) स्वर्ण संख्या अधिक होने पर, कोलॉइड की रक्षी क्षमता अधिक होती है  
 (B) स्वर्ण संख्या कम होने पर, रक्षी क्षमता अधिक होती है  
 (C) स्कन्दन मान अधिक होने पर, स्कन्दन क्षमता अधिक होती है  
 (D) स्कन्दन मान कम होने पर स्कन्दन क्षमता अधिक होती है **SC0074**
15. स्वर्ण संख्या दर्शाती है  
 (A) कोलॉइडों की रक्षी प्रकृति को (B) निलम्बन में स्वर्ण की शुद्धता को  
 (C) स्वर्ण के कोलॉइडी विलयन पर आवेश को (D) प्रति लीटर स्वर्ण के g-मोल को **SC0075**

## Question No. 16 &amp; 19 (4 questions)

निम्न प्रश्नों में दो कथन दिये गए हैं, एक को कथन तथा दूसरे को कारण के रूप में अंकित किया गया है। निम्न प्रश्नों के उत्तर देते समय आप निम्न विकल्पों में से किसी एक का चयन कर सकते हैं।

- (A) यदि दोनों कथन और कारण सत्य हैं तथा कारण, कथन का सही स्पष्टीकरण है।  
 (B) यदि दोनों कथन और कारण सत्य हैं परन्तु कारण, कथन का सही स्पष्टीकरण नहीं है।  
 (C) यदि कथन सत्य है परन्तु कारण असत्य है।  
 (D) यदि कथन असत्य है परन्तु कारण सत्य है।
16. **कथन** : जब  $\text{AgNO}_3$  को पोटैशियम आयोडाइड के आधाक्य के साथ उपचारित किया जाता है, कोलॉइड कण एनोड की ओर आकर्षित होते हैं।  
**कारण** : अवक्षेप सम आयनों (आधाक्य) को अधिशोषित करता है व इस प्रकार आवेशित हो जाता है। **SC0076**
17. **कथन** : अधिशोषण के लिए  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  सभी का मान ऋणात्मक होता है।  
**कारण** : अधिशोषण स्वतः उष्माक्षेपी प्रक्रम है जिसमें अधिशोषक व अधिशोष्य के मध्य आर्कषण बलों के कारण यादृच्छिकता घटती है। **SC0077**
18. **कथन** : उच्च क्रान्तिक ताप वाली गैस, निम्न क्रान्तिक ताप वाली गैस से अधिक मात्रा में अवशोषित होती है।  
**कारण** : आसानी से द्रवीकृत होने वाले गैसों कम मात्रा में अधिशोषित होती हैं। **SC0078**
19. **कथन** : मिसेल, पृष्ठ सक्रिय अणु द्वारा क्रान्तिक मिसेल सान्द्रता से अधिक सान्द्रता बनाते हैं (CMC).  
**कारण** : CMC पर एक ऐसे विलेय विलयन का चालकता जिसमें पृष्ठ सक्रियक अणु उपस्थित हो तेजी से घटती है। **SC0079**



20.

## List-I

- (P) इक्षु शर्करा का प्रतिपन  
(Q) स्टार्च का माल्टोज में परिवर्तन  
(R) ग्लूकोज का ईथाइल में परिवर्तन  
(S) दूध का दही में परिवर्तन

## List-II

- (1) डाईटेज  
(2) लेक्टो बेसीलाई एंजाइम  
(3) इन्वर्टेज  
(4) जाईमेज

Code:

	P	Q	R	S
(A)	3	4	1	2
(B)	3	4	2	1
(C)	3	1	4	2
(D)	2	4	1	2

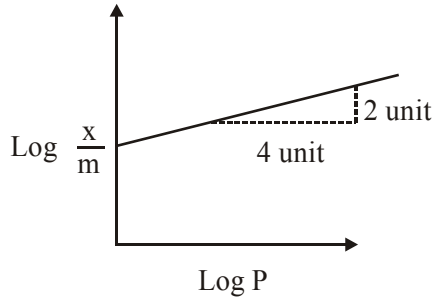
SC0080

## EXERCISE # J-MAIN

1. भौतिक अधिशोषण के सम्बन्ध में दिये निम्न कथनों में कौन असत्य है ? [AIIEE-2009]
- (1) उच्च दाब पर अधिशोषक सतह पर बहुआणवी तह बन जाती है।  
 (2) अधिशोषण की एन्थैल्पी ( $\Delta H_{\text{अधिशोषण}}$ ) निम्न और धनात्मक होती है।  
 (3) यह वॉण्डर वाल्स बलों के कारण होता है।  
 (4) अधिक सरलता से द्रवीभूत होने वाली गैसों सरलता से अधिशोषित होती है। SC0081
2. फ्रैण्डलिक अधिशोषण समतापी के अनुसार निम्न में से क्या सत्य है ? [AIIEE-2012]
- (1)  $\frac{x}{m} \propto p^0$   
 (2)  $\frac{x}{m} \propto p^1$   
 (3)  $\frac{x}{m} \propto p^{1/n}$   
 (4) विभिन्न दाब के अन्यान्य परास के लिये सभी उपरोक्त सही है SC0082
3. आर्सेनिक सल्फाइड सॉल के लिये  $\text{Na}^+$ ,  $\text{Al}^{3+}$  और  $\text{Ba}^{2+}$  आयनों वाले विद्युत अपघट्यों का स्कंदन बल निम्न क्रम में बढ़ता है: [J-Main 2013]
- (1)  $\text{Al}^{3+} < \text{Ba}^{2+} < \text{Na}^+$  (2)  $\text{Na}^+ < \text{Ba}^{2+} < \text{Al}^{3+}$   
 (3)  $\text{Ba}^{2+} < \text{Na}^+ < \text{Al}^{3+}$  (4)  $\text{Al}^{3+} < \text{Na}^+ < \text{Ba}^{2+}$  SC0083
4. एक विशिष्ट अधिशोषण प्रक्रम में निम्न अभिलक्षण होते हैं-
- (i) यह वाण्डर वाल्स बलों के कारण उत्पन्न होता है तथा (ii) यह उत्क्रमणीय होता है। सही कथन का चयन कीजिये जो कि उपरोक्त अधिशोषण प्रक्रम को वर्णित करता है-
- (1) अधिशोषण की एन्थैल्पी  $100 \text{ kJ mol}^{-1}$  से अधिक होती है  
 (2) सक्रियण ऊर्जा कम है  
 (3) अधिशोषण एकल परतीय है  
 (4) ताप में वृद्धि के साथ अधिशोषण बढ़ता है SC0084
5. फ्रॉयण्डलिक अधिशोषण समतापी वक्र में  $\log(x/m)$  तथा  $\log p$  के बीच खींचे गये रेखीय प्लॉट के लिए निम्न में से कौनसा कथन सही है ? ( $k$  तथा  $n$  स्थिरांक हैं) [J-Main 2016]
- (1)  $\log(1/n)$  इन्टरसेप्ट के रूप में आता है।  
 (2)  $k$  तथा  $1/n$  दोनों ही स्लोप पद में आते हैं।  
 (3)  $1/n$  इन्टरसेप्ट के रूप में आता है।  
 (4) मात्र  $1/n$  स्लोप के रूप में आता है। SC0085

6. टिण्डल प्रभाव तभी दिखायी पड़ेगा जब निम्न शर्तें संतुष्ट होती हैं :- [J-Main (offline)2017]
- (a) परिक्षेपित कणों का व्यास, प्रयुक्त प्रकाश के तरंगदैर्घ्य की तुलना में बहुत छोटा हो  
 (b) परिक्षेपित कणों का व्यास, प्रयुक्त प्रकाश के तरंगदैर्घ्य की तुलना में बहुत छोटा नहीं हो  
 (c) परिक्षेपित प्रावस्था तथा परिक्षेपण माध्यम के अपवर्तनांक परिमाण लगभग एक जैसे हो  
 (d) परिक्षेपित प्रावस्था तथा परिक्षेपण माध्यम के अपवर्तनांक परिमाण बहुत भिन्न हो
- (1) (a) तथा (d)                      (2) (b) तथा (d)                      (3) (a) तथा (c)                      (4) (b) तथा (c)
- SC0086**
7. निम्नलिखित में से सही कथन है : [J-Main (online)2017]
- (1) ऐसी आशा की जाती है कि चारकोल, हाइड्रोजन सल्फाइड की तुलना में क्लोरीन का अधिक अधिशोषण करेगा।  
 (2) ब्राउनी गति बड़े कणों की तुलना में छोटे कणों में अधिक दिखाई देती है।  
 (3) हार्डी-शुल्से के नियम के अनुसार किसी आयन का जितना अधिक आमाप हो उसकी स्कंदन शक्ति भी उतनी ही अधिक होगी।  
 (4) धातु सल्फाइडों के सॉल द्रवरागी होते हैं। SC0087
8. किसी पृष्ठ पर एक गैस का अधिशोषण, फ्रॉयन्डलिक अधिशोषण समताप का अनुकरण करता है।  $\log P$  के विरुद्ध  $\log \frac{x}{m}$  का प्लॉट एक सरल रेखा देता है। जिसका स्लोप 0.5 के बराबर पाया गया, तब : [J-Main (online)2017]
- ( $\frac{x}{m}$  प्रति ग्राम अधिशोषक द्वारा अधिशोषित गैस का द्रव्यमान है।)
- (1) अधिशोषण, दाब के वर्ग के समानुपाती है।                      (2) अधिशोषण, दाब पर आश्रित नहीं है।  
 (3) अधिशोषण, दाब के वर्ग मूल के समानुपाती है।                      (4) अधिशोषण, दाब के समानुपाती है। SC0088
9. निम्न में कौनसा एक भौतिक अधिशोषण का गुणधर्म नहीं है? [J- Main (online)2018]
- (1) अधिशोषण एक-परतीय होता है।                      (2) बड़ा पृष्ठ क्षेत्रफल, ज्यादा अधिशोषण  
 (3) निम्नतर ताप, ज्यादा अधिशोषण                      (4) उच्चतर दाब, ज्यादा अधिशोषण SC0089
10. निम्न में गलत कथन है - [Jee-main(online)-2019(Jan.)]
- (1) लेटेक्स, ऐसे रबर कणों का एक कोलाइडी विलयन है जो धनावेशित हैं।  
 (2) टिण्डल प्रभाव का प्रयोग, एक कोलाइडी विलयन तथा एक सत्य विलयन को विभेदित करने में किया जा सकता है  
 (3) एक वायुयान से बादलों पर ऐसी विद्युतीकृत रेत जिस पर बादलों पर उपस्थित आवेश से विपरीत आवेश उपस्थित हो, की बौछार (throwing) कर कृत्रिम वर्षा करायी जा सकती है।  
 (4) द्रवस्नेही साल को एक वैद्युत अपघट्य मिला कर स्कंदित किया जा सकता है SC0090
11. ठोस सॉल किसका एक उदाहरण है? [Jee-main(online)-2019(Jan.)]
- (1) मक्खन                      (2) जेम स्टोन                      (3) पेन्ट                      (4) हेयर क्रीम SC0091

12. गैस का अधिशोषण फ्रेंडलिच अधिशोषण समताप का अनुसरण करता है दिये गये आरेख में  $x$ , दाब  $P$  पर अधिशोष्य (adsorbed) के  $m$  द्रव्यमान पर अधिशोषित गैस का द्रव्यमान है।  $\frac{x}{m}$  किसके समानुपाती है



[Jee-main(online)-2019(Jan.)]

- (1)  $P^{1/4}$                       (2)  $P^2$                       (3)  $P$                       (4)  $P^{1/2}$                       SC0092

13. हीमोग्लोबिन तथा गोल्ड सॉल उदाहरण है :

[Jee-main(online)-2019(Jan.)]

- (1) ऋणात्मक आवेशित सॉल का  
 (2) धनात्मक आवेशित सॉल का  
 (3) क्रमशः ऋणात्मक तथा धनात्मक आवेशित सॉल का  
 (4) क्रमशः धनात्मक तथा ऋणात्मक सॉल का

SC0093

14. कोलाइडों, जैसे पनीर (C), दूध (M) तथा धूआं (S) के विषय में परिक्षिप्त प्रावस्था तथा परिक्षेपण माध्यम का सही मेल क्रमशः होगा :

- (1) C : द्रव में ठोस; M : द्रव में ठोस; S : गैस में ठोस  
 (2) C : द्रव में ठोस ; M : द्रव में द्रव; S : ठोस में गैस  
 (3) C : ठोस में द्रव; M : ठोस में द्रव; S : गैस में ठोस  
 (4) C : ठोस में द्रव; M : द्रव में द्रव; S : गैस में ठोस

[Jee-main(online)-2019(Jan.)]

SC0094

15. पेप्टाइजेशन है :

[Jee-main(online)-2019(April)]

- (1) अवक्षेप को कोलाइडी विलयन में बदलने का प्रक्रम  
 (2) कोलाइडी विलयन को अवक्षेप में बदलने का प्रक्रम  
 (3) विलेय कणों को कोलाइडी विलयन में बदलने का प्रक्रम  
 (4) कोलाइडी अणुओं को विलयन में लाने का प्रक्रम

SC0095

16. कोलोईड के संदर्भ में निम्न में से कौनसा कथन गलत है :

- (1) वे प्रकाश को प्रकीर्णित (scatter) कर सकते हैं [Jee-main(online)-2019(April)]  
 (2) वे छोटे अणुओं की तुलना में बड़े होते हैं तथा उच्च आण्विक द्रव्यमान रखते हैं  
 (3) कोलोइडी कणों के व्यासों की परास एक तथा 1 तथा 1000 nm के मध्य होत होती है  
 (4) कोलोइडी विलयन का परासरण दाब, समान सान्द्रता के वास्तविक विलयन की तुलना में अधिक होता है

SC0096

17. एक गैस का एक पृष्ठ पर भौतिक अधिशोषण होता है और वह दिये गये फ्रायन्डलिक अधिशोष समतापी समीकरण का अनुसरण कराती है

[Jee-main(online)-2019(April)]

$$\frac{x}{m} = kp^{0.5}$$

गैस का अधिशोषण बढ़ेगा यदि :

- (1) p घटायें तथा T घटायें  
 (2) p बढ़ायें तथा T बढ़ायें  
 (3) p बढ़ायें तथा T घटायें  
 (4) p घटायें तथा T बढ़ायें

SC0097

18. एरोसॉल एक ऐसा कोलायड है जिसमें :

[Jee-main(online)-2019(April)]

- (1) ठोस में गैस परिक्षिप्त है।  
 (2) गैस में ठोस परिक्षिप्त है।  
 (3) जल में द्रव परिक्षिप्त है।  
 (4) द्रव में गैस परिक्षिप्त है।

SC0098

19. 1mM पृष्ठ सक्रियक विलयन का 10 mL एक पोलर अवस्तर पर एक मोनोलेयर बनाकर 0.24 cm<sup>2</sup> घेरता है। यदि पोलर हेड को एक घनक रूप में माना जाय तो इसके कोर की लम्बाई क्या होगी?

- (1) 2.0 pm  
 (2) 2.0 nm [Jee-main(online)-2019(April)]  
 (3) 1.0 pm  
 (4) 0.1 nm

SC0099

20. दीर्घ श्रृंखला वाले फैटी एसिड के 0.27 g को 100 cm<sup>3</sup> हेक्सेन में घोला गया। इस विलयन के 10 mL को एक गोलाकार वाच ग्लास में रखे जल की सतह पर बूँद-बूँद करके गिराया गया। हेक्सेन वाष्पीकृत हो गई और एक एकल पर्त बन गई। वाच ग्लास के किनारे से उसके केन्द्र तक की दूरी 10 cm है। उस एकल परत की ऊँचाई क्या होगी?

[फैटी एसिड का घनत्व = 0.9 g cm<sup>-3</sup>, π = 3]

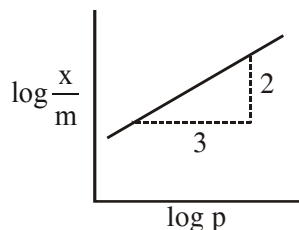
[Jee-main(online)-2019(April)]

- (1) 10<sup>-8</sup> m  
 (2) 10<sup>-6</sup> m  
 (3) 10<sup>-4</sup> m  
 (4) 10<sup>-2</sup> m

SC0100

21. एक गैस का अधिशोषण, फ्रायन्डलिक अधिशोषण समताप का पालन करता है। अधिशोषक के m द्रव्यमान पर अधिशोषित गैस का द्रव्यमान x है।  $\log \frac{x}{m}$  के विरुद्ध  $\log p$  का प्लॉट दिये गये ग्राफ में दर्शाया गया है।  $\frac{x}{m}$  जिसके अनुपातिक हैं, वह है -

[Jee-main(online)-2019(April)]



- (1) p<sup>3/2</sup>  
 (2) p<sup>3</sup>  
 (3) p<sup>2/3</sup>  
 (4) p<sup>2</sup>

SC0101

22. निम्न में से सही विकल्प है :

[Jee-main(online)-2019(April)]

- (1) द्रव विरागी सॉल में कोलाइडी कण वैद्युत कण संचलन द्वारा अवक्षेपित किये जा सकते हैं।  
 (2) कोलाइडी विलयन में यदि विलयन की श्यानता बहुत ज्यादा है तो ब्राउनियन गति तीव्रतर होती है।  
 (3) कोलाइडी औषधियाँ ज्यादा प्रभावशाली हैं क्योंकि उनका पृष्ठीय क्षेत्रफल छोटा होता है।  
 (4) पानी में फिटकिरी मिलाने से वह (पानी) पीने के अयोग्य हो जाता है।

SC0102

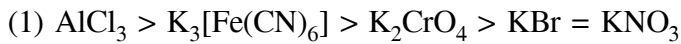
23. आर्सेनिक सल्फाइड विलयन के लिए HCl के उर्जन का मान 30 m mole L<sup>-1</sup> है। यदि आर्सेनिक सल्फाइड के उर्जन के लिए H<sub>2</sub>SO<sub>4</sub> का उपयोग किया जाए तो उपर्युक्त उद्देश्य के लिए 250 mL में आवश्यक H<sub>2</sub>SO<sub>4</sub> की मात्रा (ग्राम में) होगी \_\_\_\_\_.

(H<sub>2</sub>SO<sub>4</sub> की अणु संहति = 98 g/mol)

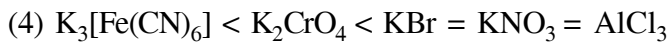
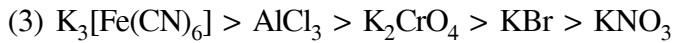
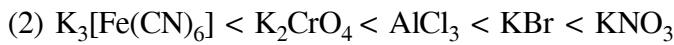
[Jee-main(online)-2020]

SC0103

24. हार्डी-सुल्से संरूपण के अनुसार, फेरिक हाइड्रॉक्साइड सॉल के लिए निम्न का ऊर्णन मान इस में है :



[Jee-main(online)-2020]



SC0104

25. निम्न कथन तथा कारण के लिए सही विकल्प है :

**कथन :** हाइड्रोजनीकरण अभिक्रिया के लिए, उत्प्रेरित क्रियाशीलता समूह 5 से समूह 11 तक बढ़ती है जिसमें समूह 7-9 के तत्वों में सबसे अधिक क्रियाशीलता होती है।

**कारण :** समूह 7-9 के तत्वों पर अभिकारकों का अधिशोषण सर्वाधिक प्रबलता से होता है।

(1) कथन तथा कारण दोनों सही हैं परन्तु कारण कथन की सही व्याख्या नहीं है।

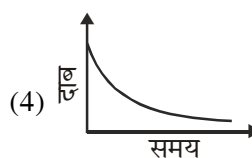
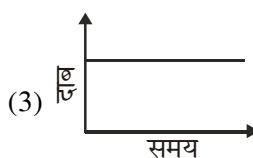
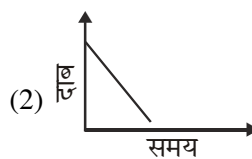
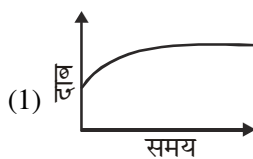
(2) कथन तथा कारण दोनों गलत है।

(3) कथन तथा कारण दोनों सही हैं तथा कारण कथन की सही व्याख्या है।

(4) कथन सही है, परन्तु कारण गलत है।

SC0105

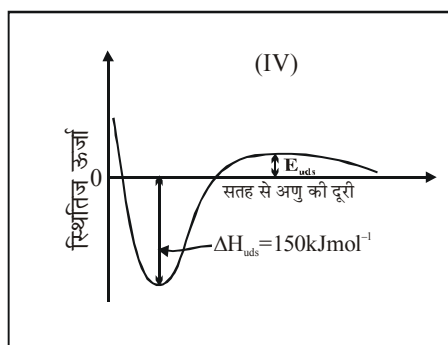
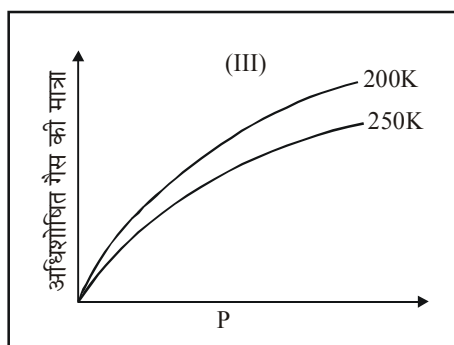
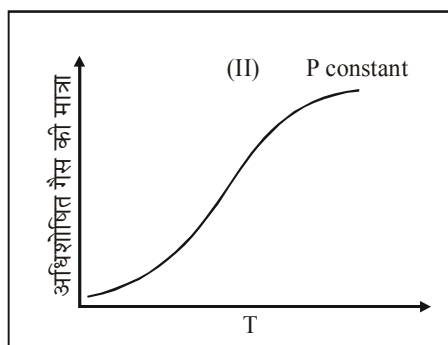
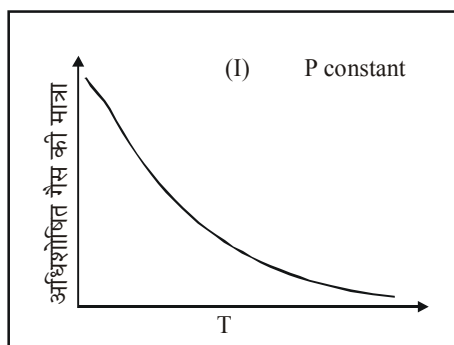
26.  $\text{O}_2$ ,  $\text{H}_2$  तथा  $\text{CO}$  गैसों के एक मिश्रण को एक बन्द पात्र में लिया जाता है जिसमें चारकोल है। आलेख जो, दाब का समय के साथ सही व्यवहार निरूपित करता है, है :



SC0106

## EXERCISE # J-ADVANCED

1. निम्न में से वह कौनसा पृष्ठ सक्रियक (surfactant) है जो व्यापक परिस्थितियों में न्यूनतम मोलर सान्द्रता पर जलीय विलयन में मिसेल बनाता है : [IIT-JEE 2008]
- (A)  $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$  (B)  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$   
 (C)  $\text{CH}_3(\text{CH}_2)_6\text{COO}^-\text{Na}^+$  (D)  $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Br}^-$  SC0110
2. विद्युत अपघट्यो  $\text{Na}_2\text{SO}_4$ ,  $\text{CaCl}_2$ ,  $\text{Al}_2(\text{SO}_4)_3$  व  $\text{NH}_4\text{Cl}$  में से  $\text{Sb}_2\text{S}_3$  सॉल के लिए अधिक उपयुक्त स्कन्दकारी (coagulating agent) है : [IIT-JEE 2009]
- (A)  $\text{Na}_2\text{SO}_4$  (B)  $\text{CaCl}_2$  (C)  $\text{Al}_2(\text{SO}_4)_3$  (D)  $\text{NH}_4\text{Cl}$  SC0111
3. ठोस -पृष्ठ पर होने वाले गैस के अधिशोषण (adsorption) के लिए सत्य कथन है (हैं) - [IIT-JEE 2011]
- (A) अधिशोषण सर्वदा उष्माक्षेपी (exothermic) है  
 (B) भौतिक अधिशोषण (Physisorption) उच्च ताप पर रासायनिक अधिशोषण (chemisorption) में परिवर्तित हो सकता है  
 (C) भौतिक अधिशोषण ताप बढ़ने के साथ बढ़ता है परन्तु रासायनिक अधिशोषण ताप बढ़ने के साथ घटता है।  
 (D) भौतिक अधिशोषण की अपेक्षा रासायनिक अधिशोषण अधिक उष्माक्षेपी है परन्तु यह अधिक सक्रियण ऊर्जा (activation energy) के कारण मन्द गति से होता है। SC0112
4. द्रवविरागी कोलाइडल कण (lyophobic colloidal particle) की स्थिरता (stability) के सही कारण चुनिए।
- (A) इनके पृष्ठ पर आयनों का विलयन से वर्णात्मक (Preferential) अधिशोषण होना। [IIT-JEE 2012]  
 (B) इनके पृष्ठ पर विलायक का विलयन से वर्णात्मक (Preferential) अधिशोषण होना।  
 (C) इनके पृष्ठक कणों के पृष्ठ पर विपरीत आवेशों के बीच आकर्षण होना।  
 (D) इनके चारों ओर स्थिर परत और विसरित परत के बीच विपरीत आवेशों के कारण विभवान्तर होना। SC0113
5. दिए हुए I, II, III और IV रेखाचित्र/उपात्त (data), मंद तापक्रम व दाब (mild temperature and pressure) पर, विभिन्न भौतिक अधिशोषण व रासायनिक अधिशोषण (प्रक्रमों) की सामान्य प्रवृत्ति दिखाते हैं। निम्नलिखित में से I, II, III और IV के संदर्भ में कौन विकल्प सही है/हैं ? [IIT-JEE 2012]



- (A) I भौतिक अधिशोषण है और II रासायनिक अधिशोषण है  
 (B) I भौतिक अधिशोषण है और III रासायनिक अधिशोषण है  
 (C) IV रासायनिक अधिशोषण है और II रासायनिक अधिशोषण है  
 (D) IV रासायनिक अधिशोषण है और III रासायनिक अधिशोषण है

SC0114

6. 25°C तापमान पर एक जलीय विलयन से मेथिलिन ब्लू का सक्रियित चारकोल पर अधिशोषण किया गया। इस प्रक्रम के लिये सही कथन है-

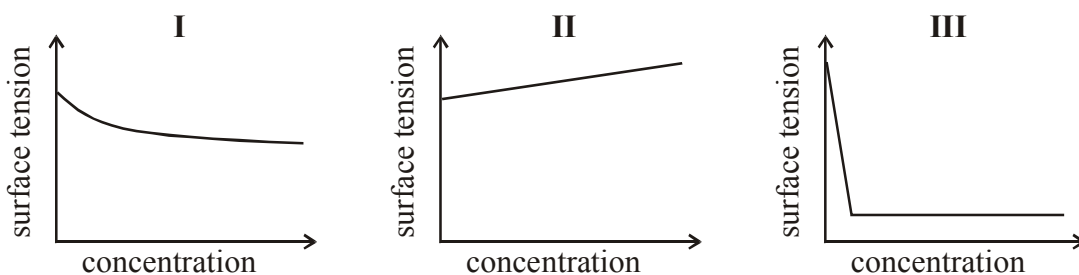
[J-Adv. 2013]

- (A) अधिशोषण को 25°C पर सक्रियण की आवश्यकता होती है  
 (B) अधिशोषण प्रक्रम में एन्थैल्पी घटती है  
 (C) अधिशोषण तापमान बढ़ाने पर बढ़ता है  
 (D) अधिशोषण अनुक्रमणीय है

SC0115

7. नीचे दिये गुणात्मक I, II तथा III सामान्य ताप KCl, CH<sub>3</sub>OH तथा CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>OSO<sub>3</sub><sup>-</sup> Na<sup>+</sup> के तीन भिन्न जलीय विलयनों की मोलर सान्द्रता (concentration) के साथ पृष्ठ तनाव (surface tension) के परिवर्तन को दर्शाती है। -

[J. Adv. 2016]



- |  |   |  |
|--|---|--|
| (A) I : KCl  | II : CH <sub>3</sub> OH   | III : CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup> |
| (B) I : CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup> | II : CH <sub>3</sub> OH   | III : KCl  |
| (C) I : KCl  | II : CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup> | III : CH <sub>3</sub> OH   |
| (D) I : CH <sub>3</sub> OH   | II : KCl  | III : CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> OSO <sub>3</sub> <sup>-</sup> Na <sup>+</sup> |

SC0116

8. पृष्ठ गुणों (surface properties) के बारे में सही कथन है/हैं -

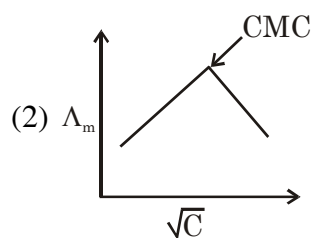
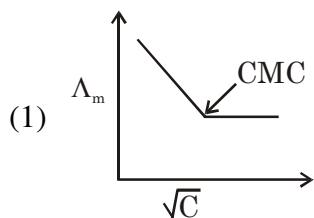
[JEE 2017]

- (A) बादल एक इमल्शन प्रकार का कोलोइड है जिसमें द्रव परिक्षिप्त प्रावस्था (dispersed phase) तथा गैस परिक्षेपण माध्यम (dispersed) है  
 (B) अधिशोषण (Adsorption), निकाय की एन्ट्रॉपी घटने तथा एन्थैल्पी घटने के साथ होता है  
 (C) कोलोइडी कणों की ब्राउनी गति कणों के आकार पर निर्भर नहीं होती परन्तु विलयन की श्यानता पर निर्भर करती है  
 (D) ऐथेन तथा नाइट्रोजन के क्रांतिक तापक्रम क्रमशः 563 K तथा 126 K है। एक दिये गये तापक्रम पर सक्रियित चारकोल की समान मात्रा पर ऐथेन का अधिशोषण नाइट्रोजन की तुलना में अधिक होगा

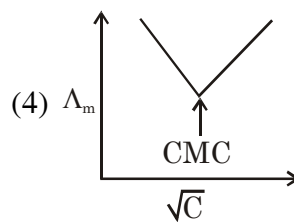
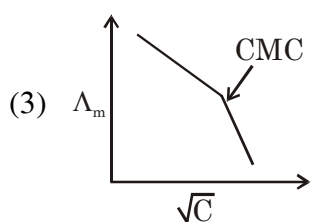
SC0117



9. सोडियम स्टीरेट (sodium stearate) के जलीय विलयन, जो एक प्रबल वैद्युत अपघट्य (electrolyte) जैसा व्यवहार दर्शाता है, की मोलर चालकता ( $\Lambda_m$ ) को विभिन्न सान्द्रताओं ( $c$ ) में मापा गया। निम्न चित्रों में से मिसेल विरचन (micelle formation) दर्शाने वाला सही चित्र कौनसा है? (क्रांतिक मिसेल सान्द्रता (critical micelle concentration, CMC) को चित्रों में तीर द्वारा दर्शाया गया है )



[JEE 2019]



SC0118

**ANSWER-KEY****EXERCISE # S-I**

- |               |               |               |
|---------------|---------------|---------------|
| 1. Ans. (200) | 2. Ans. (0.6) | 3. Ans. (1)   |
| 4. Ans. (5)   | 5. Ans. (3)   | 6. Ans. (30)  |
| 7. Ans. (5)   | 8. Ans. (9)   | 9. Ans. (600) |
| 10. Ans. (4)  |               |               |

**EXERCISE # S-II**

- |                            |  |                         |
|----------------------------|--|-------------------------|
| 1. Ans. (3)                | 2. Ans. (1)                                      | 3. Ans. (3)             |
| 4. Ans. (2)                | 5. Ans. $2.4 \times 10^6 \text{ cm}^2/\text{gm}$ |                         |
| 6. Ans. 4 sec              | 7. Ans. (6)                                      | 8. Ans. $\frac{3}{140}$ |
| 9. Ans. $2.35 \times 10^9$ | 10. Ans. $10^4$ times                            |                         |

**EXERCISE # O-I**

- |              |              |              |
|--------------|--------------|--------------|
| 1. Ans. (B)  | 2. Ans. (B)  | 3. Ans. (A)  |
| 4. Ans. (B)  | 5. Ans. (B)  | 6. Ans. (B)  |
| 7. Ans. (B)  | 8. Ans. (C)  | 9. Ans. (B)  |
| 10. Ans. (D) | 11. Ans. (A) | 12. Ans. (D) |
| 13. Ans. (C) | 14. Ans. (B) | 15. Ans. (C) |
| 16. Ans. (A) | 17. Ans. (B) | 18. Ans. (A) |
| 19. Ans. (B) | 20. Ans. (C) | 21. Ans. (B) |
| 22. Ans. (C) | 23. Ans. (B) | 24. Ans. (B) |
| 25. Ans. (D) | 26. Ans. (C) | 27. Ans. (D) |
| 28. Ans. (D) | 29. Ans. (B) | 30. Ans. (B) |
| 31. Ans. (C) | 32. Ans. (B) | 33. Ans. (C) |
| 34. Ans. (A) | 35. Ans. (B) | 36. Ans. (D) |
| 37. Ans. (B) | 38. Ans. (B) | 39. Ans. (A) |
| 40. Ans. (C) |              |              |

**EXERCISE # O-II**

- |                 |                 |                |
|-----------------|-----------------|----------------|
| 1. Ans. (A,B,D) | 2. Ans. (A,B,D) | 3. Ans. (A, B) |
| 4. Ans. (A,B,D) | 5. Ans. (B,C,D) | 6. Ans. (A, B) |
| 7. Ans. (B,C,D) | 8. Ans. (D)     | 9. Ans. (C)    |
| 10. Ans. (B)    | 11. Ans. (A, C) | 12. Ans. (A)   |
| 13. Ans. (D)    | 14. Ans. (B, D) | 15. Ans. (A)   |
| 16. Ans. (A)    | 17. Ans. (A)    | 18. Ans. (C)   |
| 19. Ans. (B)    | 20. Ans. (C)    |                |

**EXERCISE # J-MAIN**

- |     |          |     |                     |     |          |
|-----|----------|-----|---------------------|-----|----------|
| 1.  | Ans. (2) | 2.  | Ans. (4)            | 3.  | Ans. (2) |
| 4.  | Ans. (2) | 5.  | Ans. (4)            | 6.  | Ans. (2) |
| 7.  | Ans. (2) | 8.  | Ans. (4)            | 9.  | Ans. (1) |
| 10. | Ans. (1) | 11. | Ans. (2)            | 12. | Ans. (4) |
| 13. | Ans. (4) | 14. | Ans. (4)            | 15. | Ans. (2) |
| 16. | Ans. (4) | 17. | Ans. (3)            | 18. | Ans. (2) |
| 19. | Ans. (1) | 20. | Ans. (2)            | 21. | Ans. (3) |
| 22. | Ans. (1) | 23. | Ans. (0.36 to 0.38) | 24. | Ans. (4) |
| 25. | Ans. (4) | 26. | Ans. (4)            |     |          |

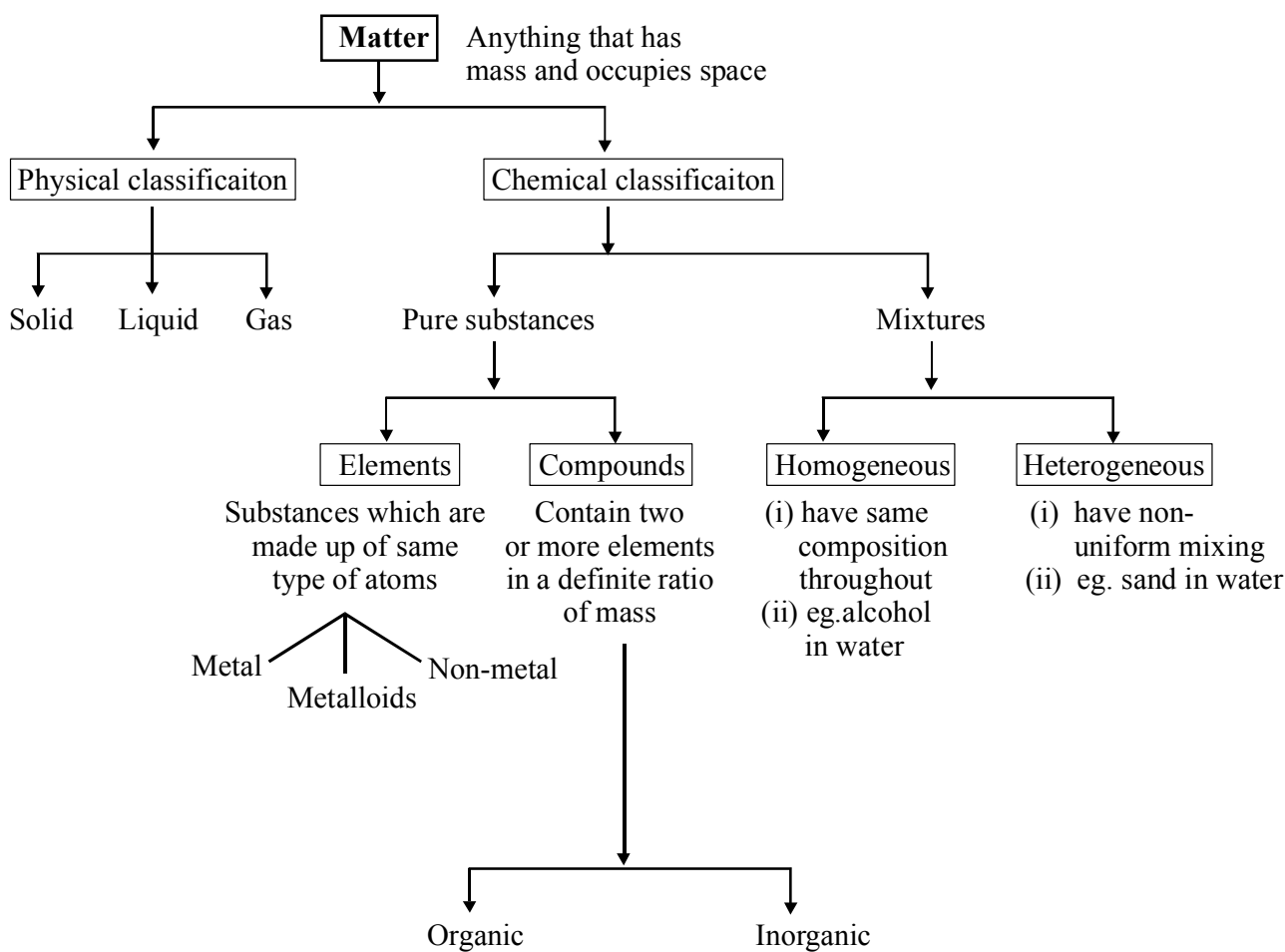
**EXERCISE # J-ADVANCED**

- |    |           |    |           |    |             |
|----|-----------|----|-----------|----|-------------|
| 1. | Ans.(A)   | 2. | Ans.(C)   | 3. | Ans.(A,B,D) |
| 4. | Ans.(A,D) | 5. | Ans.(A,C) | 6. | Ans.(B)     |
| 7. | Ans.(D)   | 8. | Ans.(B,D) | 9. | Ans.(3)     |



# QUANTUM NUMBER & ELECTRONIC CONFIGURATION

## MATTER & ITS CLASSIFICATION



**Example.1** Which of the following is homogeneous mixture :

- (A) Oil + Water (B) Milk  
(C) Salt dissolved in water (D) All of these

**Example.2** Which of the following molecule is tetra-atomic :

- (A)  $\text{CH}_2\text{Cl}_2$  (B)  $\text{NH}_3$  (C)  $\text{H}_2\text{O}$  (D) Both (B) and (C)

**ATOM** : An atom is the smallest particle of an element (made up of still smaller particle like electrons, protons, neutrons etc.) which can take part in a chemical reaction. It may or may not exist free in nature.

Name of particle	Mass	Nature of charge	Amount of charge	Presence in the atom
(i) Electron symbol = (e) Notation = ${}_{-1}\text{e}^{\circ}$ Discoverer J.J. Thomson (1897)	$9.11 \times 10^{-28}$ g $\frac{1}{1837}$ th of H-atom	Negatively charged	$-1.602 \times 10^{-19}$ Coulomb or $-4.8 \times 10^{-10}$ e.s.u	Outside the nucleus
(ii) Proton symbol = (p) Notation = $({}_{1}\text{H}^1)$ Discoverer Rutherford (1911)	$1.6725 \times 10^{-24}$ g	Positively charged	$+ 1.602 \times 10^{-19}$ coulomb  $+ 4.8 \times 10^{-10}$ e.s.u.	Inside the nucleus of an atom
(ii) Neutron symbol = (n) Notation = $({}_{0}\text{n}^1)$ Discoverer J. Chadwick (1932)	$1.675 \times 10^{-24}$ g	Neutral	0	Inside the nucleus of an atom

Representation of atom :  ${}_Z\text{X}^A$

A → Mass number : (total number of protons + total number of neutrons present in an atom.)

Z → Atomic number : (total number of protons present in an atom.)

⇒ **Isotope** : Atoms of given element which have same atomic number but different mass number are called isotope : e.g.  ${}_1\text{H}^1$ ,  ${}_1\text{H}^2$ ,  ${}_1\text{H}^3$  etc.

⇒ **Isobar** : Atoms of different elements with the same mass number but different atomic number .  
e.g.  ${}_{18}\text{Ar}^{40}$ ,  ${}_{19}\text{K}^{40}$  and  ${}_{20}\text{Ca}^{40}$

⇒ **Iso-electronic species** : Species (atom, molecules or ions) having same number of electrons are called iso-electronic e.g.  $\text{H}^-$ , He,  $\text{Li}^+$  and  $\text{Be}^{2+}$  have 2 valence electrons each.

**Note** : Now a days this concept is extended to consider the same valence shell electron also.

⇒ **Iso-sters** : Species having same number of electrons & same number of atoms. eg.  $\text{N}_2\text{O}$ ,  $\text{CO}_2$

⇒ **Iso-diaphers** : Species having same difference in number of neutrons and protons or same number of excess of neutron. eg.  $^{19}_9\text{F}$ ,  $^{23}_{11}\text{Na}$

⇒ **Orbital** : An orbital is defined as that zone in space where electron is most likely to be found. The orbitals are characterized by a set of 3 quantum numbers (n, l, m).

**QUANTUM NUMBERS** : Quantum numbers give complete information about an electron or orbital in an atom.

### 1. Principal Quantum number (n) :

- Permissible value of **n** → 1 to  $\infty$
- It represents shell number/energy level
- The energy states corresponding to different principal quantum numbers are denoted by letters K, L, M, N etc.

<b>n</b>	:	1	2	3	4	5	6
Designation of shell	:	K	L	M	N	O	P

- It indicates the distance of an electron from the nucleus.
- It also determines the energy of the electron. In general higher the value of 'n', higher is the energy of a electron.
- It give an idea of total number of orbitals & electron (which may) present in a shell & that equal to  $n^2$  &  $2n^2$  respectively.

### 2. Azimuthal Quantum number (l) :

- The values of *l* depends upon the value of 'n' and possible values are '0' to (n-1).
- It gives the name of subshells associated with the energy level and number of subshells within an energy level.
- The different value of '*l*' indicates the shape of orbitals and designated as follows :

Value	Notation	Name	Shape
$l = 0$	s	Sharp	Spherical
$l = 1$	p	Principal	Dumbell
$l = 2$	d	Diffused	Double Dumbell
$l = 3$	f	Fundamental	Complex

- It also determines the energy of orbital along with n.  
For a particular energy level/shell energy of subshell is in the following order → **s < p < d < f**
- It gives the total number of orbitals in a subshell & that equals to **(2l + 1)** and number of electron in a subshell = **2(2l + 1)**

### 3. Magnetic Quantum number ( $m$ or $m_l$ ) :

- (i) The value of  $m$  depends upon the value of  $l$  and it may have integral value  $-l$  to  $+l$  including zero.
- (ii) It gives the number of orbitals in a given subshell and orientation of different orbitals in space.  
e.g. for  $n = 4$ ,  $l = 0$  to 3.

$l$	0	1	2	3
$m$	0	+1, 0, -1	+2, 1, 0, -1, -2	+3, +2, +1, 0, -1, -2, -3
Possible Orientation	1	3	5	7
Orbitals	s	$p_x, p_y, p_z$	$d_{z^2}, d_{x^2-y^2}$ $d_{xy}, d_{yz}, d_{xz}$	Not in syllabus

- (iii) The orbitals having same value of  $n$  and  $l$  but different value of  $m$ , have same energy in absence of external electric & magnetic field. These orbitals having same energy of a particular subshell is known as Degenerate orbitals.

### 4. Spin Quantum number ( $s$ ) OR magnetic spin quantum number ( $m_s$ ) :

- (i) While moving around the nucleus, the electron always spins about its own axis either clockwise or anticlockwise. The magnetic spin quantum number represents the direction of electron spin (rotation) around its own axis (clockwise or anticlockwise).
- (ii) There are two possible values of  $m_s$  are  $+\frac{1}{2}$  &  $-\frac{1}{2}$  and represented by the two arrows  $\uparrow$  (spin up) and  $\downarrow$  (spin down).

## RULES FOR FILLING ELECTRONS :

### 1. Pauli's exclusion principle

'No two electrons in an atom can have same values of all the four quantum numbers.

An orbital accommodates two electron with opposite spin. These two electrons have same values of principal, azimuthal and magnetic quantum number but the fourth, i.e. magnetic spin quantum number will be different. i.e.

For K, shell ( $n = 1$ )

$$l = 0, m = 0$$

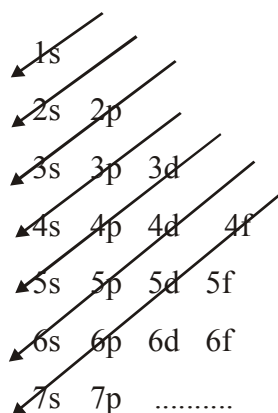
For 1<sup>st</sup> Electron  $n = 1, l = 0, m = 0, m_s = +\frac{1}{2}$

For 2<sup>nd</sup> Electron  $n = 1, l = 0, m = 0, m_s = -\frac{1}{2}$



2. Aufbau Principle (Means Building up) :

The electrons are added progressively to the various orbitals in the order of increasing energies starting with the orbital of the lowest energy



$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$$

Alternatively, the order of increase of energy of orbitals can be calculated from  $(n + l)$  rule.

- (i) Lower the value of  $(n + l)$  for an orbital, the lower will be its energy.
- (ii) If two orbitals have the same  $(n + l)$  value, then orbital with lower value of  $n$  has the lower energy.

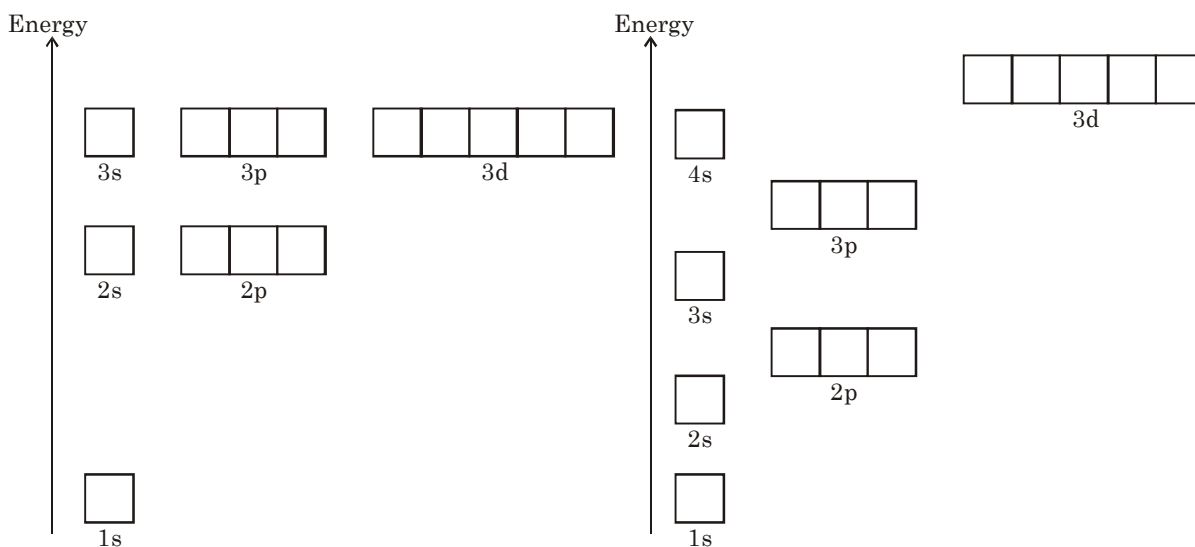
e.g. 2p & 3s

For 2p,  $n = 2, l = 1, (n + l) = 2 + 1 = 3$

For 3s,  $n = 3, l = 0, (n + l) = 3 + 0 = 3$

Then for 2p,  $n$  is lesser than for 3s, so 2p has lower energy than 3s.

- (iii)  $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f \dots$  energy order of different orbitals for single electron system like H,  $\text{He}^+$ ,  $\text{Li}^{+2}$  etc.



(A) For single electron or hydrogenic atom

(B) Multi electronic atoms

Energy level diagram for few electronic shells :

**Example.4** Write the increasing order of energies of 4s, 3p, 4p and 3d.

**Ans.** For 4s,  $n = 4, l = 0, (n + l) = 4$   
 For 3p,  $n = 3, l = 1, (n + l) = 4$   
 For 4p,  $n = 4, l = 1, (n + l) = 5$   
 For 3d,  $n = 3, l = 2, (n + l) = 5$   
 $\Rightarrow 3p < 4s < 3d < 4p$  increasing order

3. **Hund's rule of maximum multiplicity :**

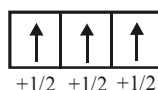
This rule deals with the filling of electrons into the orbitals belonging to the same subshell i.e. orbitals of equal energy, called degenerate orbitals.

“Electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electron with parallel spins.”

“Pairing of electrons in the orbitals belonging to the same subshell (p, d, f) does not take place until each orbital belonging to that subshell has got one electron each i.e. singly occupied. Moreover, the singly occupied orbitals must have the electrons with the parallel spin multiplicity”

Multiplicity =  $2|S| + 1$ , where S = Total spin.

i.e.

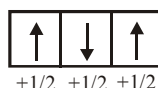


Find total spin & multiplicity

$$\text{Total spin } S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$$\text{Multiplicity} = 2 \times \frac{3}{2} + 1 = 4$$

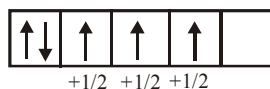
i.e.



$$\text{Total spin } S = \frac{1}{2} - \frac{1}{2} + \frac{1}{2} = \frac{1}{2}$$

$$\text{Multiplicity} = 2 \times \frac{1}{2} + 1 = 2$$

i.e.



$$\text{Total spin } S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$$\text{Multiplicity} = 2 \times \frac{3}{2} + 1 = 4$$

i.e.

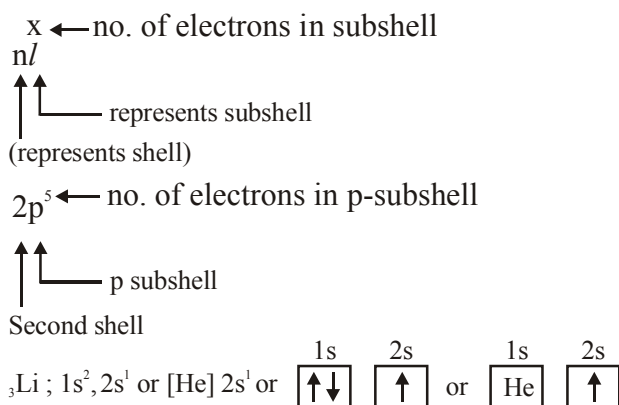


$$\text{Total spin } S = 5 \times \frac{1}{2} = \frac{5}{2}$$

$$\text{Multiplicity} = 2 \times \frac{5}{2} + 1 = 6$$

**ELECTRONIC CONFIGURATION OF ATOMS :**

The distribution of electrons in various shells, subshells and orbitals, in an atom of an element, is called its electronic configuration.

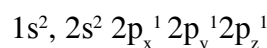


**Electronic configuration :**

**Example.5**

Nitrogen

**Ans.**



or

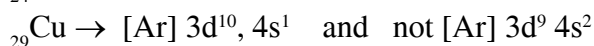
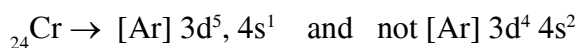


or



**Extra stability of Half-filled and fully-filled orbitals.**

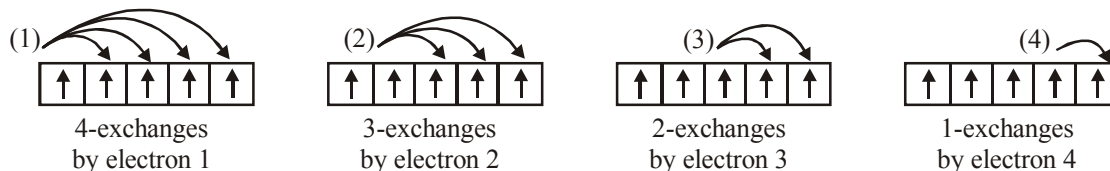
The electronic configuration of most of the atoms follows the Aufbau's rule. However, in certain elements such as Cr, Cu etc. Where the two subshells (4s and 3d) differ slightly in their energies ( $4s < 3d$ ), an electron shifts from a subshell of lower energy (4s) to a subshell of higher energy (3d), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half-filled.



It has been found that there is extra stability associated with these electronic configuration. This stabilization is due to the following two factors.

- (i) **Symmetrical distribution of electron :** It is well known that symmetry leads to stability. The completely filled or half-filled subshell have symmetrical distribution of electron in them and are therefore more stable. This effect is more dominant in d and f-orbitals. This means three or six electrons in p-subshell, 5 or 10 electrons in d-subshell and 7 or 14 in f-subshell forms a stable arrangement.

- (ii) **Exchange energy** : This stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or fully filled. As a result the exchange energy is maximum and so is the stability.



**Total exchange pairs = 10**

$$\frac{n(n-1)}{2} \rightarrow \text{Number of exchange pairs}$$

$n \rightarrow$  Number of electron with parallel spins.



Only 6 total exchange possible

### Exceptional electronic configuration

S.No.	Element	Z	Configuration
1	Cr	24	$[\text{Ar}]4s^1 3d^5$
2.	Cu	29	$[\text{Ar}]4s^1 3d^{10}$
3.	Nb	41	$[\text{Kr}]5s^1 4d^4$
4.	Mo	42	$[\text{Kr}]5s^1 4d^5$
5.	Ru	44	$[\text{Kr}]5s^1 4d^7$
6.	Rh	45	$[\text{Kr}]5s^1 4d^8$
7.	Pd	46	$[\text{Kr}]4d^{10}$
8.	Ag	47	$[\text{Kr}]5s^1 4d^{10}$
9.	La	57	$[\text{Xe}]6s^2 5d^1$
10.	Pt	78	$[\text{Xe}]6s^1 4f^{14} 5d^9$
11.	Au	79	$[\text{Xe}]6s^1 4f^{14} 5d^{10}$
12.	Ac	89	$[\text{Rn}]7s^2 6d^1$
13.	Th	90	$[\text{Rn}]7s^2 6d^2$

**MAGNETIC PROPERTIES :**❖ **Paramagnetism :**

- (i) The substances which are weakly attracted by magnetic field are paramagnetic and this phenomenon is known as paramagnetism.
- (ii) Their magnetic character is retained till they are in magnetic field and lose their magnetism when removed from magnetic field.

❖ **Diamagnetism :**

- (i) The substances which are weakly repelled by magnetic field are diamagnetic and this phenomenon is known as diamagnetism.
- (ii) Diamagnetic substances lack unpaired electrons and their spin magnetic moment is zero e.g., NaCl, N<sub>2</sub>O<sub>4</sub> etc.

❖ **Spin magnetic moment :**

The spin magnetic moment of electron (excluding orbit magnetic moment) is given by :

$$\mu = \sqrt{[n(n+2)]} \text{ B.M.}$$

Where n is number of unpaired electron in species.

The magnetic moment is expressed in Bohr magneton (B.M.)

**Example.6** A compound of vanadium has magnetic moment of 1.73 BM. Work out the electronic configuration of vanadium ion in the compound.

**Ans.** Vanadium belongs to 3d series with Z = 23. The magnetic moment of 3d series metal is given by spin only formula.

$$\mu = \sqrt{n(n+2)} \text{ BM (BM = Bohr's magneton)}$$

$$\therefore 1.73 = \sqrt{3}$$

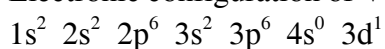
$$\Rightarrow n(n+2) = 3 \Rightarrow n = 1$$

⇒ Magnetic moment correspond to one unpaired electron.

⇒ Electronic configuration of vanadium atom 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>3</sup>.

For one unpaired electron 4 electron must be removed in which first 2 electron are lost from 4s orbital (outermost).

Electronic configuration of V<sup>4+</sup>

**Nodal Planes of different orbitals :**

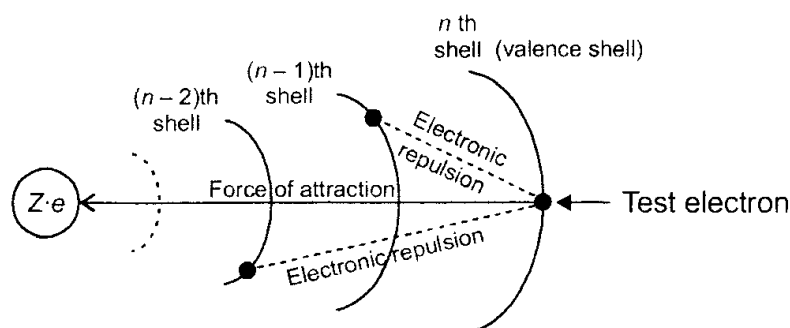
Nodal plane is a plane at which the probability of finding an electron becomes zero.

eg.	Orbital	Nodal plane	Orbital	Nodal plane
	s	None	d <sub>xy</sub>	XZ & YZ planes
	p <sub>x</sub>	YZ plane	d <sub>yz</sub>	XZ & XY planes
	p <sub>y</sub>	XZ plane	d <sub>xz</sub>	XY & YZ planes
	p <sub>z</sub>	XY plane	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	Planes perpendicular to XY plane, passing through origin (nucleus) and inclined at 45° to X & Y axis.
			d <sub>z<sup>2</sup></sub>	None (two nodal cones are available)

### SCREENING EFFECT ( $\sigma$ ) AND EFFECTIVE NUCLEAR CHARGE ( $Z_{\text{eff}}$ )

- Valence shell electron suffer force of attraction due to nucleus and force of repulsion due to inner shell electrons.
- The decrease in force of attraction on valence electron due to inner shell electron is called screening effect or shielding effect. (i.e. total repulsive force is called shielding effect.)
- Due to screening effect, valence shell electron experiences less force of attraction by nucleus.
- Due to screening effect, net attractive force felt by the electron is measured by effective nuclear charge,  $Z_{\text{eff}}$
- If nuclear charge =  $Z$ , then effective nuclear charge =  $Z - \sigma$  (Where  $\sigma$  'sigma' is called screening constant/shielding constant)

$$\text{So, } Z_{\text{eff}} = Z - \sigma$$



#### CALCULATION OF $\sigma$ (using Slater's rule)

To calculate the shielding constant ( $\sigma$ ):

- Write the electronic configuration of the element in the following order and groupings :  
(1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d), (4f), (5s, 5p), etc.

#### For s and p electrons :

- Electrons in any group to the right of the (ns, np) group contribute nothing to the shielding constant.  
(n-shell no. of the electron for which  $\sigma$  is calculated)
- All of the other electrons in the (ns, np) group, shield the concern electron to an extent of 0.35 each. (Except for the 1s orbital for which value is 0.30).
- All electrons in the (n - 1) shell shield to an extent of 0.85 each.
- All electrons (n - 2) or lower group shield completely ; that is, their contribution is 1.00 each.

#### For d and f electrons :

- Electrons in any group to the right of the nd or nf group contribute nothing to the shielding constant.
- All the other electrons in the nd or nf group, shield the valence electron to an extent of 0.35 each.
- All electrons in groups lying to the left of the nd or nf group contribute 1.00.

(Effective Nuclear charge of elements of second period)						
Element	Electronic Configuration	Z	$\sigma$ of ns & np electron	$\sigma$ (n-1) orbital	Total Screening Constant	Effective nuclear charge#
			(a)	(b)	(a + b)	$Z^* = Z - \sigma$
${}_3\text{Li}$	$1s^2 2s^1$	3	–	$0.85 \times 2 = 1.70$	1.70	1.30
${}_4\text{Be}$	$1s^2, 2s^2$	4	$1 \times 0.35 = 0.35$	$0.85 \times 2 = 1.70$	2.05	1.95
${}_5\text{B}$	$1s^2, 2s^2, 2p^1$	5	$2 \times 0.35 = 0.70$	$0.85 \times 2 = 1.70$	2.40	2.60
${}_6\text{C}$	$1s^2, 2s^2, 2p^2$	6	$3 \times 0.35 = 1.05$	$0.85 \times 2 = 1.70$	2.75	3.25
${}_7\text{N}$	$1s^2, 2s^2, 2p^3$	7	$4 \times 0.35 = 1.40$	$0.85 \times 2 = 1.70$	3.10	3.90
${}_8\text{O}$	$1s^2, 2s^2, 2p^4$	8	$5 \times 0.35 = 1.75$	$0.85 \times 2 = 1.70$	3.45	4.55
${}_9\text{F}$	$1s^2, 2s^2, 2p^5$	9	$6 \times 0.35 = 2.10$	$0.85 \times 2 = 1.70$	3.80	5.20

# Calculated for valence electron.

**Key Points :**

- (a) From left to right in a period  $Z_{\text{eff}}$  increases
- (i) For s and p-block elements,  $Z_{\text{eff}}$  in a period increases by 0.65 where atomic number increases by 1, and hence atomic size decreases considerably.
- (ii) In transition series Z increase by + 1 but screening constant increases by 0.85 So  $Z_{\text{eff}}$  is increased by 0.15  
 $(1 - 0.85 = 0.15)$  [Because  $e^-$  enters in  $(n - 1)$  orbit which has value of  $\sigma = 0.85$ ]
- (b) From top to bottom in a group  $Z_{\text{eff}}$  remain constant for s-block elements, after Li and Be.

Element	Li	Na	K	Rb	Cs	Fr
$Z_{\text{eff}}$	1.30	2.20	2.20	2.20	2.20	2.20

**Example-7 :**

What is the effective nuclear charge at the periphery of nitrogen atom when an extra electron is added during the formation of an anion. Also find the value of  $Z_{\text{eff}}$  when the atom is ionized to  $\text{N}^+$ .

**Ans.** Ground state electron configuration of  $\text{N}(Z = 7) = 1s^2 2s^2 2p^3$

Electron configuration of  $\text{N}^- = (1s^2) (2s^2 2p^4)$

Shielding constant for the last 2p electron,

$\sigma = [(2 \times 0.85) + (5 \times 0.35)] = 3.45$

So  $Z_{\text{eff}} = Z - \sigma = 7 - 3.45 = 3.55$

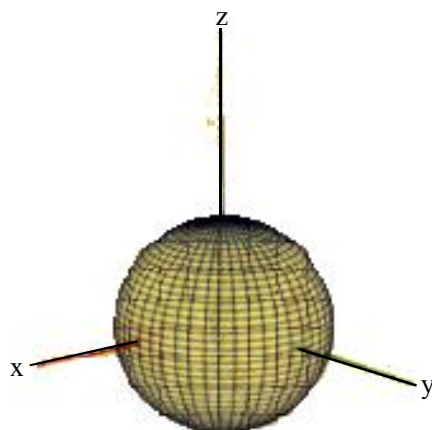
Electron configuration of  $\text{N}^+ = (1s^2) (2s^2 2p^2)$

Shielding constant for the last 2p electron,

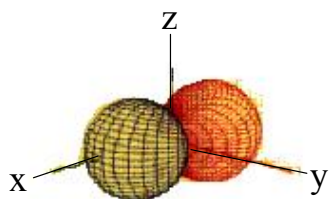
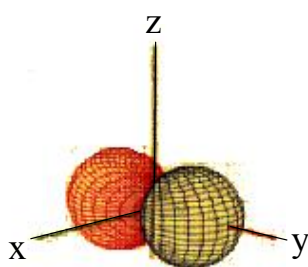
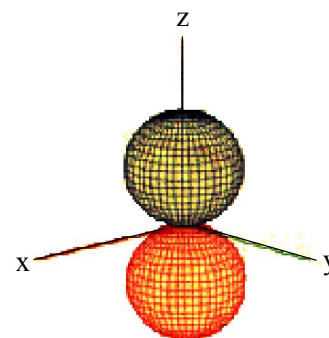
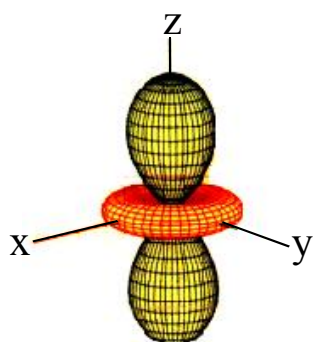
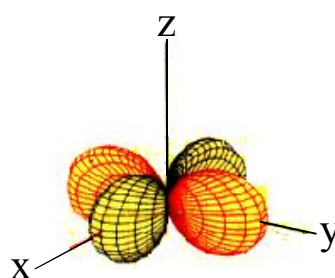
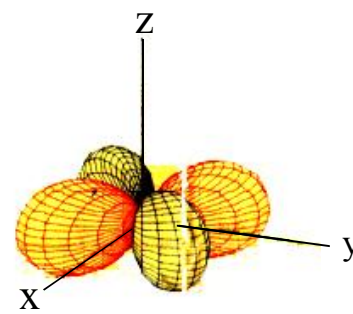
$\sigma = [(2 \times 0.85) + (3 \times 0.35)] = 2.75$

So  $Z_{\text{eff}}$  for last electron on  $\text{N}^+ = 7 - 2.75 = 4.25$

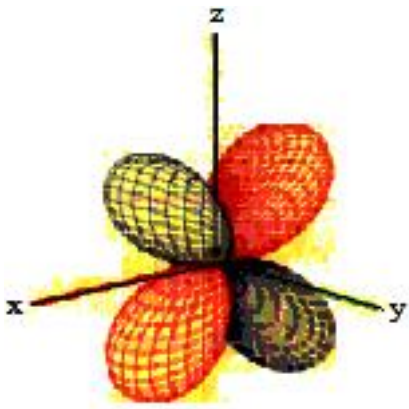
## SHAPES OF ATOMIC ORBITALS



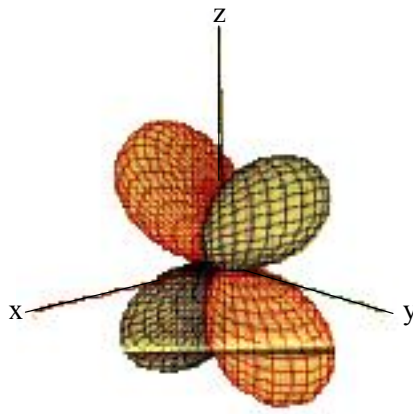
S

 $p_x$  $p_y$  $p_z$  $d_{z^2}$  $d_{x^2-y^2}$  $d_{xy}$

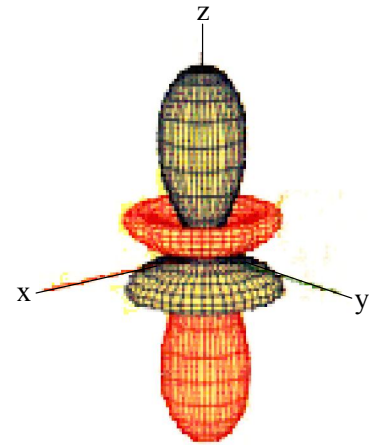




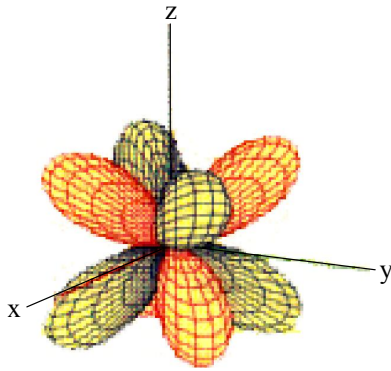
$d_{xz}$



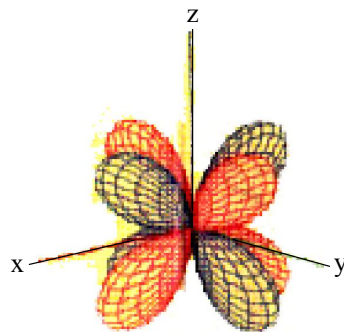
$d_{yz}$



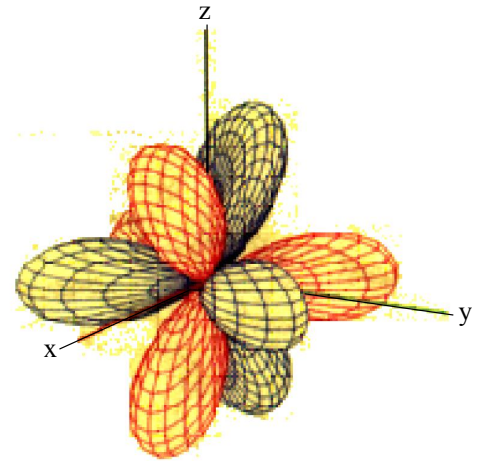
$f_z^3$



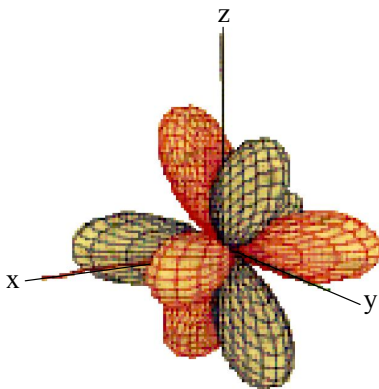
$f_{xyz}$



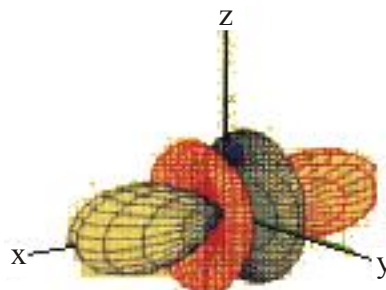
$f_{z(x^2-y^2)}$



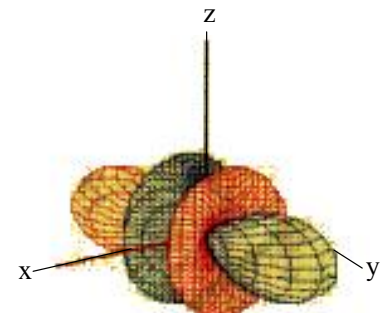
$f_{x(y^2-z^2)}$



$f_{y(z^2-x^2)}$



$f_x^3$



$f_y^3$

## EXERCISE # O-1

## General Introduction :

1. The total number of neutrons in dipositive zinc ion with mass number 70 is  
(A) 34 (B) 40 (C) 36 (D) 38 QN0001
2. It is known that atom contain protons, neutrons and electrons. If the mass of neutron is assumed to half of its original value where as that of proton is assumed to be twice of its original value then the atomic mass of  ${}^6_{14}\text{C}$  will be -  
(A) same (B) 25% more (C) 14.28 % more (D) 28.5% less QN0002
3. Two monoatomic cations  $x^{\oplus}$  and  $y^{2+}$  are isoelectronic then select the correct statement : (Both elements are consecutive)  
(A) Both element x and y have same number of electrons  
(B) Total number of valence electrons are more in element x, than element 'y'  
(C) Total number of valence electrons are more in element y, than element 'x'  
(D) Both (A) and (B) are correct QN0003
4. Which of the following sets contain only isoelectronic ions?  
(A)  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Al}^{3+}$  (B)  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Cl}^-$   
(C)  $\text{P}^{3-}$ ,  $\text{S}^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Zn}^{+2}$  (D)  $\text{Ti}^{4+}$ ,  $\text{Ar}$ ,  $\text{Cr}^{3+}$ ,  $\text{V}^{5+}$  QN0004

## Quantum number

5. Which quantum number will determine the shape of the orbital  
(A) Principal quantum number (B) Azimuthal quantum number  
(C) Magnetic quantum number (D) Spin quantum number QN0005
6. In Palladium (Atomic no.-46), number of electron having ( $\ell = 2$ ) will be -  
(A) 20 (B) 18 (C) 16 (D) 22 QN0006
7. For an electron present in which of the following orbital for which  $(n + l + m + s)$  value is maximum. Consider maximum possible value for 'm' and minimum possible value of  $m_s$  (where ever applicable).  
(A) 3p (B) 5p (C) 4d (D) 5s QN0007
8. Choose the correct option for the quantum numbers of the last electron of  $\text{K}^+$ .  
(A) 4, 0, 0,  $+1/2$  (B) 3, 1,  $-1$ ,  $-1/2$  (C) 4, 1, 0,  $-\frac{1}{2}$  (D) 3, 0, 1,  $\frac{1}{2}$  QN0008
9. Find the sum of maximum number of electrons having  $+1$  and  $-1$  value of 'm' in Ti (Atomic number = 22)  
(A) 6 (B) 8 (C) 10 (D) 12 QN0009

10. The number of electrons in Ca having minimum value of  $\left| \frac{n}{\ell \times m_\ell} \right|$  is.

(Consider only non-zero values of  $\ell$  and  $m$ )

- (A) 6 (B) 3 (C) 4 (D) None of these

QN0010

**Electronic Configuration**

11. A neutral atom of an element has two K, eight L, nine M and two N electrons then electronic configuration of the element is

- (A)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^1$  (B)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$   
 (C)  $1s^2 2s^2 2p^6 3s^2 3d^2 3p^6 4s^1$  (D)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

QN0011

12. The explanation for the presence of three unpaired electrons in the nitrogen atom can be given by

- (A) Pauli's exclusion principle (B) Hund's rule  
 (C) Aufbau's principle (D) Uncertainty principle

QN0012

13. If the nitrogen atom had electronic configuration  $1s^7$ , it would have energy lower than that of normal ground state configuration  $1s^2 2s^2 2p^3$ , because the electrons would be closer to the nucleus. Yet  $1s^7$  is not observed because it violates :-

- (A) Uncertainty principle (B) Hund's rule  
 (C) Pauli's exclusion principle (D) Bohr postulate of stationary orbits

QN0013

**Effective Nuclear charge ( $Z_{\text{eff}}$ ) :**

14. The  $Z_{\text{eff}}$  for (as Slater's rule)

3d electron of Cr

4s electron of Cr

3d electron of  $\text{Cr}^{3+}$

3s electron of  $\text{Cr}^{3+}$  are in the order respectively

- (A) 4.6, 2.95, 4.95, 8.05 (B) 4.95, 2.95, 4.6, 8.05  
 (C) 4.6, 2.95, 5.3, 12.75 (D) none of these

QN0014

15. Total number of possible shells in uranium atom (atomic no.  $z = 92$ )

- (A) 7 (B) 1 (C) 6 (D) None of these

QN0015

16. Which of the following has the maximum number of unpaired electrons ?

- (A)  $\text{Mg}^{2+}$  (B)  $\text{Ti}^{3+}$  (C)  $\text{V}^{3+}$  (D)  $\text{Fe}^{2+}$

QN0016

17. Gaseous state electronic configuration of nitrogen atom can be represented as :

- (A)  $\uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \uparrow$  (B)  $\uparrow\downarrow \uparrow\downarrow \uparrow \downarrow \uparrow$   
 (C)  $\uparrow\downarrow \uparrow\downarrow \uparrow \downarrow \downarrow$  (D)  $\uparrow\downarrow \uparrow\downarrow \downarrow \downarrow \uparrow$

QN0017

## EXERCISE # O-2

**General Introduction :**

1. Isotones are :
- (A) The atoms of different elements  
 (B) Have same number of neutrons  
 (C) Have same number of (neutrons + protons)  
 (D) Have same difference of mass number and atomic number

QN0018

**Quantum number**

2. For an electron present in which of the following orbital for which  $(n + l)$  value is maximum.  
 (A) 3p (B) 5p (C) 4d (D) 5s

QN0019

3. Correct set of four quantum numbers for valence electron of rubidium ( $Z = 37$ ) is

- (A)  $5, 0, 0, +\frac{1}{2}$  (B)  $5, 0, 0, -\frac{1}{2}$  (C)  $5, 1, 1, +\frac{1}{2}$  (D)  $6, 0, 0, +\frac{1}{2}$

QN0020

4. The correct set of quantum numbers for the unpaired electron of chlorine atom is

- |     | <b>n</b> | <b>ℓ</b> | <b>m</b> |     | <b>n</b> | <b>ℓ</b> | <b>m</b> |
|-----|----------|----------|----------|-----|----------|----------|----------|
| (A) | 2        | 1        | 0        | (B) | 2        | 1        | 1        |
| (C) | 3        | 1        | 1        | (D) | 3        | 1        | 0        |

QN0021

5. Which of the following sets of quantum numbers represent an impossible arrangement ?

- |     | <b>n</b> | <b>ℓ</b> | <b>m</b> | <b>m<sub>s</sub></b> |     | <b>n</b> | <b>ℓ</b> | <b>m</b> | <b>m<sub>s</sub></b> |
|-----|----------|----------|----------|----------------------|-----|----------|----------|----------|----------------------|
| (A) | 3        | 3        | -2       | $\frac{1}{2}$        | (B) | 4        | 0        | 0        | $\frac{1}{2}$        |
| (C) | 3        | 2        | -3       | $\frac{1}{2}$        | (D) | 5        | 3        | 0        | $\frac{1}{2}$        |

QN0022

6. The quantum numbers for the 19<sup>th</sup> electron of Cr ( $Z = 24$ ) are

- (A)  $n = 3, \ell = 0, m = 0, m_s = +\frac{1}{2}$  (B)  $n = 4, \ell = 0, m = 0, m_s = +\frac{1}{2}$   
 (C)  $n = 3, \ell = 2, m = 2, m_s = +\frac{1}{2}$  (D)  $n = 4, \ell = 0, m = 0, m_s = -\frac{1}{2}$

QN0023

7. The maximum number of electron having  $n \times \ell \times m = 0$  in  $Zn^{2+}$  is equal to the -

- (A) Atomic number of Mg  
 (B) 12  
 (C) Total number of electron in Zn which have  $n + \ell = 0$   
 (D) 'p' electrons in Ar

QN0024

**Electronic Configuration**

8. The species which have same number of electrons in outer most and penultimate shell -  
 (A) Ca (B) Ar (C)  $V^{+3}$  (D)  $Sc^{3+}$  QN0025
9. Which sub-shell fill completely before the 4f?  
 (A) 6s (B) 5p (C) 5d (D) 4d QN0026
10. The electronic configuration of a carbon atom is  $1s^2, 2s^2, 2p^2$  and consider the following four arrangements of the 2p electrons. Which arrangement have lowest energy ?  
 (A)  $\boxed{\uparrow\downarrow} \boxed{\phantom{\uparrow\downarrow}} \boxed{\phantom{\uparrow\downarrow}}$  (B)  $\boxed{\uparrow} \boxed{\uparrow\downarrow} \boxed{\phantom{\uparrow\downarrow}}$  (C)  $\boxed{\uparrow} \boxed{\phantom{\uparrow\downarrow}} \boxed{\phantom{\uparrow\downarrow}}$  (D)  $\boxed{\uparrow} \boxed{\phantom{\uparrow\downarrow}} \boxed{\phantom{\uparrow\downarrow}}$  QN0027
11. Hund's rule is applicable for :-  
 (A) d-subshell (B) p-subshell (C) s-subshell (D) f-subshell QN0028
12. Which of the following has maximum number of unpaired electron.  
 (A) Fe (B) Fe (II) (C) Fe (III) (D) Mn (II) QN0029
13.  $Mn (Z = 25) = 1s^3 1p^9 2s^3 2p^9 2d^1$   
 Which of the following change is required so that Mn have above ground state electronic configuration :  
 (A) Change in the value of  $\ell$  (azimuthal quantum number) for any subshell  
 (B) Change in the possible values of  $\ell$  (azimuthal quantum number)  
 (C) Change in the Pauli rule  
 (D) Change in the  $(n + \ell)$  rule QN0030
14. The number of d- electrons in  $Mn^{2+}$  is equal to that of  
 (A) p-electrons in N (B) s-electron in Na  
 (C) d-electrons in  $Fe^{+3}$  (D) p-electrons in  $O^{-2}$  QN0031
15. Select incorrect statement(s) :  
 (A)  $d_{z^2}$  orbital has different shape from rest of all d-orbitals  
 (B) For the formation of cation electrons are always removed from 4s.  
 (C) Zinc is a p-block element.  
 (D) Principal quantum number depend upon the value of azimuthal quantum number QN0032

## EXERCISE # S-1

*Integer Answer Type (0 to 9) :*

1. Find total no. of orbitals in nickel which have  $|m| \leq 1$  and at least one electron is present, where 'm' is magnetic quantum number.

(Given your ans. as sum of digits for example. If your ans is 57 then  $5 + 7 = 12$  and  $1 + 2 = 3$ )

QN0033

2. Minimum number of electrons having  $m_s = \left(-\frac{1}{2}\right)$  in Cr is “\_\_\_\_\_”.

QN0034

3. How many elements are possible for the I<sup>st</sup> period of periodic table if azimuthal quantum number can have integral values from 0 to  $(n + 1)$ . [ $n$  = shell number & other rules are remaining same to form periodic table.

QN0035

4. Find number of unpaired electrons when Fe does not follow  $(n + \ell)$  rule and filling of electron takes place shell after shell and Hund's rule is also not obeyed.

QN0036

5. Find the maximum number of electrons having same  $Z_{\text{eff}}$  value for sulphur atom

QN0037

6. Find the sum of maximum unpaired  $e^-$  present in one 5g & one 6g orbital.

QN0038

7. Find out the maximum number of electrons that can involve in the shielding of an electron, having quantum numbers :  $n = 2, \ell = 1, m = 0, m_s = +\frac{1}{2}$ , in an atom.

QN0039

8. Find the sum of minimum and maximum possible value of  $x$  in  $\text{Fe}^{+x}$  ion, if magnetic moment of  $\text{Fe}^{+x} = 4.89$  B.M.

QN0040

**EXERCISE # S-2***Paragraph for Question 1 to 3*

The general electronic configuration of outer most and penultimate shell is given as  $(n-1)s^2(n-1)p^6(n-1)d^xns^2$ . Then for an element with  $n = 4$  and  $x = 6$ .

- The number of protons present in the divalent cation of the element of above configuration is :-  
(A) 24 (B) 25 (C) 26 (D) 27 QN0041
- The element is :  
(A) Mn (B) Fe (C) Co (D) Li QN0041
- The number of unpaired electrons in the divalent cation of the given element in isolated gaseous state is :-  
(A) 0 (B) 3 (C) 4 (D) 1 QN0041

*Paragraph for Question 4 & 5*

Consider a hypothetical atom where  $p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}$  and  $d_{x^2-y^2}$  orbitals are present for principal quantum number  $n = 4$ .

- Find the number of other orbital which lobes are fully present in the nodal plane of  $p_x$  orbital :-  
(A) 2 (B) 4 (C) 3 (D) 5 QN0042
- Which of the following orbitals lobe is not present at all either in the nodal plane of  $p_x$  orbital or in the nodal plane of  $p_y$  orbital.  
(A)  $d_{xy}$  (B)  $d_{yz}$  (C)  $d_{x^2-y^2}$  (D)  $p_z$  QN0042

*Paragraph for Question 6 & 7*

Isotopes, Isobars and Iso-diaphers are some basic definitions related to the atom, which are based upon the variation in no. of electron, proton or neutrons.

- Which of the following pair represents the Isobar species :-  
(A)  ${}_{18}\text{Ar}^{40}, {}_6\text{C}^{12}$  (B)  ${}_8\text{O}^{16}, {}_7\text{N}^{14}$  (C)  $\text{N}_2\text{O}, \text{CO}_2$  (D) None of these QN0043
- Which of the following pair is correct for isosters :-  
(A)  $\text{N}_2\text{O}, \text{CH}_4$  (B)  $\text{N}_2\text{O}, \text{CO}_2$  (C)  $\text{CO}_2, \text{SO}_2$  (D)  $\text{N}_2\text{O}, \text{HOCl}$  QN0043

- | Column-I<br>Element | Column-II<br>Max. value of $n$ and $l$ respectively ; consider filled subshell only |
|---------------------|---|
| (P) P               | (1) 6, 2  |
| (Q) N               | (2) 3, 1  |
| (R) Pb              | (3) 6, 3  |
| (S) Cs              | (4) 2, 1  |

Code :

- |     | P | Q | R | S |     | P | Q | R | S |
|-----|---|---|---|---|-----|---|---|---|---|
| (A) | 4 | 1 | 2 | 3 | (B) | 2 | 4 | 1 | 3 |
| (C) | 3 | 1 | 2 | 4 | (D) | 2 | 4 | 3 | 1 |

QN0044

9. Match the following:

**Column-I**

- (P) Same number of unpaired electrons are present in (excluding zero)  
 (Q) Same number of electrons in s & p subshells.  
 (R) Same number of electrons with the  $l = 1$   
 (S) Same number of total electrons

**Column-II**

- (1)  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{F}^-$   
 (2)  $\text{F}^-$ ,  $\text{Mg}$ ,  $\text{O}^{2-}$   
 (3)  $\text{Mg}$ ,  $\text{Ne}$ ,  $\text{O}^{2-}$   
 (4)  $\text{Li}$ ,  $\text{Na}$ ,  $\text{K}$

Code :

	P	Q	R	S
(A)	1, 2	3, 4	1	4
(B)	4, 2	3, 1	2, 3	4, 1
(C)	4	1	1, 2, 3	1
(D)	3	1, 2	3, 4	1, 3, 4

QN0045

10. Match the following :

**Column-I (Orbital)**

- (P) s  
 (Q)  $p_x$   
 (R)  $d_{xy}$   
 (S)  $d_{x^2-y^2}$

**Column-II (Property)**

- (1) Have electron density at all three axes  
 (2) YZ plane is nodal plane  
 (3) dumbbell shape  
 (4) have azimuthal quantum no.  $l = 2$

Code :

	P	Q	R	S
(A)	1, 3	2, 3	3	3, 4
(B)	1	2, 3	2, 4	4
(C)	1	2, 3, 4	3, 4	1, 4
(D)	2	3, 4	2, 3	1, 4

QN0046

**Match The Column :**

11. Match the following :

**Column-I ( $e^-$  configuration)**

- (A)  $d^8$   
 (B)  $d^{10}$   
 (C)  $d^6$   
 (D)  $d^5$

**Column-II (Property)**

- (P) Symmetrical distribution  
 (Q) Unsymmetrical distribution  
 (R) No of exchange pair are maximum among these  
 (S) two electrons must be present in  $d_{x^2-y^2}$  orbital  
 (T) at least one electron is present in orbital having  $m = -1$

QN0047



12. Column-I

- (A)  $Zn^{2+}$
- (B)  $Ga^+$
- (C)  $Fe^{3+}$
- (D)  $Br^-$

Column-II

- (P) Diamagnetic
- (Q) Spin magnetic moment =  $\sqrt{35}$  BM
- (R)  $18 e^-$  in outer most shell
- (S) 3d subshell is fully filled
- (T) All the orbital of outer most shell are fully filled

QN0048

MATCHING LIST TYPE 1 × 3 Q. (THREE LIST TYPE Q.)

Column - I	Column - II	Column - III
(A) Paramagnetic set	(i) $Na^+, Mg^{+2}, F^-$	(P) same value of principal quantum number for last electron
(B) Isoelectronic set	(ii) Li, Na, K	(Q) The non zero number(s) of $e^-(s)$ for $n = 3$ and $\ell \geq 1$ is
(C) The set for which value(s) of spin multiplicity is $\geq 1$	(iii) $Fe^{+3}, Co^{+2}, Ni^{+2}$	(R) The value of " $m_s$ " must be $+\frac{1}{2}$ for last electron
(D) The set of elements belongs to same period in periodic table	(iv) $S, Cl^-, P^{-3}$	(S) Set for which the value of $m = \pm 2$ is possible for electron(s)

13. Which one of the following options is the **CORRECT** combination?

- (A) (A, i, P)
- (B) (B, iv, S)
- (C) (D, iii, S)
- (D) (C, iii, R)

QN0049

14. Which one of the following options is the **INCORRECT** combination?

- (A) (A, iii, P)
- (B) (C, ii, P)
- (C) (B, i, P)
- (D) (B, iv, Q)

QN0049

15. Which one of the following options is the **CORRECT** set of species with number of nodal planes for filled/partially filled orbitals is  $\leq 1$  for all given species in set?

- (A) (B, ii, R)
- (B) (B, iv, P)
- (C) (A, i, Q)
- (D) (D, iii, S)

QN0049

## EXERCISE # JEE-MAIN

1. The electrons identified by quantum numbers  $n$  and  $l$  :-  
**[JEE-1999, AIEEE-2012, JEE-MAIN, (ONLINE)-2012]**  
 (a)  $n = 4, l = 1$       (b)  $n = 4, l = 0$       (c)  $n = 3, l = 2$       (d)  $n = 3, l = 1$   
 Can be placed in order of increasing energy as  
 (1) (a) < (c) < (b) < (d)      (2) (c) < (d) < (b) < (a)  
 (3) (d) < (b) < (c) < (a)      (4) (b) < (d) < (a) < (c)  
**QN0050**
2. Which of the following paramagnetic ions would exhibit a magnetic moment (spin only) of the order of 5 BM ?  
**[JEE-MAIN, (ONLINE)-2012]**  
 (At. No : Mn = 25, Cr = 24, V = 23, Ti = 22)  
 (1)  $V^{2+}$       (2)  $Ti^{2+}$       (3)  $Mn^{2+}$       (4)  $Cr^{2+}$   
**QN0051**
3. In an atom how many orbital (s) will have the quantum numbers;  $n = 3, l = 2$  and  $m_l = +2$  ?  
**[JEE-MAIN, (ONLINE)-2013]**  
 (1) 1      (2) 5      (3) 3      (4) 7  
**QN0052**
4. The numbers of protons, electrons and neutrons in a molecule of heavy water are respectively  
**[JEE-MAIN, (ONLINE)-2013]**  
 (1) 10, 10, 10      (2) 8, 10, 11  
 (3) 10, 11, 10      (4) 11, 10, 10  
**QN0053**
5. Given  
**[JEE-MAIN, (ONLINE)-2013]**  
 (a)  $n=5, m_l = +1$       (b)  $n = 2, l = 1, m_l = -1, m_s = -1/2$   
 The maximum number of electron(s) in an atom that can have the quantum numbers as given in (a) and (b) are respectively :  
 (1) 8 and 1      (2) 25 and 1      (3) 2 and 4      (4) 4 and 1  
**QN0054**
6. The correct set of four quantum numbers for the valence electrons of rubidium atom ( $Z = 37$ ) is:  
**[JEE(Main)-2014]**  
 (1)  $5, 1, 1, +\frac{1}{2}$       (2)  $5, 0, 1, +\frac{1}{2}$       (3)  $5, 0, 0, +\frac{1}{2}$       (4)  $5, 1, 0, +\frac{1}{2}$   
**QN0055**
7. If the principal quantum number  $n = 6$ , the correct sequence of filling of electrons will be:-  
**[JEE-MAIN, (ONLINE)-2015]**  
 (1)  $ns \rightarrow (n-1)d \rightarrow (n-2)f \rightarrow np$       (2)  $ns \rightarrow np \rightarrow (n-1)d \rightarrow (n-2)f$   
 (3)  $ns \rightarrow (n-2)f \rightarrow (n-1)d \rightarrow np$       (4)  $ns \rightarrow (n-2)f \rightarrow np \rightarrow (n-1)d$   
**QN0056**
8. The total number of orbitals associated with the principal quantum number 5 is :  
**[JEE-MAIN, (ONLINE)-2016]**  
 (1) 25      (2) 5      (3) 20      (4) 10  
**QN0057**

9. The group having isoelectronic species is :- [JEE-MAIN 2017]  
 (1)  $O^{2-}$ ,  $F^-$ ,  $Na^+$ ,  $Mg^{2+}$  (2)  $O^-$ ,  $F^-$ ,  $Na$ ,  $Mg^+$   
 (3)  $O^{2-}$ ,  $F^-$ ,  $Na$ ,  $Mg^{2+}$  (4)  $O^-$ ,  $F^-$ ,  $Na^+$ ,  $Mg^{2+}$   
 QN0058
10. The isotopes of hydrogen are : [JEE-MAIN ONLINE 2019]  
 (1) Tritium and protium only  
 (2) Deuterium and tritium only  
 (3) Protium and deuterium only  
 (4) Protium, deuterium and tritium  
 QN0059
11. The quantum number of four electrons are given below - [JEE-MAIN ONLINE 2019]  
 I.  $n = 4$ ,  $l = 2$ ,  $m_l = -2$ ,  $m_s = -\frac{1}{2}$   
 II.  $n = 3$ ,  $l = 2$ ,  $m_l = 1$ ,  $m_s = +\frac{1}{2}$   
 III.  $n = 4$ ,  $l = 1$ ,  $m_l = 0$ ,  $m_s = +\frac{1}{2}$   
 IV.  $n = 3$ ,  $l = 1$ ,  $m_l = 1$ ,  $m_s = -\frac{1}{2}$   
 The correct order of their increasing energies will be -  
 (1)  $IV < III < II < I$  (2)  $IV < II < III < I$   
 (3)  $I < II < III < IV$  (4)  $I < III < II < IV$   
 QN0060
12. The isoelectronic set of ions is : [JEE-MAIN ONLINE 2019]  
 (1)  $N^{3-}$ ,  $Li^+$ ,  $Mg^{2+}$  and  $O^{2-}$  (2)  $Li^+$ ,  $Na^+$ ,  $O^{2-}$  and  $F^-$   
 (3)  $F^-$ ,  $Li^+$ ,  $Na^+$  and  $Mg^{2+}$  (4)  $N^{3-}$ ,  $O^{2-}$ ,  $F^-$  and  $Na^+$   
 QN0061
13. The number of orbitals associated with quantum numbers  $n = 5$ ,  $m_s = +\frac{1}{2}$  is : [JEE-MAIN ONLINE 2020]  
 (1) 11 (2) 25 (3) 15 (4) 50  
 QN0062
14. Hydrogen has three isotopes (A), (B) and (C). If the number of neutron(s) in (A), (B) and (C) respectively, are (x), (y) and (z), the sum of (x), (y) and (z) is : [JEE-MAIN ONLINE 2020]  
 (1) 4 (2) 3 (3) 2 (4) 1  
 QN0063

**EXERCISE # JEE-ADVANCED**

1. The maximum number of electrons that can have principal quantum number,  $n = 3$ , and spin quantum number,  $m_s = -1/2$ , is  
[JEE 2011]  
QN0064
2. In an atom, the total number of electrons having quantum numbers  $n=4$ ,  $|m_l| = 1$  and  $m_s = -\frac{1}{2}$  is:  
[JEE Advanced 2014]  
QN0065
3. Not considering the electronic spin the degeneracy of the second excited state ( $n = 3$ ) of H-atom is 9, where the degeneracy of the second excited state of  $H^-$  is [JEE Advanced 2015]  
QN0066

**ANSWER KEY**

**EXERCISE # O-1**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	B	C	C	B	B	A	C	B	C	C
Que.	11	12	13	14	15	16	17			
Ans.	B	B	C	C	D	D	A			

**EXERCISE # O-2**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A, B, D	B, C	A, B	C, D	A, C	B, D	A, B, D	B, D	A, B, D	C, D
Que.	11	12	13	14	15					
Ans.	A, B, D	C, D	B, C, D	B, C	B, C, D					

**EXERCISE # S-1**

Que.	1	2	3	4	5	6	7	8		
Ans.	4	9	8	0	8	2	9	6		

**EXERCISE # S-2**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	C	B	C	C	A	D	B	D	C	B
Que.	11					12				
Ans.	(A)-Q,T (B)-P,R,S,T (C)-Q,T (D)-P,T					(A)-P,R,S,T (B)-P,S (C)-Q (D)-P,S				
Que.	13	14	15							
Ans.	C	B	B							

**EXERCISE # JEE-MAIN**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	3	3	1	1	1	3	3	1	1	4
Que.	11	12	13	14						
Ans.	2	4	2	2						

**EXERCISE # JEE-ADVANCED**

Que.	1	2	3							
Ans.	9	6	3							

## PART-A (PERIODIC TABLE)

### INTRODUCTION :

The arrangement of all the known elements according to their properties in such a way that the elements of similar properties are grouped together in a tabular form is called periodic table.

### Development of periodic table :

#### (A) LAVOISIER CLASSIFICATION OF ELEMENTS

At first Lavoisier classified the elements into two categories.

- (i) Metal
- (ii) Non-metal

*Note : This classification cannot categories the metalloid variety.*

#### (B) DOBEREINER'S TRIAD RULE [1817]

- (i) He made groups of three elements having similar chemical properties called TRIAD.
- (ii) In Dobereiner triad, atomic weight of middle element is nearly equal to the average atomic weight of first and third element.

e.g.

[	Cl	Br	I	
	35.5	80.0	127	$\frac{35.5 + 127}{2} = 81.25$

[	Ca	Sr	Ba	
	40	87.5	137	$\frac{40 + 137}{2} = 88.5$

[	Li	Na	K	
	7	23	39	At. wt of Na = $\frac{7 + 39}{2} = 23$

- (iii) Other examples – (K, Rb, Cs), (P, As, Sb), (S, Se, Te), (H, F, Cl), (Sc, Y, La)

#### (C) NEWLAND'S OCTAVE RULE [1865]

- (i) He arranged the elements in the increasing order of their atomic mass and observed that properties of every 8<sup>th</sup> element was similar to the 1<sup>st</sup> one, like in the case of musical vowels notation.

Sa	Re	Ga	Ma	Pa	Dha	Ni	Sa
1	2	3	4	5	6	7	8

- (ii) At that time inert gases were not known.

Li	Be	B	C	N	O	H
Na	Mg	Al	Si	P	S	F
K	Ca					Cl

- (iii) The properties of Li are similar to 8<sup>th</sup> element i.e. Na, Be are similar to Mg and so on.

#### Drawbacks or Limitations :

- (a) This rule is valid only upto Ca. because after Ca due to filling of d-orbitals there is difference of 18 elements instead of 8 element.
- (b) After the discovery of inert gas this law had to be dropped out.
- (c) He failed in the case of heavier metals as Fe has been placed along with O and S.

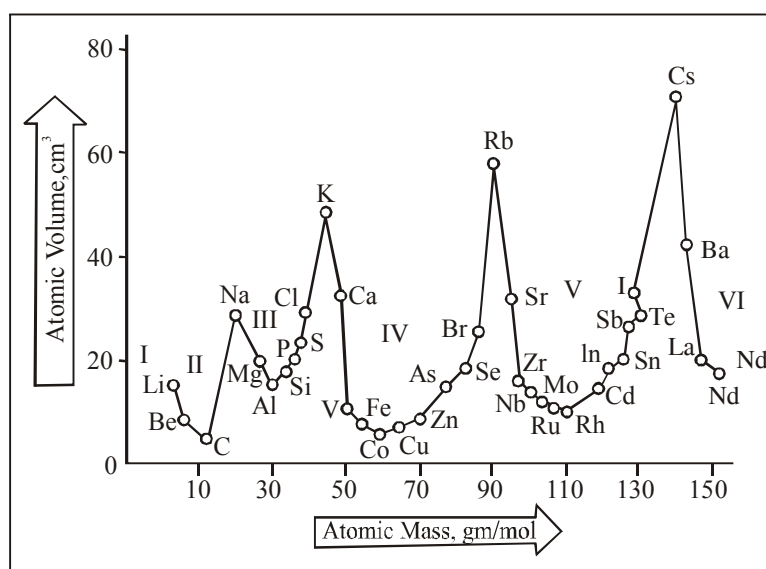
**(D) LOTHER MEYER'S CURVE [1869]**

- (i) He plotted a curve between atomic weight and atomic volume of different elements.
- (ii) The following observations can be made from the curve –
  - (a) Most electropositive elements i.e. alkali metals (Li, Na, K, Rb, Cs etc.) occupy the peak portions of the curve.
  - (b) Less electropositive i.e. alkaline earth metals (Be, Mg, Ca, Sr, Ba) occupy the descending portions of the curve.
  - (c) Metalloids (B, Si, As, Te, At etc.) and transition metals occupy bottom part of the curve.
  - (d) Most electronegative i.e. halogens (F, Cl, Br, I) occupy the ascending portion of the curve.

**Note :** Elements having similar properties occupy similar portions of the curve.

**Conclusion :**

On the basis of this curve, Lotser Meyer proposed that the physical properties of the elements are periodic function of their atomic weight and this became the basis of Mendeleev's periodic table.

**(E) MENDELEEV'S PERIODIC TABLE [1869]**

- (i) **Mendeleev's periodic law** – The physical and chemical properties of elements are the periodic function of their atomic weight
- (ii) **Characteristic of Mendeleev's periodic table** –
  - (a) It is based on atomic weight
  - (b) 63 elements were known, noble gases were not discovered.
  - (c) He was the first scientist to classify the elements in a systematic manner i.e. in horizontal rows and in vertical columns.
  - (d) Horizontal rows are called periods and there were 7 periods in Mendeleev's Periodic table.
  - (e) Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table.
  - (f) Each group upto VII<sup>th</sup> is divided into A & B subgroups. 'A' sub group elements are called normal elements and 'B' sub group elements are called transition elements.
  - (g) The VIII<sup>th</sup> group consists of 9 elements in three rows.
  - (h) The elements belonging to same group exhibit similar properties.

**(iii) Merits or advantages of Mendeleev's periodic table –**

- (a) **Study of elements** – For the first time, all known elements were classified in groups according to their similar properties. So study of the properties of elements became easier.
- (b) **Prediction of new elements** – It gave encouragement to the discovery of new elements as some gaps were left in it.

Sc (Scandium), Ga (Gallium), Ge (Germanium), Tc (Technetium) were the elements whose position and properties were well defined by Mendeleev even before their discoveries and he left the blank spaces for them in his table.

e.g. - Blank space at atomic weight 72 in silicon group was called Eka silicon (means properties like silicon) and element (*discovered later*) was named Germanium .

Similarly other elements discovered after mendeleev periodic table were :

Eka aluminium – Gallium(Ga)

Eka Boron – Scandium (Sc)

Eka Silicon – Germanium (Ge)

Eka Manganese – Technetium (Tc)

- (c) **Correction of doubtful atomic weights**–Corrections were done in atomic weight of some elements.

$$\text{Atomic Weight} = \text{Valency} \times \text{Equivalent weight.}$$

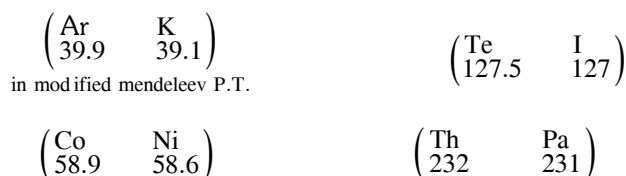
Initially, it was found that equivalent weight of Be is 4.5 and it is trivalent ( $V = 3$ ), so the weight of Be was 13.5 and there is no space in Mendeleev's table for this element. So, after correction, it was found that Be is actually divalent ( $V = 2$ ). So, the weight of Be became  $2 \times 4.5 = 9$  and there was a space between Li and B for this element in Mendeleev's table.

Corrections were done in atomic weight of elements are – U, Be, In, Au, Pt.

**(iv) Demerits of Mendeleev's periodic table –**

- (a) **Position of hydrogen** – Hydrogen resembles both, the alkali metals (IA) and the halogens (VIIA) in properties so Mendeleev could not decide where to place it.
- (b) **Position of isotopes** – As atomic weight of isotopes differs, they should have been placed in different position in Mendeleev's periodic table. But there was no such place for isotopes in Mendeleev's table.
- (c) **Anomalous pairs of elements** – There were some pair of elements which did not follow the increasing order of atomic wts.

eg : Ar and Co were placed before K and Ni respectively in the periodic table, but having higher atomic weights.

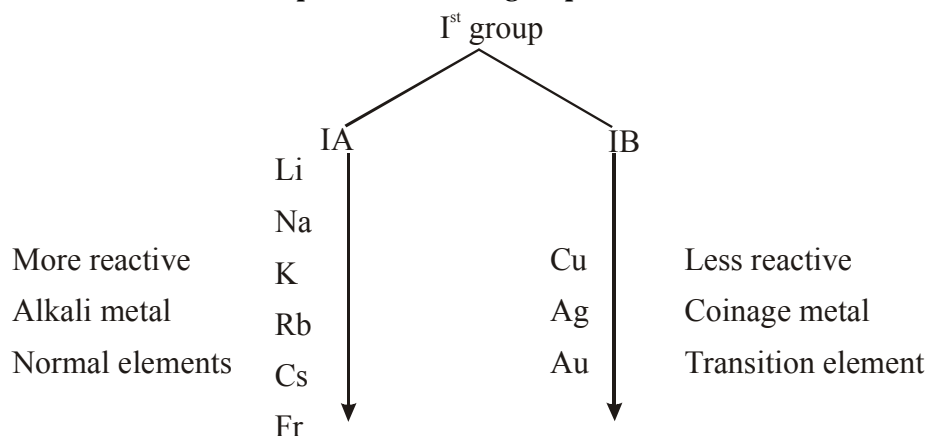
**(d) Like elements were placed in different groups.**

There were some elements like Platinum (Pt) and Gold (Au) which have similar properties but were placed in different groups in Mendeleev's table.

Pt	Au
VIII	IB



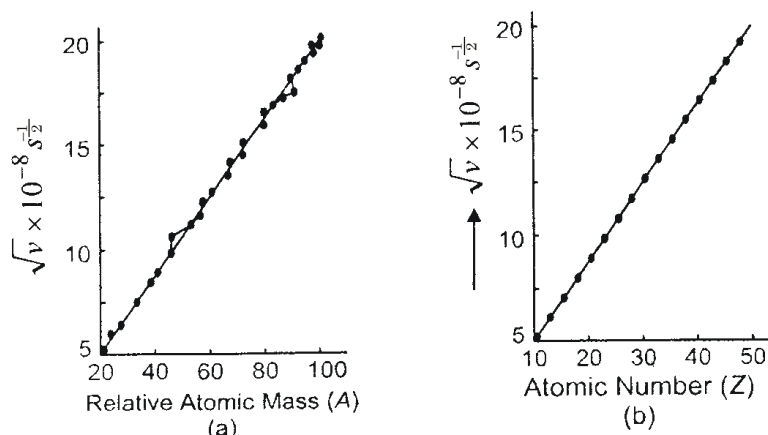
(e) Unlike elements were placed in same group.



Cu, Ag and Au placed in 1<sup>st</sup> group along with Na, K etc. While they differ in their properties (Only similar in having  $ns^1$  electronic configuration)

**(F) MODERN PERIODIC TABLE (MODIFIED MENDELEEV PERIODIC TABLE)**

- (i) It was proposed by Moseley (1913).
- (ii) Modern periodic table is based on atomic number.
- (iii) Moseley did an experiment in which he bombarded high speed electron on different metal surfaces and obtained X-rays.



Moseley's Experiment

He found out that  $\sqrt{\nu} \propto Z$  (where  $\nu$  = frequency) of X-rays from this experiment, Moseley concluded that the physical and chemical properties of the elements are periodic function of their atomic number. It means that when the elements are arranged in the increasing order of their atomic number, elements having similar properties gets repeated after a regular interval. This is also known as 'Modern Periodic Law'.

- (iv) **Modern periodic law** – The physical & chemical properties of elements are a periodic function of their atomic number.
- (v) **Characteristics of modern periodic table** –
  - (a) 9 vertical columns called groups.
  - (b) IA to VIIA, IB to VIIB, VIII and 0
  - (c) Inert gases were introduced in periodic table by Ramsay.
  - (d) 7 horizontal series called periods.

**(G) LONG FORM / PRESENT FORM OF MODERN PERIODIC TABLE**

(It is also called as 'Bohr-Burry & Rang, Werner Periodic Table.)

- (i) It is based on the Bohr-Burry electronic configuration concept and atomic number.
- (ii) This model was proposed by Rang & Werner
- (iii) It consists of 7 horizontal periods and 18 vertical columns (groups)
- (iv) According to I. U. P. A. C. 18 vertical columns are named as 1<sup>st</sup> to 18<sup>th</sup> group.
- (v) The co-relation between the groups in long form of periodic table and in modern form of periodic table are given below.

IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA, 0

1 2 3 4 5 6 7  $\overbrace{8, 9, 10}$  11 12 13 14 15 16 17 18

- (vi) Elements belonging to same group have same no. of electrons in the outermost shell so their properties are similar.

**Description of periods :**

Period	n	Sub shell	No. of elements	Element	Name of Period
1.	1	1s	2	${}_1\text{H} - {}_2\text{He}$	Shortest
2.	2	2s, 2p	8	${}_3\text{Li} - {}_{10}\text{Ne}$	Short
3.	3	3s, 3p	8	${}_{11}\text{Na} - {}_{18}\text{Ar}$	Short
4.	4	4s, 3d, 4p	18	${}_{19}\text{K} - {}_{36}\text{Kr}$	Long
5.	5	5s, 4d, 5p	18	${}_{37}\text{Rb} - {}_{58}\text{Xe}$	Long
6.	6	6s, 4f, 5d, 6p	32	${}_{55}\text{Cs} - {}_{86}\text{Rn}$	Longest
7.	7	7s, 5f, 6d, 7p	32	${}_{87}\text{Fr} - {}_{118}\text{Og}$	Longest

# Extended or Long Form of the Periodic Table

s-Block Elements (1) → p-Block Elements (18) → d-Block Elements (10) → f-Block Elements (14)

Metals (White), Non metals (Green), Metalloids (Black)

Group	IA (1)	IIA (2)	d-Block Elements										IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	0 (18)										
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18										
1	<b>H</b> 1.0079 Hydrogen																		<b>He</b> 4.0026 Helium									
2	<b>Li</b> 6.940 Lithium	<b>Be</b> 9.0122 Beryllium												<b>B</b> 10.811 Boron	<b>C</b> 12.011 Carbon	<b>N</b> 14.007 Nitrogen	<b>O</b> 15.999 Oxygen	<b>F</b> 18.998 Fluorine	<b>Ne</b> 20.180 Neon									
3	<b>Na</b> 22.990 Sodium	<b>Mg</b> 24.305 Magnesium											<b>Al</b> 26.982 Aluminium	<b>Si</b> 28.086 Silicon	<b>P</b> 30.974 Phosphorus	<b>S</b> 32.066 Sulphur	<b>Cl</b> 35.453 Chlorine	<b>Ar</b> 39.948 Argon										
4	<b>K</b> 39.098 Potassium	<b>Ca</b> 40.078 Calcium											<b>Ga</b> 69.723 Gallium	<b>Ge</b> 72.61 Germanium	<b>As</b> 74.922 Arsenic	<b>Se</b> 78.96 Selenium	<b>Br</b> 79.904 Bromine	<b>Kr</b> 83.80 Krypton										
5	<b>Rb</b> 85.468 Rubidium	<b>Sr</b> 87.62 Strontium											<b>In</b> 114.82 Indium	<b>Sn</b> 118.71 Tin	<b>Sb</b> 121.76 Antimony	<b>Te</b> 127.60 Tellurium	<b>I</b> 126.90 Iodine	<b>Xe</b> 131.29 Xenon										
6	<b>Cs</b> 132.91 Cesium	<b>Ba</b> 137.33 Barium											<b>Tl</b> 204.38 Thallium	<b>Pb</b> 207.2 Lead	<b>Bi</b> 208.98 Bismuth	<b>Po</b> 210 Polonium	<b>At</b> 210 Astatine	<b>Rn</b> 222 Radon										
7	<b>Fr</b> 223 Francium	<b>Ra</b> 226 Radium											<b>Nh</b> 285 Nihonium	<b>Fl</b> 289 Flerovium	<b>Mc</b> 288 Moscovium	<b>Lv</b> 293 Livermorium	<b>Ts</b> 294 Tennessine	<b>Og</b> 294 Oganesson										
													<b>Sc</b> 44.956 Scandium	<b>Ti</b> 47.867 Titanium	<b>V</b> 50.941 Vanadium	<b>Cr</b> 51.996 Chromium	<b>Mn</b> 54.938 Manganese	<b>Fe</b> 55.847 Iron	<b>Co</b> 58.933 Cobalt	<b>Ni</b> 58.693 Nickel	<b>Cu</b> 63.546 Copper	<b>Zn</b> 65.39 Zinc	<b>Ga</b> 69.723 Gallium	<b>Ge</b> 72.61 Germanium	<b>As</b> 74.922 Arsenic	<b>Se</b> 78.96 Selenium	<b>Br</b> 79.904 Bromine	<b>Kr</b> 83.80 Krypton
													<b>Y</b> 88.906 Yttrium	<b>Zr</b> 91.224 Zirconium	<b>Nb</b> 92.906 Niobium	<b>Mo</b> 95.94 Molybdenum	<b>Tc</b> 98 Technetium	<b>Ru</b> 101.07 Ruthenium	<b>Rh</b> 102.91 Rhodium	<b>Pd</b> 106.42 Palladium	<b>Ag</b> 107.87 Silver	<b>Cd</b> 112.41 Cadmium	<b>In</b> 114.82 Indium	<b>Sn</b> 118.71 Tin	<b>Sb</b> 121.76 Antimony	<b>Te</b> 127.60 Tellurium	<b>I</b> 126.90 Iodine	<b>Xe</b> 131.29 Xenon
													<b>La*</b> 138.91 Lanthanum	<b>Hf</b> 178.49 Hafnium	<b>Ta</b> 180.95 Tantalum	<b>W</b> 183.84 Tungsten	<b>Re</b> 186.21 Rhenium	<b>Os</b> 190.23 Osmium	<b>Ir</b> 192.22 Iridium	<b>Pt</b> 195.08 Platinum	<b>Au</b> 196.97 Gold	<b>Hg</b> 200.59 Mercury	<b>Tl</b> 204.38 Thallium	<b>Pb</b> 207.2 Lead	<b>Bi</b> 208.98 Bismuth	<b>Po</b> 210 Polonium	<b>At</b> 210 Astatine	<b>Rn</b> 222 Radon
													<b>Ac**</b> 227 Actinium	<b>Rf</b> 267 Rutherfordium	<b>Db</b> 270 Dubnium	<b>Sg</b> 271 Seaborgium	<b>Bh</b> 270 Bohrium	<b>Hs</b> 277 Hassium	<b>Mt</b> 276 Meitnerium	<b>Ds</b> 281 Darmstadtium	<b>Rg</b> 282 Roentgenium	<b>Cn</b> 285 Copernicium	<b>Nh</b> 285 Nihonium	<b>Fl</b> 289 Flerovium	<b>Mc</b> 288 Moscovium	<b>Lv</b> 293 Livermorium	<b>Ts</b> 294 Tennessine	<b>Og</b> 294 Oganesson

f-Block Elements

6	<b>* Lanthanide Series</b>	<b>Ce</b> 140.12 Cerium	<b>Pr</b> 140.91 Praseodymium	<b>Nd</b> 144.24 Neodymium	<b>Pm</b> 145 Promethium	<b>Sm</b> 150.36 Samarium	<b>Eu</b> 151.96 Europium	<b>Gd</b> 157.25 Gadolinium	<b>Tb</b> 158.93 Terbium	<b>Dy</b> 162.50 Dysprosium	<b>Ho</b> 164.93 Holmium	<b>Er</b> 167.26 Erbium	<b>Tm</b> 168.93 Thulium	<b>Yb</b> 173.07 Ytterbium	<b>Lu</b> 174.97 Lutetium
7	<b>** Actinide Series</b>	<b>Th</b> 232.04 Thorium	<b>Pa</b> 231.04 Protactinium	<b>U</b> 238.03 Uranium	<b>Np</b> 237 Neptunium	<b>Pu</b> 244 Plutonium	<b>Am</b> 243 Americium	<b>Cm</b> 247 Curium	<b>Bk</b> 247 Berkelium	<b>Cf</b> 251 Californium	<b>Es</b> 252 Einsteinium	<b>Fm</b> 257 Fermium	<b>Md</b> 258 Mendelevium	<b>No</b> 259 Nobelium	<b>Lr</b> 262 Lawrencium

IUPAC designations of groups of elements are given in brackets

**CLASSIFICATION OF ELEMENTS INTO s , p , d & f BLOCK ELEMENTS:****s – block :**

- (i) configuration  $ns^{1-2}$  (ii) last  $e^-$  enters in s orbital  
 (iii) two groups I A or 1 ; II A or 2

**p – block :**

- (i) configuration  $ns^2 np^{1-6}$  (ii) last  $e^-$  enters in p orbital  
 (iii) six groups III A , IV A , V A , VI A , VII A , zero or 13 , 14 , 15 , 16 , 17 , 18

**d – block : [ Transition Elements ]**

- (i) configuration  $(n-1)d^{1-10} ns^{0-2}$  (ii) last  $e^-$  enters in d orbital  
 (iii) their two outermost shell are incomplete  
 (iv) 10 groups III B , IV B , V B , VI B , VII B , VIII (Triad) , I B , II B or 3 , 4 , 5 , 6 , 7 , (8 , 9 , 10) , 11 , 12 .  
 (v) four series 3d , 4d , 5d , 6d belong to 4<sup>th</sup> , 5<sup>th</sup> , 6<sup>th</sup> & 7<sup>th</sup> period respectively in long form of Periodic table.

**f – block : [ Inner Transition ]**

- (i) configuration  $(n-2)f^{0-14} (n-1)d^{0-2} ns^2$   
 (ii) last  $e^-$  enters in f orbital  
 (iii) two series 4f Lanthanides & 5f Actinides belong to 6<sup>th</sup> & 7<sup>th</sup> period respectively in long form of Periodic table.

**Neil Bohr's classification of elements :**

Using electronic configuration as the criteria, elements are of four types. The classification of the elements into these groups is dependent on the extent to which the s, p, d and f orbitals are filled.

**Inert Gases :**

- (a) s – and p-orbitals of the outer most shell of these elements are completely filled. The outermost electronic configuration is  $ns^2 np^6$ .  
 (b) Helium is also inert gas but its electronic configuration is  $1s^2$

**Representative or Normal Elements :**

- (a) Outermost shell of these elements is incomplete. The number of electrons in the outermost shell is less than eight.  
 (b) s-and p-block elements except inert gases are called normal or representative elements.

**Transition Elements :**

- (a) These metals were placed between s-block metals and p-block elements so, are named transition metals.  
 (b) Their outermost electronic configuration is similar to d-block elements i.e.  $(n-1)d^{1-10} ns^{1-2}$ .  
 (c) Last two shells of these elements namely outermost and penultimate shells are incomplete.  
 (d) The last shell contains one or two electrons and the penultimate shell may contain more than eight and up to eighteen electrons.  
 (e) According to definition of transition elements, those elements which have partly filled d-orbitals in neutral state or in any stable oxidation state are called transition elements. According to this definition Zn, Cd and Hg (IIB group) are d-block elements but not transition elements because these elements have  $d^{10}$  configuration in neutral as well as in stable +2 oxidation state.

**Inner Transition Elements :**

- In these elements last three shells i.e. last, penultimate and prepenultimate shells are incomplete.
- These are related to IIIB i.e. group 3.
- The last shell contains two electrons. Penultimate shell may contain eight or nine electrons and pre-penultimate shell contains more than 18, up to 32 electrons.
- Their outmost electronic configuration is similar to f-block element  
i.e.  $(n - 2) f^{0-14} (n - 1) d^{0-2} ns^2$

**METALS, NON-METALS & METALLOIDS**

Apart from classifying elements into s, p, d and f-blocks, there is yet another broad classification of elements based on their properties. The elements can be broadly classified into

**(a) Metals:**

Majority of the elements in periodic table are metals and appears on the left side of the periodic table.

**Properties:**

- These are usually solid at room temperature [exception - mercury]
- They have high melting and boiling point [exception Gallium & Cesium have very low melting point (303 K and 302 K respectively)]
- They are good conductor of heat and electricity.
- They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires)

**(b) Non-Metals:**

These are placed at the top right hand side of periodic table. As we move horizontally along a period, the property of elements changes from metallic (on left) to non-metallic (on the right).

**Properties :**


- These are usually solids or gases at room temperature.
- They have low melting point and boiling point (exception : Boron, Carbon).
- Most Non-metallic solids are brittle and are neither malleable nor ductile.

**(c) Metalloids (Semi-metals):**

Properties of these elements show the characteristics of both metals and non-metals. Silicon (Si), Germanium(Ge), Arsenic(As), Antimony(Sb) and Tellurium(Te) are metalloids.

**ESTIMATING POSITION OF AN ELEMENT FROM ITS ELECTRONIC CONFIGURATION**

The last electron enters in which subshell gives idea of its block.

 **Think** :  $1s^1$  and  $1s^2$  belongs to which block]

Period number = Principal quantum number of valence shell electron in ground state electronic configuration.

Group number for s block = number of valence shell electrons

Group number for p block = 10 + number of valence shell electrons

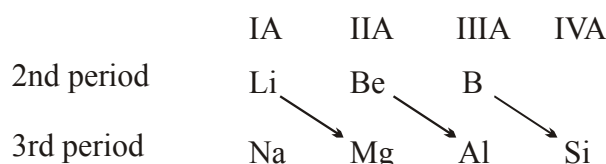
Group number for d block = number of  $[ns + (n-1) d]$  electrons

Group number for f-block = 3

 **Use these carefully while locating the position.]**

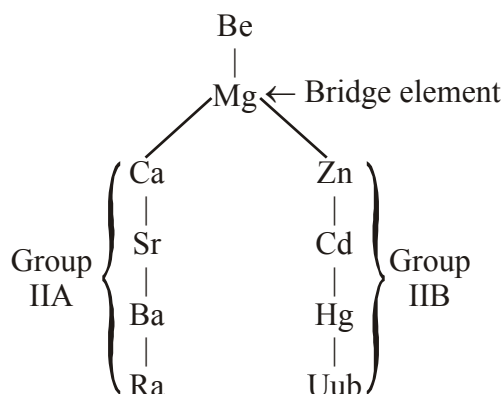
### SOME COMMONLY USED TERMS

- Noble Gases** : Element of group 18 are called noble gases. These are also called as inert gases because their outermost ns and np orbitals are completely filled (except He and  $1s^2$ ) and these gases are non-reactive in nature under ordinary conditions.
- Typical elements** : Elements of second and third period are known as typical elements.
- Diagonal relationship** : Properties of elements of second period resemble with the element of third period. This resemblance between properties of 2<sup>nd</sup> & 3<sup>rd</sup> period is called diagonal relationship.



#### 4. Bridge elements :

The typical elements of third period are also called bridge elements as the division between two subgroups A and B starts from these elements. In second group Mg acts as a bridge element. The properties of bridge element are some what mixed of the elements of two subgroups as magnesium shows similarities with alkaline earth metals (IIA) on one hand and with zinc metals (IIB) on the other.



### IUPAC NOMENCLATURE OF THE ELEMENT :

The names are derived by using roots for the three digits in the atomic number of the element and adding the ending -ium. The roots for the number are

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Thus element with atomic number 109 will be named as **une** (u for 1, n for 0 and e for 9). Table summarises the names of the elements with atomic number above 100.

## PART-B (PERIODIC PROPERTIES)

### PERIODICITY :

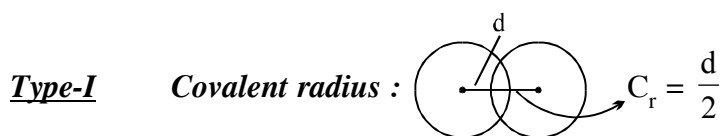
- (a) The regular gradation in properties from top to bottom in a group and from left to right in a period is called periodicity in properties.
- (b) In a period, the ultimate shell remain same, but the number of electrons gradually increases.
- (c) In a group, the number of electrons in the ultimate shell remains same, but the values of n increases.

#### Cause of periodicity

- (a) The cause of periodicity in properties is due to the same outermost shell electronic configuration repeating over regular intervals.
- (b) In the periodic table, elements with similar properties occur at intervals of 2, 8, 8, 18, 18 and 32. These numbers are called magic numbers.

### ATOMIC RADIUS :

Since there is a problem in calculating actual size of atom, three types of radii can be defined :

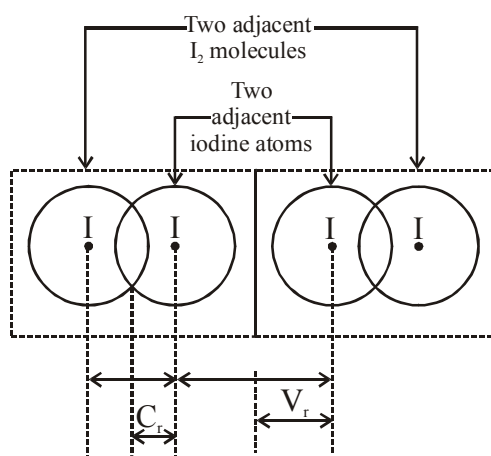


[Used for H<sub>2</sub>, Cl<sub>2</sub> and such molecules]



[Used for metals]

#### **Type-III VanderWaal's Radius or Collision radius**



**VanderWaal's radius =  $\frac{1}{2} \times$  Internuclear distance between nuclei of two neighbouring atoms belonging to nearest molecules.**

VanderWaal's radius > Metallic radius > Covalent radius

The VanderWaal's radius and covalent radius of chlorine atom are 1.80 Å and 0.99 Å respectively.

### Ionic Radius

A neutral atom changes to a cation by the loss of one or more electrons and to an anion by the gain of one or more electrons. The magnitude of charge on cation and anion is equal to the number of electrons lost or gained respectively. The ionic radii of the ions present in an ionic crystal may be calculated from the internuclear distance between the two ions.

(a) **Radius of Cation**

Radius of cation is smaller than that of corresponding atom. Since due to removal of electron(s),  $Z_{\text{eff}}$  increases.

(b) **Radius of an Anion**

Radius of an anion is invariably larger than that of the corresponding atom, since due to addition of electron(s)  $Z_{\text{eff}}$  decreases.

### Factors affecting atomic radius:

- (a)  $Z_{\text{eff}}$  increases, atomic radius decreases  $\text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}$   
 (b) Number of shell(n) increases, atomic radius increases  $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$   
 (c) Screening effect increases, atomic radius increases.  
 (d) Magnitude of -ve charge increases, atomic radius increases  $\text{O} < \text{O}^- < \text{O}^{2-}$   
 (e) Magnitude of +ve charge increases, atomic radius decreases  $\text{Mn} > \text{Mn}^{+2} > \text{Mn}^{+3} > \text{Mn}^{+4}$   
 (f) Bond order increases, atomic radius decreases  $>\text{N}-\text{N}< >-\text{N}=\text{N}- > \text{N}\equiv\text{N}$

### Periodic Trend :

(a) **For normal elements:**

(i) **Across a period :** It decreases from left to right in a period as  $Z_{\text{eff}}$  increases.

**Ex.**  $\text{Ne} > \text{Li} > \text{Be} > \text{B} > \text{C} > \text{N} > \text{O} > \text{F}$

(ii) **In a group :** It increases from top to bottom in a group as number of shells increases.

**Ex.**  $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$

**Note :** In III A group size of Al and Ga is nearly same (transition contraction)

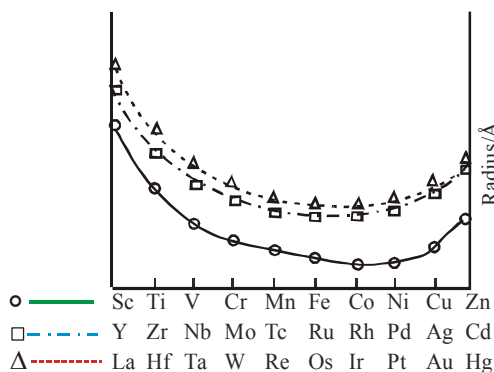
(b) **For inert gases:**

In respective period generally, the atomic radius of inert gas is largest, because for inert gas VanderWaal's radius is defined. The VanderWaal's radius of inert gases also increases on moving from top to bottom in the group.

(c) **For transition elements:**

**From left to right in a period:**

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Covalent radius (Å)	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25



Trends in atomic radii of transition elements



**In a group :**

- (i) The atomic radius of elements increases on moving down the first transition series (3d) to second transition series (4d). This is due to the increases in number of shells with the increase in atomic number.
- (ii) The atomic radii of second (4d) and third (5d) transition series in a group is almost same except Y(39) and La(57)
- (d) **For inner transition elements:**

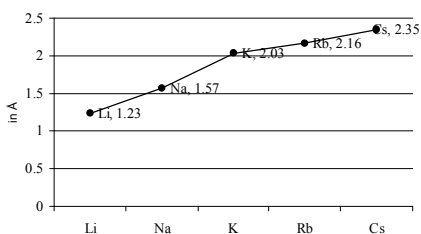
As we move along the lanthanide series, there is a decrease in atomic as well as ionic radius. The decrease in size is regular in ions but not so regular in atoms. This is called lanthanide contraction\*.

**Exceptions :**

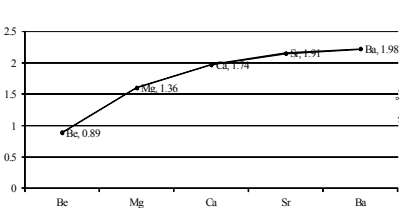
- (1) Noble gases have largest atomic sizes [Vander waal radii]. However, their covalent radii are smaller e.g. Xe.
- (2) Size of Al > Ga, [ $Z_{\text{eff}}$  increasing]
- (3) Size of Hf & Zr are same (lanthanide contraction)

**Graphical representation of atomic radius :**

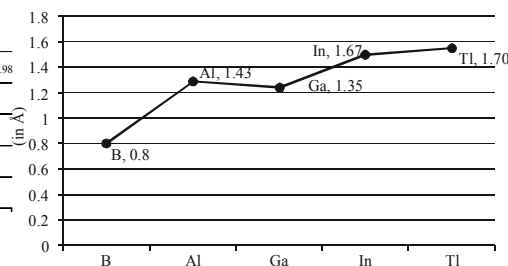
**ALKALI METALS**



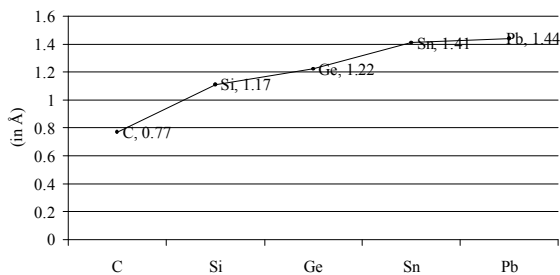
**ALKALINE EARTH METALS**



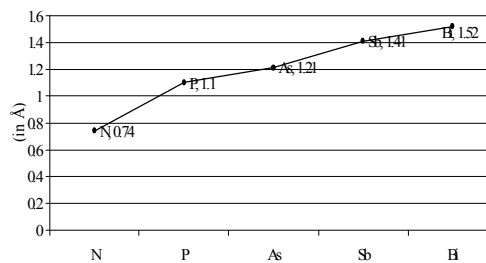
**BORON FAMILY**



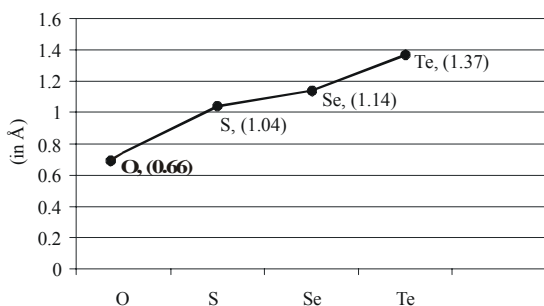
**CARBON FAMILY**



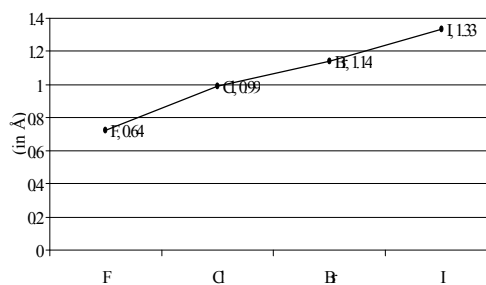
**NITROGEN FAMILY (PNICOGENS)**



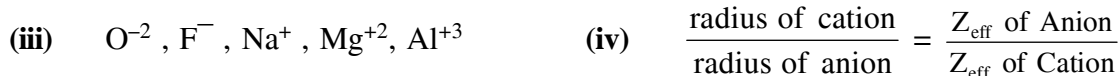
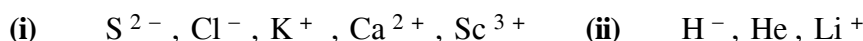
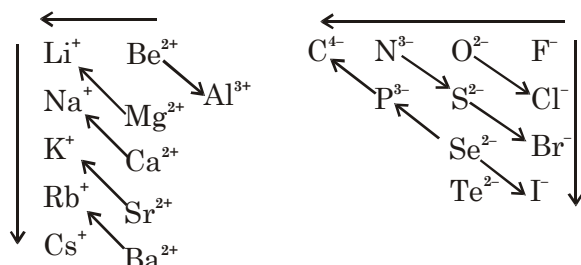
**CHALCOGENS**



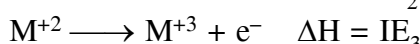
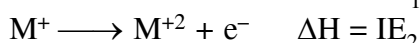
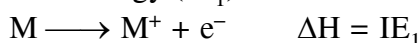
**HALOGENS**



☺ what can you predict or say about the increment in size along a group and decrement along a period]

**ISOELECTRONIC MONOATOMIC SPECIES [Size  $\propto 1/Z$ ]:****Note:-** In the direction of arrow ( $\rightarrow$ ) ionic size increases.**IONISATION ENERGY :**

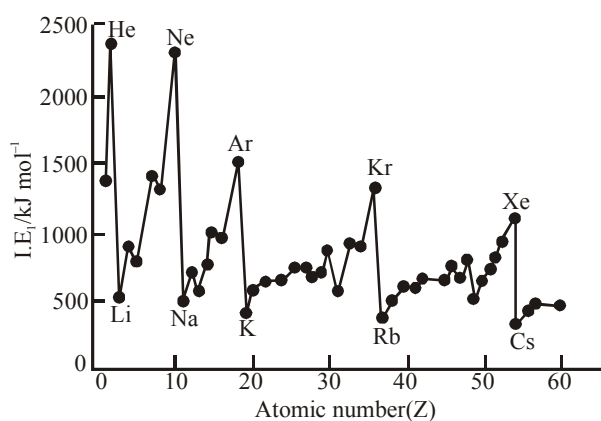
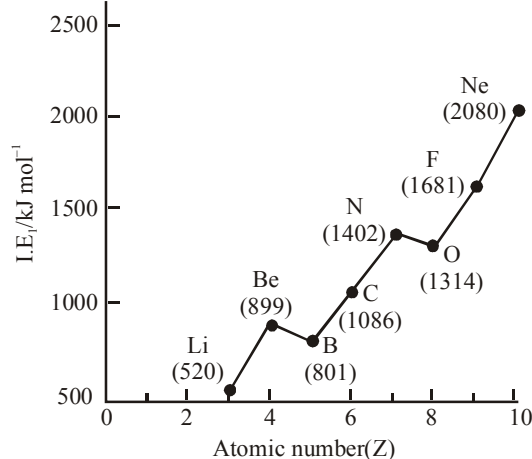
Amount of energy required to remove the most loosely bonded electron from an isolated gaseous atom from its ground state electronic configuration.

Units :  $\text{kJ mol}^{-1}$ ,  $\text{k cal mol}^{-1}$ ,  $\text{eV per atom}$ .Ionisation is endothermic (endoergic) i.e. requires energy. Hence  $\Delta H_{\text{ionisation}}$  is +ve.

Successive ionisation energy

 $\text{IE}_3 > \text{IE}_2 > \text{IE}_1$  (always)**FACTORS AFFECTING IONISATION ENERGY :**

- (1) Atomic size : Varies inversely
- (2) Screening effect : Varies inversely
- (3) Nuclear charge ( $Z$ ) : Varies directly
- (4) Special electronic configuration of outermost electron (half filled / fully filled)
- (5) Type of orbitals involved in Ionisation :  $s > p > d > f$ .

**Note :** Half filled and full filled inner orbitals, affects d-block and f-block trends.**General Trend:** Along period I.E. increases [with some exception] [ $Z_{\text{eff}} \uparrow$ ]Along a group I.E. decrease [ $Z_{\text{eff}}$  constant,  $n \uparrow$ ]Variation of first ionization energy ( $\text{IE}_1$ ) with atomic number for elements with  $Z = 1$  to 60First ionization energy ( $\text{IE}_1$ ) of elements of the second period as a function of atomic number ( $Z$ )

**Exception :**

- (1) Along a period, half filled and fully filled configurations have higher I.E.  
e.g. Be > B and N > O.
- (2) along a group, Ga ≈ Al

**PROPERTIES AFFECTED BY IONISATION ENERGY :**

- (1) Metallic character (Varies inversely)
- (2) Reducing power (Varies inversely)
- (3) Tendency to stay in which state  $A^{+1}$ ,  $A^{+2}$  or  $A^{+3}$

**Note :**

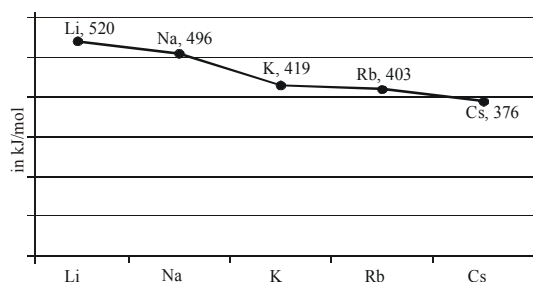
- (a) Helium (He) has the highest ionisation energy ( $IE_1$ ) among all the elements and Caesium (Cs) has the least ( $IE_1$ ) value.
- (b) Ionisation potential of inert gases is very high due to most stable  $s^2p^6$  electronic configuration.

Element	He	Ne	Ar	Kr	Xe	Rn
$IE_1$ (eV)	24.5	21.6	15.8	14.0	12.1	10.7

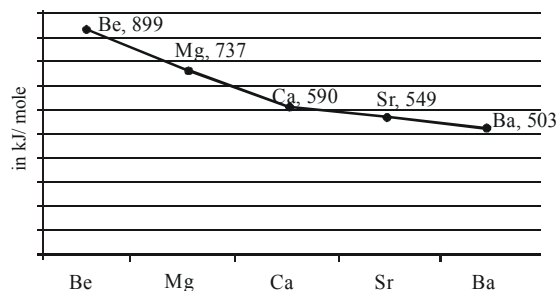
- (c) For isoelectronic species I.E. increases with positive charge and decreases with negative charge.  
e.g.  $Al^{+3} > Mg^{+2} > Na^+ > F^- > O^{-2} > N^{-3}$

**Graphical representation of ionisation energy :**

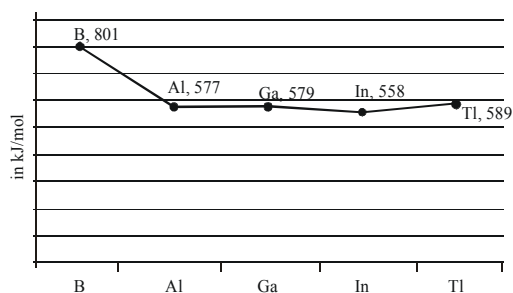
**ALKALI METALS**



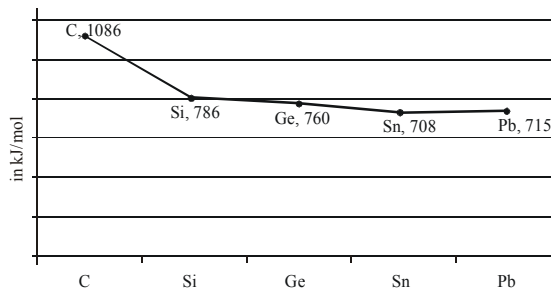
**ALKALINE EARTH METALS**



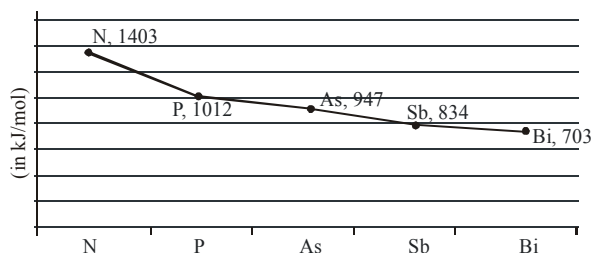
**BORON FAMILY**



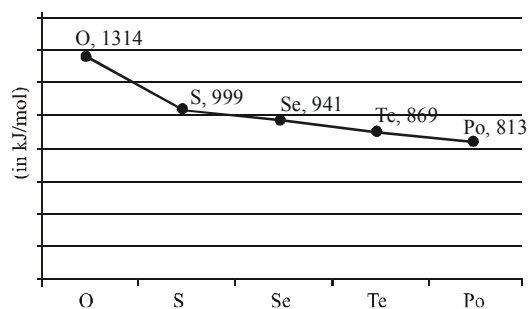
**CARBON FAMILY**



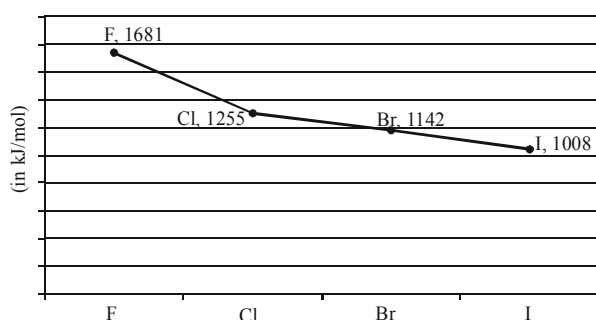
## NITROGEN FAMILY (PNICOGENS)



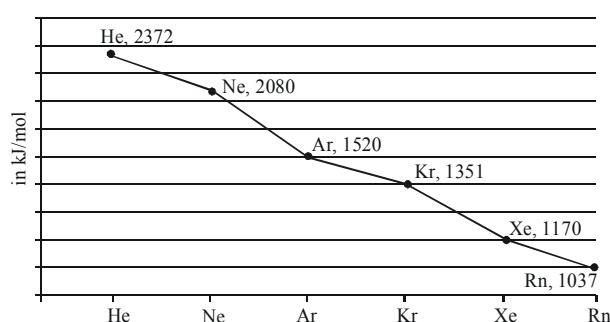
## CHALCOGENS



## HALOGENS



## NOBLE GASES

**Ionisation energy of d-block elements :**

1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> IE's are increasing from left to right for 1<sup>st</sup> Transition series, but not regularly.

For 2<sup>nd</sup> IE Cr > Fe > Mn and Cu > Zn

For 3<sup>rd</sup> IE Mn > Cr > Fe and Zn has highest.

Element	Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Electronic configuration										
M	3d <sup>1</sup> 4s <sup>2</sup>	3d <sup>2</sup> 4s <sup>2</sup>	3d <sup>3</sup> 4s <sup>2</sup>	3d <sup>5</sup> 4s <sup>1</sup>	3d <sup>5</sup> 4s <sup>2</sup>	3d <sup>6</sup> 4s <sup>2</sup>	3d <sup>7</sup> 4s <sup>2</sup>	3d <sup>10</sup> 4s <sup>2</sup>	3d <sup>10</sup> 4s <sup>1</sup>	3d <sup>10</sup> 4s <sup>2</sup>
M <sup>2+</sup>	3d <sup>1</sup>	3d <sup>2</sup>	3d <sup>3</sup>	3d <sup>4</sup>	3d <sup>5</sup>	3d <sup>6</sup>	3d <sup>7</sup>	3d <sup>8</sup>	3d <sup>9</sup>	3d <sup>10</sup>
M <sup>3+</sup>	[Ar]	3d <sup>1</sup>	3d <sup>2</sup>	3d <sup>3</sup>	3d <sup>4</sup>	3d <sup>5</sup>	3d <sup>6</sup>	3d <sup>7</sup>	—	—
Enthalpy of atomisation, Δ <sub>a</sub> H <sup>o</sup> /kJ mol <sup>-1</sup>	326	473	515	397	281	416	425	430	339	126
Ionisation Enthalpy, Δ <sub>1</sub> H <sup>o</sup> /kJ mol <sup>-1</sup>										
Δ <sub>1</sub> H <sup>o</sup>	I	631	656	650	653	717	762	758	736	745
	II	1235	1309	1414	1592	1509	1561	1644	1752	1958
	III	2393	2657	2833	2990	3260	2962	3243	3402	3556

**ELECTRON AFFINITY & ELECTRON GAIN ENTHALPY (EGE) :**

**Electron Affinity :** Amount of energy released when an electron is added to an isolated gaseous atom.

**Units :** k J mol<sup>-1</sup>, k Cal mol<sup>-1</sup> and eV per atom.

Addition of electron results in release of energy in most of the cases but for addition of second electron energy is always required. The sum of EA<sub>1</sub> & EA<sub>2</sub> is +ve (energy required)

$$E A \propto \frac{1}{\text{atomic size}} \propto Z_{\text{eff}} \quad (\text{Cl has the highest E.A.})$$

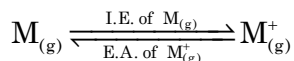
**Electron gain Enthalpy (EGE) :** When expressed in terms of enthalpy change ( $\Delta H_{eg}$ ) then it is termed as EGE Remember that  $\Delta H = -ve$  for exothermic change.

For  $EA_1$ , energy is released  $\therefore \Delta H_{eg1} = -ve$  (Not always)

For  $EA_2, EA_3$  .....energy is required  $\therefore \Delta H_{eg2} = +ve$  (always)

In general  $EA_1 + EA_2$ , energy is required.  $\therefore (\Delta H_{eg1} + \Delta H_{eg2}) > 0$

**Note :**  $\Delta H_{e.g.} \approx -EA$



Ionisation energy of element is equal to electron affinity of its cation.

**FACTORS AFFECTING ELECTRON AFFINITY :**

- (1) **Atomic size :** Varies inversely
- (2) **Nuclear charge :** Varies directly
- (3) For stable electronic configuration i.e. half filled and fully filled shells EA decreases.

**General Trend :** Along a period, electron affinity increases [with a few exceptions] as  $Z_{eff} \uparrow$ .

Along a group, electron affinity decreases after 3<sup>rd</sup> period. Between 2<sup>nd</sup> and 3<sup>rd</sup> period in p block electron affinity of 2<sup>nd</sup> period is lesser.

**Exception :**

- (1) A fully filled and half filled configuration have low values of EA or even sometimes energy is required rather than getting released.
- (2) 2<sup>nd</sup> period has lower value than 3<sup>rd</sup> owing to repulsion between electrons in small sized 2<sup>nd</sup> period elements.

**Electron affinity of the main-group elements (in electron volts)**

1							18
<b>H</b>							<b>He</b>
+0.754	2	13	14	15	16	17	-0.5
<b>Li</b>	<b>Be</b>	<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>	<b>Ne</b>
+0.618	$\leq 0$	$\leq +0.277$	+1.263	-0.07	+1.461	+3.399	-1.2
<b>Na</b>	<b>Mg</b>	<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>	<b>Ar</b>
+0.548	$\leq 0$	+0.441	+1.385	+0.747	+2.077	+3.617	-1.0
<b>K</b>	<b>Ca</b>	<b>Ga</b>	<b>Ge</b>	<b>As</b>	<b>Se</b>	<b>Br</b>	<b>Kr</b>
+0.502	-	+0.03	+1.2	+0.81	+2.021	+3.365	-1.0
<b>Rb</b>	<b>Sr</b>	<b>In</b>	<b>Sn</b>	<b>Sb</b>	<b>Te</b>	<b>I</b>	<b>Xe</b>
+0.486	-	+0.3	+1.2	+1.07	+1.971	+3.059	-0.8

**ELECTRO NEGATIVITY :****Property of an atom in a molecule**

F has highest electronegativity in the periodic table.

Decreasing order  $\rightarrow$  F > O > Cl  $\approx$  N > Br > S  $\approx$  C > I > H.

**Pauling Scale :**  $|X_A - X_B| = 0.208\sqrt{\Delta_{A-B}}$   $\Delta$  in kcal/mol

$|X_A - X_B| = 0.102\sqrt{\Delta_{A-B}}$   $\Delta$  in kJ/mol

$\Delta_{A-B} = E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2}$

Where,  $E_{A-B}$  = Bond energy of A-B;  $E_{A-A}$  = Bond energy of A-A;  $E_{B-B}$  = Bond energy of B-B

**Mulliken's Scale :**  $X_M = \frac{IP + EA}{2}$  (IP & EA are expressed in eV)

Mulliken's values of EN are about 2.8 times higher than values on Pauling's scale.

i.e.  $X_P = \frac{X_M}{2.8}$

**Allred-Rochow's Scale :**  $X_{AR} = \frac{0.359Z_{eff}}{r^2}$  ;  $X_P = X_{AR} + 0.744$

$r$  = covalent radius of atom (in Å)

$Z_{eff}$  = Effective nuclear charge on periphery


**FACTORS AFFECTING ELECTRO NEGATIVITY :**

- (1) **Nuclear attraction :** Varies directly
- (2) **Atomic radius :** Varies inversely
- (3) **Charge on ions :** More positive charge, more electronegativity and more -ve charge, less electronegativity.
- (4) **Hybridisation :** To be discussed later in chemical bonding chapter.

**General Trends :** Along a period, electronegativity increases

Along a group, electronegativity decreases

**Exceptions :** Not Noteworthy.

 **Note:** Electronegativity of F > Cl but Electron affinity of Cl > F

**Electronegativity of Some Elements (on Pauling's Scale)**

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9					

In Pauling's Scale, elements having almost same electronegativity are-

C  $\approx$  S  $\approx$  I  $\approx$  2.5

N = Cl = 3.0

P = H = 2.1

Cs = Fr = 0.7

Be = Al = 1.5

**PROPERTIES DEPENDENT ON ELECTRO NEGATIVITY :**

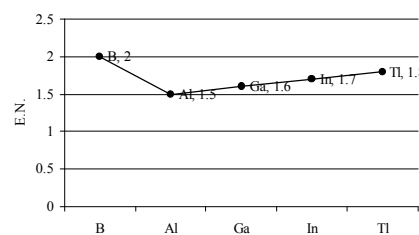
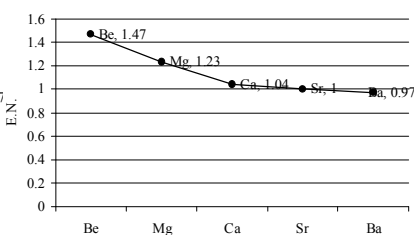
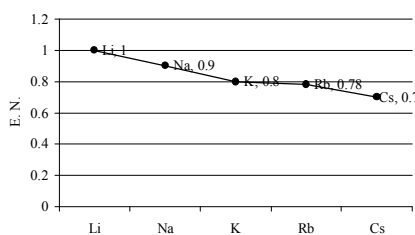
- (1) % ionic character
- (2) Strength of bond
- (3) Bond Length
- (4) Nature of hydrides
- (5) Nature of hydroxide.

*Graphical representation of Electronegativity :*

**ALKALI METALS**

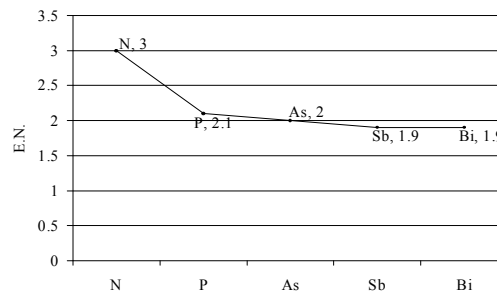
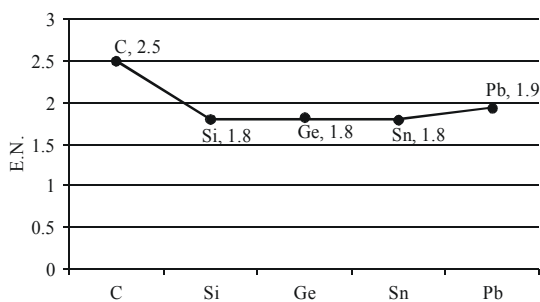
**ALKALINE EARTH METALS**

**BORON FAMILY**



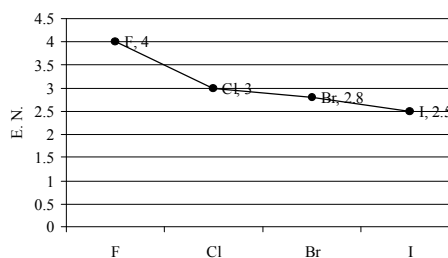
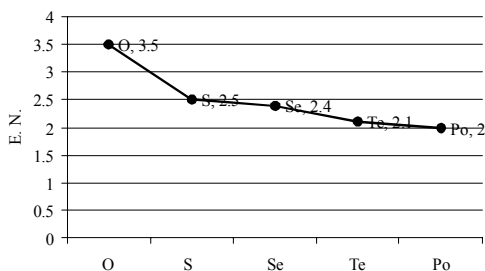
**CARBON FAMILY**

**NITROGEN FAMILY (PNICOGENS)**



**CHALCOGENS**

**HALOGENS**



**LATTICE ENERGY :**

The amount of energy released during the formation of 1 mole crystal lattice from constituent gaseous ions.



OR

The lattice energy of an ionic compound is the energy required to separate 1 mole of solid ionic substance completely into gaseous ions.



Lattice energies are large and positive because of attraction between positive and negative ions. The potential energy of two interacting charged particles is given by:

$$E = K \frac{Q_1 Q_2}{r} \quad \text{where, } r = r^+ + r^- ; r^+ \rightarrow \text{radius of cation, } r^- \rightarrow \text{radius of anion}$$

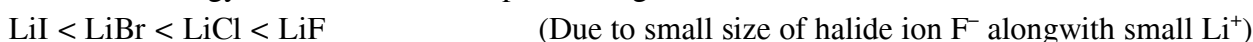
Where  $Q_1$  and  $Q_2$  are the charge on the particles in coulombs, and  $r$  is the distance between their centres in meters. The constant  $K$  has the value  $9.0 \times 10^9 \text{ J - m/C}^2$ .

**Factors affecting lattice energy :**

- The lattice energy increases as the charge on the ions increases and as their radii decreases.
- The magnitude of lattice energies however depends primarily on the ionic charges because ionic radii do not vary over a wide range.

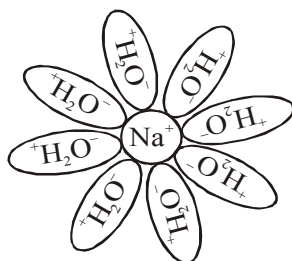
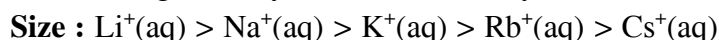
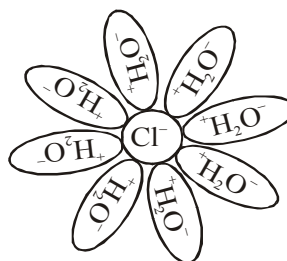
**For Example :**

The lattice energy order for some compounds is given below.

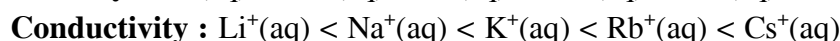
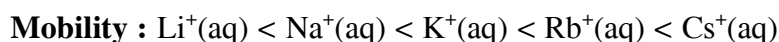
**HYDRATION ENERGY :**

It is the energy released when 1 mol of gaseous ions are hydrated in water. It is directly proportional to nuclear charge and inversely proportional to size. It always decreases down the group.

- As the charge density of ion increases hydrated size (or aqueous radius) increases.

Hydration of  $\text{Na}^+$ Hydration of  $\text{Cl}^-$ 

- As the hydrated size of ion increases ionic mobility decreases, which thus, decreases conductivity of ions.



- Hydration energy also affects the solubility of ionic compounds. If hydration energy is greater than lattice energy then ionic compound will be soluble in water. More is the hydration energy, greater is the solubility, whereas, if lattice energy decreases, solubility of ionic compound increases.

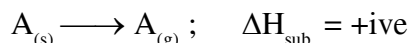


**BORN-HABER CYCLE :**

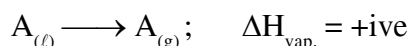
The Born-Haber cycle is an approach to analyze reaction energies.

**Various energy terms**

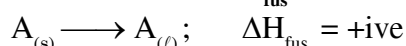
⇒ **Heat of sublimation ( $\Delta H_{\text{sub.}}$ ) :** It is heat required to change one mole of a substance from solid state to gaseous state.



⇒ **Heat of vaporisation ( $\Delta H_{\text{vap.}}$ ) :** It is heat required to change one mole of liquid substance into gas.

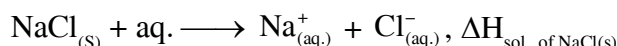


⇒ **Heat of fusion ( $\Delta H_{\text{fus}}$ ) :** It is heat required to change one mole of solid substance into liquid.



⇒ **Heat of atomization ( $\Delta H_{\text{atm}}$ ) :** It is change in enthalpy when one mole of a substance is converted into its constituent gaseous atoms.

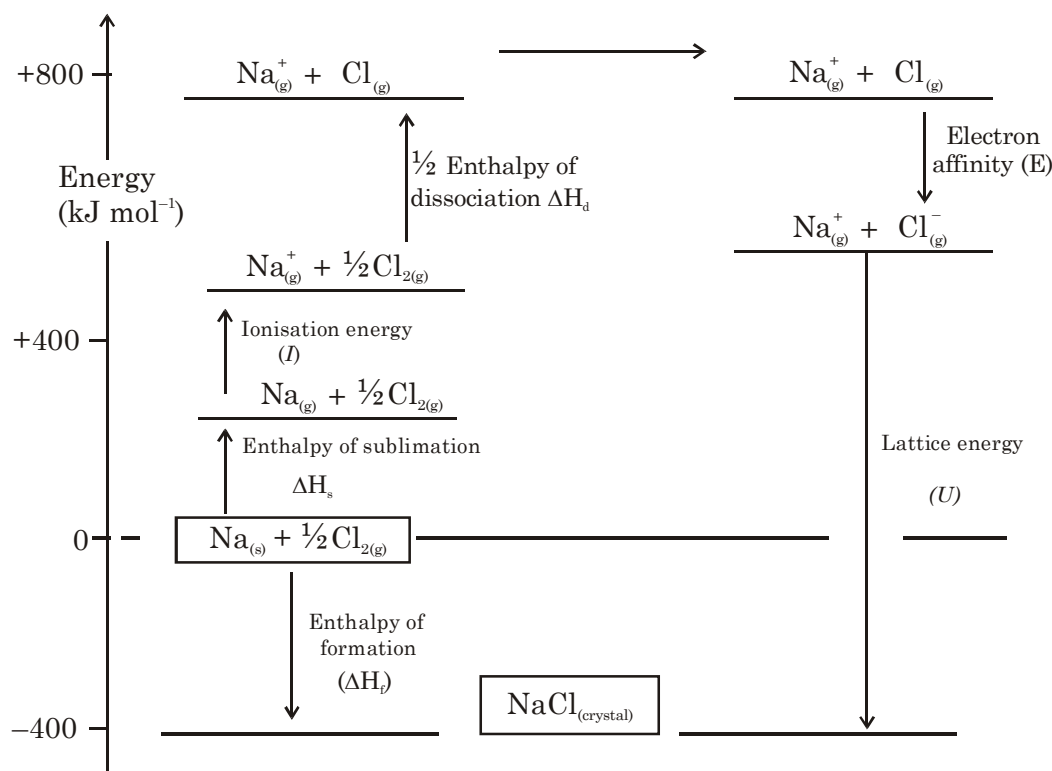
⇒ **Heat of solution ( $\Delta H_{\text{sol.}}$ ) :** It is the change in enthalpy when one mole of a solute is dissolved in excess amount of solvent.



⇒ **Bond dissociation energy (B.D.E.) and Bond Energy (B.E.) :** It is the amount of heat require to break one mole of bond between two atoms of a gaseous molecule into gaseous atoms.

⇒ **Heat of formation ( $\Delta H_f$ ) :** It is the change in enthalpy when one mole of substance is formed from it's element in standard state.

**Born -Haber cycle for  $\text{NaCl}_{(s)}$ .**



$$\Delta H_f = \Delta H_s + I + \frac{1}{2}\Delta H_d + E + U$$

Examples :  $\text{MgO}$ ,  $\text{AlF}_3$

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**MISCELLANEOUS CHEMICAL PROPERTIES :**


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**1. Periodicity of hydra acids :**

- (a) Acidic character of hydra acid increases from left to right in a period.
- (b) Acidic character of hydra acid increases from top to bottom in a group.

**2. Periodicity of oxy acids :**

- (a) Acidic character of oxy acid increases from left to right in a period.
- (b) Acidic character of oxy acid decreases from top to bottom in a group.

**3. Periodicity of nature of oxide :**

- (a) On moving from left to right in a period acidic nature of oxide generally increases.  
e.g.  $\text{CO}_2 < \text{P}_2\text{O}_5 < \text{SO}_3 < \text{Cl}_2\text{O}_7$
- (b) On moving from top to bottom in a group acidic nature of oxide generally decreases.

**4. General trends**

- (a) **Hydration energy** decreases along a group.
- (b) **Lattice energy** decreases along a group.

**:: Some points to Remember ::**

(without considering radioactive elements)

1. Second most electronegative element is Oxygen
2. Hydrogen is the lightest element and Lithium is lightest metal.
3. Helium has the highest value of I.P.
4. In periodic table metalloids are only in p-block.
5. Total gaseous elements are 11 (He, Ne, Ar, Kr, Xe, Rn,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{F}_2$ )
6. Liquid metal at room temperature is – Hg.
7. Diamond is hardest natural substance.
8. Halogens have highest electron affinity and amongst them, Cl has the highest amongst them.
9. The largest cation of the periodic table =  $\text{Cs}^+$ .
10. The smallest cation of the periodic table =  $\text{H}^+$ .
11. The smallest anion of the periodic table =  $\text{F}^-$ .
12. The biggest element of periodic table = Fr.
13. The smallest element of periodic table = H.
14. Br is liquid non-metal element at room temperature.
15. Osmium is the heaviest element known.
16. Fluorine is the most electronegative element.

## EXERCISE # O-1

## Periodic Table

1. Which is not anomalous pair of elements in the Mendeleev's periodic table:-  
(A) Ar and K            (B) Co and Ni            (C) Te and I            (D) Al and Si  
**PT0001**
2. Representative elements belong to :  
(A) s-and p-block            (B) d-block            (C) d- and f-block            (D) f-block  
**PT0002**
3. True statement is :-  
(A) All the transuranic elements are synthetic elements  
(B) Elements of third period are called transition elements  
(C) Element of  $[\text{Ar}] 3d^{10}4s^2$  configuration is placed in IIA group  
(D) Electronic configuration of elements of a group is same  
**PT0003**
4. Which of the following match is correct :-  
(A) Last natural element – Uub  
(B) General electronic configuration of IA group –  $ns^2$   
(C) Inert gas elements lies between 2<sup>nd</sup> – 6<sup>th</sup> period  
(D) Typical elements – 3<sup>rd</sup> period elements  
**PT0004**
5. The electronic configuration of elements X and Z are  $1s^2 2s^2 2p^6 3s^2 3p^5$  and  $1s^2 2s^2 2p^5$  respectively. What is the position of element X with respect to position of Z in the periodic table -  
(A) Just below element Z            (B) Just above Z  
(C) Left to the Z            (D) right to the Z  
**PT0005**
6. Which of the following is not a Dobereiner triad :  
(A) H, F, Cl            (B) N, O, F            (C) P, As, Sb            (D) S, Se, Te  
**PT0006**
7. Select the incorrect statement for Lotser Meyer's curve :  
(A) Curve is plotted between atomic weight and atomic volume  
(B) Alkali metals occupy maxima of curve  
(C) Halogens occupy descending portions of the curve  
(D) Transition metals occupy bottom portions of the curve  
**PT0007**

*Atomic & Ionic Radii*

8. The size of the following species increases in the order:  
 (A)  $\text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$  (B)  $\text{F}^- < \text{Na}^+ < \text{Mg}^{2+}$   
 (C)  $\text{Mg}^{2+} < \text{F}^- < \text{Na}^+$  (D)  $\text{Na}^+ < \text{F}^- < \text{Mg}^{2+}$  **PT0008**
9. Highest size will be of  
 (A)  $\text{Br}^-$  (B)  $\text{I}$  (C)  $\text{I}^-$  (D)  $\text{I}^+$  **PT0009**
10. Element Cu has two oxidation states  $\text{Cu}^{+1}$  &  $\text{Cu}^{+2}$ . the right order of radii of these ions.  
 (A)  $\text{Cu}^{+1} > \text{Cu}^{+2}$  (B)  $\text{Cu}^{+2} > \text{Cu}^{+1}$  (C)  $\text{Cu}^{+1} = \text{Cu}^{+2}$  (D)  $\text{Cu}^{+2} \geq \text{Cu}^{+1}$  **PT0010**
11. The correct order of increasing atomic size of element N, F, Si & P.  
 (A)  $\text{N} < \text{F} < \text{Si} < \text{P}$  (B)  $\text{F} > \text{N} < \text{P} < \text{Si}$  (C)  $\text{F} < \text{N} < \text{P} < \text{Si}$  (D)  $\text{F} < \text{N} < \text{Si} < \text{P}$  **PT0011**
12. The correct order of atomic or ionic size  
 (A)  $\text{N} < \text{Li} < \text{B}$  (B)  $\text{Cl} < \text{Mg} < \text{Ca}$  (C)  $\text{Ca}^{+2} < \text{S}^{-2} < \text{Cl}^-$  (D)  $\text{Na}^+ < \text{Mg}^{+2} < \text{Cl}^-$  **PT0012**
13. In isoelectronic series largest difference between size is observed in  $\text{N}^{3-}$ ,  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  :  
 (A)  $\text{N}^{3-}$ ,  $\text{Mg}^{2+}$  (B)  $\text{N}^{3-}$ ,  $\text{O}^{2-}$  (C)  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  (D)  $\text{F}^-$ ,  $\text{Na}^+$  **PT0013**
14. Mg,  $\text{Mg}^{2+}$ , Al and  $\text{Al}^{3+}$  are arranged in decreasing order of size 1 > 2 > 3 > 4. Species which are present at 1 and 4 position respectively are :  
 (A) Al,  $\text{Mg}^{2+}$  (B) Mg,  $\text{Al}^{3+}$  (C)  $\text{Mg}^{2+}$ , Al (D)  $\text{Al}^{3+}$ , Mg **PT0014**

*Ionization Energy or Potential*

15. In which of the following electronic configuration, ionisation energy will be maximum in  
 (A)  $[\text{Ne}] 3s^2 3p^1$  (B)  $[\text{Ne}] 3s^2 3p^2$  (C)  $[\text{Ne}] 3s^2 3p^3$  (D)  $[\text{Ar}] 3d^{10} 4s^2 4p^3$  **PT0015**
16. The correct order of second ionisation potential of C, N, O and F is:  
 (A)  $\text{C} > \text{N} > \text{O} > \text{F}$  (B)  $\text{O} > \text{N} > \text{F} > \text{C}$  (C)  $\text{O} > \text{F} > \text{N} > \text{C}$  (D)  $\text{F} > \text{O} > \text{N} > \text{C}$  **PT0016**
17. The ionization energy will be maximum for which process?  
 (A)  $\text{Ba} \rightarrow \text{Ba}^+$  (B)  $\text{Be} \rightarrow \text{Be}^+$  (C)  $\text{Cs} \rightarrow \text{Cs}^+$  (D)  $\text{Li} \rightarrow \text{Li}^+$  **PT0017**
18. Amongst the following, the incorrect statement is  
 (A)  $\text{IE}_1(\text{Al}) < \text{IE}_1(\text{Mg})$  (B)  $\text{IE}_1(\text{Na}) < \text{IE}_1(\text{Mg})$   
 (C)  $\text{IE}_2(\text{Mg}) > \text{IE}_2(\text{Na})$  (D)  $\text{IE}_3(\text{Mg}) > \text{IE}_3(\text{Al})$  **PT0018**

19. Decreasing ionization potential for K, Ca & Ba is  
 (A) Ba > K > Ca (B) Ca > Ba > K  
 (C) K > Ba > Ca (D) K > Ca > Ba

**PT0019**

20. Alkaline earth metals always form dipositive ions due to  
 (A)  $IE_2 - IE_1 > 10 \text{ eV}$  (B)  $IE_2 - IE_1 = 17 \text{ eV}$   
 (C)  $IE_2 - IE_1 < 10 \text{ eV}$  (D) None of these

**PT0020**

21. The correct order of second I.P.  
 (A) Na < Mg > Al < Si (B) Na > Mg < Al > Si  
 (C) Na > Mg > Al < Si (D) Na > Mg > Al > Si

**PT0021**

*Electron affinity or Electron Gain Enthalpy*

22. The process requires absorption of energy is  
 (A)  $F \rightarrow F^-$  (B)  $Cl \rightarrow Cl^-$  (C)  $O^- \rightarrow O^{2-}$  (D)  $H \rightarrow H^-$

**PT0022**

23. Of the following elements, which possesses the highest electron affinity?  
 (A) As (B) O (C) S (D) Se

**PT0023**

24. Electron affinities of O, F, S and Cl are in the order.  
 (A) O < S < Cl < F (B) O < S < F < Cl  
 (C) S < O < Cl < F (D) S < O < F < Cl

**PT0024**

25. Increasing order of Electron affinity for following configuration.  
 (a)  $1s^2, 2s^2 2p^2$  (b)  $1s^2, 2s^2 2p^4$   
 (c)  $1s^2, 2s^2 2p^6 3s^2 3p^4$  (d)  $1s^2, 2s^2 2p^6, 3s^2 3p^3$   
 (A) d < a < b < c (B) d < a < c < b (C) a < b < c < d (D) a < b < d < c

**PT0025**

26. Highest electron affinity is shown by  
 (A)  $F^-$  (B)  $Cl^-$  (C)  $Li^+$  (D)  $Na^+$

**PT0026**

27. Which of the following statements is not true?  
 (A) F atom can hold additional electron more tightly than Cl atom  
 (B) Cl atom can hold additional electron more tightly than F atom  
 (C) The incoming electron encounters greater repulsion for F atom than for Cl atom  
 (D) It is easier to remove an electron from  $F^-$  than  $Cl^-$ .

**PT0027**

*Electronegativity*

28. The outermost electronic configuration of most electronegative element amongst the following is :  
 (A)  $ns^2 np^3$  (B)  $ns^2 np^4$  (C)  $ns^2 np^5$  (D)  $ns^2 np^6$  **PT0028**
29. In the following, which is the correct representation ?  
 (A)  $\overset{\delta+}{C}-\overset{\delta-}{F}$  (B)  $\overset{\delta+}{C}-\overset{\delta+}{Cl}$  (C)  $\overset{\delta+}{F}-\overset{\delta-}{Cl}$  (D)  $\overset{\delta-}{O}-\overset{\delta+}{F}$  **PT0029**
30. On the Pauling's electronegativity scale, which element is next to F .  
 (A) Cl (B) O (C) Br (D) Ne **PT0030**
31. Which one is not correct order of electronegativity.  
 (A)  $F > Cl > Br > I$  (B)  $Si > Al > Mg > Na$   
 (C)  $Cl > S > P > Si$  (D) None of these **PT0031**
32. The increasing order of acidic nature of  $Li_2O$ ,  $BeO$ ,  $B_2O_3$   
 (A)  $Li_2O > BeO < B_2O_3$  (B)  $Li_2O < BeO < B_2O_3$   
 (C)  $Li_2O < BeO > B_2O_3$  (D)  $Li_2O > BeO > B_2O_3$  **PT0032**
33. The lowest electronegativity of the element from the following atomic number is.  
 (A) 37 (B) 55 (C) 9 (D) 35 **PT0033**

*Miscellaneous*

34. Which of the following does not reflect the periodicity of element  
 (A) Bonding behaviour (B) Electronegativity  
 (C) Ionisation potential (D) Neutron/ Proton ratio **PT0034**
35. Among the following, which species is/are paramagnetic ?  
 (i)  $Sr^{2+}$  (ii)  $Fe^{3+}$  (iii)  $Co^{2+}$  (iv)  $S^{2-}$  (v)  $Pb^{2+}$   
 (A) i, iv, v (B) i, ii, iii (C) ii, iii (D) iv, v **PT0035**
36. Choose the s-block element from the following:  
 (A)  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$  (B)  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$   
 (C)  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$  (D) all of the above **PT0036**
37. False statement for periodic classification of elements is  
 (A) The properties of the elements are periodic function of their atomic numbers.  
 (B) No. of non-metallic elements is less than the no. of metallic elements.  
 (C) First ionization energy of elements does not increase regularly with the increase in atomic number in a period.  
 (D) d-subshell is filled by final electron with increasing atomic number of inner transition elements. **PT0037**

38. Which of the following order is incorrect against the property indicated :
- (A)  $Mg < Ar < Na$  (2nd I.E.) (B)  $Be < F < Cl$  ( $|\Delta H_{eg}|$ )  
 (C)  $Rb < Na < K > Ca$  (atomic radius) (D)  $P < S < N$  (electronegativity) **PT0038**
39. If each orbital can hold a maximum of three electrons, the number of elements in 9<sup>th</sup> period of periodic table (long form) will be
- (A) 48 (B) 162 (C) 50 (D) 75 **PT0039**
40. Which of the following element has highest metallic character .
- | Element | IP    |
|---------|-------|
| (A) P   | 17 eV |
| (B) Q   | 2 eV  |
| (C) R   | 10 eV |
| (D) S   | 13 eV |
- PT0040**
41. The electronic configuration of an element is  $1s^2 2s^2 2p^6 3s^2 3p^4$ . The atomic number and the group number of the element 'X' which is just below the above element in the periodic table are respectively.
- (A) 24 & 6 (B) 24 & 15 (C) 34 & 16 (D) 34 & 8 **PT0041**
42. The number of d- electrons in  $Mn^{2+}$  is equal to that of
- (A) p-electrons in N (B) s-electrons in Na  
 (C) d-electrons in  $Fe^{+2}$  (D) p-electrons in  $O^{-2}$  **PT0042**
43. Which of the following has the maximum number of unpaired electrons
- (A)  $Mg^{2+}$  (B)  $Ti^{3+}$  (C)  $V^{3+}$  (D)  $Fe^{2+}$  **PT0043**
44. EN of the element (A) is  $E_1$  and IP is  $E_2$ . Hence EA will be according to mulliken
- (A)  $2E_1 - E_2$  (B)  $E_1 - E_2$  (C)  $E_1 - 2E_2$  (D)  $(E_1 + E_2)/2$  **PT0044**
45. Moving from right to left in a periodic table, the atomic size is:
- (A) Increased (B) Decreased (C) Remains constant (D) None of these **PT0045**
46. One element has atomic weight 39. Its electronic configuration is  $1s^2, 2s^2 2p^6, 3s^2 3p^6 4s^1$ . The true statement for that element is:
- (A) High value of IE (B) Transition element (C) Isotone with  ${}_{18}Ar^{38}$  (D) None **PT0046**
47. The number of paired electrons in oxygen atom is:
- (A) 6 (B) 16 (C) 8 (D) 32 **PT0047**
48. The decreasing size of  $K^+, Ca^{2+}, Cl^-$  &  $S^{2-}$  follows the order:
- (A)  $K^+ > Ca^{+2} > S^{-2} > Cl^-$  (B)  $K^+ > Ca^{+2} > Cl^- > S^{-2}$   
 (C)  $Ca^{+2} > K^+ > Cl^- > S^{-2}$  (D)  $S^{-2} > Cl^- > K^+ > Ca^{+2}$  **PT0048**

**EXERCISE : O-2***Atomic & Ionic Radius*

1. Select correct order of size :

- (A)  $Ti^{2+} < Ti < Zr$       (B)  $Ti^{2+} < Ti < Hf$       (C)  $Zr^{2+} < Zr \approx Hf$       (D)  $Hf^{2+} < Hf \approx Zr$

PT0049

2. Which of the following orders of atomic / Ionic radius is correct ?

- (A)  $B < Al \approx Ga$       (B)  $Sc > Cu < Zn$       (C)  $C < O < N$       (D)  $Al^{+3} < Al^{+2} < Al^{+}$

PT0050

*Electron Affinity*

3. Which of the following is correct order of EA.

- (A)  $N < C < O < F$       (B)  $F > Cl > Br > I$       (C)  $Cl > F > Br > I$       (D)  $C < N < O < F$

PT0051

4. The electron affinity of the members of oxygen family of the periodic table, follows the sequence

- (A)  $O > S > Se$       (B)  $S > O < Se$       (C)  $O < S > Se$       (D)  $Se > O > S$

PT0052

*Ionisation Energy*

5. Considering the following ionisation steps :



Select the correct statements :

- (A)  $IE_1$  of  $A(g)$  is 100 eV      (B)  $IE_1$  of  $A^{+}(g)$  is 150 eV  
(C)  $IE_2$  of  $A(g)$  is 150 eV      (D)  $IE_2$  of  $A(g)$  is 250 eV

PT0053

6. Which of the following are correct ?

- (A)  $IE_2(Mg) < IE_2(Na)$       (B)  $EA(N) < EA(P)$   
(C) Atomic size  $Mg^{+2} >$  Atomic size  $(Li^{+})$       (D)  $IP$  of  $Na < Mg < Al$

PT0054

*Electronegativity*

7. Amongst the following statements, which is / are correct?

- (A) Electronegativity of sulphur is greater than that of oxygen.  
(B) Electron affinity of oxygen is smaller than that of sulphur.  
(C) Electron gain enthalpy of fluorine is most negative  
(D) Electron gain enthalpy of chlorine is most negative

PT0055

8. An element 'E' have  $IE = x$  eV/atom and  $EA = y$  eV / atom and EN on Pauling scale is 1.2. Find EN of 'E' on Mullikan scale :

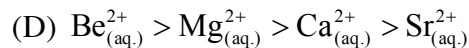
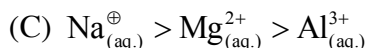
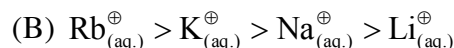
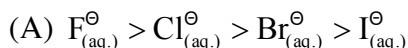
- (A)  $\frac{x+y}{2}$       (B)  $1.2 \times 2.8$       (C)  $\frac{x+y}{2.8} - 1.2$       (D)  $1.2 - \frac{x+y}{2}$

PT0056



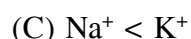
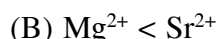
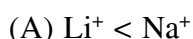
*Hydration Energy*

9. Choose the INCORRECT order of hydrated size of the ions -



PT0057

10. Find the correct ionic mobility order in aqueous solution from the following options-



PT0058

*Miscellaneous*

11. Select the correct statement(s).

(A) The value of electron gain enthalpy of an element can be -ve or +ve.

(B) In the periodic table, metallic character of the elements increases down the group and decreases across the period

(C) The  $Cl^-$  &  $S^{2-}$  are isoelectronic species but first one is not smaller in size than the second

(D) Ionization enthalpy of an atom is equal to electron gain enthalpy of cation

PT0059

12. In halogens, which of the following properties increase from iodine to fluoroine

(A) Ionisation energy

(B) Electronegativity

(C) Bond length

(D) Electron affinity

PT0060

13. In which of the following set of elements 1<sup>st</sup> element is more metallic than second.

(A) Ba, Ca

(B) Sb, Sn

(C) Ge, S

(D) Na, F

PT0061

14. Which of the following order(s) is / are **CORRECT** :

(A)  $Li < Be < B < C$  ( $IE_1$ )

(B)  $HF < HCl < HBr < HI$  (Bond length)

(C)  $Na_2O < MgO < Al_2O_3 < SiO_2 < P_2O_5$  (Acidic)

(D)  $Li^+(g) < Na^+(g) < K^+(g) < Cs^+(g)$  (Ionic radius)

PT0062

15. Which of the following order is correct :

(A)  $P < Si < Be < Mg < Na$  (Metallic character)

(B)  $Mg^{2+} < Na^+ < F^- < O^{2-}$  (Ionic radius)

(C)  $Li < B < Be < C < N < O$  (2<sup>nd</sup> ionization energy)

(D)  $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$  (Ionic mobility)

PT0063

16. The ionic compound  $A^+ B^-$  is formed easily when the
- (A) electron affinity of B is high                      (B) ionization energy of A is low  
(C) lattice energy of AB is high                      (D) lattice energy of AB is low

PT0064

17. Which of the following is/are correct?
- (A) For  $A(g) + e^- \longrightarrow A^-(g)$   $\Delta H$  may be negative  
(B) For  $A^-(g) + e^- \longrightarrow A^{2-}(g)$   $\Delta H$  may be negative  
(C) For  $A^-(g) + e^- \longrightarrow A^{2-}(g)$   $\Delta H$  must be positive  
(D) For  $Ne(g) + e^- \longrightarrow Ne^-(g)$   $\Delta H$  may be zero

PT0065

## EXERCISE # S-1

- Find out the atomic number of element whose IUPAC name is Unnilpentium.  
*Fill your answer as sum of digits (excluding decimal places) till you get the single digit answer.*  
PT0066
- Select total number of acidic compounds out of given below.  
CsOH, OC(OH)<sub>2</sub>, SO<sub>2</sub>(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>, BrOH, NaOH, O<sub>2</sub>NOH  
PT0067
- Total number of enthalpy(s) (out of given eight) of A(g) which is/are **not** associated with conversion of  
 $A_{(g)}^- \longrightarrow A_{(g)}^{+4}$ :  
IE<sub>1</sub>, IE<sub>2</sub>, IE<sub>3</sub>, IE<sub>4</sub>, IE<sub>5</sub>, IE<sub>6</sub>, EGE<sub>1</sub>, EGE<sub>2</sub>  
(IE = ionization energy, EGE = electron gain enthalpy)  
PT0068
- Write the number of pairs in which size of first element or ion is higher as compared to II<sup>nd</sup> out of following eight pairs.  
(O,S), (He, Ne), (Kr, Ne), (Na, Na<sup>+</sup>), (Cl, Cl<sup>-</sup>), (I<sup>-</sup>, Cl<sup>-</sup>), (Li, Na), (Li<sup>+</sup>, Na<sup>+</sup>)  
PT0069
- Total number of elements which have less IE<sub>1</sub> than that of 'N'.  
Be, B, C, F, P, He  
PT0070
- Size of H<sup>-</sup> is smaller than how many elements among these ?  
H, Li, Be, B, C, N, O, F, F<sup>-</sup>  
PT0071
- How many orders are **CORRECT**  
(a) Acidic strength  $\Rightarrow$  ClOH < BrOH < IOH  
(b) Basic strength  $\Rightarrow$  MgO < CaO < SrO < BeO  
(c) Electronegativity  $\Rightarrow$  I < Br < N < O < F  
(d) Electron affinity  $\Rightarrow$  Mg < Na < Si < S < Cl  
(e) % Ionic character  $\Rightarrow$  NaF < KF < RbF  
PT0072
- \_\_\_\_\_ is higher for fluorine as compared to chlorine.  
Find the number of properties given below to fill the blank space to make a correct statement.  
Atomic mass, Covalent radius, Ionic radius (X<sup>-</sup>), Ionization energy, Electron affinity, Electronegativity, Hydration energy of uninegative ion (X<sup>-</sup>),  
PT0073

9. Upto argon find the number of elements which have lower  $IE_1$  as compared to He. **PT0074**
10. The number of pairs, in which EA of the second element is more than that of the first element is :  
[O, S], [C, N], [O, N], [N, P], [Cl<sup>-</sup>, F<sup>-</sup>], [K<sup>+</sup>, Na<sup>+</sup>]  
**PT0075**
11. For an element the successive ionisation energy values (in eV/atom), are given below.  
14.534, 29.601, 47.448, 77.472, 97.888, 552.057, 667.029  
Find the number of valence shell electrons in that element. **PT0076**
- Subjective :*
12. Calculate E.N. of chlorine atom on Pauling scale if I.E. of Cl<sup>-</sup> is 4eV & of E.A. of Cl<sup>-</sup> is + 13.0 eV. **PT0077**
13. Increasing order of ionic size :  
N<sup>3-</sup>, Na<sup>+</sup>, F<sup>-</sup>, O<sup>2-</sup>, Mg<sup>2+</sup>  
**PT0078**

## EXERCISE # S-2

## Paragraph for Questions 1 to 2

First electron gain enthalpy (in  $\frac{\text{kJ}}{\text{mol}}$ ) of few elements are given below :

Elements	$\Delta H_{\text{eg}}$
I	-60
II	-45
III	-328
IV	-295
V	+48

Answer the following questions on the basis of above data:

- Which element may be an inert gas  
(A) I (B) III (C) IV (D) V
- Which element is most non-metallic among all the elements -  
(A) I (B) II (C) III (D) IV

PT0079

PT0079

## Paragraph for Questions 3 to 4

The  $IE_1$  and the  $IE_2$  in KJ/mol of a few elements designated by U, V, W, X are shown below.

Atom	$IE_1$	$IE_2$
U	2464	6110
V	610	7542
W	928	1810
X	1588	3410

Based on the above information answer the following question :-

- Which of the elements represent a noble gas.  
(A) U (B) V (C) W (D) X
- Which of the following element belongs to group 1 (IA).  
(A) U (B) V (C) W (D) X

PT0080

PT0080

## Paragraph for Question 5 to 7

Nature of bond can be predicted on the basis of electronegativity of bonded atoms, greater difference in electronegativity (X), more will be the polarity of bond, and polar bond are easily broken in polar solvent like water. For hydroxy acids  $X_O - X_A$  difference predict the nature of oxide formed by the element A.

$|X_O - X_A| > |X_O - X_H|$  then A-O-H show basic nature (NaOH)

$|X_O - X_A| < |X_O - X_H|$  then A-O-H show acidic nature (H-O-Cl)

With the help of EN values [ $EN_A = 1.8$ ,  $EN_B = 2.6$ ,  $EN_C = 1.6$ ,  $EN_D = 2.8$ ] answer the following questions for the compounds HAO, HBO, HCO, HDO.

- Compounds whose aqueous solution is acidic and order of their acidic strength  
(A) AOH, COH ; AOH < COH (B) HDO, HBO ; HDO > HBO  
(C) AOH, COH ; AOH > COH (D) HDO, HBO ; HDO < HBO

PT0081

6. Compounds whose aqueous solution is basic and order of their basic strength  
 (A) AOH, COH ; AOH < COH (B) HDO, HBO ; HDO > HBO  
 (C) AOH, COH ; AOH > COH (D) HDO, HBO ; HDO < HBO

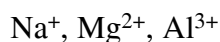
PT0081

7. Percentage ionic character of compound AB is  
 (A) 42.42% (B) 24.24% (C) 15.04% (D) None of these

PT0081

*Paragraph for Question 8 to 12*

All the simple salt dissolve in water, producing ions and consequently the solution conduct electricity. In this process water molecule surround both the cations and anions & release energy. This process is called hydration & energy released is called hydration energy & it depends on size of gaseous ions. Answer the following questions with respect to given cations.



8. Order of extent of hydration  
 (A)  $\text{Na}^+ = \text{Mg}^{2+} = \text{Al}^{3+}$  (B)  $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$   
 (C)  $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$  (D)  $\text{Al}^{3+} > \text{Mg}^{2+} < \text{Na}^+$

PT0082

9. Order of hydration energy  
 (A)  $\text{Na}^+ = \text{Mg}^{2+} = \text{Al}^{3+}$  (B)  $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$   
 (C)  $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$  (D)  $\text{Al}^{3+} > \text{Mg}^{2+} < \text{Na}^+$

PT0082

10. Order of size of hydrated ion.  
 (A)  $\text{Na}^+ = \text{Mg}^{2+} = \text{Al}^{3+}$  (B)  $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$   
 (C)  $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$  (D)  $\text{Al}^{3+} > \text{Mg}^{2+} < \text{Na}^+$

PT0082

11. Order of ionic mobility  
 (A)  $\text{Na}^+ = \text{Mg}^{2+} = \text{Al}^{3+}$  (B)  $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$   
 (C)  $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$  (D)  $\text{Al}^{3+} > \text{Mg}^{2+} < \text{Na}^+$

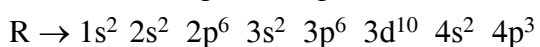
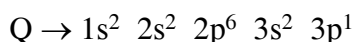
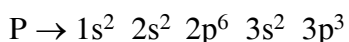
PT0082

12. Order of size of gaseous ions.  
 (A)  $\text{Na}^+ = \text{Mg}^{2+} = \text{Al}^{3+}$  (B)  $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$   
 (C)  $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$  (D)  $\text{Al}^{3+} > \text{Mg}^{2+} < \text{Na}^+$

PT0082

Paragraph for Question 13 to 14 are based on the following information.

Four elements P, Q, R & S have ground state electronic configuration as:



13. Comment which of the following option represent the correct order of true (T) & false (F) statement.

I size of P < size of Q

II size of R < size of S

III size of P < size of R (appreciable difference) IV size of Q < size of S (appreciable difference)

(A) TTTT

(B) TTTF

(C) FFTT

(D) TTFF

PT0083

14. Order of  $IE_1$  values among the following is

(A)  $P > R > S > Q$

(B)  $P < R < S < Q$

(C)  $R > S > P > Q$

(D)  $P > S > R > Q$

PT0083

Matching List

15. Column-I

Element

(P) Si

(Q) Sc

(R) Ga

(S) Tl

Column-II

Period and group number respectively

(1) 4, 3

(2) 3, 14

(3) 6, 13

(4) 4, 13

Code :

	P	Q	R	S
(A)	2	1	3	4
(B)	1	2	4	3
(C)	2	1	4	3
(D)	4	3	1	2

PT0084

Match the column

16. Match the column :

Column I

(A) Highest density

(B) Metallic character

(C) Lightest Metal

(D) Liquid at room temperature

Column II

(P) Lithium

(Q) Osmium

(R) Mercury

(S) Bromine

PT0085

17. If electrons are filled in the sub shells of an atom in the following order 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f..... then match the following element in List I with block in List II.

**List-I**

- (A) K(19)  
 (B) Fe(26)  
 (C) Ga(31)  
 (D) Sn(50)

**List-II**

- (P) s-Block  
 (Q) p-Block  
 (R) d-Block  
 (S) f-block

PT0086

18. Match the characteristics mentioned in List II with the process in List I.

**List I**

- (A)  $O(g) + e^- \rightarrow O^-(g)$   
 (B)  $O^-(g) + e^- \rightarrow O^{2-}(g)$   
 (C)  $Na^-(g) \rightarrow Na(g) + e^-$   
 (D)  $Mg^+(g) + e^- \rightarrow Mg(g)$

**List II**

- (P) Positive electron gain enthalpy  
 (Q) Negative electron gain enthalpy  
 (R) Exothermic  
 (S) Endothermic

PT0087

19. Match the column :

**Column I**

- (A) Cl  
 (B) F  
 (C) Cu  
 (D) He

**Column II**

- (P) Metal  
 (Q) Highest negative electron gain enthalpy  
 (R) Most Electronegative element  
 (S) Highest ionisation energy.

PT0088



## EXERCISE # JEE-MAIN

1. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I, having atomic number 9, 17, 35 and 53 respectively, is :- [AIIEEE-2011]

- (1)  $I > Br > Cl > F$  (2)  $F > Cl > Br > I$   
 (3)  $Cl > F > Br > I$  (4)  $Br > Cl > I > F$

PT0089

2. The increasing order of the ionic radii of the given isoelectronic species is :- [AIIEEE-2012]

- (1)  $K^+, S^{2-}, Ca^{2+}, Cl^-$  (2)  $Cl^-, Ca^{2+}, K^+, S^{2-}$   
 (3)  $S^{2-}, Cl^-, Ca^{2+}, K^+$  (4)  $Ca^{2+}, K^+, Cl^-, S^{2-}$

PT0090

3. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar ? [JEE-MAIN-2013]

- (1)  $Ca < S < Ba < Se < Ar$  (2)  $S < Se < Ca < Ba < Ar$   
 (3)  $Ba < Ca < Se < S < Ar$  (4)  $Ca < Ba < S < Se < Ar$

PT0091

4. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of  $Na^+$  will be :- [JEE-MAIN-2013]

- (1)  $-2.55$  eV (2)  $-5.1$  eV (3)  $-10.2$  eV (4)  $+2.55$  eV

PT0092

5. Electron gain enthalpy with negative sign of fluorine is less than that of chlorine due to :

[JEE-MAIN 2013 (On-Line)]

- (1) Smaller size of chlorine atom (2) Bigger size of 2p orbital of fluorine  
 (3) High ionization enthalpy of fluorine (4) Smaller size of fluorine atom

PT0093

6. Given [JEE-MAIN 2013 (On-Line)]

Reaction	Energy Change (in kJ)
$Li(s) \longrightarrow Li(g)$	161
$Li(g) \longrightarrow Li^+(g)$	520
$\frac{1}{2} F_2(g) \longrightarrow F(g)$	77
$F(g) + e^- \longrightarrow F^-(g)$	(Electron gain enthalpy)
$Li^+(g) + F^-(g) \longrightarrow LiF(s)$	-1047
$Li(s) + \frac{1}{2} F_2(g) \longrightarrow LiF(s)$	-617

Based on data provided, the value of electron gain enthalpy of fluorine would be :

- (1)  $-300$  kJ mol<sup>-1</sup> (2)  $-328$  kJ mol<sup>-1</sup> (3)  $-350$  kJ mol<sup>-1</sup> (4)  $-228$  kJ mol<sup>-1</sup>

PT0094

7. The order of increasing sizes of atomic radii among the elements O, S, Se and As is :  
[JEE-MAIN 2013 (On-Line)]
- (1) As < S < O < Se (2) O < S < As < Se  
(3) Se < S < As < O (4) O < S < Se < As
- PT0095
8. Which is the correct order of second ionization potential of C, N, O and F in the following ?  
[JEE-MAIN 2013 (On-Line)]
- (1) O > F > N > C (2) O > N > F > C  
(3) C > N > O > F (4) F > O > N > C
- PT0096
9. Which of the following series correctly represents relations between the elements from X to Y ?  
[JEE-MAIN 2014 (On-Line)]
- X  $\longrightarrow$  Y
- (1)  ${}_{18}\text{Ar} \rightarrow {}_{54}\text{Xe}$  Noble character increases  
(2)  ${}_{3}\text{Li} \rightarrow {}_{19}\text{K}$  Ionization enthalpy increases  
(3)  ${}_{6}\text{C} \rightarrow {}_{32}\text{Ge}$  Atomic radii increases  
(4)  ${}_{9}\text{F} \rightarrow {}_{35}\text{Br}$  Electron gain enthalpy with negative sign increases
- PT0097
10. The ionic radii (in Å) of  $\text{N}^{3-}$ ,  $\text{O}^{2-}$  and  $\text{F}^{-}$  are respectively :- [JEE-MAIN 2015 (Off-Line)]
- (1) 1.71, 1.40 and 1.36 (2) 1.71, 1.36 and 1.40  
(3) 1.36, 1.40 and 1.71 (4) 1.36, 1.71 and 1.40
- PT0098
11. In the long form of the periodic table, the valence shell electronic configuration of  $5s^2 5p^4$  corresponds to the element present in:  
[JEE-MAIN 2015 (On-Line)]
- (1) Group 16 and period 5 (2) Group 17 and period 6  
(3) Group 17 and period 5 (4) Group 16 and period 6
- PT0099
12. Which of the following atoms has the highest first ionization energy ?  
[JEE-MAIN 2016 (Off-Line)]
- (1) Sc (2) Rb (3) Na (4) K
- PT0100
13. The non-metal that does not exhibit positive oxidation state is :  
[JEE-MAIN 2016 (On-Line)]
- (1) Oxygen (2) Fluorine (3) Iodine (4) Chlorine
- PT0101
14. The electronic configuration with the highest ionization enthalpy is:- [JEE-MAIN 2017]
- (1)  $[\text{Ar}] 3d^{10} 4s^2 4p^3$  (2)  $[\text{Ne}] 3s^2 3p^1$   
(3)  $[\text{Ne}] 3s^2 3p^2$  (4)  $[\text{Ne}] 3s^2 3p^3$
- PT0102

15. Consider the following ionization enthalpies of two elements 'A' and 'B' :

Element	Ionization enthalpy (kJ/mol)		
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
A	899	1757	14847
B	737	1450	7731

[JEE-MAIN 2017]

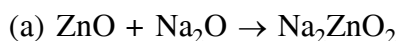
Which of the following statements is correct ?

- (1) Both A and B belong to group-2 where A comes below B
- (2) Both A and B belong to group-1 where A comes below B
- (3) Both A and B belong to group-1 where B comes below A
- (4) Both A and B belong to group-2 where B comes below A

PT0103

16. In the following reactions, ZnO is respectively acting as a/an :

[JEE-MAIN 2017]

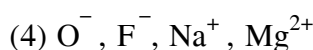
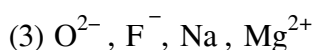
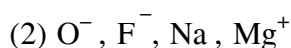
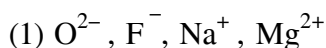


- (1) base and acid      (2) base and base      (3) acid and acid      (4) acid and base

PT0104

17. The group having isoelectronic species is :-

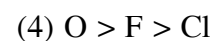
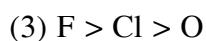
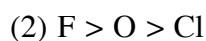
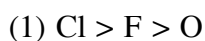
[JEE-MAIN 2017]



PT0105

18. The correct order of electron affinity is :-

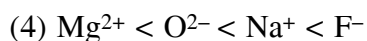
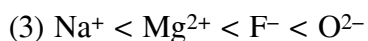
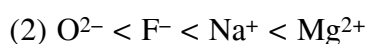
[JEE-MAIN 2018]



PT0106

19. For  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{F}^-$  and  $\text{O}^{2-}$ ; the correct order of increasing ionic radii is :

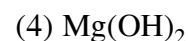
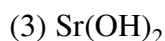
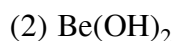
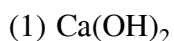
[JEE-MAIN 2018]



PT0107

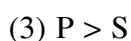
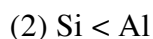
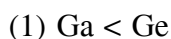
20. The amphoteric hydroxide is :

[JEE-MAIN ONLINE 2019]



PT0108

21. The correct option with respect to the Pauling electronegativity values of the elements is :-



[JEE-MAIN ONLINE 2019]

PT0109

22. The effect of lanthanoid contraction in the lanthanoid series of elements by and large means :  
 (1) decrease in both atomic and ionic radii [JEE-MAIN ONLINE 2019]  
 (2) increase in atomic radii and decrease in ionic radii  
 (3) increase in both atomic and ionic radii  
 (4) decrease in atomic radii and increase in ionic radii  
 PT0110
23. When the first electron gain enthalpy ( $\Delta_{eg}H$ ) of oxygen is  $-141$  kJ/mol, its second electron gain enthalpy is :  
 (1) almost the same as that of the first [JEE-MAIN ONLINE 2019]  
 (2) negative, but less negative than the first  
 (3) a positive value  
 (4) a more negative value than the first  
 PT0111
24. The correct order of hydration enthalpies of alkali metal ions is - [JEE-MAIN ONLINE 2019]  
 (1)  $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$   
 (2)  $Li^+ > Na^+ > K^+ > Cs^+ > Rb^+$   
 (3)  $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$   
 (4)  $Na^+ > Li^+ > K^+ > Cs^+ > Rb^+$   
 PT0112
25. The IUPAC symbol for the element with atomic number 119 would be : [JEE-MAIN ONLINE 2019]  
 (1) unh (2) uun (3) une (4) uue  
 PT0113
26. The element having greatest difference between its first and second ionization energies, is :  
 (1) Ca (2) K (3) Ba (4) Sc [JEE-MAIN ONLINE 2019]  
 PT0114
27. The correct statements among I to III regarding group 13 element oxides are,  
 (I) Boron trioxide is acidic. [JEE-MAIN ONLINE 2019]  
 (II) Oxides of aluminium and gallium are amphoteric.  
 (III) Oxides of indium and thallium are basic.  
 (1) (I), (II) and (III) (2) (II) and (III) only (3) (I) and (III) only (4) (I) and (II) only  
 PT0115
28. Consider the hydrated ions of  $Ti^{2+}$ ,  $V^{2+}$ ,  $Ti^{3+}$  and  $Sc^{3+}$ . The correct order of their spin-only magnetic moments is :  
 (1)  $Sc^{3+} < Ti^{3+} < Ti^{2+} < V^{2+}$  (2)  $Ti^{3+} < Ti^{2+} < Sc^{3+} < V^{2+}$  [JEE-MAIN ONLINE 2019]  
 (3)  $Sc^{3+} < Ti^{3+} < V^{2+} < Ti^{2+}$  (4)  $V^{2+} < Ti^{2+} < Ti^{3+} < Sc^{3+}$   
 PT0116

29. The pair that has similar atomic radii is : **[JEE-MAIN ONLINE 2019]**  
(1) Sc and Ni            (2) Ti and Hf            (3) Mo and W            (4) Mn and Re  
**PT0117**
30. Within each pair of elements of F & Cl, S & Se, and Li & Na, respectively, the elements that release more energy upon an electron gain are- **[JEE-MAIN ONLINE 2020]**  
(1) F, Se and Na  
(2) F, S and Li  
(3) Cl, S and Li  
(4) Cl, Se and Na  
**PT0118**
31. The atomic radius of Ag is closest to : **[JEE-MAIN ONLINE 2020]**  
(1) Cu                      (2) Hg                      (3) Au                      (4) Ni  
**PT0119**
32. The third ionization enthalpy is minimum for : **[JEE-MAIN ONLINE 2020]**  
(1) Fe                      (2) Ni                      (3) Co                      (4) Mn  
**PT0120**
33. B has a smaller first ionization enthalpy than Be. Consider the following statements :  
(I) It is easier to remove 2p electron than 2s electron  
(II) 2p electron of B is more shielded from the nucleus by the inner core of electrons than the 2s electrons of Be.  
(III) 2s electron has more penetration power than 2p electron.  
(IV) atomic radius of B is more than Be  
(Atomic number B = 5, Be = 4)  
The correct statements are : **[JEE-MAIN ONLINE 2020]**  
(1) (I), (II) and (III)  
(2) (II), (III) and (IV)  
(3) (I), (III) and (IV)  
(4) (I), (II) and (IV)  
**PT0121**

## EXERCISE # JEE-ADVANCED

1. **Statement-1** : F atom has a less negative electron gain enthalpy than Cl atom. [JEE 2000]  
**Statement-2** : Additional electron is repelled more efficiently by 3p electron in Cl atom than by 2p electron in F atom.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true. PT0122
2. The correct order of radii is: [JEE 2000]  
 (A)  $N < Be < B$       (B)  $F^- < O^{2-} < N^{3-}$       (C)  $Na < Li < K$       (D)  $Fe^{3+} < Fe^{2+} < Fe^{4+}$  PT0123
3. The  $IE_1$  of Be is greater than that of B. [T/F] [JEE 2001] PT0124
4. The set representing correct order of  $IP_1$  is [JEE 2001]  
 (A)  $K > Na > Li$       (B)  $Be > Mg > Ca$       (C)  $B > C > N$       (D)  $Fe > Si > C$  PT0125
5. Identify the least stable ion amongst the following: [JEE 2002]  
 (A)  $Li^-$       (B)  $Be^-$       (C)  $B^-$       (D)  $C^-$  PT0126
6. The increasing order of atomic radii of the following group 13 elements is [JEE 2016]  
 (A)  $Al < Ga < In < Tl$       (B)  $Ga < Al < In < Tl$   
 (C)  $Al < In < Ga < Tl$       (D)  $Al < Ga < Tl < In$  PT0127
7. The option(s) with only amphoteric oxides is (are): [JEE 2017] PT0128  
 (A)  $Cr_2O_3, CrO, SnO, PbO$   
 (B)  $NO, B_2O_3, PbO, SnO_2$   
 (C)  $Cr_2O_3, BeO, SnO, SnO_2$   
 (D)  $ZnO, Al_2O_3, PbO, PbO_2$

## ANSWERS KEY

### EXERCISE # O-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	D	A	A	D	A	B	C	A	C	A
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	C	B	A	B	C	C	B	C	B	C
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	B	C	C	B	A	C	A	C	A	B
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	D	B	B	D	C	C	D	C	D	B
Que.	41	42	43	44	45	46	47	48		
Ans.	C	B	D	A	A	C	A	D		

### EXERCISE # O-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A,B,C,D	A, B, D	A, C	B, C	A, B, C	A, B	B, D	A, B	B, C	A,B,C,D
Que.	11	12	13	14	15	16	17			
Ans.	A, B, D	A, B	A, C, D	B, C, D	A, B, D	A, B, C	A, C			

### EXERCISE # S-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	6	4	3	3	4	0	3	3	17	4
Que.	11	12	13							
Ans.	5	3.03 (Pauling)	$Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$							

### EXERCISE # S-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	D	C	A	B	B	A	C	C	C	C
Que.	11	12	13	14	15	16				
Ans.	B	B	B	A	C	(A)→Q;(B)→P,Q,R ;(C)→P;(D)→R, S				
Que.	17					18				
Ans.	(A)→R ; (B)→R ; (C)→Q ; (D)→S					(A) → Q,R ; (B) → P,S ; (C) → S ; (D) → Q,R				
Que.	19									
Ans.	(A) → Q ; (B) → R ; (C) → P ; (D) → S									

**EXERCISE # JEE-MAIN**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	3	4	3	2	4	2	4	1	3	1
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	1	1	2	4	4	4	1	1	1	2
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	1	1	3	1	4	2	1	1	3	3
Que.	31	32	33							
Ans.	3	1	1							

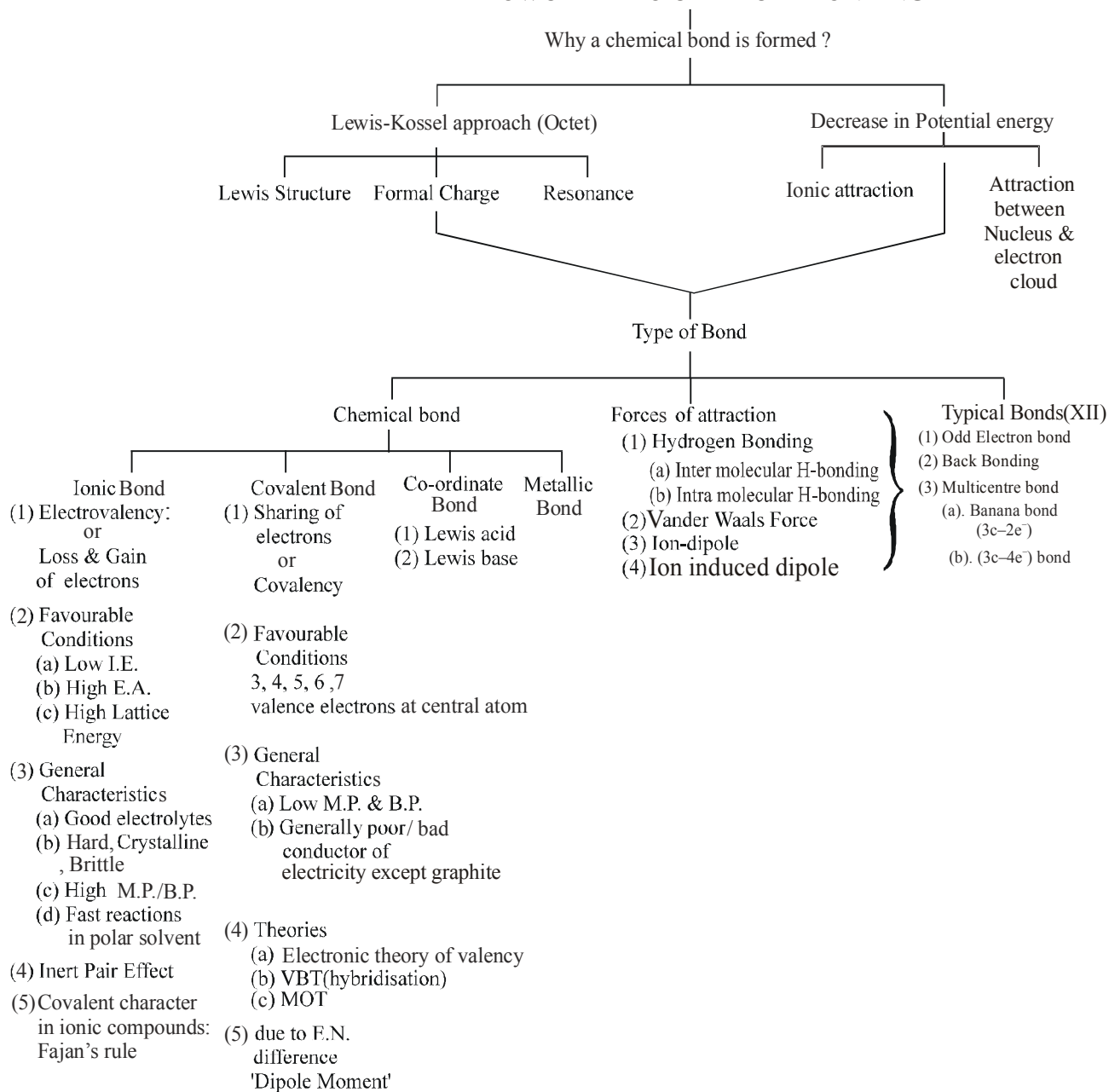
**EXERCISE # JEE-ADVANCED**

Que.	1	2	3	4	5	6	7			
Ans.	C	B	T	B	B	B	C, D			



# CHEMICAL BONDING

## FLOWCHART TO CHEMICAL BONDING



## KEY CONCEPT

### CHEMICAL BOND

- The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.
- It is the combination of two or more chemical species involving redistribution of  $e^-$  among them.
- This process is accompanied with decrease in energy.
- Decrease in energy strengthens the bond.
- Therefore, molecules are more stable than atoms.

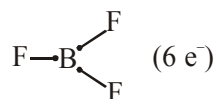
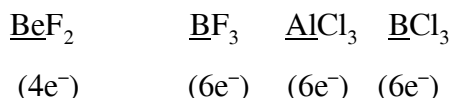
### CAUSE OF CHEMICAL COMBINATION

- Tendency to acquire minimum energy :
- Tendency to acquire noble gas configuration (Octet rule) :

Atoms combine to complete an octet of electrons in their outer most shell. Hence all atoms have a tendency to acquire octet ( $ns^2np^6$ ) configuration or to attain nearest noble gas configuration in their outermost orbit. This can be achieved by combining with other atom or ion.

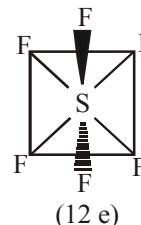
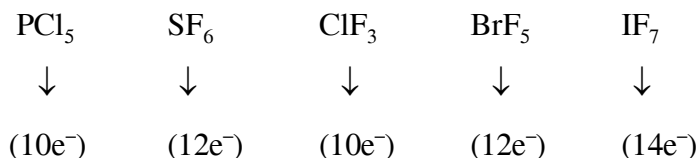
### LIMITATION OF OCTET RULE

- Contraction of octet (incomplete octet)



These compounds are hypovalent.

- Expansion of Octet (due to empty d-orbitals)



These compounds are hypervalent.

- Odd electron species

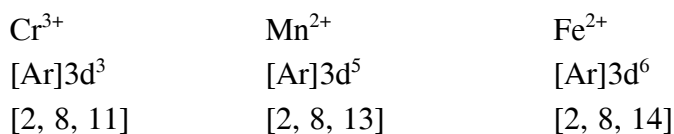
Ex. NO, NO<sub>2</sub>, ClO<sub>2</sub> etc.

### OTHER EXCEPTIONS OF OCTET RULE

- Compounds of Noble gases

Noble gases which have already completed their octets (or duplet in case of He.) should not form compounds. However, their compounds like XeF<sub>2</sub>, XeF<sub>6</sub> & KrF<sub>2</sub> etc., have been actually prepared.

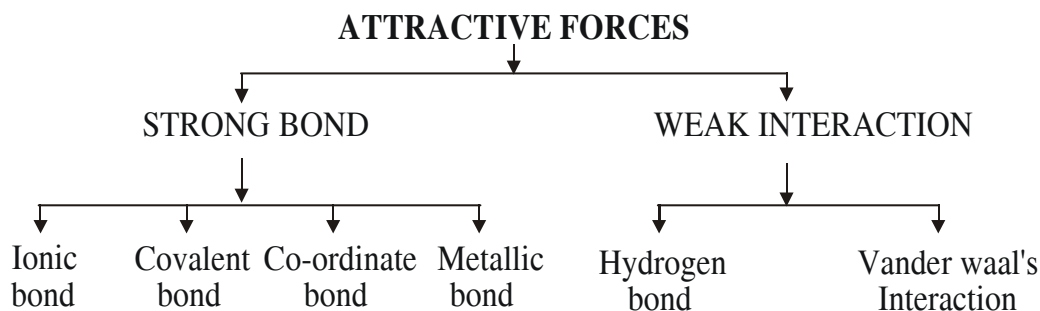
- Transition metal ions



- Pseudo inert gas configuration  $[(ns^2np^6nd^{10})]$



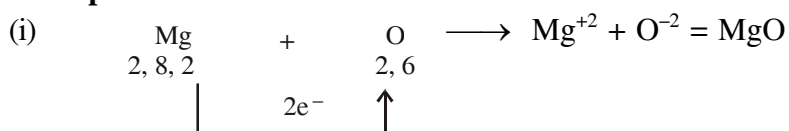
## CLASSIFICATION OF BONDS



## ELECTROVALENT OR IONIC BOND

(a) The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called as Ionic or electrovalent bond.

**Example**



electrovalency of Mg = 2

electrovalency of O = 2

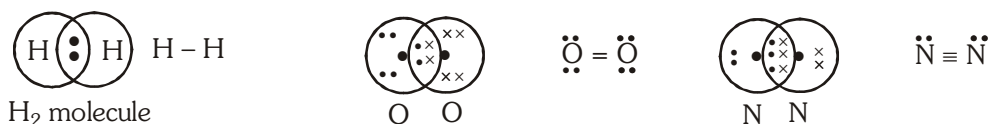
**Note :** Ionic bond is non-directional.

## FACTORS FAVOURING IONIC BONDING

- Less Ionization energy of atom forming cation
- Higher electron affinity of atom forming anion
- Greater Lattice energy of formed product.
- Greater Electronegativity difference between atoms forming cation & anion.

## COVALENT BOND

(a) A covalent bond is formed by the mutual sharing of electrons between two atoms.

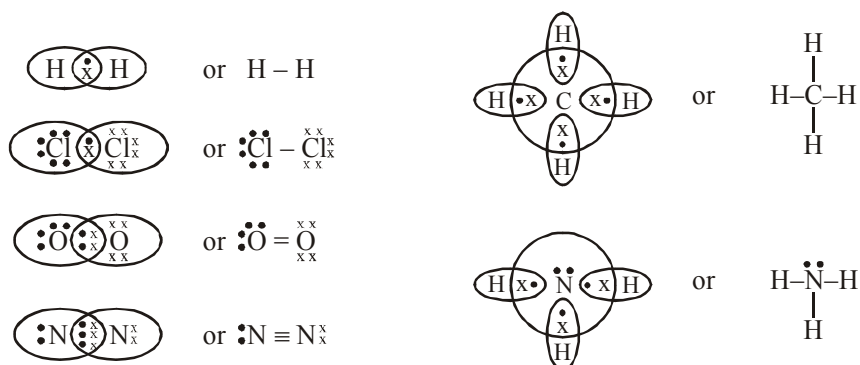


(b) The shared pair of electrons must have opposite spins, and are localised between two atoms concerned.

(c) On the basis of electrons being shared between two atoms the bonds are of three types –

**Covalency :** Capacity to form covalent bond is known as covalency

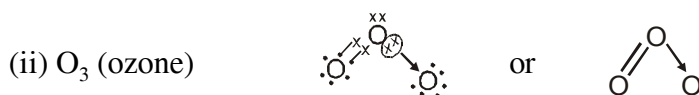
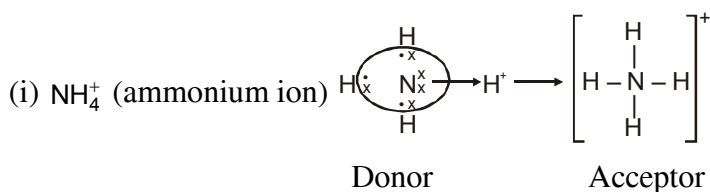
It is represented by (–) small line. – means single bond ; = means double bond ; ≡ means triple bond.



★ **Covalent bonds are directional in nature**

## COORDINATE BOND (DATIVE BOND)

The bond formed between two atom in which contribution of an electron pair is made by one of them while the sharing is done by both.

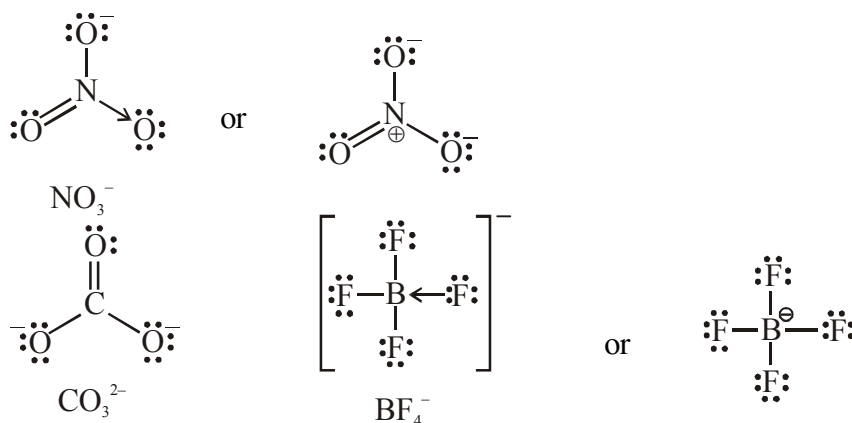


### Lewis Dot structures:

- ✦ Arrangement of various atoms in a molecule & types of bonding present in it but no idea of geometry of the molecule.
- ✦ In most cases we can construct a Lewis structure in three steps :
  - (1) Decide on the number of electrons that are included in the structure by adding together the number of all the valence electrons provided by the atoms.
  - (2) Write the chemical symbols of the atoms in the arrangement that shows which atoms are bonded together.
  - (3) Distribute the electrons in pairs so that there is one pair of electrons forming a single bond between each pair of atom bonded together and then supply electron pairs (to form lone pairs or multiple bonds) until each atom has an octet.
- ✦ In oxy acids all 'H' atoms are attached to oxygen as  $-\text{OH}$  groups except in  $\text{H}_3\text{PO}_3$  (dibasic),  $\text{H}_3\text{PO}_2$  (monobasic) &  $\text{H}_4\text{P}_2\text{O}_5$  (dibasic). Which are directly bonded to central atom.

### Applications :

- ✦ To know various linkages present
- ✦ To calculate formal charge of various elements.



### FORMAL CHARGE

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom.

$$\text{Formal Charge} : Q_F = N_A - N_{L.P.} - \frac{1}{2} N_{B.P.}$$

Where :

$N_A$  = Total number of valence electron in the free atom

$N_{L.P.}$  = Total number of non bonding (lone pair) electrons

$N_{B.P.}$  = Total number of bonding (shared) electrons

Molecule	Structure	Formal Charge
$O_3$		$O(1) = 6 - 2 - \frac{1}{2} (6) = +1$ $O(2) = 6 - 4 - \frac{1}{2} (4) = 0$ $O(3) = 6 - 6 - \frac{1}{2} (2) = -1$
$CO$		$C = 4 - 2 - \frac{1}{2} \times 6 = -1$ $O = 6 - 2 - \frac{1}{2} \times 6 = +1$
$NH_4^+$		$N = 5 - 0 - \frac{1}{2} (8) = +1$ On each H = $1 - 0 - \frac{1}{2} (2) = 0$

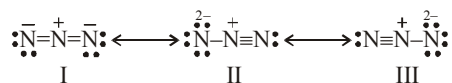
### RESONANCE\*

When a molecule cannot be completely represented by a single Lewis structure but its characteristic properties can be described by two or more different structures, with similar energy position of nuclei, bonding and non-bonding pairs of electrons, then the true structure is said to be resonance hybrid of these structures. The phenomenon is called resonance and different contributing structures are called resonating structures or canonical structures.

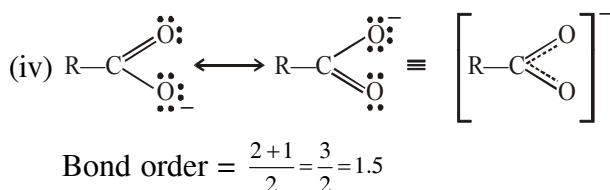
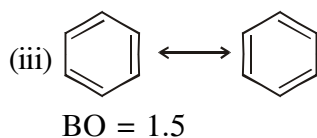
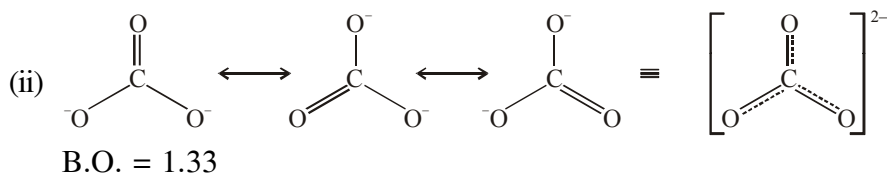
- ❖ Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single canonical structure.
- ❖ Resonance averages the bond characteristics as a whole.
- ❖ The canonical forms have no real existence.

**Resonance Structure of Some Molecules/Ions :****(i) Azide ion,  $N_3^-$  :**

The azide ion may be represented as -



The structures II and III contribute equally and the molecule has almost double bond character in each N-N bond.



\*Descriptive discussion of concept of resonance will be done in **Organic Chemistry**.

**VALENCE BOND THEORY**

**Valence bond theory** was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals and the hybridization of atomic orbitals.

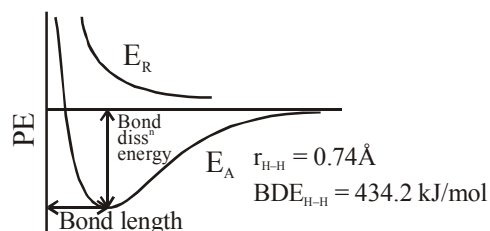
**Formation of  $H_2$  molecule :**

When two 'H'-atoms approaches towards each other for the formation of  $H_2$  molecule. The following interactions takes place.

- (i) e-e repulsion
- (ii) e-p attraction
- (iii) p-p repulsion

Experimentally, it has been found that the magnitude of attractive forces is more than the repulsive forces. As a result, when two atoms approach each other then potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy.

At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm. Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms.

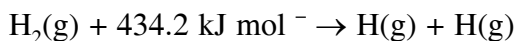


The potential energy curve for the formation of  $H_2$  molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of  $H_2$ .

**Bond Length :** Internuclear distance at minimum potential energy is called bond length.

**Bond Dissociation Energy :** The amount of energy released when one mole of same type of bonds are formed is called B.D.E.

434.2 kJ/mol of energy is required to dissociate one mole of  $H_2$  molecule.



## ORBITAL OVERLAP CONCEPT

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons, present in the valence shell having opposite spins.

### Directional Properties of Bonds :

The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like  $CH_4$ ,  $NH_3$  and  $H_2O$ , etc. in terms of overlap and hybridisation of atomic orbitals.

### Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into following types depending upon the types of overlapping :-

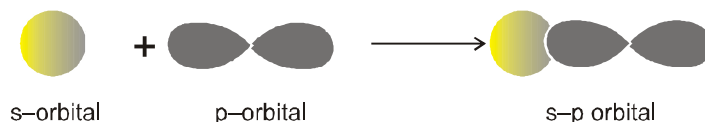
(i) sigma ( $\sigma$ ) bond (ii) pi ( $\pi$ ) bond (iii) delta ( $\delta$ ) bond

(i) **Sigma ( $\sigma$ ) bond :** This type of covalent bond is formed by the end to end (head on or axial) overlap of bonding orbitals along the internuclear axis. This can be formed by any one of the following types of combinations of atomic orbitals.

- s-s overlapping : In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below :



- s-p overlapping: This type of overlap occurs between half filled s-orbital of one atom and half filled p-orbital of another atom.

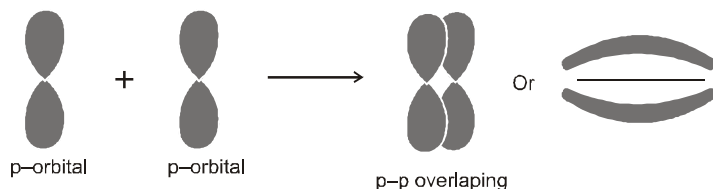


- p-p overlapping : This type of overlap takes place between half filled similar p-orbitals of the two approaching atoms.

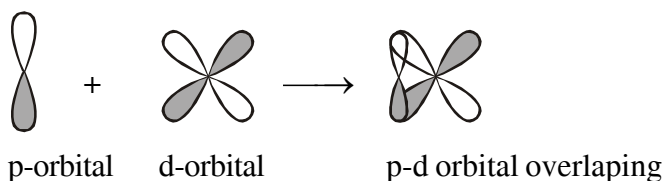


- (ii)  **$\pi$  bond** : In the formation of  $\pi$  bond the atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.

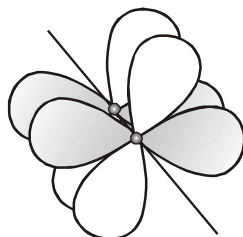
(a)  **$p_{\pi}-p_{\pi}$**



(b)  **$p_{\pi}-d_{\pi}$**



- (iii)  **$\delta$  bond** : are the covalent bonds where four lobes of d-orbital of one atom overlap with four lobes of the similar d-orbital of other atom. Except  $d_{z^2}$  all d orbitals form  $\delta$  bond.



**Strength of sigma and pi Bonds :**

Basically the strength of a bond depends upon the extent of overlapping- In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds)

**Advantages of VBT :**

- ❖ It explain various bond characteristics e.g., bond length, bond strength.
- ❖ It explains the quantitative relationship between the extent of overlapping and bond dissociation energy.
- ❖ This theory accounts for shape and nature of bonding of the molecule whose covalency is not according to the number of half-filled orbitals present in the ground state.
- ❖ This theory redefined the stability of molecules e.g.  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{PCl}_5$ ,  $\text{SF}_6$  etc which are exception to octet rule.

**Disadvantages of VBT :**

- ❖ According to this theory three bond angle in  $\text{CH}_4$  should be  $90^\circ$ , as these are formed by p-p overlapping, but actually it has four  $109^\circ 28'$  angles. In  $\text{NH}_3$  &  $\text{H}_2\text{O}$ , angle should be  $90^\circ$ . This is in disagreement with the actual bond angles of  $107^\circ$  &  $104.5^\circ$  in  $\text{NH}_3$  &  $\text{H}_2\text{O}$  molecules respectively.
- ❖ In order to explain the characteristic geometrical shapes of polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  etc. Pauling introduced the concept of hybridisation.



## HYBRIDISATION

The phenomenon of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new  $sp^3$  hybrid orbitals.

**Salient features of hybridisation:** The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

### Important conditions for hybridisation

- (i) The orbitals present in the valence shell of the atom are hybridised.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.
- (iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

### Types of Hybridisation

There are various types of hybridisation involving s, p and d orbitals. The different types of hybridisation are as under :

- (i)  $sp$  hybridisation
- (ii)  $sp^2$  hybridisation
- (iii)  $sp^3$  hybridisation
- (iv)  $sp^3d$  hybridisation:
- (v)  $sp^3d^2$  hybridisation:
- (vi)  $sp^3d^3$  hybridisation:

### Determination of hybridisation state –

To predict hybridisation following formula may be used :

Number of hybrid orbital = Steric Number (S.N.) = Number of  $\sigma$ -bond around that atom + Number of lone pair on that atom.

Molecule	Method	Hybridisation
$NH_4^+$	S.N. = 4 + 0 = 4	$sp^3$ hybridisation.

Number of hybrid orbitals	Hybridisation
two	$sp$
three	$sp^2$
four	$sp^3$
five	$sp^3d$
six	$sp^3d^2$
seven	$sp^3d^3$

**Hybridisation in Ionic solid species :**

Species	Cationic part	Anionic part
$\text{PCl}_5$	$\text{PCl}_4^+$ ( $\text{sp}^3$ )	$\text{PCl}_6^-$ ( $\text{sp}^3\text{d}^2$ )
$\text{PBr}_5$	$\text{PBr}_4^+$ ( $\text{sp}^3$ )	$\text{Br}^-$
$\text{XeF}_6$	$\text{XeF}_5^+$ ( $\text{sp}^3\text{d}^2$ )	$\text{F}^-$
$\text{N}_2\text{O}_5$	$\text{NO}_2^+$ ( $\text{sp}$ )	$\text{NO}_3^-$ ( $\text{sp}^2$ )
$\text{N}_2\text{O}_3(\text{s})$	$\text{NO}^+$	$\text{NO}_2^-$ ( $\text{sp}^2$ )
$\text{N}_2\text{O}_4(\text{s})$	$\text{NO}^+$	$\text{NO}_3^-$ ( $\text{sp}^2$ )
$\text{I}_2\text{Cl}_6$ (liquid)	$\text{ICl}_2^+$ ( $\text{sp}^3$ )	$\text{ICl}_4^-$ ( $\text{sp}^3\text{d}^2$ )
$\text{I}_2$ (liquid)	$\text{I}_3^+$ ( $\text{sp}^3$ )	$\text{I}_3^-$ ( $\text{sp}^3\text{d}$ )
$\text{Cl}_2\text{O}_6$	$\text{ClO}_2^+$ ( $\text{sp}^2$ )	$\text{ClO}_4^-$ ( $\text{sp}^3$ )

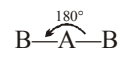
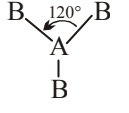
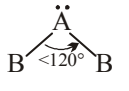
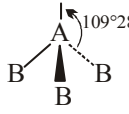
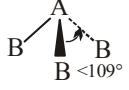
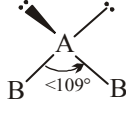
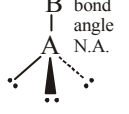
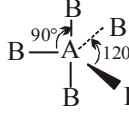
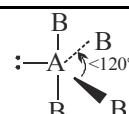
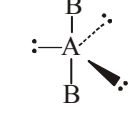
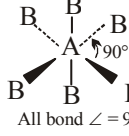
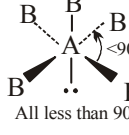
$\text{PF}_5(\text{s})$  exist in form of trigonal bipyramidal geometry.

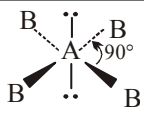
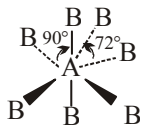
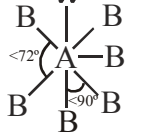
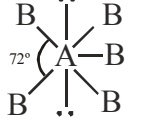
**VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)**

- (a) Molecules having covalent bond have definite geometry as covalent bonding has directional characteristics. A simple theory was given for the molecular shape of the covalent molecules by Gillespie and Nyholm in 1957.
- (b) This theory predicts the shape of the molecule by considering the most stable configuration of the bond angles in the molecule. This theory states
- Electron pairs in the valence shell of the central atom of a molecule, whether bonding or lone pairs are regarded as occupying localised orbitals. These orbitals arrange themselves in so as to minimize the mutual electronic repulsions.
  - The magnitude of the different types of electronic repulsions follows the order given below:
 

**lone pair-lone pair > lone pair - bonded pair > bonded pair - bonded pair**
  - The electronic repulsion between two pairs of electrons will be minimum if they are as far apart as possible.
  - The actual shape of the molecules containing lone pairs is a little distorted from the basic shape as in the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules, the bond angles are not  $109^\circ 28'$  but  $107^\circ$  and  $104.5^\circ$  respectively due to presence of one lone pair in  $\text{NH}_3$  and two lone pairs in  $\text{H}_2\text{O}$ .

SHAPES OF MOLECULES BASED ON VSEPR THEORY

Total no. of hybrid orbitals	No. of b.p. (bond pairs)	No. of unshared pair i.e. $l_p$	General formula	Type of hybridisation	Stereo chemical formula/str.	Shape	Exam.
2	2	0	$AB_2$	$sp$		linear	$BeCl_2$
3	3	0	$AB_3$	$sp^2$		Trigonal planar	$BCl_3$ , $NO_3^-$ , $GaF_3$ , $CO_3^{2-}$
3	2	1	$AB_2$	$sp^2$		V or Bent or angular	$SnCl_2$ , $O_3$ , $SO_2$
4	4	0	$AB_4$	$sp^3$		Tetrahedron	$CH_4$ , $SiF_4$ , $NH_4^+$
4	3	1	$AB_3$	$sp^3$		Trigonal pyramidal	$NH_3$ , $CH_3^-$
4	2	2	$AB_2$	$sp^3$		V or Bent or angular	$H_2O$ , $SF_2$
4	1	3	$AB$	$sp^3$		linear	$ClO^-$
5	5	0	$AB_5$	$sp^3d$		Trigonal bipyramidal	$PF_5$ , $SF_5^+$ , $SbBr_5$ , $XeO_3F_2$
5	4	1	$AB_4$	$sp^3d$		Seesaw	$SF_4$
5	3	2	$AB_3$	$sp^3d$		T-shaped	$ClF_3$ , $BrF_3$
5	2	3	$AB_2$	$sp^3d$		Linear	$ICl_2^-$ , $XeF_2$ , $I_3^-$
6	6	0	$AB_6$	$sp^3d^2$		Octahedral or Square bipyramidal	$SF_6$ , $IF_6^+$
6	5	1	$AB_5$	$sp^3d^2$		Square pyramidal	$IF_5$ , $XeOF_4$ , $BrF_5$

6	4	2	$AB_4$	$sp^3d^2$		Square planar	$IF_4^-$ , $XeF_4$ , $ICl_4$
7	7	0	$AB_7$	$sp^3d^3$		Pentagonal bipyramidal	$IF_7$
7	6	1	$AB_6$	$sp^3d^3$		Distorted octahedral	$XeF_6$ , $IF_6^-$
7	5	2	$AB_5$	$sp^3d^3$		Pentagonal planar	$XeF_5^-$

## BOND PARAMETERS

(I) Bond order

(II) Bond Length (Bond distance)

(III) Bond Angle

(IV) Bond Enthalpy

(I) Bond order :

The Bond Order is given by the number of bonds between the two atoms in a molecule.

The bond order, for example in  $H_2$  (with a single shared electron pair), in  $O_2$  (with two shared electron pairs) and in  $N_2$  (with three shared electron pairs) is 1,2,3 respectively.

**Note :** Isoelectronic molecules and ions have identical bond orders; for example,  $F_2$  and  $O_2^{2-}$  have bond order 1.  $N_2$ , CO and  $NO^+$  have bond order 3.

**Note :** A general correlation useful for understanding the stabilities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases.

(II) Bond Length :-

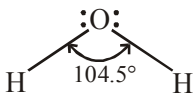
**Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.** Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques about which you will learn in higher classes.

**Factors affecting bond length**

- |                             |   |
|-----------------------------|---|
| (a) Size of atoms           | (b) Effect of bond order or number of bonds |
| (c) Effect of Resonance     | (d) Effect of Electronegativity difference  |
| (e) Effect of Hybridisation |   |

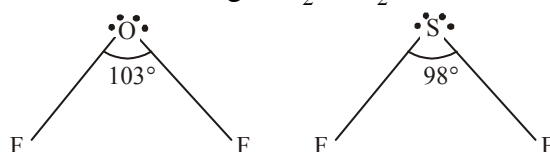
(III) Bond angle :

It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods. For example  $H-\hat{O}-H$  bond angle in water can be represented as under :



**Comparison of bond angles.**

- (a) If central atoms are in different hybridisations then it can be compared.
- (b) If same hybridisation but different central atoms then bond angle would be more of the molecule in which central atom is more E.N. eg.  $\text{OF}_2$ ,  $\text{SF}_2$



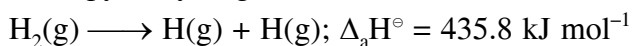
- (c) Molecules having same C.A. but different substituent then bond angle increases as the size of attached atom increases except in symmetrical molecules and  $\text{H}_2\text{O}$  /  $\text{F}_2\text{O}$ ,  $\text{NH}_3$  /  $\text{NF}_3$

**Factors affecting bond angle**

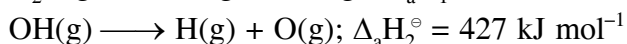
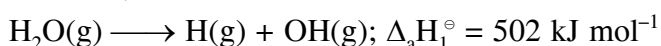
- (a) State of Hybridisation
- (b) Presence of lone pair
- (c) Electronegativity of central atom
- (d) Electronegativity of surrounding atom
- (e) Size of surrounding atom
- (f) Lone pairs may sometimes be transferred from a filled shell of one atom to an unfilled shell of another bonded atom, causing less repulsion.
- (g) Multiple bond orbital repel other orbitals more strongly than single bond orbitals.

**(IV) Bond Enthalpy**

It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is  $\text{kJ mol}^{-1}$ . For example, the H – H bond enthalpy in hydrogen molecule is  $435.8 \text{ kJ mol}^{-1}$ .

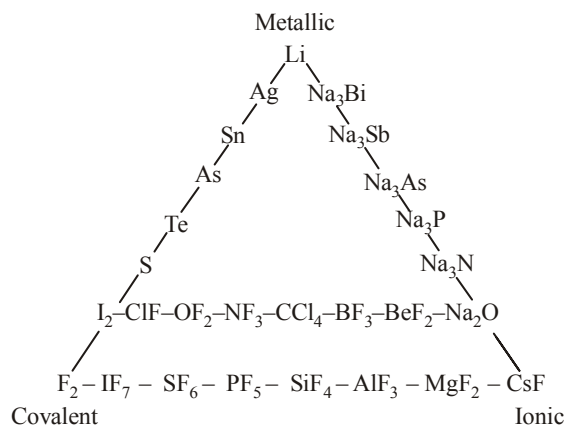


⇒ In polyatomic molecules the **term mean or average bond enthalpy** is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule,



$$\text{Average bond enthalpy} = \frac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}$$

**SUMMARY OF THE THREE MAIN TYPES OF BONDS**

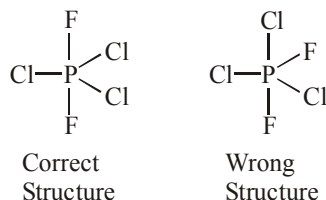


**BENT'S RULE**

- (i) A lone pair of electron prefers to occupy that hybrid orbitals which has greater percentage of s-character.
- (ii) A more electronegative atom/group prefers to occupy that hybrid orbital which has smaller percentage of s-character.

Ex. Draw the geometry of  $\text{PCl}_3\text{F}_2$

Sol.



Because highly electronegative atom occupy axial position (axial position has smaller percentage of s-character).

**DRAGO'S RULE**

On the basis of experimental bond angles of certain molecules fulfilling the following three conditions,

- (i) Central atom belongs to third or lower period in periodic table
- (ii) Central atom must contain atleast one lone pair of electron, and
- (iii) Electronegativity of surrounding atom is  $\leq 2.5$

Drago generalised that in such molecules justification of experimental bond angle can be made satisfactorily if one considers no hybridisation, i.e., overlapping of almost pure atomic orbitals from central atom.

In such molecules bond angle is approximately  $90^\circ$ .

Group 15	Bond angle	Group 16	Bond angle
$\text{NH}_3$	$107^\circ 48'$	$\text{H}_2\text{O}$	$104^\circ 28'$
$\text{PH}_3$	$93^\circ 36'$	$\text{H}_2\text{S}$	$92^\circ$
$\text{AsH}_3$	$91^\circ 48'$	$\text{H}_2\text{Se}$	$91^\circ$
$\text{SbH}_3$	$91^\circ 18'$	$\text{H}_2\text{Te}$	$90.5^\circ$

- Right order of bond angle.

(a)  $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$

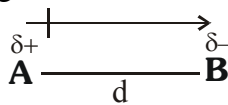
(b)  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$

**MOLECULES THAT DO NOT EXIST**

- (1)  $\text{SF}_4$ ,  $\text{SF}_6$  &  $\text{PF}_5$  exist while.  $\text{OF}_4$ ,  $\text{OF}_6$ ,  $\text{NF}_5$  do not exist
- (2) (a)  $\text{PI}_5(\text{vap})$  &  $\text{SCl}_6$  do not exist  
 (b)  $\text{SCl}_6$  does not exist while  $\text{TeCl}_6$  exist  
 (c)  $\text{PI}_5$  (Solid) exist
- (3)  $\text{SF}_6$ ,  $\text{PF}_5$ ,  $\text{XeF}_6$ ,  $\text{XeF}_4$  &  $\text{XeF}_2$  exist while  $\text{SH}_6$ ,  $\text{PH}_5$ ,  $\text{XeH}_6$ ,  $\text{XeH}_4$ ,  $\text{XeH}_2$  do not exist

**DIPOLE MOMENT**

- The degree of polarity of covalent bond is given by the dipole moment ( $\mu$ )
- It is the product of the either charge and the distance between them.



Electronegativity of A < Electronegativity of B

$$\mu = \delta \times d$$

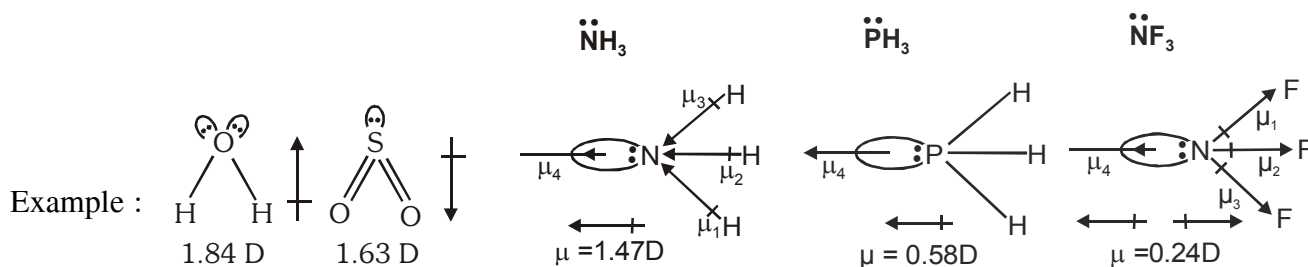
- Dipole moment is a vector quantity.  
The direction of dipole moment is represented by  $\text{---} \rightarrow$
- Units = Cm (S.I.) or esu cm (CGS) or Debye (common unit)
- 1 D =  $10^{-18}$  esu cm =  $3.33 \times 10^{-30}$  coulomb m

**Dipole moment depends on**

- Electronegativity difference between bonded atoms
- Direction of bond dipole moment
- Angle between various bonds
- Influence of unshared  $e^-$  pairs
- Magnitude of polarity of the molecule
- Symmetrical / Unsymmetrical shape.

**Application of dipole moment**

- To determine the polarity and geometry of molecules



- To calculate the percentage of ionic character

$$\% \text{ ionic character} = \frac{\text{observed } \mu}{\text{calculated } \mu \text{ (for 100 \% ionic)}} \times 100 \%$$

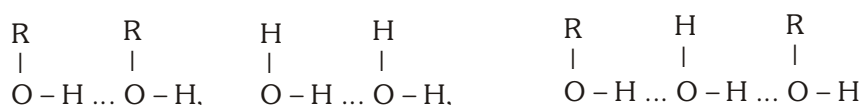
**HYDROGEN BONDING**

- Hydrogen bonding:** When a hydrogen atom is bonded to a highly electronegative atom (like F, O or N) comes under the influence of another strongly electronegative atom, then a weak electrostatic force of attraction is developed between them, which is called as hydrogen bond.

**Types of H-bonding:**

- Intermolecular H-bond

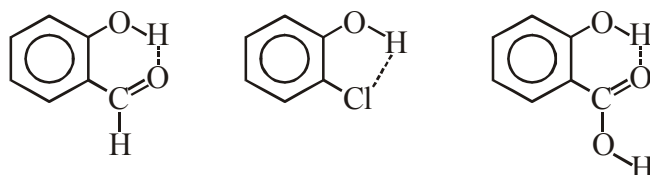
- This type of H-bonding takes place between two molecules. **Ex.** ROH, H<sub>2</sub>O, R - OH & H<sub>2</sub>O



- In such compounds molecular wt., M.P. & B.P. are high.
- Extent of Inter molecular H-bonding  $\uparrow$  viscosity & density  $\uparrow$ .

★ Intramolecular H-bond

Normally when 2 hydroxyl groups are present on the same carbon atom i.e. gem diols are unstable, but "chloralhydrate" is a stable molecule due to formation of H-bond.



**Properties influenced by hydrogen bonding**

- Abnormal behaviour of water.
- Association of molecules eg. dimerisation of  $\text{CH}_3\text{COOH}$ ,  $\text{HCOOH}$
- Dissociation of a polar species.
- Abnormal melting point & boiling point.
- Enhanced solubility in water.

★ **Metallic bonds :**

Electron gas model or sea model, with metal atom existing as kernels along with less firmly held valence electrons & bonds between various kernels ( at the lattice site) & valence electrons are known as metallic bonds.

**QUESTION OF HYDROGEN BONDING**

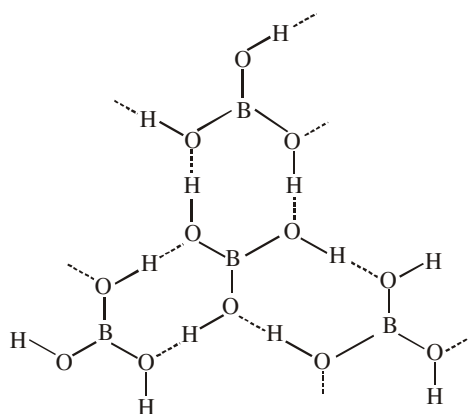
- Q.1 Explain the structure of Boric acid in solid state.
- Q.2 Boiling point of o-Nitrophenol is less than meta and para nitrophenol. Why?
- Q.3 Maleic acid is more acidic than fumaric acid. Why?
- Q.4 H – F is only liquid among halogen acid. Why?
- Q.5 Ammonia is more easily liquefied than HCl, explain.
- Q.6 Why ice floats on water?
- Q.7 Water shows maximum density at  $4^\circ\text{C}$ . Why?
- Q.8 HI is the strongest halogen acid, whereas H–F is the weakest. Why?
- Q.9 Wood pieces are used to hold ice-cream. Why?
- Q.10  $\text{KHF}_2$  is possible but not  $\text{KBr}_2$  or  $\text{KI}_2$ . Why?
- Q.11 O – Nitrophenol is less soluble in  $\text{H}_2\text{O}$  than p – Nitrophenol. Why?
- Q.12 o-Hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid.
- Q.13 Glycerol is more viscous than ethanol. Explain.
- Q.14  $\text{CH}_4$  and  $\text{H}_2\text{O}$  have nearly same molecular weight. Yet  $\text{CH}_4$  has a boiling point 112 K and water 373 K. Explain.



- Q.15 The experimental molecular weight of acetic acid is just double than theoretical molecular weight of acetic acid. Why?
- Q.16 Although chlorine has same electronegativity as nitrogen but the former does not form effective H-bonding. Explain.
- Q.17 Molar entropy change of vapourization of acetic acid is less than that of water. Explain
- Q.18 Heat of vapourization of water is higher than HF, however strength of H-bond in HF is higher than water. Explain

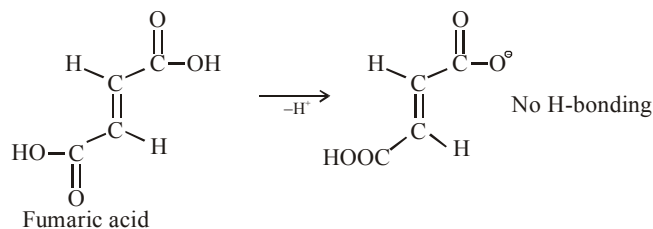
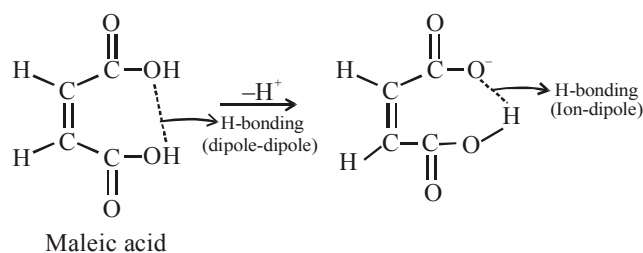
**ANSWER OF HYDROGEN BONDING**

1.

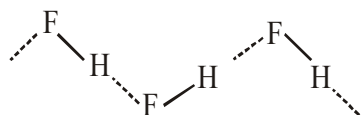


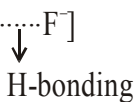
Structure of boric acid; the dotted lines represent hydrogen bonds

2. Inter molecular H-Bonding in case of para nitro phenol is strong enough to increase boiling point which is not favoured in o-Nitro phenol.
3. Maleic acid anion gets stabilize due to intra molecular H-bonding which is not possible in anion of Fumaric acid. So  $H^+$  releasing tendency is more in case of maleic acid

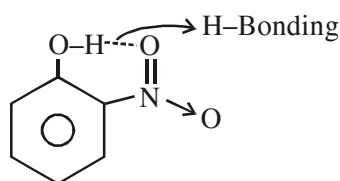


4. Due to strong H-Bonding in H-F



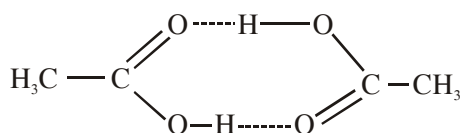
5. Due to H-Bonding in  $\text{NH}_3$ .
6. Density of ice is higher than that of water due to cage like structure of ice volume of ice increases and density decreases.
7. On heating ice in temperature range  $0-4^\circ\text{C}$  H-bonds of ice break down, which decreases volume, hence density of  $\text{H}_2\text{O}$  increases. On heating ice after  $4^\circ\text{C}$  thermal vibrations of  $\text{H}_2\text{O}$  molecules increases which increases effective volume of ice, so density of ice again decreases.
8. H-I bond is weak as compare to H-F so it can be dissociated easily and can give  $\text{H}^+$  easily.
9. The organic matter in wood participate in H-bonding with water molecules in ice-cream.
10.  $\text{K}^+[\text{F}-\text{H}\cdots\text{F}]$  But  $\text{K}\text{HBr}_2$  &  $\text{K}\text{HI}_2$  can't form H-Bond.  


11. In o-Nitrophenol intra molecular H-bond is present which decreases it's solubility in water.



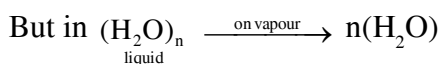
Ortho Nitro-phenol

12. In o-hydroxy benzaldehyde intramolecular H-bond is present which is less stronger than intermolecular H-bond in p-hydroxy benzaldehyde.
13. Extent of H-bonding in glycerol is more as compare to ethanol so it is more viscous.
14. Due to H-bonding in  $\text{H}_2\text{O}$
15. Due to H-bonding in acetic acid it forms dimer so overall molecular weight is just double of original

Dimer of  $\text{CH}_3\text{COOH}$ 

16. Due to bigger size of 'Cl' atom it's interaction is not enough to evolve the amount of energy which lies in the range of H-bond.
17.  $(\text{AcOH})_n$   $\xrightarrow[\text{liquid}]{\text{on vapour}}$   $\frac{n}{2} (\text{AcOH})_2$

} Not completely converted



Here all  $\text{H}_2\text{O}$  molecule gets vapourised. So entropy change is more

18. As extent of H-bond is more in  $\text{H}_2\text{O}$  as compare to HF, heat of vaporisation of water is higher than HF.

## VANDER WAAL'S FORCES

- ⇒ These are the weakest type of inter molecular forces that exist among the chemical species which bring about a significant change in physical properties.
- ⇒ These are non-directional, non-valence cohesive forces. These attractive forces being played between the two molecules are independent of the presence of other molecules.
- ⇒ Solid, liquid or gaseous states of many molecules are explained on the basis of inter molecular forces other than covalent, ionic or metallic bonds. Although inert gases do not form any type of bond but may exist in liquid and solid states. This shows that the atoms of inert gases are attracted by each other through some type of inter molecular forces. These intermolecular forces are called Vander Waals forces.

### Types of Vander Waal's Forces

- (1) **Dipole-dipole interaction (Keesom forces)** : The force of attraction between the oppositely charged poles of two polar molecules (for example :  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ,  $\text{PH}_3$  etc.) is called dipole-dipole attraction.
- (2) **Dipole-induced dipole interaction (Debye forces)** : This type of cohesive forces occurs in a mixture of polar and non polar molecules. The former induce polarity in non polar molecules by disturbing their electron system. for example force of attraction between  $\text{Cl}_2$  and  $\text{H}_2\text{O}$ .
- (3) **Instantaneous dipole-Induced dipole interaction (Dispersion forces/London forces)** : The weak intermolecular forces operating in similar non polar gaseous molecules are called London forces. These forces are very weak in nature and exist only at low temperature. For example weak intermolecular forces in  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{N}_2$ , molecules and in noble gases.

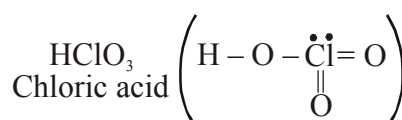
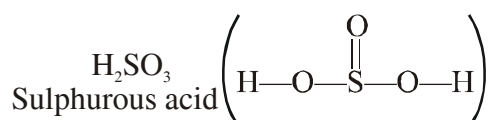
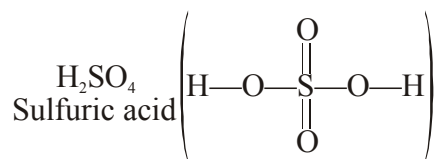
(Note :- London forces present in both polar and non polar species)

### Other Weak Interactions

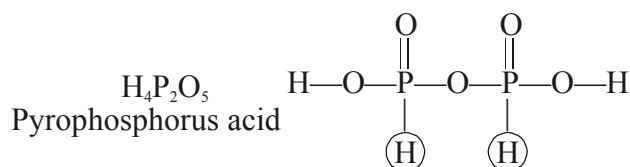
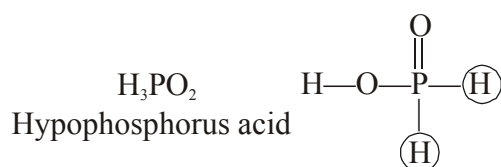
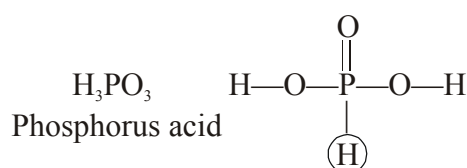
- (1) **Ion-dipole interaction** : Polar molecules are attracted by ions. The negative pole is attracted by cation and positive pole attracted by the anion. This type of attraction is called ion dipole attraction, ion-dipole attraction is observed generally in the process of solvation when sodium chloride ( $\text{Na}^+ \text{Cl}^-$ ) is dissolved in water because negative poles of water aggregate around  $\text{Na}^+$  ions and positive poles around  $\text{Cl}^-$  ions.
- (2) **Ion-induced dipole interaction** : When non polar molecules come in contact with ions, its electron cloud gets polarised and the oppositely charged end of it is attracted by the ion. For example attraction between  $\text{I}^-$  and  $\text{I}_2$  molecule.

### □ OXY-ACIDS

Those compounds which contain X–O–H bond are called oxy-acids. Where X is usually a non-metal. But sometimes X may also be a metal.

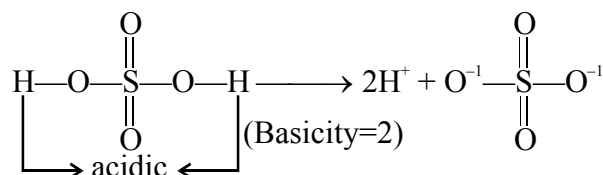


In oxy acids, all the hydrogens are attached with oxygen. Although there are a very few exceptions (as given below), in which all hydrogens are not attached with oxygen.

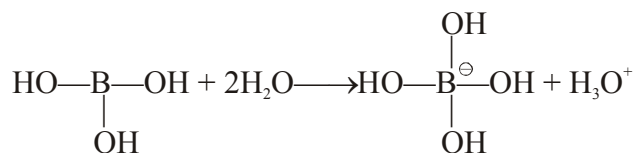


In these three oxyacids circled hydrogens are not attached with oxygen.

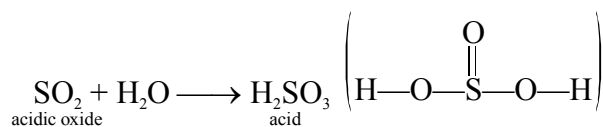
In oxyacids, those hydrogens which are attached with oxygen are acidic in nature, i.e., they ionise in solution.

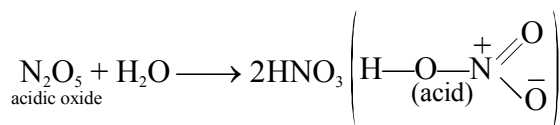
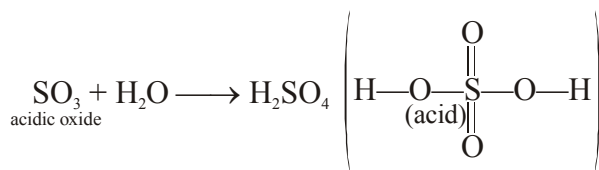


No. of hydrogens attached with oxygen is known as basicity of the acid. One notable exception is  $\text{H}_3\text{BO}_3$  in which all the three hydrogens are attached with oxygen yet, they do not ionise in solution. In fact,  $\text{H}_3\text{BO}_3$  when dissolved in water, it behaves as a monobasic acid.



Oxyacids are actually aqueous solutions of acidic oxides.



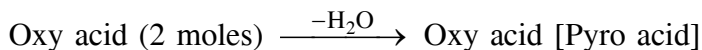


- Some acids have suffix-ic acid and some has-ous acid. Usually, when the central atom in oxy acid is in higher oxidation state the name of the acid ends with -ic acid and when the central atom is in lower oxidation state, it's name ends with -ous acid.

**Oxyacids can be classified as**

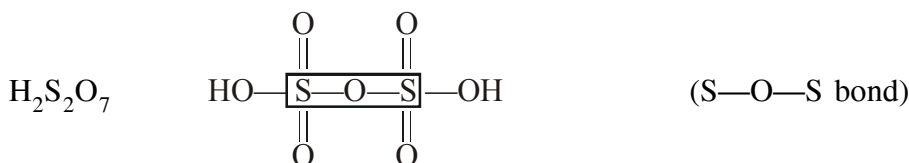
□ **PYRO ACIDS :**

When one mole of water is removed from two moles of an oxyacid, the resultant oxy acid is known as pyro acid. In general pyro acids contain X—O—X bonds.



- $\text{H}_2\text{SO}_4$  (2 moles) =  $\text{H}_4\text{S}_2\text{O}_8 \xrightarrow{-\text{H}_2\text{O}} \text{H}_2\text{S}_2\text{O}_7$  [Pyrosulphuric acid]  
[Sulphuric acid]

In general Pyro acids contain X—O—X bond.



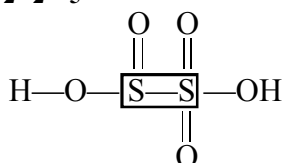
- $\text{H}_3\text{PO}_4$  (2 moles) =  $\text{H}_6\text{P}_2\text{O}_8 \xrightarrow{-\text{H}_2\text{O}} \text{H}_4\text{P}_2\text{O}_7$  [Pyrophosphoric acid]  
[Orthophosphoric acid]



- $2\text{H}_3\text{PO}_3$  (phosphorus acid)  $\xrightarrow{-\text{H}_2\text{O}}$   $\text{H}_4\text{P}_2\text{O}_5$  (pyrophosphorus acid)  $\text{HO}-\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \boxed{\text{P}-\text{O}-\text{P}}-\text{OH} \\ \parallel \quad \quad \parallel \\ \text{H} \quad \quad \text{H} \end{array}-\text{OH}$

- $2\text{H}_2\text{SO}_3 \xrightarrow{-\text{H}_2\text{O}} \text{H}_2\text{S}_2\text{O}_5$  (Pyrosulfurous acid)

**Exception :  $\text{H}_2\text{S}_2\text{O}_5$  [Pyrosulfurous acid] does not contain S—O—S linkage.**

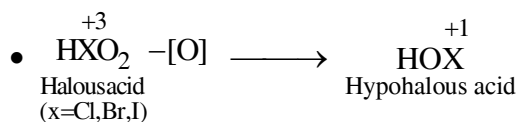
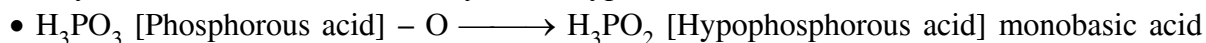


Pyrosulfurous acid

### □ HYPO ACID :

Hypo prefix is added to those oxy acids which is obtained when one oxygen atom is removed from its form of (usually) acids.

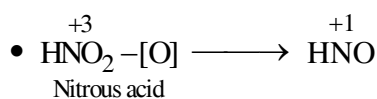
Oxy acid(-ous form)  $\xrightarrow{-O}$  Oxy acid (Hypo -ous acid)



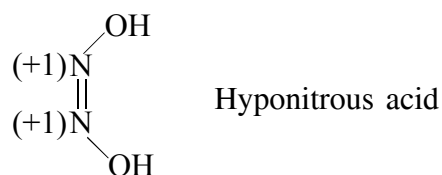
$\text{HOCl}$  - Hypochlorous acid

$\text{HOBr}$  - Hypobromous acid

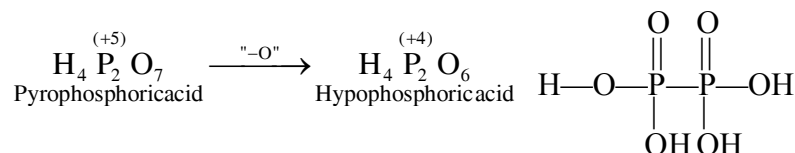
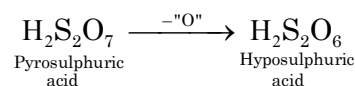
$\text{HOI}$  - Hypoiodous acid



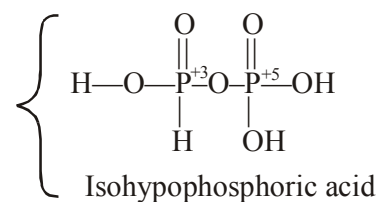
$\text{HNO}$  exist in dimeric form i.e. as  $(\text{HNO})_2 = \text{H}_2\text{N}_2\text{O}_2$



**If one O is removed from pyro 'ic' acid it produce hypo 'ic' acid**

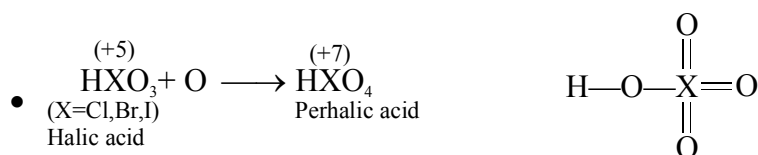


Exception : (It may be exist as isohypophosphoric acid)



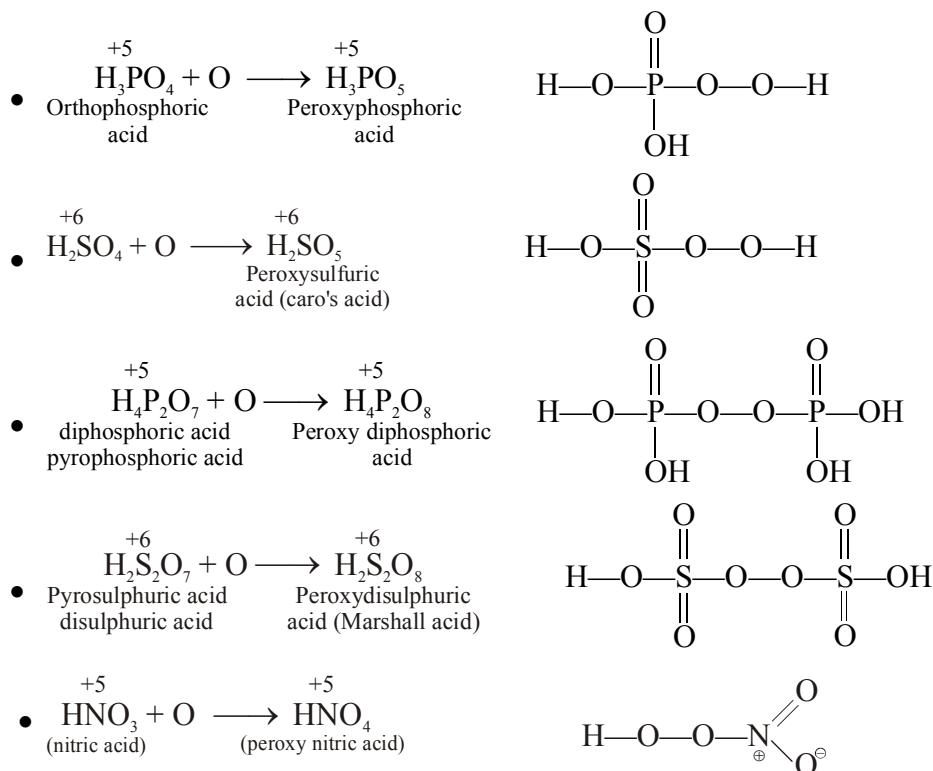
### □ PER ACID AND PEROXY ACID :

When one oxygen is added to -ic form of acid and if the oxidation number of central atom in resulting oxy acid is more than the -ic form of acid, then it is per acid.



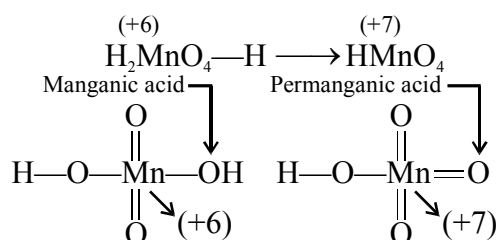
$\text{HClO}_4$  perchloric acid  $\text{HBrO}_4$  - Perbromic acid.

**Peroxy prefix** is added to those oxy acids which are obtained when one oxygen is added to -ic form of acid and the oxidation number of central atom remains the same. Peroxy acids contain peroxy linkage ( $-\text{O}-\text{O}-$ ).



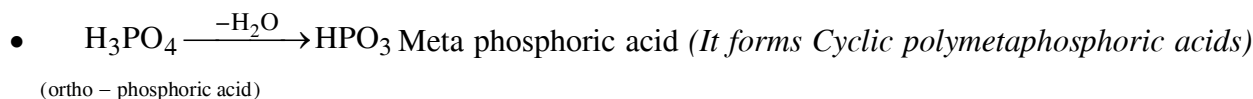
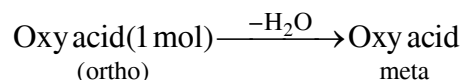
Note : Peroxynitric acid does not contain N—O—H bond, yet it is considered to be oxy acid.

**Exception :**  $\overset{+6}{\text{H}_2\text{MnO}_4}$  is manganic acid when one hydrogen is removed from  $\text{H}_2\text{MnO}_4$ ,  $\text{HMnO}_4$  is formed which is named as permanganic acid.

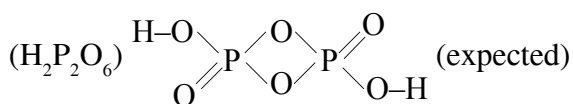


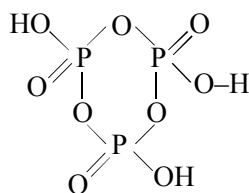
□ **ORTHO ACIDS AND META ACIDS :-**

When one mole of  $\text{H}_2\text{O}$  is removed from one mole of an oxy acid, the resulting compound, if an oxy acid (i.e. it contains at least one X—OH bond) then the oxy acid from which  $\text{H}_2\text{O}$  is removed is named as ortho acid and the product oxyacid is known as META ACID.

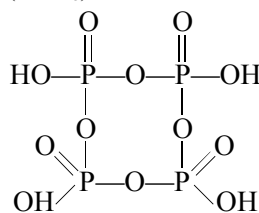


◆ **Cyclic polymetaphosphoric acids :**  
 $(\text{HPO}_3)_2$  - Dimetaphosphoric acid

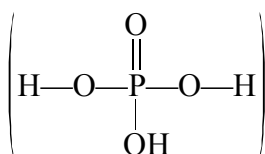




Trimetaphosphoric acid

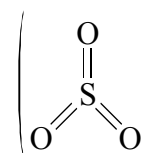
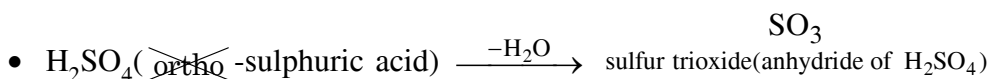
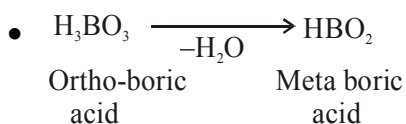


Tetrametaphosphoric acid



Orthophosphoric acid

An ortho acid must contain at least three hydrogens.

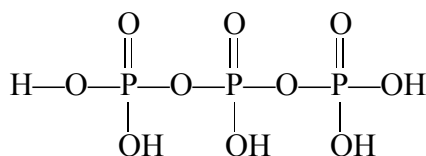


As  $\text{SO}_3$  does not contain any hydrogen (i.e., X-OH/S-OH bond), so  $\text{SO}_3$  is not an oxy acid rather it is anhydride of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) so,  $\text{H}_2\text{SO}_4$  can't be prefixed with ortho, and its name does not contain any prefix and it is named as sulphuric acid.

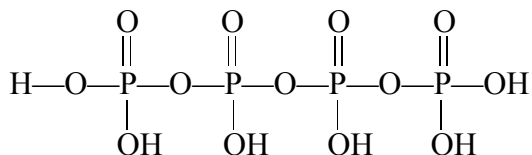
### □ POLYPHOSPHORIC ACID :

Oxy acids having general formula  $\text{H}_{(n+2)}\text{P}_n\text{O}_{(3n+1)}$  are known as polyphosphoric acids. These contain  $(n-1)$  P-O-P bonds.

$\text{H}_5\text{P}_3\text{O}_{10}$  - Tripolyphosphoric acid



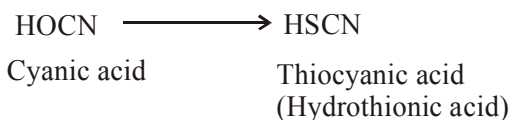
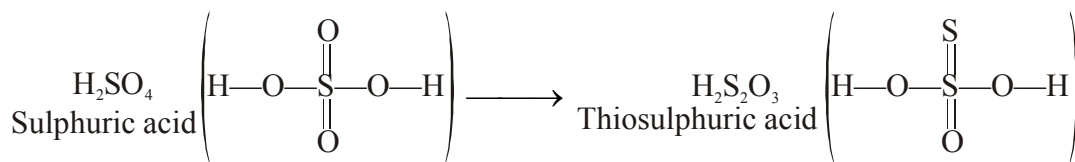
$\text{H}_6\text{P}_4\text{O}_{13}$  - Tetrapolyphosphoric acid



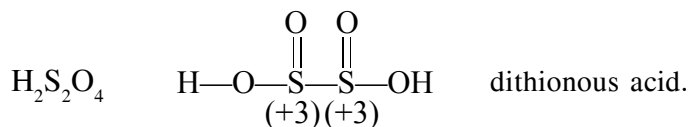


❑ THIO ACID :

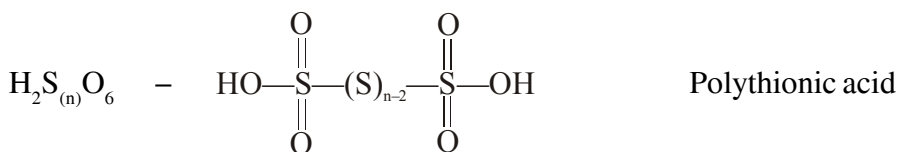
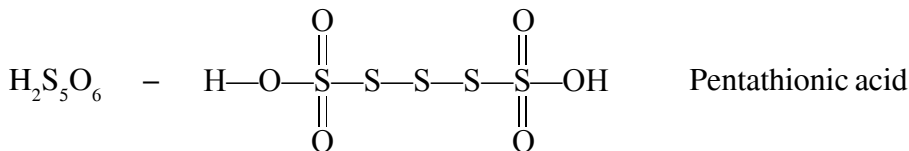
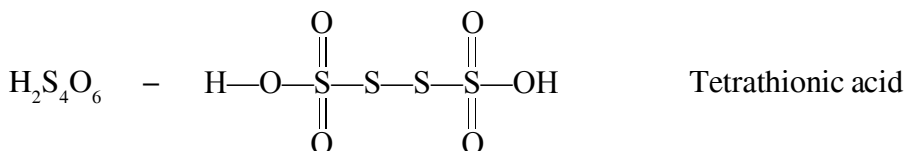
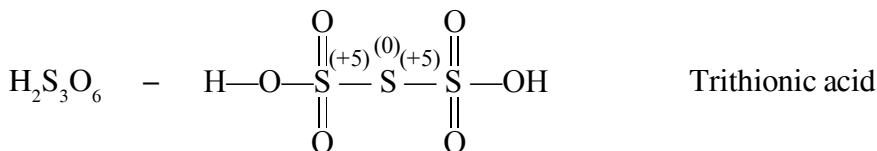
- ◆ 1. Oxy acids in which one oxygen atom are replaced by sulphur are considered as thio acid.  
For example :-



- ◆ 2. Oxy acids of sulphur containing S—S bonds are known as thio acids.



**Thionic acids :** Oxy acids of sulphur containing S—S bond and having general formula  $\text{H}_2\text{S}_{(n+2)}\text{O}_6$  are known as thionic acids





- ♦ **Naming of salts of oxy acids : The name of salt ends with – “ate” if the name of the oxy acid ends with - ic acid and all prefix remain same eg. :-**

$H_2SO_4$ Sulphuric acid	$Na_2SO_4$ - Sodium sulfate $K_2SO_4$ - Potassium sulfate $BaSO_4$ - Barium sulfate $FeSO_4$ - Ferrous sulfate $Al_2(SO_4)_3$ - Aluminium sulfate
$H_3PO_4$ Orthophosphoric acid	$Na_3PO_4$ - Sodium orthophosphate $K_3PO_4$ - Potassium orthophosphate $Ca_3(PO_4)_2$ - Calcium Orthophosphate $AlPO_4$ - Aluminium orthophosphate
$HPO_3$ meta phosphoric acid	$NaPO_3$ - Sodium metaphosphate $KPO_3$ - Potassium metaphosphate $Ca(PO_3)_2$ - Calcium metaphosphate $Al(PO_3)_3$ - Aluminium metaphosphate
$HClO_3$ chloric acid	$KClO_3$ - Potassium chlorate $NaClO_3$ - Sodium chlorate $Ca(ClO_3)_2$ - Calcium chlorate
$HClO_4$ Perchloric acid	$NaClO_4$ - Sodium perchlorate $KClO_4$ - Potassium perchorate $NH_4ClO_4$ - Ammonium perchlorate $Ca(ClO_4)_2$ - Calcium perchlorate
$H_3PO_4$ Orthophosphoric acid $(HPO_3)_6 = H_6P_6O_{18}$ Hexametaphosphoric acid	$KH_2PO_4$ potassium dihydrogen orthophosphate $Ca(H_2PO_4)_2$ calcium dihydrogen orthophosphate $Na_6P_6O_{18}$ Sodium hexametaphosphate
$HBO_2$ metaboric acid	$NaBO_2$ sodium metaborate
$H_2SO_5$ Peroxy sulphuric acid	$Na_2SO_5$ - Sodium peroxy sulfate
$H_4P_2O_7$ Pyrophosphoric acid	$Na_4P_2O_7$ - Sodium pyrophosphate

**If the name of the oxy acid ends with ous acid then the name of the salt ends with “ite”**

$HClO_2$ chlorous acid	$NaClO_2$ sodium chlorite $KClO_2$ potassium chlorite $Ca(ClO_2)_2$ calcium chlorite
$H_3PO_3$ Phosphorous acid (dibasic acid)	$Na_2HPO_3$ sodium phosphite $K_2HPO_3$ Potassium phosphite $CaHPO_3$ calcium phosphite
$H_2SO_3$ sulfurous acid	$Na_2SO_3$ sodium sulfite $K_2SO_3$ potassium sulfite
$HNO_2$ Nitrous acid	$NaNO_2$ sodium nitrite $KNO_2$ potassium nitrite
$HOCl$	$NaOCl$ sodium hypochlorite

Hypochlorous acid

KOBr potassium hypobromite



NaOI sodium hypoiodite

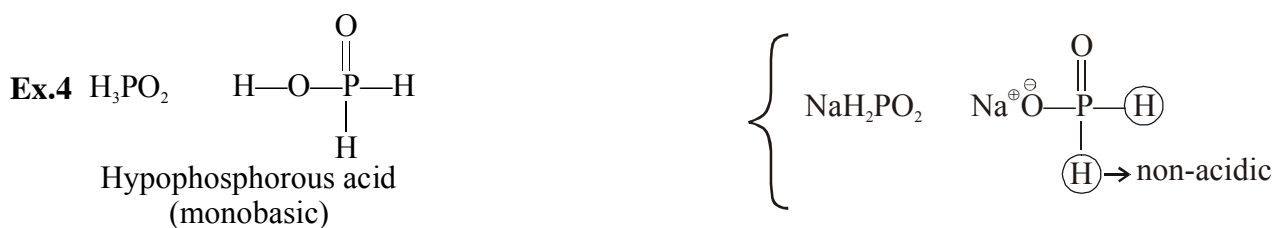
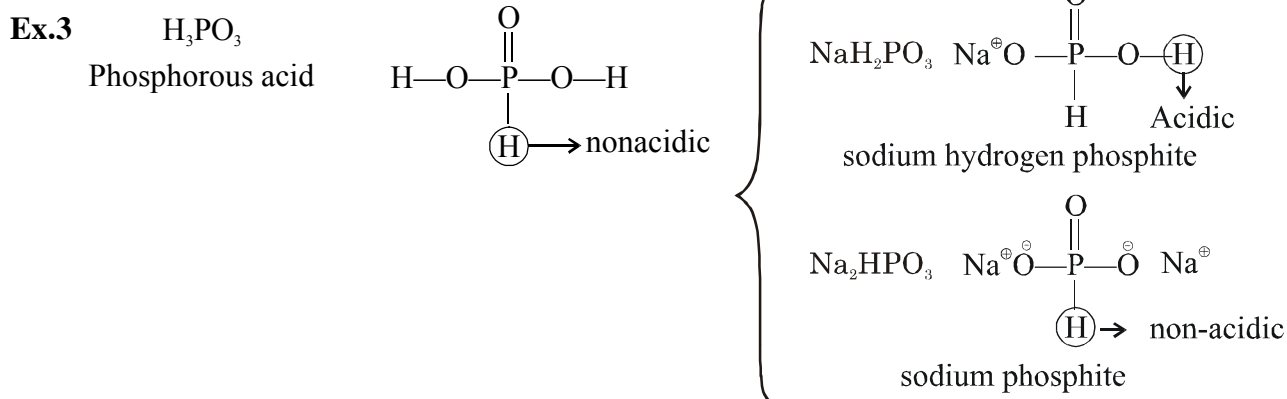
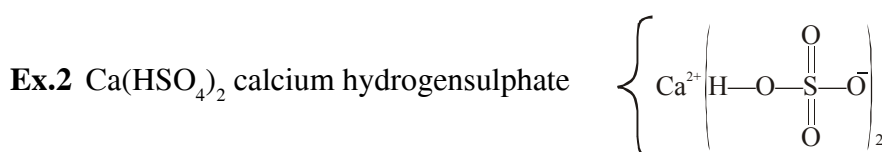
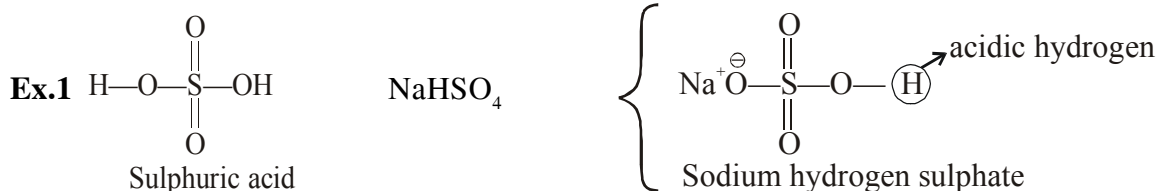
Hypophosphorous acid

$\text{NaH}_2\text{PO}_2$  sodium hypophosphite

(monobasic acid)

$\text{Ba}(\text{H}_2\text{PO}_2)_2$  Barium hypophosphite

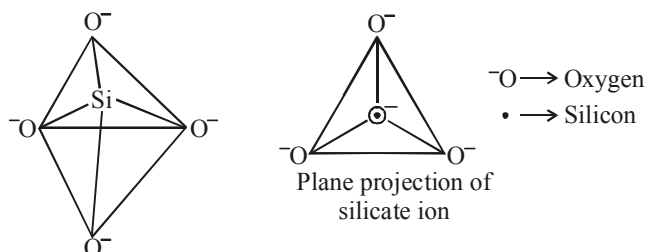
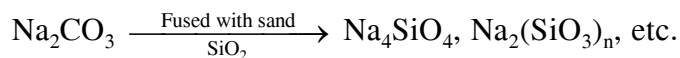
*If all the ionisable hydrogens are not removed from the acid to form salt, then the hydrogen word is added to the name of the salt containing acidic hydrogens (H attached with oxygen)*



sodium hypophosphite but not sodium dihydrogen phosphite as H is not acidic.

**SILICATES**

Silicates are metal derivatives of silicic acid,  $H_4SiO_4$  or  $Si(OH)_4$ . Silicates are formed by heating metal oxide or metal carbonates with sand, e.g.,



Silicates have basic unit of  $SiO_4^{4-}$ , each silicon atom is bonded with four oxide ions tetrahedrally. There are following types of silicates

Silicates	Sharing of O-atom / Basic Tetrahedral unit	Contribution of O-atom/Basic Tetrahedral unit	General formula
Ortho	0	4	$SiO_4^{4-}$
Pyro	1	3.5	$Si_2O_7^{6-}$
Cyclic	2	3	$(SiO_3)_{2n}^{2n-}$
Simple chain (pyroxene)	2	3	$(SiO_3)_n^{2n-}$
Double chain (Amphibole)	(3, 2) av = 2.5	$\frac{11}{4} = \left(\frac{5.5}{2}\right)$	$(Si_4O_{11})_n^{6n-}$
2D or (Sheet)	3	2.5	$(Si_2O_5)_n^{2n-}$
3D	4	2	$(SiO_2)_n$

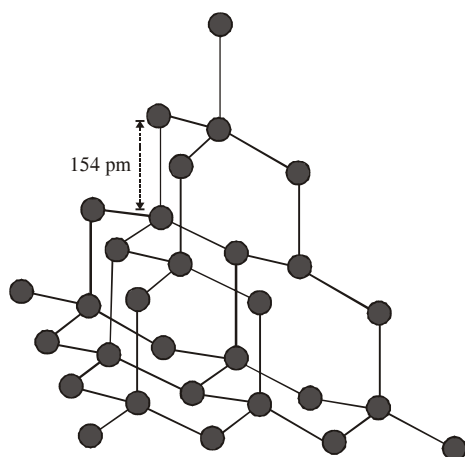
## ALLOTROPE OF CARBON FAMILY

⇒ **Diamond** (*kinetically most stable allotrope of carbon, meta stable phase of carbon*)

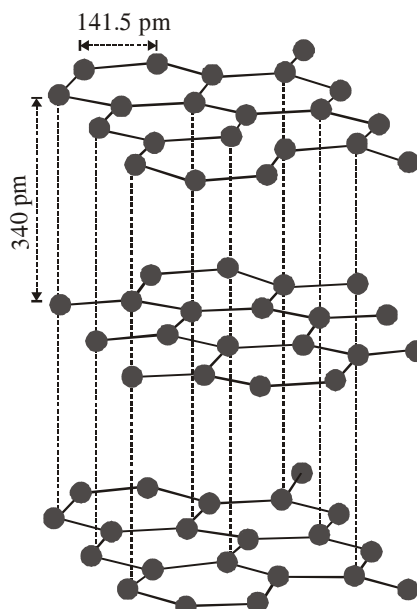
- It has a **crystalline lattice**. A rigid three dimensional network of carbon atoms.
- Each carbon atom undergoes  **$sp^3$  hybridisation** and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion.
- **C–C bond length is 154 pm.**
- It is very difficult to break **extended covalent bonding** and, therefore, diamond is a **very hard** substance.

Uses :-

- Used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.
- Diamond is a precious stone and used in jewellery. It is measured in **carats** (1 carat = 200 mg).



The structure of diamond



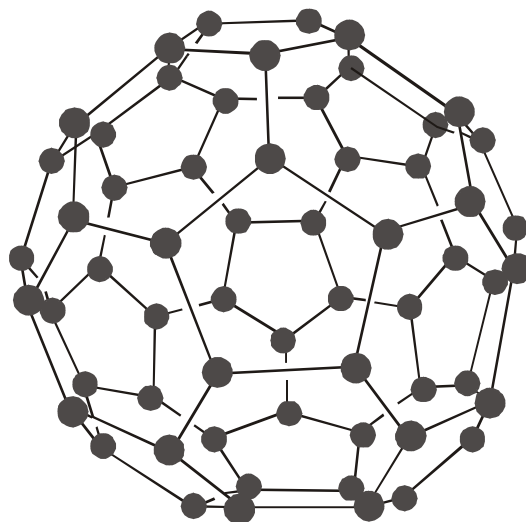
The structure of graphite

⇒ **Graphite** (*Thermodynamically most stable allotrope of carbon*)

- Layered structure. **Layers are held by van der Waals forces** and distance between two **layers is 340 pm.**
- Each layer is composed of **planar hexagonal rings** of carbon atoms. C—C bond length within the **layer is 141.5 pm.**
- Each carbon atom in hexagonal ring **undergoes  $sp^2$  hybridisation** and makes three sigma bonds with three neighbouring carbon atoms. **Fourth electron forms a  $\pi$  bond.** The electrons are delocalised over the whole sheet. Thus, graphite is lustrous.
- Electrons are mobile and, therefore, graphite conducts electricity along the sheet.
- Graphite cleaves easily between the layers and, therefore, it is very soft and slippery.
- **Uses :-** Due to slippery nature graphite is used as a **dry lubricant** in machines running at high temperature, where oil cannot be used as a lubricant.
- **Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis.**

### Fullerenes

- Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon.
- The sooty material formed by condensation of vapourised  $C_n$  small molecules consists of mainly  $C_{60}$  with smaller quantity of  $C_{70}$  and traces of fullerenes consisting of even number of carbon atoms up to 350 or above.
- **Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules.**
- **Fullerene  $C_{60}$  :- molecule has a shape like soccer ball and called Buckminsterfullerene. It contains 20, six- membered rings and 12, five membered rings.**
- This ball shaped molecule has **60 vertices** and each one is occupied by one carbon atom and it also **contains both single and double bonds** with C–C distances of 143.5 pm and 138.3 pm respectively. **Spherical fullerenes are also called *bucky balls* in short.**
- A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings.
- All the carbon atoms are equal and they undergo  $sp^2$  hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms.
- The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule. However, because of non-planar nature of fullerenes, their aromatic character gets diminished and reactivity increases.



[The structure of  $C_{60}$  Buckminsterfullerene : Note that molecule has the shape of a soccer ball (football)]

### IMPORTANT POINTS FOR CARBON

- **Thermodynamic stability order** : Graphite > Diamond > Fullerene  $C_{60}$
- It is very important to know that **graphite is thermodynamically most stable allotrope of carbon and, therefore,  $\Delta H_f$  of graphite is taken as zero.  $\Delta H_f$  values of diamond and fullerene,  $C_{60}$  are 1.90 and 38.1 kJ mol<sup>-1</sup>, respectively.**
- Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes.
  - ⇒ **Carbon black** is obtained by burning hydrocarbons in a limited supply of air.
  - ⇒ **Charcoal and coke** are obtained by heating wood or coal respectively at high temperatures in the absence of air.

#### Uses of Carbon

- **Graphite fibres** embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes.
- **Crucibles** made from graphite are inert to dilute acids and alkalis.
- Being **highly porous, activated charcoal** is used in adsorbing poisonous gases; also used in water filters to remove organic contaminants and in airconditioning system to control odour.
- **Carbon black** is used as black pigment in black ink and as filler in automobile tyres.
- **Coke** is used as a fuel and largely as a reducing agent in metallurgy.

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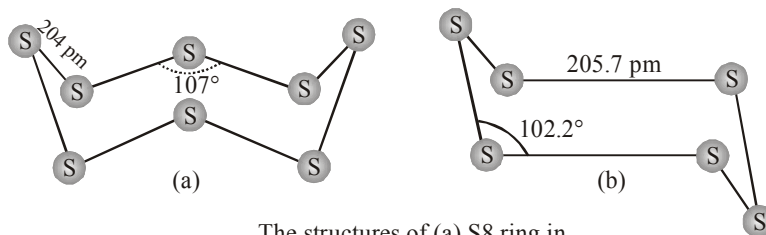
### ALLOTROPES OF OXYGEN FAMILY

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- **Oxygen**  
Two non-metallic forms, dioxygen  $O_2$  and ozone  $O_3$ . Dioxygen  $O_2$  is stable as a diatomic molecule.  $O_3$  molecule is diamagnetic while  $O_2$  is paramagnetic.
- Six allotropes of **selenium** are known.
- **Tellurium** has only one crystalline form, which is silvery white and semimetallic.
- This is similar to grey Se, but has stronger metallic interaction.
- **Sulphur Allotropic forms** :
  - Sulphur forms numerous allotropes of which the **yellow rhombic** ( $\alpha$ -sulphur) and **monoclinic** ( $\beta$ -sulphur) forms are the most important.
  - The **stable form** at room temperature is **rhombic sulphur**, which transforms to monoclinic sulphur when heated above 369 K.



- ⇒ **Rhombic sulphur ( $\alpha$ -sulphur)** (*Most stable sulphur allotrope at room temperature*)
- This allotrope is **yellow in colour, m.p. 385.8 K and specific gravity 2.06**. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in  $\text{CS}_2$ .
  - It is **insoluble in water** but dissolves to some extent in benzene, alcohol and ether. It is **readily soluble** in  $\text{CS}_2$ .
- ⇒ **Monoclinic sulphur ( $\beta$ -sulphur)**
- Its m.p. is 393 K and specific gravity 1.98. It is **soluble in  $\text{CS}_2$  while water insoluble**.
  - This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, **colourless needle shaped crystals of  $\beta$ -sulphur are formed**.
  - **It is stable above 369 K and transforms into  $\alpha$ -sulphur below it**. Conversely,  $\alpha$ -sulphur is stable below 369 K and transforms into  $\beta$ -sulphur above this. At 369 K, both the forms are stable. This temperature is called **transition temperature**.
  - **Both rhombic and monoclinic sulphur have  $\text{S}_8$  molecules**. These  $\text{S}_8$  molecules are packed to give different crystal structures. **The  $\text{S}_8$  ring in both the forms is puckered and has a crown shape**. The molecular dimensions are given in the figure.



The structures of (a)  $\text{S}_8$  ring in rhombic sulphur and (b)  $\text{S}_6$  form

### EXTRA POINTS

- Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades.
- In cyclo- $\text{S}_6$ , the ring adopts the chair form and the molecular dimensions are as shown in figure.
- At elevated temperatures ( $\sim 1000$  K),  $\text{S}_2$  is the dominant species and is paramagnetic just like  $\text{O}_2$ .
- **Engel's sulphur ( $\epsilon$ -sulphur)** is unstable and contains  $\text{S}_6$  rings arranged in the chair conformation. It is made by pouring  $\text{Na}_2\text{S}_2\text{O}_3$  solution into concentrated HCl and extracting the S with toluene.
- Plastic sulphur- $(\chi)$  is obtained by pouring liquid sulphur into water.

### Allotropes of Nitrogen Family :

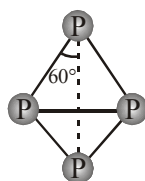
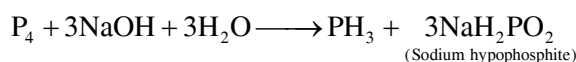
Solid As, Sb and Bi each exist in several allotropic forms. Arsenic vapour contains tetrahedral  $\text{As}_4$  molecules. A reactive yellow form of the solid resembles white phosphorus and is thought to contain tetrahedral  $\text{As}_4$  units. Sb also has a yellow form. All three elements have much less reactive metallic or  $\alpha$ -forms.

### PHOSPHORUS ALLOTROPIC FORMS

Phosphorus is found in many allotropic forms, the important ones being white, red and black.

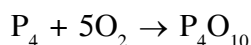
#### ⇒ White phosphorus

- Translucent, white, waxy solid.
- It is poisonous, **insoluble in water** but **soluble in carbon disulphide** and glows in dark (chemiluminescence).
- It dissolves in boiling NaOH solution in an inert atmosphere giving  $\text{PH}_3$ .



Discrete tetrahedral  $\text{P}_4$  unit of White Phosphorus

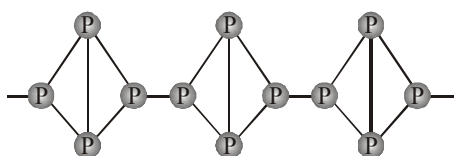
- White phosphorus is **less stable** and therefore, **more reactive** than the other solid phases under normal conditions **because of angular strain** in the  $\text{P}_4$  molecule where the angles are only  $60^\circ$ . It readily catches fire in air to give dense white fumes of  $\text{P}_4\text{O}_{10}$ .



#### ⇒ Red phosphorus

- Obtained by heating white phosphorus at 573K in an inert atmosphere for several days.
- When red phosphorus is heated under high pressure, a series of phases of black phosphorus is formed.
- Red phosphorus possesses **iron grey lustre**. It is **odourless, nonpoisonous and insoluble** in water as well as in **carbon disulphide**.
- Chemically, red phosphorus is **much less reactive than white phosphorus**. **It does not glow in the dark**.

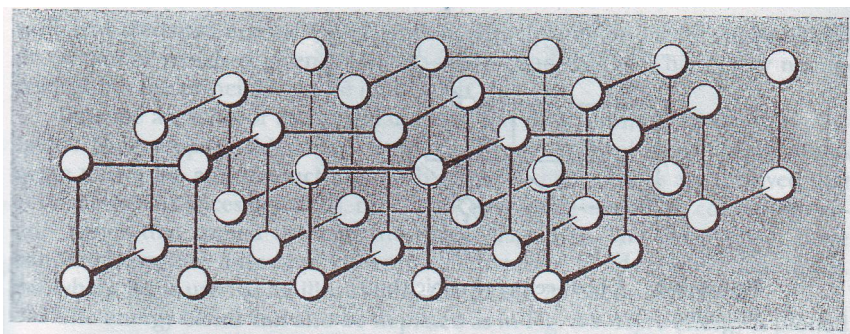
It is polymeric, consisting of chains of  $\text{P}_4$  tetrahedra linked together in the manner as shown in Fig.



Red Phosphorus

⇒ **Black phosphorus**

- Two forms  $\alpha$ -black phosphorus and  $\beta$ -black phosphorus.
- $\alpha$ -Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It does not oxidise in air.
- $\beta$ -Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

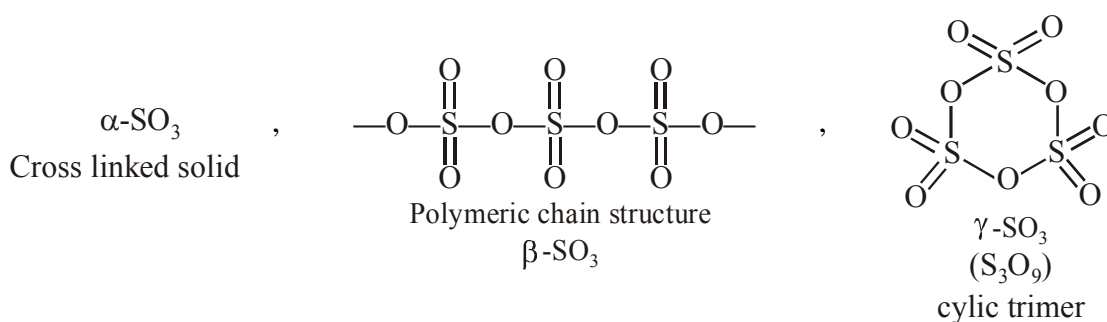


**Thermodynamic stability order :** Black phosphorus > Red phosphorus > White phosphorus

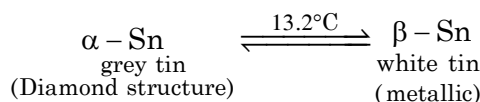
**Reactivity order :** Black phosphorus < Red phosphorus < White phosphorus

**ALLOTROPIC FORM OF SO<sub>3</sub>**

SO<sub>3</sub> have three allotropic forms  $\alpha$ -SO<sub>3</sub> ,  $\beta$ -SO<sub>3</sub> and  $\gamma$ -SO<sub>3</sub>



**NOTE:-** Si, Ge and Sn have a diamond type of structure, though Sn exists as a metallic form. Pb exists only in the metallic form. Ge is unusual because the liquid expands when it forms the solid. This property is unique to Ga, Ge and Bi.



## EXERCISE # O-1

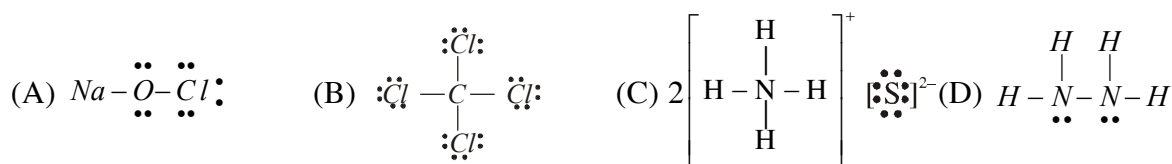
## IONIC BOND

(Only one option is correct)

1. The compound which contains ionic as well as covalent bonds is  
 (A)  $C_2H_4Cl_2$  (B)  $CH_3I$  (C)  $KCN$  (D)  $H_2O_2$  **CBO0001**
2. A bond formed between two like atoms cannot be  
 (A) ionic (B) covalent (C) coordinate (D) metallic **CBO0002**
3. An ionic bond  $A^+B^-$  is most likely to be formed when :  
 (A) the ionization energy of  $A$  is high and the electron gain enthalpy of  $B$  is low  
 (B) the ionization energy of  $A$  is low and the electron gain enthalpy of  $B$  is high  
 (C) the ionization energy of  $A$  and the electron gain enthalpy of  $B$  both are high  
 (D) the ionization energy of  $A$  and the electron gain enthalpy of  $B$  both are low **CBO0003**

## COVALENT BOND, CO-ORDINATE BOND &amp; LEWIS STRUCTURE

4. Which of the following species are hypervalent?  
 (1)  $PCl_5$ , (2)  $BF_3$ , (3)  $XeF_2$ , (4)  $CO_3^{2-}$   
 (A) 1, 2, 3 (B) 1, 3 (C) 3, 4 (D) 1, 2 **CBO0004**
5. The types of bond present in  $N_2O_5(g)$  are  
 (A) only covalent (B) only ionic (C) ionic and covalent (D) covalent & coordinate **CBO0005**
6. Which of the following molecule does not have coordinate bonds?  
 (A)  $CH_3-NC$  (B)  $CO$  (C)  $O_3$  (D)  $CO_3^{2-}$  **CBO0006**
7. Which of the following Lewis dot diagrams is(are) incorrect ?

**CBO0007**

## V.B.T., HYBRIDISATION &amp; VSEPR THEORY

8. Which of the following has a geometry different from the other three species (having the same geometry)?  
 (A)  $BF_4^-$  (B)  $SO_4^{2-}$  (C)  $XeF_4$  (D)  $PH_4^+$  **CBO0008**
9. Maximum bond energy is in :  
 (A)  $F_2$  (B)  $N_2$  (C)  $O_2$  (D) equal **CBO0009**

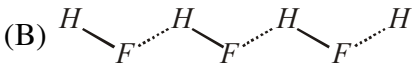
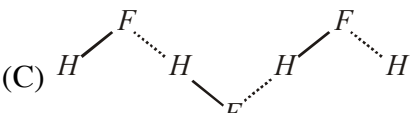
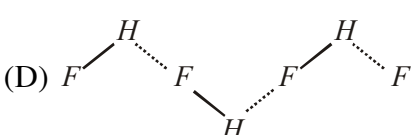
10. The hybridisation and shape of  $\text{BrF}_3$  molecule are :  
 (A)  $sp^3d$  and bent T shape (B)  $sp^2d^2$  and tetragonal  
 (C)  $sp^3d$  and bent (D) none of these  
**CBO0010**
11. The shape of methyl cation ( $\text{CH}_3^+$ ) is likely to be:  
 (A) linear (B) pyramidal (C) planar (D) spherical  
**CBO0011**
12. The structure of  $\text{XeF}_2$  involves hybridization of the type :  
 (A)  $sp^3$  (B)  $sp^2$  (C)  $sp^3d$  (D)  $sp^3d^2$   
**CBO0012**
13. Which of the following has been arranged in increasing order of length of the hybrid orbitals ?  
 (A)  $sp < sp^2 < sp^3$  (B)  $sp^3 < sp^2 < sp$  (C)  $sp^2 < sp^3 < sp$  (D)  $sp^2 < sp < sp^3$   
**CBO0013**
14. In the context of carbon, which of the following is arranged in the correct order of electronegativity :  
 (A)  $sp > sp^2 > sp^3$  (B)  $sp^3 > sp^2 > sp$  (C)  $sp^2 > sp > sp^3$  (D)  $sp^3 < sp < sp^2$   
**CBO0014**
15. When  $2s-2s$ ,  $2p-2p$  and  $2p-2s$  orbitals overlap, the bond strength decreases in the order :  
 (A)  $p-p > s-s > p-s$  (B)  $p-p > p-s > s-s$   
 (C)  $s-s > p-p > p-s$  (D)  $s-s > p-s > p-p$   
**CBO0015**
16. Carbon atoms in  $\text{C}_2(\text{CN})_4$  are :  
 (A)  $sp$ -hybridized (B)  $sp^2$ -hybridized  
 (C)  $sp$ - and  $sp^2$  hybridized (D)  $sp$ ,  $sp^2$  and  $sp^3$ - hybridized  
**CBO0016**
17. The structure of  $\text{XeF}_6$  in vapour phase is  
 (A) pentagonal bipyramidal (B) trigonal bipyramidal  
 (C) capped octahedron (D) square bipyramidal  
**CBO0017**

### BENT'S RULE AND DRAGO'S RULE

18. C-H bond distance is the longest in:  
 (A)  $\text{C}_2\text{H}_2$  (B)  $\text{C}_2\text{H}_4$  (C)  $\text{C}_2\text{H}_6$  (D)  $\text{C}_2\text{H}_2\text{Br}_2$   
**CBO0018**
19. The bond angle and hybridization in ether ( $\text{CH}_3\text{OCH}_3$ ) is :  
 (A)  $106^\circ 51'$ ,  $sp^3$  (B)  $104^\circ 31'$ ,  $sp^3$  (C)  $110^\circ$ ,  $sp^3$  (D)  $109^\circ 28'$ ,  $sp^3$   
**CBO0019**
20. Which of the following has been arranged in order of decreasing bond length ?  
 (A)  $\text{P-O} > \text{Cl-O} > \text{S-O}$  (B)  $\text{P-O} > \text{S-O} > \text{Cl-O}$   
 (C)  $\text{S-O} > \text{Cl-O} > \text{P-O}$  (D)  $\text{Cl-O} > \text{S-O} > \text{P-O}$   
**CBO0020**

21. Select the **CORRECT** set of statements :  
As the s-character of a hybrid orbital decreases  
(I) The bond angle decreases (II) The bond strength increases  
(III) The bond length increases (IV) Size of orbital increases  
(A) (I), (III) and (IV) (B) (II), (III) and (IV) (C) (I) and (II) (D) All are **CORRECT**  
**CBO0021**
22. Among the following, the **CORRECT** statement is :  
(A) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional  
(B) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
(C) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
(D) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional  
**CBO0022**
23. In which of the following molecule C—C bond length will be highest ?  
(A)  $\text{CF}_3 - \text{CF}_3$  (B)  $\text{F}_2\text{CH} - \text{CHF}_2$  (C)  $\text{FCH}_2 - \text{CH}_2\text{F}$  (D)  $\text{CH}_3 - \text{CF}_3$   
**CBO0023**
24. In  $\text{BClBrI}$  molecule the maximum % s-character provided from the central atom is in bond :  
(A) B - I (B) B - Cl (C) B - Br (D) Can not predict  
**CBO0024**
25. Which of the following order is **CORRECT** for increasing p-character in orbital used for bonding by central atom  
(A)  $\text{SiH}_4 > \text{CH}_4$  (B)  $\text{H}_2\text{S} > \text{H}_2\text{O}$  (C)  $\text{PH}_4^+ > \text{PH}_3$  (D)  $\text{NH}_3 > \text{PH}_3$   
**CBO0025**
- MOLECULE DOES NOT EXIST**
26.  $\text{PCl}_5$  exists but  $\text{NCl}_5$  does not because :  
(A) Nitrogen has no vacant 2d-orbitals (B)  $\text{NCl}_5$  is unstable  
(C) Nitrogen atom is much smaller than P (D) Nitrogen is highly inert  
**CBO0026**
27. Which of the following molecules do not exist.  
(A)  $\text{BF}_6^{3-}$  (B)  $\text{NCl}_3$  (C)  $\text{NOF}_3$  (D)  $\text{XeF}_5^-$   
**CBO0027**
28. Select non existing species  
(A)  $\text{PH}_3$  (B)  $\text{PH}_4^+$  (C)  $[\text{PF}_6]^-$  (D) None of these  
**CBO0028**
29. Among the fluorides below, the one which does not exist is -  
(A)  $\text{XeF}_4$  (B)  $\text{BeF}_4$  (C)  $\text{SF}_4$  (D)  $\text{CF}_4$   
**CBO0029**
30. Which of the following compound exist -  
(A)  $\text{XeH}_2$  (B)  $\text{ClF}_7$  (C)  $\text{PH}_5$  (D)  $\text{ICl}_3$   
**CBO0030**

**DIPOLE MOMENT & HYDROGEN BONDING**

31. Which of the following has been arranged in order of decreasing dipole moment ?  
 (A)  $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$  (B)  $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$   
 (C)  $\text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I} > \text{CH}_3\text{F}$  (D)  $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{I} > \text{CH}_3\text{Br}$   
**CBO0031**
32. The experimental value of the dipole moment of  $\text{HCl}$  is  $1.03 \text{ D}$ . The length of the  $\text{H}-\text{Cl}$  bond is  $1.275 \text{ \AA}$ . The percentage of ionic character in  $\text{HCl}$  is nearly :  
 (A) 43 (B) 21 (C) 17 (D) 7  
**CBO0032**
33. Ethanol has a higher boiling point than dimethyl ether though they have the same molecular weight. This is due to :  
 (A) resonance (B) coordinate bonding  
 (C) hydrogen bonding (D) ionic bonding  
**CBO0033**
34. Which of the following compounds would have significant intermolecular hydrogen bonding ?  
 $\text{HF}, \text{CH}_3\text{OH}, \text{N}_2\text{O}_4, \text{CH}_4$   
 (A)  $\text{HF}, \text{N}_2\text{O}_4$  (B)  $\text{HF}, \text{CH}_4, \text{CH}_3\text{OH}$  (C)  $\text{HF}, \text{CH}_3\text{OH}$  (D)  $\text{CH}_3\text{OH}, \text{CH}_4$   
**CBO0034**
35. For  $\text{H}_2\text{O}_2, \text{H}_2\text{S}, \text{H}_2\text{O}$  and  $\text{HF}$ , the correct order of decreasing strength of hydrogen bonding is :  
 (A)  $\text{H}_2\text{O} > \text{HF} > \text{H}_2\text{O}_2 > \text{H}_2\text{S}$  (B)  $\text{HF} > \text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{H}_2\text{S}$   
 (C)  $\text{HF} > \text{H}_2\text{O} > \text{H}_2\text{O}_2 > \text{H}_2\text{S}$  (D)  $\text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{HF} > \text{H}_2\text{S}$   
**CBO0035**
36. Which one of the following does not have intermolecular H-bonding?  
 (A)  $\text{H}_2\text{O}$  (B) *o*-nitro phenol (C)  $\text{HF}$  (D)  $\text{CH}_3\text{COOH}$   
**CBO0036**
37. The order of strength of hydrogen bonds is:  
 (A)  $\text{NH}\dots\text{N} > \text{OH}\dots\text{O} > \text{FH}\dots\text{F}$  (B)  $\text{NH}\dots\text{N} < \text{OH}\dots\text{O} < \text{FH}\dots\text{F}$   
 (C)  $\text{NH}\dots\text{N} > \text{OH}\dots\text{O} < \text{FH}\dots\text{F}$  (D)  $\text{NH}\dots\text{N} < \text{OH}\dots\text{O} > \text{FH}\dots\text{F}$   
**CBO0037**
38. The  $\text{H}$  bond in solid  $\text{HF}$  can be best represented as:  
 (A)  $\text{H} - \text{F}\dots\text{H} - \text{F}\dots\text{H} - \text{F}$  (B)   
 (C)   
 (D)   
**CBO0038**

## VANDERWAAL FORCES

39. **Statement-1** : The melting point of noble gases increases as its atomic mass increases.  
**Statement-2** : Instantaneous dipole induced dipole attraction increases with increase in atomic mass of noble gases.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CBO0039

40. The critical temperature of water is higher than that of  $O_2$  because the  $H_2O$  molecule has :
- (A) fewer electrons than  $O_2$  (B) two ionic bonds  
 (C) V-shape (D) dipole moment

CBO0040

41. Which of the following boiling point order is correct -
- (A)  $He > T_2 > D_2$  (B)  $He < T_2 < D_2$  (C)  $T_2 > He > D_2$  (D)  $He < D_2 < T_2$

CBO0041

42. Which is the incorrect match for the energy distance function for following interaction -
- (A) Debye force :  $r^{-6}$  (B) Ion-induced dipole interaction :  $r^{-2}$   
 (C) London force :  $r^{-6}$  (D) Keesom force :  $r^{-3}$

CBO0042

43. Identify the incorrect order of boiling point in the following pair.
- (A)  $B(OH)_3 < B(OCH_3)_3$  (B)  $NF_3 < N(CH_3)_3$   
 (C)  $BF_3 < B(CH_3)_3$  (D)  $C_2H_6 < C_2F_6$

CBO0043

## SILICATE

44. The number of corners or O-atoms shared per tetrahedron for pyroxene chain silicate is -
- (A) 3 (B) 2 (C) 2.5 (D) 1
45. The mineral  $Na_2Fe^{II}Fe^{III}[Si_8O_{22}](OH)_2$  (chrocidolite) is a :
- (A) Pyroxene chain silicate (B) Sheet silicate  
 (C) Amphiboles chain silicate (D) 3D-silicate
46. The silicate anion in the mineral kinoite is a chain of three  $SiO_4$  tetrahedra that share corners with adjacent tetrahedra. The mineral also contains  $Ca^{2+}$  ions,  $Cu^{2+}$  ions, and water molecules in a 1:1:1 ratio mineral is represented as :
- (A)  $CaCuSi_3O_{10} \cdot H_2O$  (B)  $CaCuSi_3O_{10} \cdot 2H_2O$   
 (C)  $Ca_2Cu_2Si_3O_{10} \cdot 2H_2O$  (D) none of these

CBO0046



47. Silicate thortveitite ( $\text{Sc}_2\text{Si}_2\text{O}_7$ ) is an example of -  
(A) Ortho silicate      (B) Pyro silicate      (C) Cyclic silicate      (D) Chain silicate  
**CBO0047**
48. Name of the structure of silicates in which three oxygen atoms of  $\text{SiO}_4^{4-}$  are shared is -  
(A) Pyro silicate      (B) Sheet silicate  
(C) Linear chain silicate      (D) Three dimensional silicate  
**CBO0048**

**MISCELLENEOUS**

49. The formal charges on the three O-atoms in  $\text{O}_3$  molecule are  
(A) 0, 0, 0      (B) 0, 0, -1      (C) 0, 0, +1      (D) 0, +1, -1  
**CBO0049**
50. The types of bonds present in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  are  
(A) electrovalent and covalent  
(B) electrovalent, coordinate covalent & H-bond  
(C) covalent, coordinate covalent & H-bonds  
(D) electrovalent, covalent, coordinate covalent & H-bond  
**CBO0050**
51. If ethylene molecule lies in X-Y plane then nodal planes of the  $\pi$ -bond will lie in  
(A) XZ plane      (B) YZ plane  
(C) In a plane that bisects C-C axis      (D) XY plane  
**CBO0051**
52. Two ice cubes are pressed over each other and unite to form one cube. Which force is responsible for holding them together :  
(A) van der Waal's forces      (B) Covalent attraction  
(C) Hydrogen bond formation      (D) Dipole-dipole attraction  
**CBO0052**

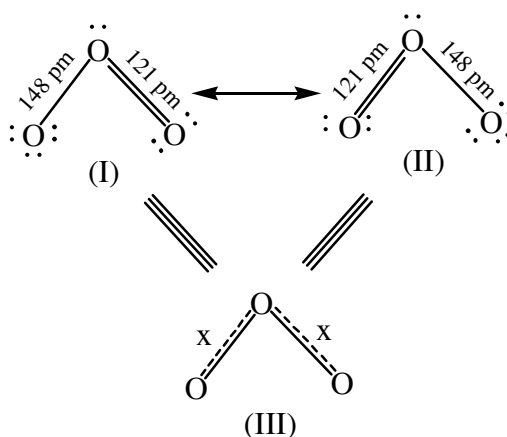
## EXERCISE # O-2

## IONIC BOND , COVALENT BOND &amp; COORDINATE BOND

1. Which of the following compounds contain ionic, covalent and co-ordinate bonds?  
 (A)  $\text{NH}_4\text{Cl}$  (B)  $\text{KCN}$  (C)  $\text{NaBF}_4$  (D)  $\text{NaOH}$  CBO0053
2. Which of the following statements is/are true?  
 (A) Covalent bonds are directional  
 (B) Ionic bonds are nondirectional  
 (C) A polar bond is formed between two atoms which have the same electronegativity value.  
 (D) The presence of polar bonds in a polyatomic molecule suggests that it has zero dipole moment CBO0054
3. To which of the following species octet rule is not applicable :  
 (A)  $\text{BrF}_5$  (B)  $\text{SF}_6$  (C)  $\text{IF}_7$  (D)  $\text{CO}$  CBO0055

## LEWIS STRUCTURE &amp; BOND LENGTH

4.  $\text{O}_3$  (ozone) molecule can be equally represented by the structures I and II shown below



which of the following values of x are not correct

- (A) 148 pm (B) 121 pm (C) less than 121 pm (D) more than 148 pm CBO0056
5. Select the correct statement -  
 (A) C–O bond length of  $\text{CO}$  molecule is higher than the C–O bond length of  $\text{CO}_2$   
 (B) C–O bond length of  $\text{CO}$  molecule is lower than the C–O bond length of  $\text{CO}_2$   
 (C) N–O bond length of  $\text{NO}_3^-$  ion is higher than the N–O bond length of  $\text{NO}_2^-$   
 (D) N–O bond length of  $\text{NO}_3^-$  ion is lower than the N–O bond length of  $\text{NO}_2^-$  CBO0057

VBT, HYBRIDISATION & VSEPR THEORY

6. Which of the following statement(s) is / are not correct?  
 (A) Hybridization is the mixing of atomic orbitals of large energy difference.  
 (B)  $sp^2$ -hybrid orbitals are formed from two  $p$  - atomic orbitals and one  $s$ - atomic orbital  
 (C)  $sp^3d^2$ -hybrid orbitals are all at  $90^\circ$  to one another  
 (D)  $sp^3$ -hybrid orbitals are directed towards the corners of a regular tetrahedron  
CBO0058
7. Which of the following species are linear ?  
 (A)  $ICl_2^-$                       (B)  $I_3^-$                       (C)  $N_3^-$                       (D)  $ClO_2^+$   
CBO0059
8. Which of the following molecules have bent shape.  
 Where A is central atom , B is surrounding atom and E is lone pair -  
 (A)  $AB_2E_2$                       (B)  $AB_2E$                       (C)  $AB_3E$                       (D)  $AB_2$   
CBO0060
9. In which of the following process(s) hybridisation of underlined atom does not change –  
 (A)  $\underline{N}H_3 + BF_3 \rightarrow H_3N.BF_3$                       (B)  $\underline{Si}F_4 + 2F^\ominus \rightarrow [SiF_6]^{2-}$   
 (C)  $BH_3 + \text{[Diagram: A five-membered ring with an oxygen atom at the bottom vertex. An arrow points from the oxygen atom to the boron atom in the reaction.]}$   $\rightarrow H_3B \leftarrow O \text{[Diagram: A five-membered ring with an oxygen atom at the bottom vertex.]}$                       (D)  $H_3\underline{B}O_3 \xrightarrow{OH^-} [B(OH)_4]^-$   
CBO0061
10. Which of the following 'd' orbital(s) participate in the hybridisation for Xe in the cationic part of  $XeF_6(s)$  :-  
 (A)  $d_{xy}$                       (B)  $d_{x^2-y^2}$                       (C)  $d_{z^2}$                       (D)  $d_{y^2}$   
CBO0062
11. Select the **CORRECT** statement if internuclear axis is y-axis :-  
 (A)  $d_{xy}$  and  $d_{xy}$  orbital of two atoms form  $\pi$ -bond  
 (B)  $p_z$  and  $p_z$  orbital of two atoms form  $\sigma$ -bond  
 (C)  $d_{x^2-y^2}$  and  $d_{x^2-y^2}$  orbital of two atoms form  $\pi$ -bond  
 (D)  $p_y$  and  $d_{zx}$  orbital of two atoms form  $\pi$ -bond  
CBO0063
12. What is the hybridisation state of Cl in cationic part of solid  $Cl_2O_6$  ?  
 (A)  $sp^3$                       (B)  $sp$                       (C)  $sp^2$                       (D)  $sp^3d$   
CBO0064

13. **INCORRECT** order of bond angle is:-

- (A)  $\text{OCl}_2 > \text{SF}_2$       (B)  $\text{H}_2\text{O} > \text{OF}_2$       (C)  $\text{SO}_4^{2-} > \text{CF}_4$       (D)  $\text{NF}_3 > \text{NH}_3$

CBO0065

14. Select the **CORRECT** statement(s) ?

- (A) Bond angle order :  $\text{CH}_4 > \text{CF}_4$       (B) Bond length order :  $d_{\text{N-O}}(\text{NO}_2^-) < d_{\text{N-O}}(\text{NO}_3^-)$   
 (C) Bond order of S-O :  $\text{SO}_4^{2-} > \text{SO}_3^{2-}$       (D) Bond angle order :  $\text{NH}_3 < \text{PH}_3$

CBO0066

**MOLECULE DOES NOT EXIST**

15. Which of the following molecules do not exist ?

- (A)  $\text{Br}_2\text{O}$       (B)  $\text{SF}_6$       (C)  $\text{NCl}_5$       (D)  $\text{OF}_4$

CBO0067

16. Which of the following do not exist ?

- (A)  $\text{SH}_6$       (B)  $\text{HFO}_4$       (C)  $\text{SiCl}_6^{-2}$       (D)  $\text{HClO}_3$

CBO0068

17. Which of the following molecule exist-

- (A)  $\text{SF}_6$       (B)  $\text{IH}_3$       (C)  $\text{SH}_2$       (D)  $\text{PCl}_5$

CBO0069

18. Which of the following molecules does not exist and non-existence reason is same as that of  $\text{SH}_6$

- (A)  $\text{OF}_4$       (B)  $\text{SH}_4$       (C)  $\text{PBr}_6^-$       (D)  $\text{XeH}_4$

CBO0070

**DIPOLE MOMENT & HYDROGEN BOND**

19. Which of the following compounds possesses zero dipole moment?

- (A) Water      (B) Benzene  
 (C) Carbon tetrachloride      (D) Boron trifluoride

CBO0071

20. Which of the following statements are correct?

- (A) The crystal lattice of ice is formed by covalent as well as hydrogen bonds  
 (B) The density of water increases when heated from  $0^\circ\text{C}$  to  $4^\circ\text{C}$   
 (C) Above  $4^\circ\text{C}$  the thermal agitation of water molecules increases. Therefore, intermolecular distance increases and water starts expanding  
 (D) The density of water decreases from  $0^\circ\text{C}$  to a maximum at  $4^\circ\text{C}$

CBO0072

21. In which of the following chemical species hydrogen bonding takes place -

- (A)  $\text{Na}_2\text{HPO}_3(\text{s})$       (B)  $\text{K}_2\text{HPO}_4(\text{s})$       (C)  $\text{KHCO}_3(\text{s})$       (D)  $\text{NaHCO}_3(\text{s})$

CBO0073

22. If  $IF_x^n$ , types species are planar and non-polar, then which of the following match is correct- (where X is number of F atoms and n is charge an species)  
 (A)  $x = 2$  and  $n = +1$  (B)  $x = 3$  and  $n = 0$  (C)  $x = 2$  and  $n = -1$  (D)  $x = 5$  and  $n = 0$

CBO0074

23. The correct order/s of boiling point is/are -  
 (A)  $H_2O > CH_3OH$  (B)  $H_3PO_4 > Me_3PO_4$  (C)  $NH_3 < H_2O$  (D)  $H_2O > HF$

CBO0075

### VANDERWAAL FORCES

24. Which of the following factors are responsible for origination of vander Waals forces ?  
 (A) Instantaneous dipole-induced dipole interaction  
 (B) Dipole-induced dipole interaction  
 (C) Dipole-dipole interaction  
 (D) Size of molecule

CBO0076

25. Which of the following are true ?  
 (A) Vander Waals forces are responsible for the formation of molecular crystals  
 (B) Branching lowers the boiling points of isomeric organic compounds due to decrease in Vander Waals forces of attraction  
 (C) In graphite, vander Waals forces act between the carbon layers  
 (D) In diamond, vander Waals forces act between the carbon layers

CBO0077

26. Iodine molecules are held in solid lattice by \_\_\_\_\_.  
 (A) London forces (B) Dipole-dipole attraction  
 (C) Covalent bonds (D) Coulombic force

CBO0078

27. Which of the following inert gas liquefies easily as compare to others -  
 (A) Kr (B) He (C) Ne (D) Ar

CBO0079

### SILICATE

28. In which of the following cases the number of corner shared per tetrahedron is '2' -  
 (A) Pyroxene chain silicate (B) Amphibole chain silicate  
 (C) 5-membered cyclic silicate (D) None of these

CBO0080

29. Which of the following minerals contain three oxygen corners shared per silicate unit ?  
 (A)  $CaMg[(SiO_3)_2]$  (B)  $BaTi[Si_3O_9]$   
 (C)  $Ca_2Mg_5[(Si_4O_{11})_2](OH)_2$  (D)  $Al_2(OH)_4[Si_2O_5]$

CBO0081

30. In Silica ( $SiO_2$ ), each silicon atom is bonded to -  
 (A) Two oxygen atoms (B) Four oxygen atoms  
 (C) One silicon and two oxygen atoms (D) One silicon and four oxygen atoms

CBO0082

31. The ratio of 'Si' atom to monovalent 'O' atom in amphibole silicate is -  
(A) 2 : 3                      (B) 4 : 5                      (C) 4 : 11                      (D) 1 : 3

CBO0083

32. In which of the following silicate/s, 'Si' atoms are  $sp^3$  hybrid -  
(A) Pyro silicate              (B) Sheet silicate              (C) Pyroxene                      (D) Amphiboles

CBO0084

**MISCELLENEOUS & STRUCTURE**

33. Which of the following oxyacids of sulphur contain  $S-S$  bonds ?

(A)  $H_2S_2O_8$                       (B)  $H_2S_2O_6$                       (C)  $H_2S_2O_4$                       (D)  $H_2S_2O_5$

CBO0085

34. Molecule(s) having both polar and non polar bonds is / are

(A)  $O_2F_2$                       (B)  $S_2Cl_2$                       (C)  $N_2H_4$                       (D)  $S_2F_{10}$

CBO0086

35. Which of the following molecule is/are planar -

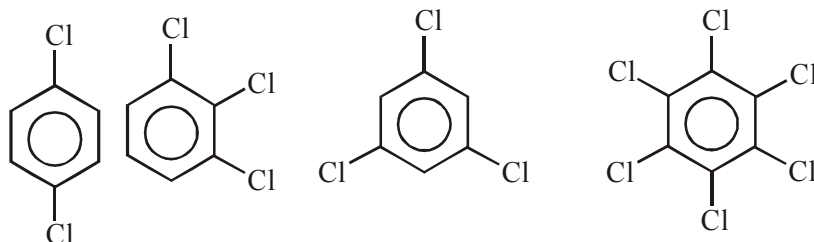
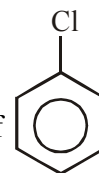
(A)  $CH_2Cl_2$                       (B)  $XeF_4$                       (C)  $SO_3$                       (D)  $NF_3$

CBO0087

EXERCISE # S-1

Integer Type Answer :

- In solid  $\text{NaCl}^+$  one  $\text{Na}^+$  is surrounded by six  $\text{Cl}^-$  ions find out total number of directional bonds formed by each  $\text{Na}^+$  with  $\text{Cl}^-$  ions. CBO0088
- Find out total number of  $p\pi-d\pi$  bonds present in  $\text{SO}_2$  molecule CBO0089
- Find out total number of  $p\pi-p\pi$  bonds present in  $\text{SO}_4^{2-}$  CBO0090
- How many number of atomic orbitals are required, so that their mixing produces hybrid orbitals each having % of s-character nearly equal to 17%. CBO0091
- Calculate the maximum number of atoms lying in one plane of  $\text{PCl}_3\text{F}_2$ . CBO0092
- Find the total number of following molecule(s) which have all bond lengths are same.  
 $\text{XeF}_4, \text{SF}_4, \text{SH}_2, \text{NO}_3^-, \text{SiF}_4, \text{ClF}_3, \text{PF}_2\text{Cl}_3, \text{XeO}_3\text{F}_2$  CBO0093
- A diatomic molecule has a dipole moment of 1.2 D. If bond length is  $1.0 \text{ \AA}$ , what percentage of an electronic charge exists on each atom.  
[Add the digits untill you are getting single digit. e.g. If the answer is 537, then  $5 + 3 + 7 = 15$ ] again  $1 + 5 = 6$  and 6 is to be written as answer. CBO0094
- Total number of  $sp^3$  hybridised atom(s) in given hydrocarbon.  
 $\text{CH}_3-\text{CH}=\text{CH}-\underset{\text{CH}_3}{\text{CH}}-\text{C}\equiv\text{CH}$  CBO0095
- Find the number of lone pair on central atom of  $\text{ICl}_4^-$  CBO0096
- Find the number of acid(s) which are having hypo prefix in it's name from the following.  
 $\text{H}_3\text{PO}_4, \text{H}_3\text{BO}_3, \text{H}_3\text{PO}_3, \text{H}_3\text{PO}_2, \text{HClO}_3, \text{HClO}, (\text{HNO})_2, \text{H}_4\text{P}_2\text{O}_6$  CBO0097
- Find the number of planar molecules/ions which are cyclic –  
 $\text{B}_3\text{N}_3\text{H}_6, \text{C}_3\text{N}_3\text{Cl}_3, (\text{BO}_2)_3, \text{S}_2\text{O}_8^{2-}$  CBO0098



CBO0099

13. Find the number of molecules having intramolecular hydrogen bonding in the following :  
ice, o-boric acid, o-nitrophenol, o-chlorophenol, chloral hydrate, o-salicylaldehyde  
**CBO0100**
14. Calculate the value of "n" in  $Zn_nCa_2(Si_3O_{10}) \cdot 2H_2O$   
**CBO0101**
15. In which of the following silicates structure, the number of corner/oxygen atoms shared per tetrahedron is '2'.  
Pyrosilicate , pyroxene chain silicate ,  
2D-silicate , 3D-silicate , 4-membered cyclic silicate  
**CBO0102**



## EXERCISE # S-2

*(Comprehension) (Q.1 to Q.2)*

Bond angle and bond polarity are important parameters associated for bonding in molecule.

1. Which of the following bond angle order is incorrect.



CBO0103

2. Which of the following molecule is polar and non-planar



CBO0103

*(Comprehension) (Q.3 to Q.4)*

During the formation of a covalent bond each participating atom usually acquires electronic configuration to that of nearest noble gas, and the shared electron pair remains localized between the bonded nuclei. Besides these shared electrons there are certain electron pairs which remains localized on C.A. or on substituent or both and are called non bonding or lone pair electrons.

3. Which of the following species does / do not follow octet rule:



CBO0104

4. In  $\text{SO}_3^{2-}$  the total number of lone pairs and bond pairs are respectively



CBO0104

*(Comprehension) (Q.5 to Q.7)*

Hybridisation is a theoretical concept, as state of hybridisation cannot be detected even by spectroscopically; unlike intermediates or transition state in various reactions. but it corrects the predictions which are based simple on overlapping of pure atomic orbitals. VSEPR theory predicts precisely shape and bond angle in a given molecule.

5. In which pair of molecules bond angles are not same:



CBO0105

6. The molecules / ions which are planar as well as polar.



CBO0105

7. The correct order of energy levels of hybrid orbitals.



CBO0105

**(Comprehension) (Q.8 to Q.10)**

As one moves from  $sp$  hybridisation to  $sp^3$ . % of s-character in hybrid orbital decreases from 50% to 25% and p-character increases from 50% to 75% and in any hybrid orbital total % of s & p-character remains 100%. By increasing p-character the hybrid orbitals become elongated hence, their overlapping extent decreases that results into weak bond energy also bond angle decreases.

8. **Statement-1** : On decreasing s-character in hybrid orbitals, bond angle decreases.

**Statement-2** : p-orbitals are at  $90^\circ$  to one another.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

CBO0106

9. The type of overlapping which produces bond of maximum bond energy is:

(A)  $sp^3 - 1s$

(B)  $sp^2 - 1s$

(C)  $sp - 1s$

(D) All have same bond energy

CBO0106

10. The molecule having bond pair in which % of s character is minimum for the central atom's hybrid orbital.

(A)  $SiF_4$

(B)  $BCl_3$

(C)  $CH_3^+$

(D)  $CO_2$

CBO0106

**Match the Column :**

11. Match the column

**Column-I (molecules)**

(A)  $\underline{P}Cl_5$  ( $\theta = 120^\circ$ ), ( $\theta' = 90^\circ$ )

(B)  $\underline{N}H_3$  ( $\theta = 107^\circ$ )

(C)  $\underline{S}iH_4$  ( $\theta = 109^\circ 28'$ )

(D)  $\underline{S}O_2$  ( $\theta = 116^\circ$ )

**Column-II (correct about molecule)**

(P) Number of the given bond angle ( $\theta$  or  $\theta'$ ) is = One

(Q) Number of the given bond angle ( $\theta$  or  $\theta'$ ) is = Three

(R) Number of the given bond angle ( $\theta$  or  $\theta'$ ) is = Six

(S) d-orbital(s) is/are involved in hybridisation of central atom

(T) Lone pair at underlined atom is present

CBO0107

12. Column I

(A)  $BrF_3$

(B)  $TeF_5^-$

(C)  $IF_7$

(D)  $XeF_4$

Column II

(P) At least one angle  $\leq 90^\circ$

(Q) Central atom is  $sp^3d^2$  hybridised

(R) Non planar

(S) Polar

CBO0108

13. Column I

(A)  $I(CN)_2^-$

(B)  $CO_3^{2-}$

(C)  $XeO_2F_2$

(D)  $SOF_4$

Column II

(P) Having  $p\pi-p\pi$  bond &  $\mu_D = 0$

(Q) Having  $p\pi-d\pi$  bond &  $\mu_D \neq 0$

(R) Planar

(S) Central atom is  $sp^3d$

CBO0109

14. Column I

- (A)  $H_2S_2O_5$
- (B)  $H_6B_2O_7^{2-}$
- (C)  $H_4P_2O_6$  (tetrabasic)
- (D)  $H_6Si_2O_7$

Column II

- (P) Central atom is  $sp^3$  hybridised
- (Q) M–O–M i.e. oxo linkage is present
- (R) M–M linkage is present
- (S) Non planar

CBO0110

15. Column-I

- (P)  $XeF_4$
- (Q)  $BrF_5$
- (R)  $ClF_3$
- (S)  $SO_3^{2-}$

Column-II

- (1)  $sp^3d$  hybridised with 2 lone pair on central atom
- (2)  $sp^3d^2$  hybridised with 2 lone pair on central atom
- (3)  $sp^3$  hybridised with 1 lone pair on central atom
- (4)  $sp^3d^2$  hybridised with 1 lone pair on central atom

Code :

	P	Q	R	S
(A)	1	2	3	4
(B)	2	4	1	3
(C)	2	4	3	1
(D)	3	1	4	2

CBO0111

16. Column-I

- (P)  $NH_4Cl$
- (Q)  $K[HF_2]$
- (R)  $B_3N_3H_6$
- (S) SiC

Column-II

- (1) diamond like structure
- (2) Benzene like structure
- (3) Both hydrogen bond and ionic bond exist
- (4) Both covalent bond and ionic bond exist

Code :

	P	Q	R	S
(A)	4	3	2	1
(B)	3	4	2	1
(C)	3	4	1	2
(D)	4	1	3	2

CBO0112

Answer Q.17, Q.18 and Q.19 by appropriately matching the information given in the three columns of the following table.

Column - I	Column - II	Column - III
(P) $d_{yz}$	(1) $p_y$	(i) 1 lobe – 1 lobe overlap
(Q) s	(2) $p_x$	(ii) 2 lobe – 2 lobe overlap
(R) $d_{xz}$	(3) $d_{yz}$	(iii) 4 lobe – 4 lobe overlap
(S) $p_z$	(4) s	(iv) Zero overlap

17. Which of the following combination results in  $\pi$ -bond formation if internuclear axis is z-axis  
 (A) (P), (1), (ii)                      (B) (P), (4), (i)                      (C) (R), (4), (iv)                      (D) (R), (3), (ii)

CBO0113

18. Which of the following combination results in  $\sigma$ -bond formation if internuclear axis is z-axis  
 (A) (P), (1), (ii)                      (B) (Q), (3), (ii)                      (C) (Q), (4), (i)                      (D) (R), (2), (ii)

CBO0113

19. Which of the following combination results in  $\delta$ -bond formation if internuclear axis is x-axis  
 (A) (P), (1), (i)                      (B) (P), (3), (iii)                      (C) (R), (3), (iv)                      (D) (P), (2), (ii)

CBO0113

20. Match the column

**Column-I**  
(Molecules)

- (A)  $\text{CH}_4$   
 (B)  $\text{CH}_2\text{F}_2$   
 (C)  $\text{CHF}_3$   
 (D)  $\text{CF}_4$

**Column-I**  
(Characteristics)

- (P) Molecule is having perfect tetrahedral shape  
 (Q) C-F bond has maximum p-character  
 (R) C-H bond has maximum s-character  
 (S) Molecule is having maximum number of equal angles  
 (T) Molecule has lowest bond angle

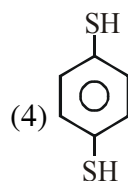
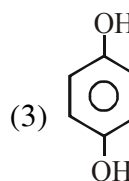
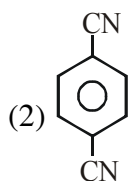
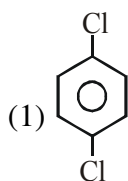
CBO0114

## EXERCISE # JEE-MAIN

1. The hybridisation of orbitals of N atom in  $\text{NO}_3^-$ ,  $\text{NO}_2^+$  and  $\text{NH}_4^+$  are respectively:- [AIEEE-2011]  
 (1)  $sp$ ,  $sp^3$ ,  $sp^2$       (2)  $sp^2$ ,  $sp^3$ ,  $sp$       (3)  $sp$ ,  $sp^2$ ,  $sp^3$       (4)  $sp^2$ ,  $sp$ ,  $sp^3$   
**CBO0115**
2. The structure of  $\text{IF}_7$  is :- [AIEEE-2011]  
 (1) octahedral      (2) pentagonal bipyramid  
 (3) square pyramid      (4) trigonal bipyramid  
**CBO0116**
3. Which of the following has maximum number of lone pairs associated with Xe [AIEEE-2011]  
 (1)  $\text{XeO}_3$       (2)  $\text{XeF}_4$       (3)  $\text{XeF}_6$       (4)  $\text{XeF}_2$   
**CBO0117**
4. The molecule having smallest bond angle is :- [AIEEE-2012]  
 (1)  $\text{PCl}_3$       (2)  $\text{NCl}_3$       (3)  $\text{AsCl}_3$       (4)  $\text{SbCl}_3$   
**CBO0118**
5. In which of the following pairs the two species are not isostructural ? [AIEEE-2012]  
 (1)  $\text{AlF}_6^{3-}$  and  $\text{SF}_6$       (2)  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$       (3)  $\text{PCl}_4^+$  and  $\text{SiCl}_4$       (4)  $\text{PF}_5$  and  $\text{BrF}_5$   
**CBO0119**
6. The number of S-S bonds in  $\text{SO}_3$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{S}_2\text{O}_6^{2-}$  and  $\text{S}_2\text{O}_8^{2-}$  respectively are :- [JEE-MAINS-2012]  
 (1) 1, 0, 1, 0      (2) 0, 1, 1, 0      (3) 1, 0, 0, 1      (4) 0, 1, 0, 1      (On line)  
**CBO0120**
7. Among the following species which two have trigonal bipyramidal shape ? [JEE-MAINS-2012]  
 (I)  $\text{NI}_3$       (II)  $\text{I}_3^-$       (III)  $\text{SO}_3^{2-}$       (IV)  $\text{NO}_3^-$       (On line)  
 (1) II and III      (2) III and IV      (3) I and IV      (4) I and III  
**CBO0121**
8. Which of the following has the square planar structure :- [JEE-MAINS-2012]  
 (1)  $\text{NH}_4^+$       (2)  $\text{CCl}_4$       (3)  $\text{XeF}_4$       (4)  $\text{BF}_4^-$       (On line)  
**CBO0122**
9. The compound of Xenon with zero dipole moment is :- [JEE-MAINS-2012]  
 (1)  $\text{XeO}_3$       (2)  $\text{XeO}_2$       (3)  $\text{XeF}_4$       (4)  $\text{XeOF}_4$       (On line)  
**CBO0123**
10. Among the following the molecule with the lowest dipole moment is :- [JEE-MAINS-2012]  
 (1)  $\text{CHCl}_3$       (2)  $\text{CH}_2\text{Cl}_2$       (3)  $\text{CCl}_4$       (4)  $\text{CH}_3\text{Cl}$       (On line)  
**CBO0124**

11. The formation of molecular complex  $\text{BF}_3 - \text{NH}_3$  results in a change in hybridisation of boron :-  
**[JEE-MAINS-2012]**  
 (1) from  $\text{sp}^3$  to  $\text{sp}^3\text{d}$  (2) from  $\text{sp}^2$  to  $\text{dsp}^2$  (On line)  
 (3) from  $\text{sp}^3$  to  $\text{sp}^2$  (4) from  $\text{sp}^2$  to  $\text{sp}^3$   
**CBO0125**
12. Trigonal bipyramidal geometry is shown by:  
**[JEE-MAINS-2013]**  
 (1)  $\text{XeO}_3\text{F}_2$  (2)  $\text{XeOF}_2$  (3)  $\text{XeO}_3$  (4)  $\text{FXeOSO}_2\text{F}$  (On line)  
**CBO0126**
13. Which one of the following molecules is polar?  
**[JEE-MAINS-2013]**  
 (1)  $\text{CF}_4$  (2)  $\text{SbF}_5$  (3)  $\text{IF}_5$  (4)  $\text{XeF}_4$  (On line)  
**CBO0127**
14. Oxidation state of sulphur in anions  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_4^{2-}$  and  $\text{S}_2\text{O}_6^{2-}$  increases in the orders :  
**[JEE-MAINS-2013]**  
 (1)  $\text{S}_2\text{O}_6^{2-} < \text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-}$  (2)  $\text{SO}_3^{2-} < \text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-}$  (On line)  
 (3)  $\text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-} < \text{S}_2\text{O}_6^{2-}$  (4)  $\text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-} < \text{SO}_3^{2-}$   
**CBO0128**
15.  $\text{XeO}_4$  molecule is tetrahedral having :  
**[JEE-MAINS-2013]**  
 (1) Two  $\text{p}\pi\text{-d}\pi$  bonds (2) Four  $\text{p}\pi\text{-d}\pi$  bonds (On line)  
 (3) One  $\text{p}\pi\text{-d}\pi$  bond (4) Three  $\text{p}\pi\text{-d}\pi$  bonds  
**CBO0129**
16. Bond distance in HF is  $9.17 \times 10^{-11}$  m. Dipole moment of HF is  $6.104 \times 10^{-30}$  Cm. The percent ionic character in HF will be : (electron charge =  $1.60 \times 10^{-19}$  C) **[JEE-MAINS-2013]**  
 (1) 61.0% (2) 38.0% (On line)  
 (3) 35.5% (4) 41.5%  
**CBO0130**
17. The shape of  $\text{IF}_6^-$  is :  
**[JEE-MAINS-2013]**  
 (1) distorted octahedron (2) Pyramidal (On line)  
 (3) Octahedral (4) Square antiprism  
**CBO0131**
18. Which has trigonal bipyramidal shape ?  
**[JEE-MAINS-2013]**  
 (1)  $\text{XeOF}_4$  (2)  $\text{XeO}_3$  (3)  $\text{XeO}_3\text{F}_2$  (4)  $\text{XeOF}_2$  (On line)  
**CBO0132**
19. The catenation tendency of C, Si and Ge is in the order  $\text{Ge} < \text{Si} < \text{C}$ . The bond energies (in  $\text{kJ mol}^{-1}$ ) of C—C, Si—Si and Ge—Ge bonds are respectively : **[JEE-MAINS-2013 (On line)]**  
 (1) 348, 260, 297 (2) 348, 297, 260 (3) 297, 348, 260 (4) 260, 297, 348  
**CBO0133**
20. In which of the following sets, all the given species are isostructural ? **[JEE-MAINS-2013 (On line)]**  
 (1)  $\text{BF}_3$ ,  $\text{NF}_3$ ,  $\text{PF}_3$ ,  $\text{AlF}_3$  (2)  $\text{PCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{BCl}_3$ ,  $\text{SbCl}_3$   
 (3)  $\text{BF}_4^-$ ,  $\text{CCl}_4$ ,  $\text{NH}_4^+$ ,  $\text{PCl}_4^+$  (4)  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{ClO}_2$ ,  $\text{SiO}_2$   
**CBO0134**

21. For which of the following molecule significant  $\mu \neq 0$  [JEE-M-2014]



(1) Only (3)

(2) (3) and (4)

(3) Only (1)

(4) (1) and (2)

CBO0135

22. Among the following oxoacids, the correct decreasing order of acid strength is :- [JEE-M-2014]

(1)  $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$

(2)  $\text{HClO}_2 > \text{HClO}_4 > \text{HClO}_3 > \text{HOCl}$

(3)  $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$

(4)  $\text{HClO}_4 > \text{HOCl} > \text{HClO}_2 > \text{HClO}_3$

CBO0136

23. The number and type of bonds in  $\text{C}_2^{2-}$  ion in  $\text{CaC}_2$  are:

[AIEEE-2005, AIEEE-2011, JEE-MAINS-2014 (On line)]

(1) Two  $\sigma$  bonds and one  $\pi$  - bond

(2) Two  $\sigma$  bonds and two  $\pi$  - bonds

(3) One  $\sigma$  bond and two  $\pi$  - bonds

(4) One  $\sigma$  bond and one  $\pi$  - bond

CBO0137

24. For the compounds [JEE-MAINS-2014]

$\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{F}$ ,

(On line)

the correct order of increasing C-halogen bond length is :

(1)  $\text{CH}_3\text{F} < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl} < \text{CH}_3\text{I}$

(2)  $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$

(3)  $\text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{F} < \text{CH}_3\text{I}$

(4)  $\text{CH}_3\text{F} < \text{CH}_3\text{I} < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl}$

CBO0138

25. Shapes of certain interhalogen compounds are stated below. Which one of them is not correctly stated?

[JEE-MAINS-2014]

(1)  $\text{IF}_7$  : Pentagonal bipyramid

(2)  $\text{BrF}_5$  : Trigonal bipyramid

(On line)

(3)  $\text{ICl}_3$  : Planar dimeric

(4)  $\text{BrF}_3$  : Planar T-shaped

CBO0139

26. Which of the following molecules has two sigma( $\sigma$ ) and two pi( $\pi$ ) bonds :- [JEE-MAINS-2014]

(1)  $\text{HCN}$

(2)  $\text{C}_2\text{H}_2\text{Cl}_2$

(3)  $\text{N}_2\text{F}_2$

(4)  $\text{C}_2\text{H}_4$

(On line)

CBO0140

27. Example of a three-dimensional silicate is : [JEE-MAINS-2014]  
 (1) Beryls (2) Zeolites (3) Feldspars (4) Ultramarines (On-line)  
 CBO0141
28. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is :- [JEE-M-2015]  
 (1) London force (2) Hydrogen bond  
 (3) ion-ion interaction (4) ion-dipole interaction  
 CBO0142
29. Which one has the highest boiling point ? [JEE-M-2015]  
 (1) Kr (2) Xe (3) He (4) Ne  
 CBO0143
30. Which intermolecular force is most responsible in allowing xenon gas to liquefy?  
 (1) Ionic [JEE (MAIN) ONLINE 2016]  
 (2) Instantaneous dipole- induced dipole  
 (3) Dipole - dipole  
 (4) Ion - dipole  
 CBO0144
31. The pair in which phosphorous atoms have a formal oxidation state of + 3 is :-  
 (1) Pyrophosphorous and pyrophosphoric acids [JEE-MAINS(offline)-2016]  
 (2) Orthophosphorous and pyrophosphorous acids  
 (3) Pyrophosphorous and hypophosphoric acids  
 (4) Orthophosphorous and hypophosphoric acids  
 CBO0145
32. The group of molecules having identical shape is : [JEE-MAINS(online)-2016]  
 (1) SF<sub>4</sub>, XeF<sub>4</sub>, CCl<sub>4</sub> (2) ClF<sub>3</sub>, XeOF<sub>2</sub>, XeF<sub>3</sub><sup>+</sup>  
 (3) PCl<sub>5</sub>, IF<sub>5</sub>, XeO<sub>2</sub>F<sub>2</sub> (4) BF<sub>3</sub>, PCl<sub>3</sub>, XeO<sub>3</sub>  
 CBO0146
33. **Assertion** : Among the carbon allotropes, diamond is an insulator, whereas, graphite is a good conductor of electricity. [JEE-MAINS(online)-2016]  
**Reason** : Hybridization of carbon in diamond and graphite are sp<sup>3</sup> and sp<sup>2</sup>, respectively.  
 (1) Assertion is incorrect statement, but the reason is correct.  
 (2) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.  
 (3) Both assertion and reason are incorrect.  
 (4) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion.  
 CBO0147



34. Aqueous solution of which salt will not contain ions with the electronic configuration  $1s^2 2s^2 2p^6 3s^2 3p^6$  ? [JEE-MAINS(online)-2016]  
 (1) NaCl (2)  $CaI_2$  (3) KBr (4) NaF  
**CBO0148**
35. The correct sequence of decreasing number of  $\pi$ -bonds in the structures of  $H_2SO_3$ ,  $H_2SO_4$  and  $H_2S_2O_7$  is:- [JEE-MAINS(online)-2017]  
 (1)  $H_2S_2O_7 > H_2SO_4 > H_2SO_3$  (2)  $H_2SO_3 > H_2SO_4 > H_2S_2O_7$   
 (3)  $H_2S_2O_7 > H_2SO_3 > H_2SO_4$  (4)  $H_2SO_4 > H_2S_2O_7 > H_2SO_3$   
**CBO0149**
36. The increasing order of the boiling points for the following compounds is :- [JEE-MAINS(online)-2017]  
 (I)  $C_2H_5OH$  (II)  $C_2H_5Cl$  (III)  $C_2H_5CH_3$  (IV)  $C_2H_5OCH_3$   
 (1) (III) < (II) < (I) < (IV) (2) (II) < (III) < (IV) < (I)  
 (3) (IV) < (III) < (I) < (II) (4) (III) < (IV) < (II) < (I)  
**CBO0150**
37. The number of P–OH bonds and the oxidation state of phosphorus atom in pyrophosphoric acid ( $H_4P_2O_7$ ) respectively are:- [JEE-MAINS(online)-2017]  
 (1) five and four (2) five and five (3) four and five (4) four and four  
**CBO0151**
38. The group having triangular planar structures is :- [JEE-MAINS(online)-2017]  
 (1)  $CO_3^{2-}, NO_3^-, SO_3$  (2)  $NCl_3, BCl_3, SO_3$  (3)  $NH_3, SO_3, CO_3^{2-}$  (4)  $BF_3, NF_3, CO_3^{2-}$   
**CBO0152**
39. The number of S=O and S–OH bonds present in peroxodisulphuric acid and pyrosulphuric acid respectively are : [JEE-MAINS(online)-2017]  
 (1) (2 and 4) and (2 and 4) (2) (4 and 2) and (2 and 4)  
 (3) (2 and 2) and (2 and 2) (4) (4 and 2) and (4 and 2)  
**CBO0153**
40. The number of P–O bonds in  $P_4O_6$  is :- [JEE-MAINS(online)-2018]  
 (1) 18 (2) 12 (3) 9 (4) 6  
**CBO0154**
41. In  $XeO_3F_2$ , the number of bond pair(s),  $\pi$ -bond(s) and lone pair(s) on Xe atom respectively are :- [JEE-MAINS(online)-2018]  
 (1) 4, 2, 2 (2) 4, 4, 0 (3) 5, 2, 0 (4) 5, 3, 0  
**CBO0155**
42. The decreasing order of bond angles in  $BF_3$ ,  $NH_3$ ,  $PF_3$  and  $I_3^-$  is :- [JEE-MAINS(online)-2018]  
 (1)  $I_3^- > BF_3 > NH_3 > PF_3$  (2)  $BF_3 > NH_3 > PF_3 > I_3^-$   
 (3)  $I_3^- > NH_3 > PF_3 > BF_3$  (4)  $BF_3 > I_3^- > PF_3 > NH_3$   
**CBO0156**
43. Identify the pair in which the geometry of the species is T-shape and square-pyramidal, respectively :- [JEE-MAINS(online)-2018]  
 (1)  $IO_3^-$  and  $IO_2F_2^-$  (2)  $XeOF_2$  and  $XeOF_4$  (3)  $ICl_2^-$  and  $ICl_5$  (4)  $ClF_3$  and  $IO_4^-$   
**CBO0157**

44. Which of the following is a lewis acid ? [JEE-MAINS(online)-2018]  
 (1) NaH (2) NF<sub>3</sub> (3) PH<sub>3</sub> (4) B(CH<sub>3</sub>)<sub>3</sub> CBO0158
45. Among the oxides of nitrogen : N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub>; the molecule(s) having nitrogen-nitrogen bond is/are :- [JEE-MAINS(online)-2018]  
 (1) N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> (2) N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub> (3) N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub> (4) Only N<sub>2</sub>O<sub>5</sub> CBO0159
46. The incorrect geometry is represented by :- [JEE-MAINS(online)-2018]  
 (1) BF<sub>3</sub> - trigonal planar (2) NF<sub>3</sub> - trigonal planar  
 (3) AsF<sub>5</sub> - trigonal bipyramidal (4) H<sub>2</sub>O - bent CBO0160
47. Which of the following conversions involves change in both shape and hybridisation ? [JEE-MAINS(online)-2018]  
 (1) BF<sub>3</sub> → BF<sub>4</sub><sup>-</sup> (2) H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup> (3) CH<sub>4</sub> → C<sub>2</sub>H<sub>6</sub> (4) NH<sub>3</sub> → NH<sub>4</sub><sup>+</sup> CBO0161
48. Which of the following are Lewis acids ? [JEE-MAINS(offline)-2018]  
 (1) AlCl<sub>3</sub> and SiCl<sub>4</sub> (2) PH<sub>3</sub> and SiCl<sub>4</sub> (3) BCl<sub>3</sub> and AlCl<sub>3</sub> (4) PH<sub>3</sub> and BCl<sub>3</sub> CBO0162
49. Total number of lone pair of electrons in I<sub>3</sub><sup>-</sup> ion is [JEE-MAINS(offline)-2018]  
 (1) 6 (2) 9 (3) 12 (4) 3 CBO0163
50. The element that shows greater ability to form pπ-pπ multiple bonds, is : [JEE-MAINS(online)-2019]  
 (1) Si (2) Ge (3) Sn (4) C CBO0164
51. The type of hybridisation and number of lone pair(s) of electrons of Xe in XeOF<sub>4</sub>, respectively, are : [JEE-MAINS(online)-2019]  
 (1) sp<sup>3</sup>d and 1 (2) sp<sup>3</sup>d and 2 (3) sp<sup>3</sup>d<sup>2</sup> and 1 (4) sp<sup>3</sup>d<sup>2</sup> and 2 CBO0165
52. The pair that contains two P-H bonds in each of the oxoacids is : [JEE-MAINS(online)-2019]  
 (1) H<sub>3</sub>PO<sub>2</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>5</sub> (2) H<sub>4</sub>P<sub>2</sub>O<sub>5</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>  
 (3) H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>2</sub> (4) H<sub>4</sub>P<sub>2</sub>O<sub>5</sub> and H<sub>3</sub>PO<sub>3</sub> CBO0166
53. The ion that has sp<sup>3</sup>d<sup>2</sup> hybridization for the central atom, is : [JEE-MAINS(online)-2019]  
 (1) [ICl<sub>2</sub>]<sup>-</sup> (2) [IF<sub>6</sub>]<sup>-</sup> (3) [ICl<sub>4</sub>]<sup>-</sup> (4) [BrF<sub>2</sub>]<sup>-</sup> CBO0167
54. C<sub>60</sub>, an allotrope of carbon contains : [JEE-MAINS(online)-2019]  
 (1) 20 hexagons and 12 pentagons. (2) 12 hexagons and 20 pentagons.  
 (3) 18 hexagons and 14 pentagons. (4) 16 hexagons and 16 pentagons. CBO0168
55. The oxoacid of sulphur that does not contain bond between sulphur atoms is : [JEE-MAINS(online)-2019]  
 (1) H<sub>2</sub>S<sub>4</sub>O<sub>6</sub> (2) H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>  
 (3) H<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (4) H<sub>2</sub>S<sub>2</sub>O<sub>4</sub> CBO0169

56. The number of pentagons in  $C_{60}$  and trigons (triangles) in white phosphorus, respectively, are:  
 (1) 12 and 3 (2) 20 and 4 [JEE-MAINS(online)-2019]  
 (3) 12 and 4 (4) 20 and 3  
**CBO0170**
57. The C–C bond length is maximum in [JEE-MAINS(online)-2019]  
 (1) graphite (2)  $C_{70}$  (3) diamond (4)  $C_{60}$   
**CBO0171**
58. The dipole moments of  $CCl_4$ ,  $CHCl_3$  and  $CH_4$  are in the order : [JEE-MAINS(online)-2020]  
 (1)  $CH_4 = CCl_4 < CHCl_3$  (2)  $CH_4 < CCl_4 < CHCl_3$   
 (3)  $CCl_4 < CH_4 < CHCl_3$  (4)  $CHCl_3 < CH_4 = CCl_4$   
**CBO0172**
59. The relative strength of interionic/intermolecular forces in decreasing order is : [JEE-MAINS(online)-2020]  
 (1) ion-dipole > ion-ion > dipole-dipole  
 (2) dipole-dipole > ion-dipole > ion-ion  
 (3) ion-dipole > dipole-dipole > ion-ion  
 (4) ion-ion > ion-dipole > dipole-dipole  
**CBO0173**
60. Arrange the following bonds according to their average bond energies in descending order : [JEE-MAINS(online)-2020]  
 $C-Cl$ ,  $C-Br$ ,  $C-F$ ,  $C-I$   
 (1)  $C-I > C-Br > C-Cl > C-F$  (2)  $C-Br > C-I > C-Cl > C-F$   
 (3)  $C-F > C-Cl > C-Br > C-I$  (4)  $C-Cl > C-Br > C-I > C-F$   
**CBO0174**
61. The predominant intermolecular forces present in ethyl acetate, a liquid, are : [JEE-MAINS(online)-2020]  
 (1) hydrogen bonding and London dispersion  
 (2) Dipole-dipole and hydrogen bonding  
 (3) London dispersion and dipole-dipole  
 (4) London dispersion, dipole-dipole and hydrogen bonding  
**CBO0175**
62. The number of bonds between sulphur and oxygen atoms in  $S_2O_8^{2-}$  and the number of bonds between sulphur and sulphur atoms in rhombic sulphur, respectively, are : [JEE-MAINS(online)-2020]  
 (1) 4 and 8 (2) 4 and 6  
 (3) 8 and 8 (4) 8 and 6  
**CBO0176**
63. The number of  $sp^2$  hybrid orbitals in a molecule of benzene is : [JEE-MAINS(online)-2020]  
 (1) 24 (2) 6 (3) 12 (4) 18  
**CBO0177**

## EXERCISE # JEE-ADVANCED

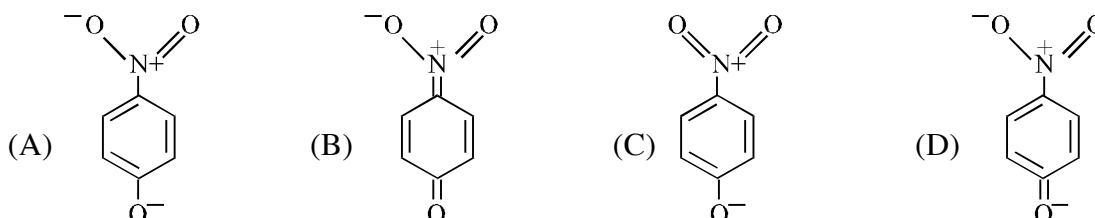
## Integer Type

- The number of water molecule(s) directly bonded to the metal centre in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is  
[JEE 2009] CBO0178
- Based on VSEPR theory, the number of 90 degree F–Br–F angles in  $\text{BrF}_5$  is [JEE 2010] CBO0179
- The difference in the oxidation numbers of the two types of sulphur atoms in  $\text{Na}_2\text{S}_4\text{O}_6$  is.  
[JEE 2011] CBO0180
- The total number of lone-pairs of electrons in melamine is [JEE Adv. 2013] CBO0181
- The sum of the number of lone pairs of electrons on each central atom in the following species is.  
[JEE 2017]  
 $[\text{TeBr}_6]^{2-}$ ,  $[\text{BrF}_2]^+$ ,  $\text{SNF}_3$  and  $[\text{XeF}_3]^-$   
[Atomic number : N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54]

CBO0182

## One or more than one correct

- The most likely representation of resonance structure of p–nitrophenoxide is:



CBO0183

- Specify hybridization of N and B atoms in a 1 : 1 complex of  $\text{BF}_3$  and  $\text{NH}_3$  [JEE 2002]  
(A) N : tetrahedral,  $sp^3$  ; B : tetrahedral,  $sp^3$  (B) N : pyramidal,  $sp^3$  ; B : pyramidal,  $sp^3$   
(C) N : pyramidal,  $sp^3$  ; B : planar,  $sp^2$  (D) N : pyramidal,  $sp^3$  ; B : tetrahedral,  $sp^3$

CBO0184

- The nodal plane in the  $\pi$ -bond of ethene is located in [JEE 2002]  
(A) the molecular plane  
(B) a plane parallel to the molecular plane  
(C) a plane perpendicular to the molecular plane which bisects, the carbon-carbon  $\sigma$  bond at right angle  
(D) a plane perpendicular to the molecular plane which contains, the carbon-carbon bond.

CBO0185

9. **Statement-1** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.  
*because*  
**Statement-2** : o-Hydroxybenzoic acid has intramolecular hydrogen bonding. [JEE 2007]  
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
(C) Statement-1 is True, Statement-2 is False.  
(D) Statement-1 is False, Statement-2 is True. CBO0186
10. **Statement-1** : In water, orthoboric acid behaves as a weak monobasic acid.  
*because*  
**Statement-2** : In water, orthoboric acid acts as a proton donor. [JEE 2007]  
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
(C) Statement-1 is True, Statement-2 is False.  
(D) Statement-1 is False, Statement-2 is True. CBO0187
11. The nitrogen oxide(s) that contain(s) N–N bond(s) is/are [JEE 2009]  
(A)  $N_2O$  (B)  $N_2O_3$  (C)  $N_2O_4$  (D)  $N_2O_5$  CBO0188
12. The value of n in the molecular formula  $Be_nAl_2Si_6O_{18}$  is [JEE 2010] CBO0189
13. The species having pyramidal shape is/are : [JEE 2010] CBO0190  
(A)  $SO_3$  (B)  $BrF_3$  (C)  $SiO_3^-$  (D)  $OSF_2$
14. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen- [JEE 2012] CBO0191  
(A)  $HNO_3$ ,  $NO$ ,  $NH_4Cl$ ,  $N_2$  (B)  $HNO_3$ ,  $NO$ ,  $N_2$ ,  $NH_4Cl$   
(C)  $HNO_3$ ,  $NH_4Cl$ ,  $NO$ ,  $N_2$  (D)  $NO$ ,  $HNO_3$ ,  $NH_4Cl$ ,  $N_2$
15. The shape of  $XeO_2F_2$  molecule is : [JEE 2012] CBO0192  
(A) Trigonal bipyramidal (B) Square planar  
(C) tetrahedral (D) see-saw
16. The compound(s) with TWO lone pairs of electrons on the central atom is(are) [JEE 2016] CBO0193  
(A)  $BrF_5$  (B)  $ClF_3$  (C)  $XeF_4$  (D)  $SF_4$

17. The crystalline form of borax has [JEE 2016]  
(A) Tetranuclear  $[B_4O_5(OH)_4]^{2-}$  unit  
(B) All boron atoms in the same plane  
(C) Equal number of  $sp^2$  and  $sp^3$  hybridized boron atoms  
(D) One terminal hydroxide per boron atom  
CBO0194
18. The order of the oxidation state of the phosphorus atom in  $H_3PO_2$ ,  $H_3PO_4$ ,  $H_3PO_3$  and  $H_4P_2O_6$  is [JEE 2017]  
(A)  $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$   
(B)  $H_3PO_3 > H_3PO_2 > H_3PO_4 > H_4P_2O_6$   
(C)  $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$   
(D)  $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$   
CBO0195
19. Based on the compounds of group 15 elements, the correct statement(s) is (are) [JEE 2018]  
(A)  $Bi_2O_5$  is more basic than  $N_2O_5$   
(B)  $NF_3$  is more covalent than  $BiF_3$   
(C)  $PH_3$  boils at lower temperature than  $NH_3$   
(D) The N–N single bond is stronger than the P–P single bond  
CBO0196
20. The total number of compounds having at least one bridging oxo group among the molecules given below is \_\_\_\_\_. [JEE 2018]  
 $N_2O_3$ ,  $N_2O_5$ ,  $P_4O_6$ ,  $P_4O_7$ ,  $H_4P_2O_5$ ,  $H_5P_3O_{10}$ ,  $H_2S_2O_3$ ,  $H_2S_2O_5$   
CBO0197

**ANSWERS KEY**

**EXERCISE # O-1**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	C	A	B	B	D	D	A	C	B	A
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	C	C	A	A	B	C	C	C	C	B
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	A	C	C	A	B	A	A	D	B	D
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	A	C	C	C	C	B	B	C	A	D
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	D	B	A	B	C	C	B	B	D	D
Que.	51	52								
Ans.	D	C								

**EXERCISE # O-2**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A,C	A,B	A,B,C	A,B,C,D	B,C	A,C	A,B,C	A,B	A,C	B,C
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	A	C	C,D	B,C	C,D	A,B,C	A,C,D	B,D	B,C,D	A,B,C
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	B,C,D	C	A,B,C,D	A,B,C	A,B,C	A	A	A,C	D	B
Que.	31	32	33	34	35					
Ans.	A	A,B,C,D	B,C,D	A,B,C,D	B,C					

**EXERCISE # S-1**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	0	1	0	6	4	4	7 (25%)	3	2	4
Que.	11	12	13	14	15					
Ans.	3	3	4	2	2					

## EXERCISE # S-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	B	A	D	C	D	B	B	B	C	A
Que.	11					12				
Ans.	(A)→Q,R,S;(B)→Q,T;(C)→R;(D)→P,T					(A)→P,S (B)→P,Q,R,S (C)→P,R (D)→P,Q				
Que.	13					14				
Ans.	(A) → P,R,S (B) → P,R (C) → Q,S (D) → Q,S					(A) → P,R,S (B) → P,Q,S (C) → P,R,S (D) → P,Q,S				
Que.	15	16	17	18	19	20				
Ans.	B	A	A	C	B	(A) → P,S (B) → Q,T (C) → R (D) → P,S				

## EXERCISE # JEE-MAIN

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	4	2	4	4	4	2	BONUS	3	3	3
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	4	1	3	3	2	4	1	3	2	3
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	2	1	3	2	2	1	2,3,4	2	2	2
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	2	2	4	4	1	4	3	1	4	2
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	4	1	2	4	3	2	1	3	2	4
Que.	51	52	53	54	55	56	57	58	59	60
Ans.	3	1	3	1	2	3	3	1	4	3
Que.	61	62	63							
Ans.	3	3	4							

## EXERCISE # JEE-ADVANCED

- Ans. 4
- Ans. 0
- Ans. 5
- Ans. 6
- Ans. 6

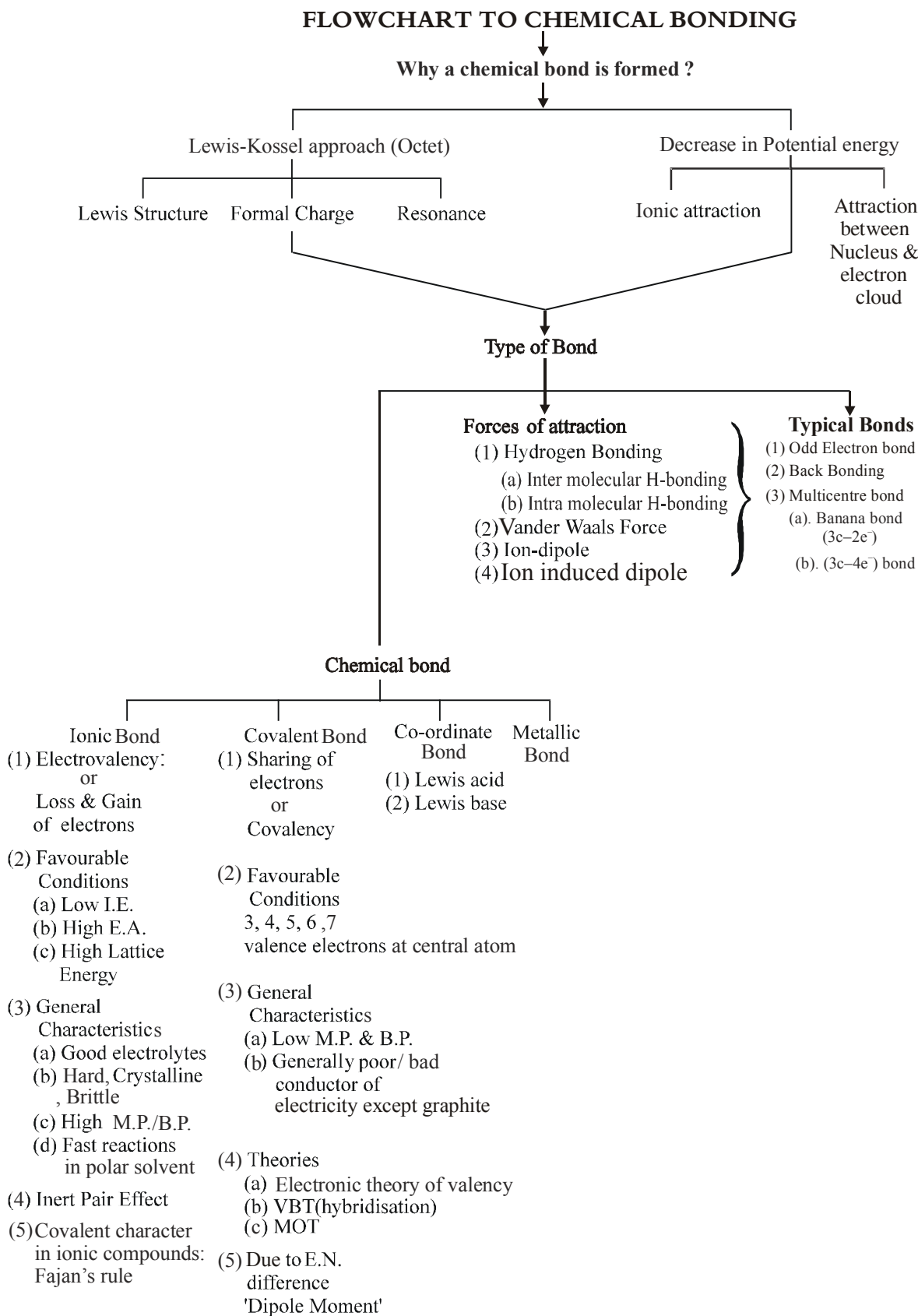
Que.	6	7	8	9	10	11	12	13	14
Ans.	A	A	A	D	C	A,B,C or A,C	3	D	B
Que.	15	16	17	18	19	20			
Ans.	D	B,C	A,C,D	A	A,B,C	5 or 6			







# CHEMICAL BONDING



**Note :** Hydrogen bond is an extreme manifestation of dipole dipole interaction.

## VANDER WAAL'S FORCES

- ⇒ These are the weakest type of inter molecular forces that exist among the chemical species which bring about significant change in physical properties.
- ⇒ These are non-directional, non-valence cohesive forces. These attractive forces being played between the two molecules are independent of the presence of other molecules.
- ⇒ Solid, liquid or gaseous states of many molecules are explained on the basis of inter molecular forces other than covalent, ionic or metallic bonds. Although inert gases do not form any type of bond but may exist in liquid and solid states. This shows that the atoms of inert gases are attracted by each other through some type of inter molecular forces. These intermolecular forces are called Vander Waals forces.

### Types of Vander Waal's Forces

- (1) **Dipole-dipole interaction (Keesom forces)** : The force of attraction between the oppositely charged poles of two polar molecules (for example :  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ,  $\text{PH}_3$  etc.) is called dipole-dipole attraction.
- (2) **Dipole-induced dipole interaction (Debye forces)** : This type of cohesive forces occurs in a mixture of polar and non polar molecules. The former induce polarity in non polar molecules by disturbing their electron system. for example force of attraction between  $\text{Cl}_2$  and  $\text{H}_2\text{O}$ .
- (3) **Instantaneous dipole-Induced dipole interaction (Dispersion forces/London forces)** : The weak intermolecular forces operating in similar non polar gaseous molecules are called London forces. These forces are very weak in nature and exists only at low temperature. For example weak intermolecular forces in  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{N}_2$ , molecules and in noble gases.

(Note :- London forces present in both polar and non polar species)

### Other Weak Interactions

- (1) **Ion-dipole interaction** : Polar molecules are attracted by ions. The negative pole is attracted by cation and positive pole attracted by the anion. This type of attraction is called ion dipole attraction, ion-dipole attraction is observed generally in the process of solvation when sodium chloride ( $\text{Na}^+ \text{Cl}^-$ ) is dissolved in water because negative poles of water aggregate around  $\text{Na}^+$  ions and positive poles around  $\text{Cl}^-$  ions.
- (2) **Ion-induced dipole interaction** : When non polar molecules come in contact with ions, its electron cloud gets polarised and the oppositely charged end of it is attracted by the ion. For example attraction between  $\text{I}^-$  and  $\text{I}_2$  molecule.

## HYBRIDISATION

The phenomenon of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new  $\text{sp}^3$  hybrid orbitals.

**Salient features of hybridisation:** The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are equivalent in energy and shape.

- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

### Important conditions for hybridisation

- The orbitals present in the valence shell of the atom are hybridised.
- The orbitals undergoing hybridisation should have almost equal energy.
- Promotion of electron is not essential condition prior to hybridisation.
- It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

### Types of Hybridisation

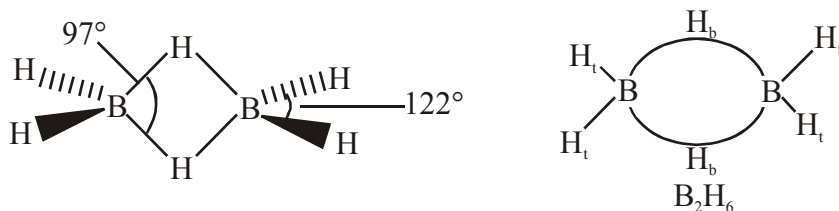
There are various types of hybridisation involving s, p and d orbitals. The different types of hybridisation are as under :

- $sp$  hybridisation
- $sp^2$  hybridisation
- $sp^3$  hybridisation
- $sp^3d$  hybridisation:
- $sp^3d^2$  hybridisation:
- $sp^3d^3$  hybridisation:

## BRIDGE BONDING

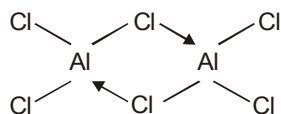
There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds which are  $2c-2e^-$  bonds (two centre two electron bonds). These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds ( $3c-2e$ ) which are present in diborane  $B_2H_6$ ,  $Al_2(CH_3)_6$ ,  $BeH_2(s)$  etc.

bonding in  $B_2H_6$  (diborane)



The structure of diborane containing four terminal (t) and two bridging (b) hydrogen atoms. The model determined by molecular orbital theory indicates that the bonds between boron and the terminal hydrogen atoms are conventional  $2c-2e^-$  covalent bonds. The bonding between the boron atoms and the bridging hydrogen atoms is, however different from that in molecules such as hydrocarbons. Having used two electrons in bonding to the terminal hydrogen atoms, each boron has one valence electron remaining for additional bonding. The bridging hydrogen atoms provide one electron each. Thus the  $B_2H_2$  ring is held together by four electrons, an example of  $3c-2e^-$  bonding. This type of bond is sometimes called as 'banana bond'. Group 13, gallium is known to form a similar compound, digallane,  $Ga_2H_6$ .

But  $\text{Al}_2\text{Cl}_6$  have covalent bond only and there is no electron deficient bonding as depicted in the given structure.



(Al – Cl – Al is 3c – 4e bond)

### INERT PAIR EFFECT

In p-block elements the stability of the lower oxidation state increases on descending the group. Because increased effective nuclear charge holds ns electrons tightly due to poor shielding effect of inner d & f orbitals and thereby, restrict their (ns electrons) participation in bonding only np electrons take part in bond formation. As a result of this, +1 oxidation state of Tl is more stable than its +3 oxidation state. Pb shows +2 stable oxidation state and Bi shows +3 stable oxidation state.

For example :

#### Group 13

B (+3)

Al (+3)

Ga (+3), (+1)

In (+3), (+1)

Tl (+3), (+1)

#### Group 14

C (+4)

Si (+4)

Ge (+4), (+2)

Sn (+4), (+2)

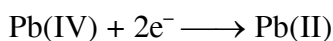
Pb (+4), (+2)

**Order of stability :**  $\text{Tl}^{+1} > \text{In}^{+1} > \text{Ga}^{+1}$  (due to inert pair effect)

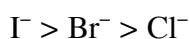
**Order of stability :**  $\text{Pb}^{+2} > \text{Sn}^{+2} > \text{Ge}^{+2}$  (due to inert pair effect)

**Ex.**  $\text{PbCl}_4$  is stable at room temperature whereas  $\text{PbI}_4$  doesn't exist.

**Sol.** Due to inert pair effect  $\text{Pb}(+4)$  is less stable than  $\text{Pb}(+2)$ . Hence it is very good oxidant.

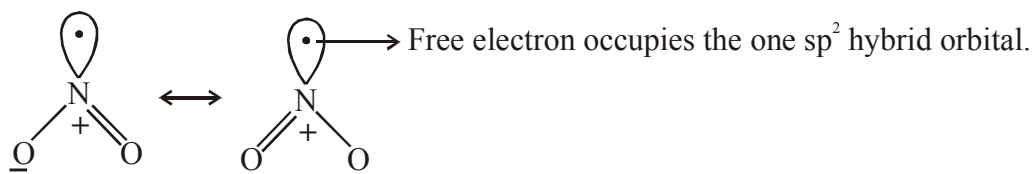


Reducing abilities of halides follows the sequence



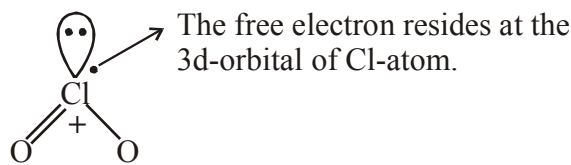
### STRUCTURE OF ODD ELECTRONIC SPECIES

(1)  $\text{NO}_2$



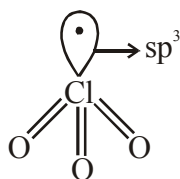
(2)  $\text{ClO}_2$

Structure :-



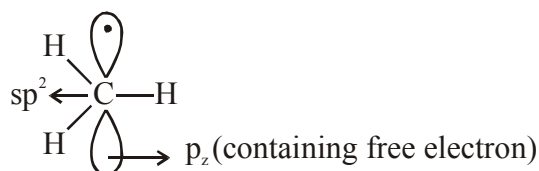
(3)  $\text{ClO}_3$  :

Structure :



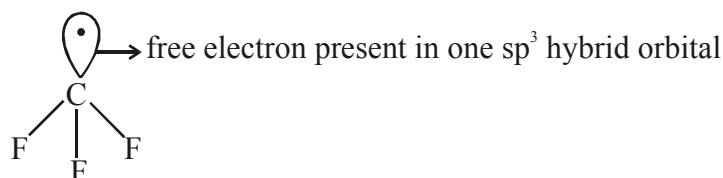
(4)  $\dot{\text{C}}\text{H}_3$  :

Structure :



(5)  $\dot{\text{C}}\text{F}_3$  :

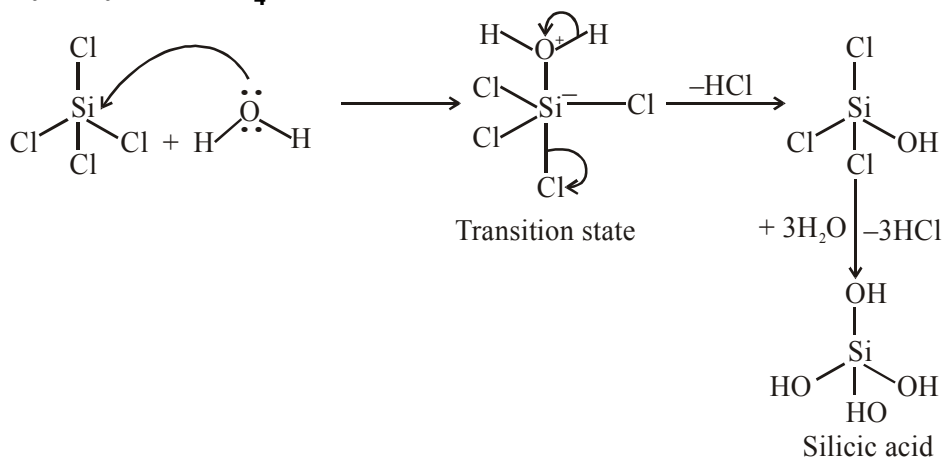
Structure :



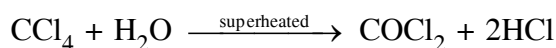
### HYDROLYSIS :

In hydrolysis of covalent molecules the nucleophilic centre of molecule is replaced by  $\text{OH}^-$  group of water generally through nucleophilic substitution reaction.

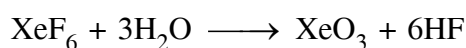
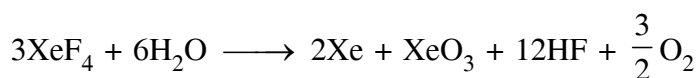
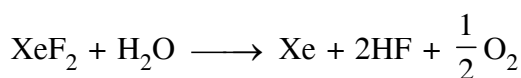
Ex. Hydrolysis of  $\text{SiCl}_4$



**Note :**  $\text{CCl}_4$ ,  $\text{NF}_3$ , is inert towards hydrolysis due to the absence of d orbital, but under drastic condition these molecules under goes hydrolysis.



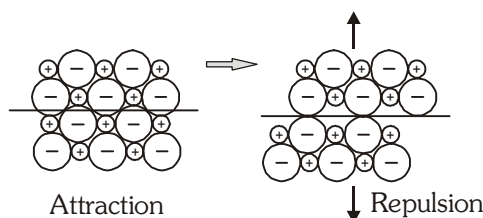
**Note :** Hydrolysis of  $\text{XeF}_2$  &  $\text{XeF}_4$  takes place through with redox reaction.



## IONIC COMPOUNDS

### Properties of ionic compound

(a) **Physical state** : Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction. Brittleness  $\rightarrow$  { Same charged ions comes nearer. So they repell each other }



(b) **Isomorphism** : The phenomenon of different ionic compounds, having same crystal arrangement of ions is termed as isomorphism

#### Condition of Isomorphism :

- Same charge on cation & anion between isomorphs
- Same radius ratio range of cation & anion between isomorphs
- Same number of water of crystalization between isomorphs

Ex. (i)  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  are isomorphous

(ii) All alums are isomorphous

(c) **Boiling point and melting point** : Ionic compounds have high boiling point and melting point due to strong electrostatic force of attraction among oppositely charged ions.

(d) **Conductivity** : It depends on ionic mobility.

- In solid state - No free ions - Bad conductor of electricity.
- In fused state or aqueous solution Due to free ions - Good conductor of electricity.

**Conductivity order** : Solid state < fused state < Aqueous solution

#### (e) Solubility :

Ionic compounds are more soluble in polar solvalents and less soluble in non polar solvents.

- Solubility of ionic compounds in water mainly depends upon hydration energy & lattice energy.

Q. Why does the solubility of alkaline earth metal hydroxides in water increase down the group?

Ans. Among alkaline earth metal hydroxides, the anion being common the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases as we go down the group.

Q. Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?



**Ans.** The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

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### FAJAN'S RULE

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**Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajans in terms of the following rules :**

- The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- The greater the charge on the cation, the greater the covalent character of the ionic bond.
- For cations of the same size and charge, the one, with electronic configuration  $(n-1)d^n ns^0$ , typical of transition metals, is more polarising than the one with a noble gas configuration,  $ns^2 np^6$ , typical of alkali and alkaline earth metal cations.
- The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond, i.e., buildup of electron charge density between the nuclei. The polarising power of the cation, the polarisability of the anion and the extent of distortion (polarisation) of anion are the factors, which determine the per cent covalent character of the ionic bond.

⇒ Polarisation power of a cation is usually called ionic potential or charge density.

$$\text{Ionic potential } \phi \text{ (phi)} = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

### APPLICATION OF THE CONCEPT OF POLARISATION :

- To compare the covalent and ionic character of molecule
- To compare the nature of oxide
- To compare the electrical conductivity of ionic compounds
- Tendency of the formation of complex compounds
- To compare the thermal stability of metal salts
- To compare the intensity of colour of compounds
- To compare the solubility of heavier metal halide in water.

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### MOLECULAR ORBITAL THEORY (MOT)

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Given by Hunds & Mulliken

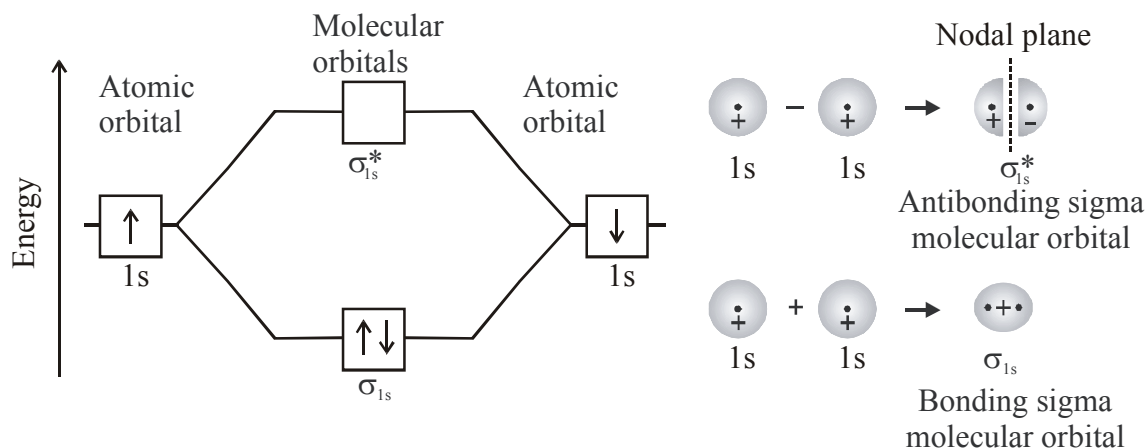
- Two atomic orbital come nearer & then overlap each other to form two molecular orbitals (MO)
- Combination of atomic orbital (AO) forms molecular orbital (MO)

### Types of molecular orbitals

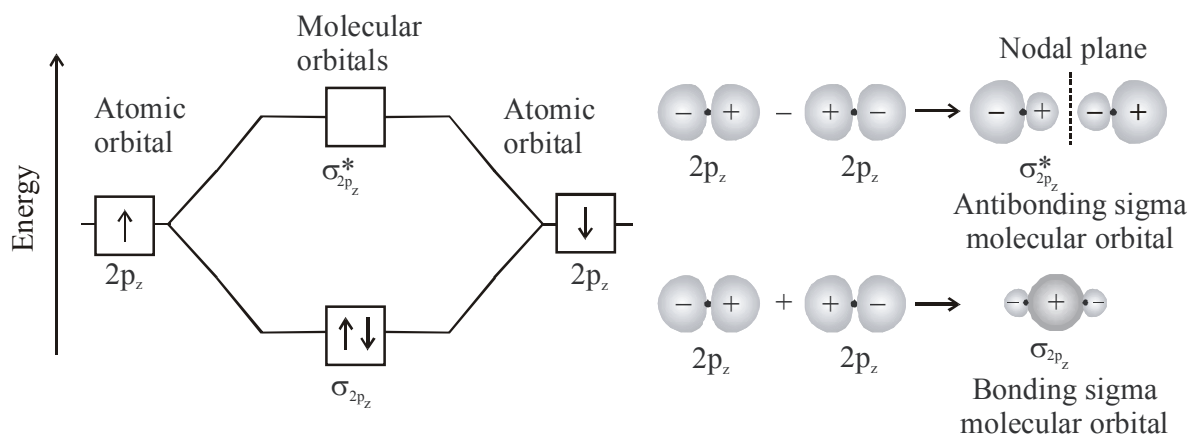
Molecular orbitals of diatomic molecules are designated as  $\sigma$ (sigma),  $\pi$ (pie),  $\delta$ (delta) etc.

In this nomenclature, the **sigma ( $\sigma$ ) molecular orbitals are symmetrical around the inter molecular axis (assumed to be z-axis) while pi ( $\pi$ ) molecular orbitals are not symmetrical.**

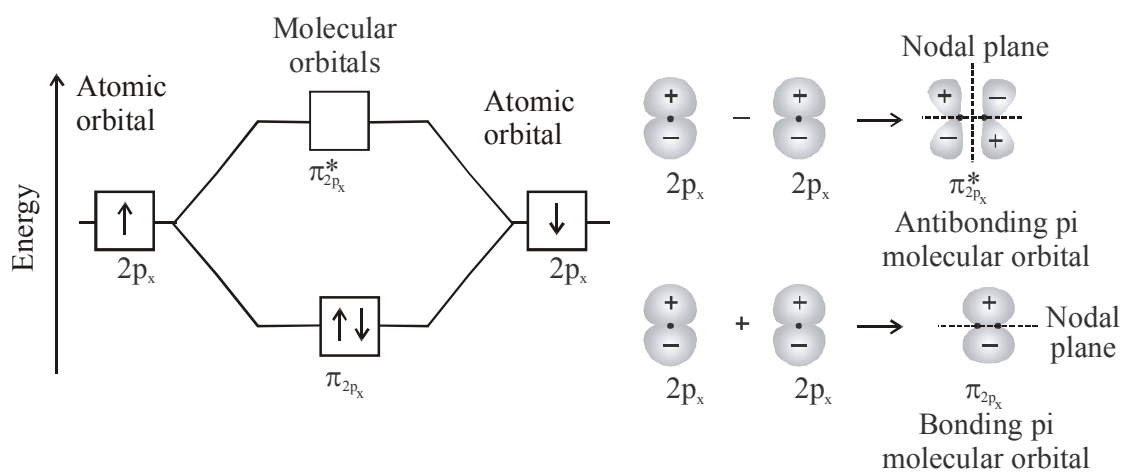
#### (1) s-s combination of orbitals



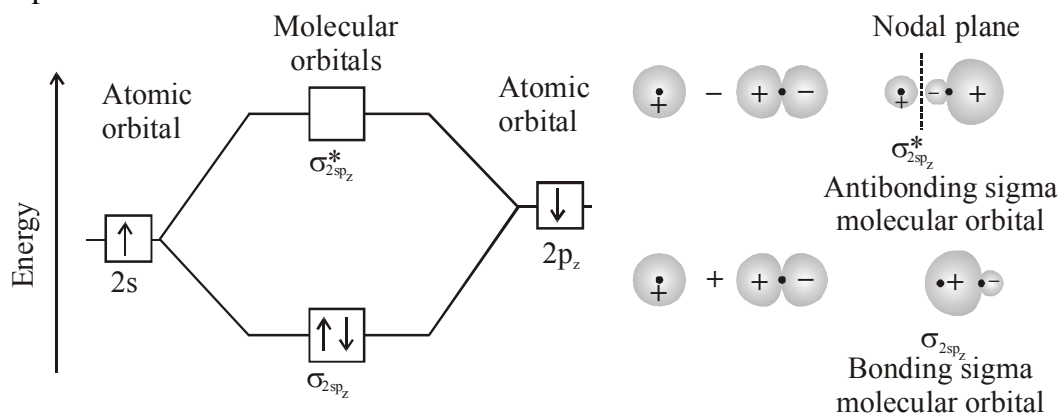
#### (2) p-p combination of orbitals(end to end overlap)



#### (3) p-p combination of orbitals (side by side overlap)



(4) s-p combination of orbitals



(c) Energy of BMO < Energy of ABMO.

(d) Molecular orbitals can be filled by electrons according to Aufbau, Hund's, Pauli's principle.

(e) Energy order of the molecular orbitals of homonuclear di-atomic molecules.

**Note : Molecular orbital energy diagram for up to N<sub>2</sub> (molecule having ≤ 14 electrons)**

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^*$$

**Note : Molecular orbital energy diagram for O<sub>2</sub> and F<sub>2</sub> (molecule having > 14 electrons)**

$$\sigma_{1s} < \sigma_{1s}^* ; < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^*$$

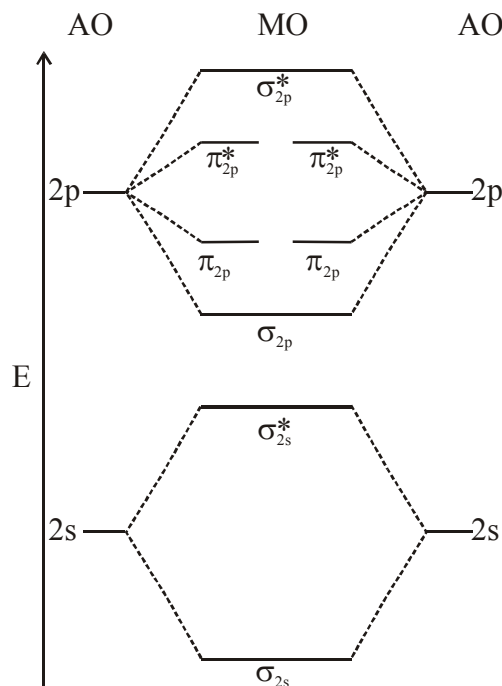
$\sigma^*, \pi^* =$  antibonding molecular orbital

$\sigma, \pi =$  bonding molecular orbital

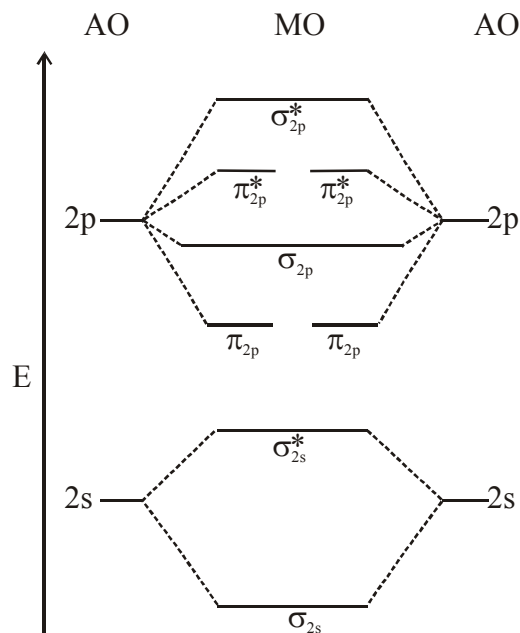
**Ex. Why molecular orbitals have different order of energy in N<sub>2</sub> & O<sub>2</sub> ?**

**Sol.** s-p mixing

**Hint**



The correct MO energy-level diagram when s-p mixing is not allowed.



The correct MO energy-level diagram when s-p mixing is allowed, the energies of the  $\sigma_{2p}$  and  $\pi_{2p}$  orbitals are reversed.

**Bond Order**

Bond order can be defined as :

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

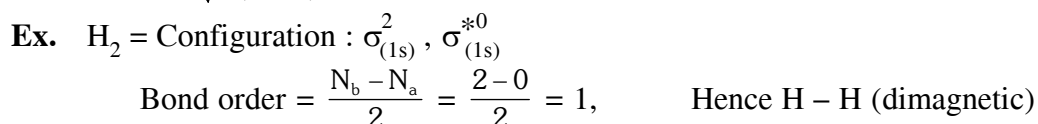
$N_b$  = No. of electron in bonding MO's

$N_a$  = No. of electron in antibonding MO's

- If bond order = 0, it means species does not exist.
- Bond order of 1, 2 & 3 corresponds to a single bond, double & triple bond respectively.
- Bond order  $\uparrow$  stability of molecule  $\uparrow$  bond length  $\downarrow$

**Magnetic behaviour**

- If the molecule has one or more unpaired electron, it will be paramagnetic,
- If all the electrons are paired it will be diamagnetic.
- Magnetic strength can be calculated by using spin only formula of magnetic moment ( $\mu$ ).
- $\mu = \sqrt{n(n+2)}$  B.M. (where n = number of unpaired electron)







13. **Statement-1** :  $\text{PCl}_3$  on hydrolysis gives  $\text{OH}-\overset{\text{O}}{\underset{\text{H}}{\text{P}}}-\text{OH}$  and  $\text{OH}-\overset{\text{OH}}{\text{P}}-\text{OH}$

**Statement-2** :  $\text{H}_3\text{PO}_3$  exists in two tautomeric forms :  $\text{OH}-\overset{\text{OH}}{\text{P}}-\text{OH} \rightleftharpoons \text{OH}-\overset{\text{H}}{\underset{\text{O}}{\text{P}}}-\text{OH}$

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CB0013

#### INERT PAIR EFFECT

14. **Statement-1** : Boron does not show univalent nature but unipositive nature of thallium is quite stable.  
**Statement-2** : Inert pair effect predominates in thallium.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CB0014

15. **Statement-1** :  $\text{PbI}_4$  doesn't exist and converts into  $\text{PbI}_2$  and  $\text{I}_2$  spontaneously at room temperature but  $\text{PbCl}_4$  needs heating to convert into  $\text{PbCl}_2$  and  $\text{Cl}_2$ .  
**Statement-2** :  $\text{Pb}^{2+}$  is more stable than  $\text{Pb}^{4+}$  due to inert pair effect.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CB0015

#### IONIC COMPOUND

16. The dissolution of ionic compounds involves :  
 (A) Evolution of heat (B) Weakening of attractive forces  
 (C) Dissociation into ions (D) All of these
17. Select correct order out of given options :  
 (A)  $\text{BeCO}_3 < \text{BaCO}_3$  : Covalent character (B)  $\text{BeO} > \text{SrO}$  : lattice energy  
 (C)  $\text{Be}^{2+} < \text{Li}^+$  : Hydration energy (D)  $\text{Be}^{2+}(\text{aq.}) > \text{Li}^+(\text{aq.})$  : Ionic mobility
18. The polarizability of the following ions is/are in the order of  
 (A)  $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$  (B)  $\text{I}^- > \text{Br}^- > \text{F}^- > \text{Cl}^-$   
 (C)  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$  (D)  $\text{I}^- < \text{Br}^- < \text{F}^- < \text{Cl}^-$

CB0016

CB0017

CB0018

19. Which of the following equilibria would have the highest value of  $K_p$  at a common temperature?  
 (A)  $\text{MgCO}_3 \rightleftharpoons \text{MgO} + \text{CO}_2$  (B)  $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$   
 (C)  $\text{SrCO}_3 \rightleftharpoons \text{SrO} + \text{CO}_2$  (D)  $\text{BaCO}_3 \rightleftharpoons \text{BaO} + \text{CO}_2$

CB0019

20. Which of the following set of characteristics lead to the increase in solubility of ionic substances?  
 (A) High dipole moment, strong attraction by an ion towards solvent and large solvation energy  
 (B) Low dipole moment, weak attraction by an ion towards solvent and high solvation energy  
 (C) High dipole moment, strong attraction by an ion towards solvent and low solvation energy  
 (D) High dipole moment, weak attraction by an ion towards solvent and large solvation energy

CB0020

21. The solubility of anhydrous  $\text{AlCl}_3$  and hydrated  $\text{AlCl}_3$  in diethyl ether are  $S_1$  and  $S_2$  respectively. Then  
 (A)  $S_1 = S_2$  (B)  $S_1 > S_2$  (C)  $S_1 < S_2$  (D)  $S_1 < S_2$  but not  $S_1 = S_2$

CB0021

22. **Statement-1** : Among alkali metal cations,  $\text{Li}^+(\text{aq.})$  has highest electrical conductance.

**Statement-2** :  $\text{Li}^+(\text{aq.})$  is largest alkali metal cation because of greater degree of hydration.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CB0022

23. **Statement-1** :  $\text{Al}(\text{OH})_3$  is amphoteric in nature.

**Statement-2** : Al–O and O–H bonds can be broken with equal ease in  $\text{Al}(\text{OH})_3$ .

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CB0023

### MOLECULAR ORBITAL THEORY

24. The bond energy order of  $\text{He}_2^+$  and  $\text{HeH}^+$  is  
 (A)  $\text{He}_2^+ > \text{HeH}^+$  (B)  $\text{HeH}^+ = \text{He}_2^+$  (C)  $\text{HeH}^+ > \text{He}_2^+$  (D) Can't be predicted

CB0024

25. Among  $\text{KO}_2$ ,  $\text{AlO}_2^-$ ,  $\text{BaO}_2$  and  $\text{NO}_2^+$  unpaired electron is present in :

- (A)  $\text{KO}_2$  only (B)  $\text{NO}_2^+$  and  $\text{BaO}_2$  (C)  $\text{KO}_2$  and  $\text{AlO}_2^-$  (D)  $\text{BaO}_2$  only

CB0025

26. During the formation of a molecular orbital from atomic orbitals, probability of electron density is

- (A) minimum in the nodal plane (B) maximum in the nodal plane  
 (C) zero in the nodal plane (D) zero on the surface of the lobe

CB0026



27. Pick out the **incorrect** statement ?  
 (A)  $N_2$  has greater dissociation energy than  $N_2^+$   
 (B)  $O_2$  has lower dissociation energy than  $O_2^+$   
 (C) Bond length in  $N_2^+$  is less than  $N_2$   
 (D) Bond length in  $NO^+$  is less than in  $NO$
- CB0027**
28. A simplified application of MO theory to the hypothetical molecule 'OF' would give its bond order as :  
 (A) 2 (B) 1.5 (C) 1.0 (D) 0.5
- CB0028**
29. Which of the following is true ?  
 (A) With increasing Bond order , Bond length decreases & Bond energy increases  
 (B) With increasing Bond order , Bond length increases & Bond energy decreases  
 (C) With increasing Bond order , Bond length decreases & Bond energy decreases  
 (D) With increasing Bond order , Bond length increases & Bond energy increases
- CB0029**
30. Which of the following has fractional bond order :  
 (A)  $O_2^{2+}$  (B)  $O_2^{2-}$  (C)  $F_2^{2-}$  (D)  $H_2^-$
- CB0030**
31. **Statement-1:**  $H_2$  molecule is more stable than He–H molecule.  
**Statement-2 :** The antibonding electron in He–H molecule decreases the bond order and there by the stability.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- CB0031**
32. **Statement-1 :** Super oxide ion is paramagnetic whereas peroxide ion is diamagnetic.  
**Statement-2 :** Super oxide ion has one unpaired electron whereas peroxide ion has no unpaired electron.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- CB0032**
33. **Statement-1:**  $\pi_p$  and  $\pi^*$  orbitals obtained from 2p orbital are lying in the same plane.  
**Statement-2 :** Bonding M.O's are formed by constructive interference while antibonding M.O's are formed by destructive interference.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- CB0033**

## EXERCISE # (O-2)

## WEAK FORCES

1. Which of the following factors are responsible for origination of vander Waals forces ?  
 (A) Instantaneous dipole-induced dipole interaction  
 (B) Dipole-induced dipole interaction  
 (C) Dipole-dipole interaction  
 (D) Size of molecule
2. Which of the following are true ?  
 (A) Vander Waals forces are responsible for the formation of molecular crystals  
 (B) Branching lowers the boiling points of isomeric organic compounds due to decrease in Vander Waals forces of attraction  
 (C) In graphite, vander Waals forces act between the carbon layers  
 (D) In diamond, vander Waals forces act between the carbon layers

CB0034

CB0035

## MULTICENTERED BOND

3. No X-X bond exists in which of the following compounds having general form of  $X_2H_6$  ?  
 (A)  $B_2H_6$                       (B)  $C_2H_6$                       (C)  $Al_2H_6$                       (D)  $Si_2H_6$
4. Three centre - two electron bonds exist in :  
 (A)  $B_2H_6$                       (B)  $Al_2(CH_3)_6$                       (C)  $BeH_2(s)$                       (D)  $BeCl_2(s)$
5. Select correct statement about  $B_2H_6$   
 (A) Bridging groups are electron-deficient with 12 valence electrons  
 (B) It has  $2c - 2e$  B-H bonds  
 (C) It has  $3c - 2e$  B-H-B bonds  
 (D) It has  $3c - 4e$  B-H-B bonds

CB0036

CB0037

CB0038

## ODD ELECTRON SPECIES

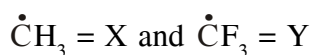
6. Select correct about  $NO_2$  :  
 (A) It is odd electron specie                      (B) N-O bond order = 1.5  
 (C) Paramagnetic specie                      (D) Isoelectronic with  $CO_2$
7. The number of specie(s) which are not perfectly planar.  
 (A)  $\dot{C}H_3$                       (B)  $\dot{C}F_3$                       (C)  $\dot{C}HF_2$                       (D)  $\dot{C}H_2F$
8. Which of the following statement is **CORRECT** :-  
 (A) The free electron of  $ClO_3$  molecule is present in d-orbital of Cl-atom  
 (B) The free electron of  $\dot{C}F_3$  is present in  $sp^3$  hybrid orbital  
 (C) NO is polar  
 (D) The free electron of  $ClO_2$  molecule is present in d-orbital of Cl-atom

CB0039

CB0040

CB0041

9. Which of the following statement(s) is / are **INCORRECT** for



- (A) When X dimerises bond angle decreases  
 (B) When X dimerises bond angle increases  
 (C) In X–Y molecule C–C bond length less than that in Y–Y molecule  
 (D) Bond angle in Y is less than X

CB0042

*HYDROLYSIS*

10. Which of the following halide(s) cannot be hydrolysed at room temperature

- (A)  $\text{SeF}_6$  (B)  $\text{SF}_6$  (C)  $\text{CCl}_4$  (D)  $\text{NF}_3$

CB0043

11. Which of the following statement is/are **INCORRECT** ?

- (A)  $\text{P}_4\text{S}_{10}$  gives rise to  $\text{H}_2\text{S}$  gas on hydrolysis  
 (B)  $\text{PCl}_5$  produces  $\text{POCl}_3$  on partial hydrolysis  
 (C)  $\text{H}_2\text{SO}_5$  gives rise to  $\text{H}_2\text{SO}_3$  on hydrolysis  
 (D) d-orbital participates in the hydrolysis of  $\text{SF}_6$  at room temperature

CB0044

*INERT PAIR EFFECT*

12. Which of the following have (18 + 2) electron configuration ?

- (A)  $\text{Pb}^{2+}$  (B)  $\text{Cd}^{2+}$  (C)  $\text{Bi}^{3+}$  (D)  $\text{SO}_4^{2-}$

CB0045

13. Which of following stability order is/are correct due to inert pair effect.

- (A)  $\text{Hg} > \text{Hg}^{2+}$  (B)  $\text{Bi}^{3+} < \text{Bi}^{5+}$  (C)  $\text{Pb}^{2+} > \text{Pb}^{4+}$  (D)  $\text{Fe}^{2+} < \text{Fe}^{3+}$

CB0046

*IONIC COMPOUND*

14. Choose the correct order(s) for the given properties.

- (A)  $\text{MgSO}_4 < \text{SrSO}_4 < \text{BaSO}_4$  : Thermal stability order  
 (B)  $\text{BeC}_2\text{O}_4 < \text{CaC}_2\text{O}_4 < \text{BaC}_2\text{O}_4$  : Solubility in water  
 (C)  $\text{LiCl} > \text{NaCl} > \text{KCl}$  : Melting point order  
 (D)  $\text{BeF}_2 > \text{CaF}_2 > \text{SrF}_2$  : Covalent character order

CB0047

15. Polarization may be called the distortion of the shape of an anion by an adjacently placed cation. Which of the following statements is/are incorrect :

- (A) Minimum polarization is brought about by a cation of low radius  
 (B) A large cation is likely to bring about a large degree of polarization  
 (C) Maximum polarization is brought about by a cation of high charge  
 (D) A small anion is likely to undergo a large degree of polarization

CB0048

16. Most ionic compounds have :
- (A) high melting points and low boiling points  
 (B) high melting points and nondirectional bonds  
 (C) high solubilities in polar solvents and low solubilities in nonpolar solvents  
 (D) three-dimensional network structures, and are good conductors of electricity in the molten state
- CB0049**
17. Choose the correct order for the given properties.
- (A)  $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$  : covalent character order.  
 (B)  $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$  : melting point order  
 (C)  $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$  : lattice energy order  
 (D)  $\text{NaF} > \text{MgF}_2 > \text{AlF}_3$  : order of polarising power of cation.

**CB0050***MOLECULAR ORBITAL THEORY*

18. Which of the following have identical bond order ?
- (A)  $\text{O}_2^{2+}$                       (B)  $\text{NO}^+$                       (C)  $\text{CN}^-$                       (D)  $\text{CN}^+$
- CB0051**
19. Which of the following statement is/are correct
- (A) The peroxide ion has a bond order of 1 while the oxygen molecule has a bond order of 2  
 (B) The peroxide ion has a weaker bond than the dioxygen molecule has.  
 (C) The peroxide ion as well as the dioxygen molecules are paramagnetic  
 (D) The bond length of the peroxide ion is greater than that of the dioxygen molecule
- CB0052**
20. Which of the following statements are true for these given species :  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CN}^-$  and  $\text{NO}^+$ .
- (A) All species are paramagnetic                      (B) The species are isoelectronic  
 (C) All the species have dipole moment                      (D) All the species are linear
- CB0053**
21. Which of the following have unpaired electron(s)
- (A)  $\text{O}_2^+$                       (B)  $\text{O}_2^-$                       (C)  $\text{NO}$                       (D)  $\text{H}_2^+$
- CB0054**
22. Which of the following is/are paramagnetic ?
- (A)  $\text{B}_2$                       (B)  $\text{O}_2$                       (C)  $\text{N}_2$                       (D)  $\text{He}_2$
- CB0055**
23. Which of the following species have a bond order of 3 ?
- (A)  $\text{CO}$                       (B)  $\text{CN}^-$                       (C)  $\text{NO}^+$                       (D)  $\text{O}_2^+$
- CB0056**

24. Which of the following is/are correct ?

- (A) During  $N_2^+$  formation, one electron is removed from the bonding molecular orbitals
- (B) During  $O_2^+$  formation, one electron is removed from the antibonding molecular orbitals
- (C) During  $O_2^-$  formation, one electron is added to the bonding molecular orbitals
- (D) During  $CN^-$  formation, one electron is added to the bonding molecular orbitals

**CB0057**

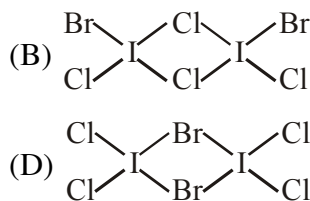
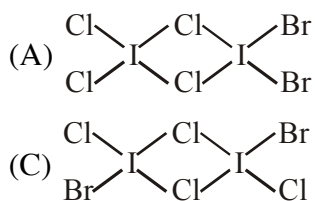
**MISCELLANEOUS**

25. Rotation around the bond (between the underlined atoms) is restricted in :

- (A)  $\underline{C}_2H_4$                       (B)  $H_2\underline{O}_2$                       (C)  $\underline{C}_2H_2$                       (D)  $\underline{C}_2H_6$

**CB0058**

26. The experimental result says that two iodine atoms are in different environments and predict the all possible incorrect arrangement for  $I_2Cl_4Br_2$ .



**CB0059**

## EXERCISE # (S-1)

- Find the number of angles less than  $120^\circ$  in  $\text{PH}_2\text{F}_3$ .  
CB0060
- Find the number of molecules which are not having 3c-2e bond from the following.  
 $\text{Al}_2(\text{CH}_3)_6$ ,  $\text{Si}_2\text{H}_6$ ,  $\text{B}_2\text{H}_6$ ,  $\text{C}_2\text{H}_6$ ,  $\text{Si}_2\text{Cl}_6$ ,  $\text{Al}_2\text{Cl}_6$   
CB0061
- Find the ratio of  $\pi$ -electrons in the  $\text{C}_2$ -molecule with that of  $\text{B}_2$  molecule according to M.O.T.  
CB0062
- The total number of bonding and antibonding electrons in  $\text{O}_2^+$  are "....." and "....." respectively.  
[If the answer is 14 and 7, then represent as 147]  
CB0063
- Find the total number of following molecule(s) which have all bond lengths are same.  
 $\text{XeF}_4$ ,  $\text{SF}_4$ ,  $\text{SH}_2$ ,  $\text{NO}_3^-$ ,  $\text{SiF}_4$ ,  $\text{ClF}_3$ ,  $\text{PF}_2\text{Cl}_3$ ,  $\text{XeO}_3\text{F}_2$   
CB0064
- Among the following total number of planar molecules is / are  
 $\text{Cl}_2\text{O}$ ,  $\text{P}(\text{CH}_3)_3$ ,  $\text{N}(\text{CH}_3)_3$ ,  $\text{ClO}_2$ ,  $\cdot\text{CH}_3$ ,  $\text{NCl}_3$   
CB0065
- How many compound(s) gives diprotic acid on hydrolysis ?  
 $\text{SO}_2\text{Cl}_2$ ,  $\text{SOCl}_2$ ,  $\text{POCl}_3$ ,  $\text{XeF}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{P}_4\text{O}_6$ ,  $\text{SF}_4$ ,  $\text{BCl}_3$   
CB0066

## EXERCISE # (S-2)

## Comprehension # 1 (1 to 3 Questions)

B is the first element of III<sup>rd</sup> group. It forms a number of electron deficient halides and hydrides. Among the hydrides diborane is an important compound.

- Which of the following halide is the strongest Lewis acid?  
(A)  $\text{BF}_3$  (B)  $\text{BCl}_3$  (C)  $\text{BBr}_3$  (D)  $\text{BI}_3$  CB0067
- Which of the following compounds has  $2p\pi - 2p\pi$  bond ?  
(A)  $\text{BF}_3$  (B)  $\text{BCl}_3$  (C)  $\text{BBr}_3$  (D)  $\text{BI}_3$  CB0067
- In  $\text{B}_2\text{H}_6$  number of  $3c - 2e$  bonds is/are  
(A) 1 (B) 2 (C) 3 (D) None CB0067

## Comprehension # 2 (4 to 6 Questions)

Molecular orbital theory is based on linear combination of atomic orbitals (LCAO). According to LCAO when respective atomic orbitals of the atoms interact, they undergoes constructive and destructive interference giving two types of molecular orbital i.e. bonding and antibonding molecular orbitals respectively.

- Which of the following specie is paramagnetic ?  
(A)  $\text{NO}^-$  (B)  $\text{O}_2^{2-}$  (C)  $\text{CN}^-$  (D) CO CB0068
- Bond order of  $\text{Be}_2$  is :  
(A) 1 (B) 2 (C) 3 (D) 0 CB0068
- Number of anti bonding electrons in  $\text{N}_2$  is :  
(A) 4 (B) 10 (C) 12 (D) 14 CB0068

## Comprehension # 3 (7 to 8 Questions)

Polarisation of anion in ionic compounds play an important role to influence the various physical and chemical properties of ionic compound.

- Amongst  $\text{LiCl}$ ,  $\text{RbCl}$ ,  $\text{BeCl}_2$  and  $\text{MgCl}_2$  the compounds with the greatest and the least ionic character, respectively are :  
(A)  $\text{LiCl}$  and  $\text{RbCl}$  (B)  $\text{RbCl}$  and  $\text{BeCl}_2$  (C)  $\text{RbCl}$  and  $\text{MgCl}_2$  (D)  $\text{MgCl}_2$  and  $\text{BeCl}_2$  CB0069
- Compound with maximum ionic character is formed from :  
(A) Na and Cl (B) Cs and F (C) Cs and I (D) Na and F CB0069

**Comprehension # 4 (9 to 10 Questions)**

"Hydrolysis is defined as the reaction of water with any substance"

9. Choose the correct order of ease of hydrolysis -

- (A)  $\text{MgCl}_2 > \text{AlCl}_3$     (B)  $\text{SF}_6 < \text{SeF}_6$     (C)  $\text{SnCl}_2 > \text{SnCl}_4$     (D) None

CB0070

10. Which of the following oxyacids are formed during the stepwise hydrolysis of  $\text{P}_4\text{O}_{10}$

- (A) tetrametaphosphoric acid    (B) tetrapolyphosphoric acid  
(C) pyrophosphoric acid    (D) All of these

CB0070

**MATCHING LIST**

11. Match list I with list II and select the correct answer:

List I (species)				List II (O-N-O angle)					
(P) $\text{NO}_2^+$				(1) $180^\circ$					
(Q) $\text{NO}_2$				(2) $134^\circ$					
(R) $\text{NO}_2^-$				(3) $120^\circ$					
(S) $\text{NO}_3^-$				(4) $115^\circ$					
				(5) $109^\circ$					
	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>	
(A)	5	4	3	2	(B)	5	2	4	3
(C)	1	2	4	3	(D)	1	4	3	2

CB0071

12. Match list I with list II and select the correct answer:

List-I (Molecule / Species)				List-II (Unpaired electron resides in)					
(P) $\text{NO}_2$				(1) d-orbital					
(Q) $\text{ClO}_2$				(2) $\text{sp}^2$ -orbital					
(R) $\text{ClO}_3$				(3) $\text{sp}^3$ -orbital					
(S) $\cdot\text{CH}_3$				(4) p-orbital					
<b>Code :</b>	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>	
(A)	2	4	1	3	(B)	2	1	3	4
(C)	1	4	2	3	(D)	3	1	2	4

CB0072





Answer Q.17 to Q.19 by appropriately matching the information given in the three columns of the following table

Molecular Orbital	Number of nodal plane	Symmetry of Molecular Orbital
(1) $\sigma_s$	(P) 3	(I) BMO, gerade
(2) $\pi_p$	(Q) 2	(II) ABMO, ungerade
(3) $\sigma_{p_z}^*$	(R) 1	(III) BMO, ungerade
(4) $\delta^*$	(S) 0	(IV) ABMO, gerade

17. Which of the following matching is **INCORRECT**.

- (A) (1), S, I                      (B) (2), R, I                      (C) (3), R, II                      (D) (4), P, II

CB0077

18. How many orbitals are occupied with set (1)(S)(I) in  $F_2$

- (A) 0                      (B) 1                      (C) 2                      (D) 3

CB0077

19. If z axis is the molecular axis then **CORRECT** matching for  $d_{xy} + d_{xy}$  orbital is 4, P, II for the subtraction of wave function.

Which of the following matching is **CORRECT** for the addition of wave function for same combination of orbitals.

- (A) P, IV                      (B) P, III                      (C) Q, II                      (D) Q, I

CB0077

## EXERCISE # J-MAIN

1. The bond order in NO is 2.5 while that in  $\text{NO}^+$  is 3. Which of the following statement is true for these two species ? [AIEEE-2004]  
 (1) Bond length in  $\text{NO}^+$  is equal to that NO (2) Bond length in NO is greater than  $\text{NO}^+$   
 (3) Bond length in  $\text{NO}^+$  is greater than NO (4) Bond length is unpredictable  
**CB0078**
2. The states of hybridization of boron and oxygen atoms in boric acid ( $\text{H}_3\text{BO}_3$ ) are respectively [AIEEE-2004]  
 (1)  $\text{sp}^3$  and  $\text{sp}^2$  (2)  $\text{sp}^2$  and  $\text{sp}^3$  (3)  $\text{sp}^2$  and  $\text{sp}^2$  (4)  $\text{sp}^3$  and  $\text{sp}^3$   
**CB0079**
3. The maximum number of  $90^\circ$  angles between bond pair-bond pair of electrons is observed in :- [AIEEE-2004]  
 (1)  $\text{dsp}^2$  hybridization (2)  $\text{sp}^3\text{d}$  hybridization  
 (3)  $\text{dsp}^3$  hybridization (4)  $\text{sp}^3\text{d}^2$  hybridization  
**CB0080**
4. Which one of the following specie is diamagnetic in nature ? [AIEEE-2005]  
 (1)  $\text{He}_2^+$  (2)  $\text{H}_2$  (3)  $\text{H}_2^+$  (4)  $\text{H}_2^-$   
**CB0081**
5. Which of the following molecule/ion does not contain unpaired electrons? [AIEEE-2006]  
 (1)  $\text{N}_2^+$  (2)  $\text{O}_2$  (3)  $\text{O}_2^{2-}$  (4)  $\text{B}_2$   
**CB0082**
6. Among the following mixtures, dipole-dipole as the major interaction, is present in [AIEEE-2006]  
 (1) KCl and water (2) benzene and carbon tetrachloride  
 (3) benzene and ethanol (4) acetonitrile and acetone  
**CB0083**
7. A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statement about these chlorides is correct ? [AIEEE-2006]  
 (1)  $\text{MCl}_2$  is more ionic than  $\text{MCl}_4$   
 (2)  $\text{MCl}_2$  is more easily hydrolysed than  $\text{MCl}_4$   
 (3)  $\text{MCl}_2$  is more volatile than  $\text{MCl}_4$   
 (4)  $\text{MCl}_2$  is more soluble in anhydrous ethanol than  $\text{MCl}_4$   
**CB0084**
8. The decreasing values of bond angles from  $\text{NH}_3$  ( $106^\circ$ ) to  $\text{SbH}_3$  ( $91^\circ$ ) down group-15 of the periodic table is due to [AIEEE-2006]  
 (1) decreasing lp – bp repulsion (2) increasing electronegativity  
 (3) increasing bp – bp repulsion (4) increasing p-orbital character in  $\text{sp}^3$   
**CB0085**

9. In which of the following ionization process, the bond order has increased and the magnetic behaviour has changed [AIEEE-2007]  
 (1)  $\text{NO} \rightarrow \text{NO}^+$       (2)  $\text{O}_2 \rightarrow \text{O}_2^+$       (3)  $\text{N}_2 \rightarrow \text{N}_2^+$       (4)  $\text{C}_2 \rightarrow \text{C}_2^+$   
**CB0086**
10. Which of the following species exhibits the diamagnetic behaviour [AIEEE-2007]  
 (1)  $\text{O}_2^+$       (2)  $\text{O}_2$       (3)  $\text{NO}$       (4)  $\text{O}_2^{2-}$   
**CB0087**
11. which one of the following pairs of species have the same bond order? [AIEEE-2008]  
 (1)  $\text{CN}^-$  and  $\text{NO}^+$       (2)  $\text{CN}^-$  and  $\text{CN}^+$       (3)  $\text{O}_2^-$  and  $\text{CN}^-$       (4)  $\text{NO}^+$  and  $\text{CN}^+$   
**CB0088**
12. The bond dissociation energy of B–F in  $\text{BF}_3$  is  $646 \text{ kJ mol}^{-1}$  whereas that of C–F in  $\text{CF}_4$  is  $515 \text{ kJ mol}^{-1}$ . The correct reason for higher B–F bond dissociation energy as compared to that of C–F is :- [AIEEE-2009]  
 (1) Significant  $p\pi - p\pi$  interaction between B and F in  $\text{BF}_3$  whereas there is not possibility of such interaction between C and F in  $\text{CF}_4$ .  
 (2) Lower degree of  $p\pi - p\pi$  interaction between B and F in  $\text{BF}_3$  than that between C and F in  $\text{CF}_4$   
 (3) Smaller size of B-atom as compared to that of C-atom  
 (4) Stronger  $\sigma$  bond between B and F in  $\text{BF}_3$  as compared to that between C and F in  $\text{CF}_4$   
**CB0089**
13. Using MO theory predict which of the following species has the shortest bond length ? [AIEEE-2009]  
 (1)  $\text{O}_2^-$       (2)  $\text{O}_2^{2-}$       (3)  $\text{O}_2^{2+}$       (4)  $\text{O}_2^+$   
**CB0090**
14. Among the following the maximum covalent character is shown by the compound :- [AIEEE-2011]  
 (1)  $\text{AlCl}_3$       (2)  $\text{MgCl}_2$       (3)  $\text{FeCl}_2$       (4)  $\text{SnCl}_2$   
**CB0091**
15. Which one of the following molecules is expected to exhibit diamagnetic behaviour ?  
 (1)  $\text{C}_2$       (2)  $\text{N}_2$       (3)  $\text{O}_2$       (4)  $\text{S}_2$  [AIEEE-2013]  
**CB0092**
16. In which of the following pairs of molecules/ions, both the species are not likely to exist ?  
 (1)  $\text{H}_2^+, \text{He}_2^{2-}$       (2)  $\text{H}_2^-, \text{He}_2^{2-}$       (3)  $\text{H}_2^{2+}, \text{He}_2$       (4)  $\text{H}_2^-, \text{He}_2^{2+}$  [JEE-M-2013]  
**CB0093**
17. Stability of the species  $\text{Li}_2$ ,  $\text{Li}_2^-$  and  $\text{Li}_2^+$  increases in the order of :- [JEE-M-2013]  
 (1)  $\text{Li}_2 < \text{Li}_2^+ < \text{Li}_2^-$       (2)  $\text{Li}_2^- < \text{Li}_2^+ < \text{Li}_2$       (3)  $\text{Li}_2 < \text{Li}_2^- < \text{Li}_2^+$       (4)  $\text{Li}_2^- < \text{Li}_2 < \text{Li}_2^+$   
**CB0094**



26. Which of the following species is not paramagnetic :- [JEE-MAINS-2017]  
 (1) NO (2) CO (3) O<sub>2</sub> (4) B<sub>2</sub> CB0103
27. Which of the following is paramagnetic ? [JEE-MAINS-2017 (On-line)]  
 (1) CO (2) O<sub>2</sub><sup>2-</sup> (3) NO<sup>+</sup> (4) B<sub>2</sub> CB0104
28. sp<sup>3</sup>d<sup>2</sup> hybridization is not displayed by : [JEE-MAINS-2017 (On-line)]  
 (1) [CrF<sub>6</sub>]<sup>3-</sup> (2) BrF<sub>5</sub> (3) PF<sub>5</sub> (4) SF<sub>6</sub> CB0105
29. The number of S=O and S–OH bonds present in peroxodisulphuric acid and pyrosulphuric acid respectively are : [JEE-MAINS-2017 (On-line)]  
 (1) (2 and 4) and (2 and 4) (2) (4 and 2) and (2 and 4)  
 (3) (2 and 2) and (2 and 2) (4) (4 and 2) and (4 and 2) CB0106
30. The correct sequence of decreasing number of π-bonds in the structures of H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>S<sub>2</sub>O<sub>7</sub> is:- [JEE-MAINS-2017 (On-line)]  
 (1) H<sub>2</sub>S<sub>2</sub>O<sub>7</sub> > H<sub>2</sub>SO<sub>4</sub> > H<sub>2</sub>SO<sub>3</sub> (2) H<sub>2</sub>SO<sub>3</sub> > H<sub>2</sub>SO<sub>4</sub> > H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>  
 (3) H<sub>2</sub>S<sub>2</sub>O<sub>7</sub> > H<sub>2</sub>SO<sub>3</sub> > H<sub>2</sub>SO<sub>4</sub> (4) H<sub>2</sub>SO<sub>4</sub> > H<sub>2</sub>S<sub>2</sub>O<sub>7</sub> > H<sub>2</sub>SO<sub>3</sub> CB0107
31. The increasing order of the boiling points for the following compounds is:- [JEE-MAINS-2017 (On-line)]  
 (I) C<sub>2</sub>H<sub>5</sub>OH (II) C<sub>2</sub>H<sub>5</sub>Cl (III) C<sub>2</sub>H<sub>5</sub>CH<sub>3</sub> (IV) C<sub>2</sub>H<sub>5</sub>OCH<sub>3</sub>  
 (1) (III) < (II) < (I) < (IV) (2) (II) < (III) < (IV) < (I)  
 (3) (IV) < (III) < (I) < (II) (4) (III) < (IV) < (II) < (I) CB0108
32. The number of P–OH bonds and the oxidation state of phosphorus atom in pyrophosphoric acid (H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) respectively are :- [JEE-MAINS-2017 (On-line)]  
 (1) five and four (2) five and five (3) four and five (4) four and four CB0109
33. The group having triangular planar structures is :- [JEE-MAINS-2017 (On-line)]  
 (1) CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>3</sub> (2) NCl<sub>3</sub>, BCl<sub>3</sub>, SO<sub>3</sub> (3) NH<sub>3</sub>, SO<sub>3</sub>, CO<sub>3</sub><sup>2-</sup> (4) BF<sub>3</sub>, NF<sub>3</sub>, CO<sub>3</sub><sup>2-</sup> CB0110
34. Which of the following are Lewis acids ? [JEE-MAINS-2018]  
 (1) AlCl<sub>3</sub> and SiCl<sub>4</sub> (2) PH<sub>3</sub> and SiCl<sub>4</sub> (3) BCl<sub>3</sub> and AlCl<sub>3</sub> (4) PH<sub>3</sub> and BCl<sub>3</sub> CB0111
35. According to molecular orbital theory, which of the following will not be a viable molecule ? [JEE-MAINS-2018]  
 (1) He<sub>2</sub><sup>+</sup> (2) H<sub>2</sub><sup>-</sup> (3) H<sub>2</sub><sup>2-</sup> (4) He<sub>2</sub><sup>2+</sup> CB0112

36. Which of the following compounds contain(s) no covalent bond(s) ? [JEE-MAINS-2018]

KCl, PH<sub>3</sub>, O<sub>2</sub>, B<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>SO<sub>4</sub>

- (1) KCl, H<sub>2</sub>SO<sub>4</sub>      (2) KCl      (3) KCl, B<sub>2</sub>H<sub>6</sub>      (4) KCl, B<sub>2</sub>H<sub>6</sub>, PH<sub>3</sub>

CB0113

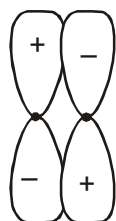
37. In KO<sub>2</sub>, the nature of oxygen species and the oxidation state of oxygen atom are, respectively

[JEE-MAINS-2018 (Online)]

- (1) Superoxide and -1/2      (2) Oxide and -2  
(3) Peroxide and -1/2      (4) Superoxide and -1

CB0114

38. Which of the following best describes the diagram below of a molecular orbital ?



[JEE-MAINS-2018 (Online)]

- (1) An antibonding  $\pi$  orbital      (2) An antibonding  $\sigma$  orbital  
(3) A non-bonding orbital      (4) A bonding  $\pi$  orbital

CB0115

39. In the molecular orbital diagram for the molecular ion, N<sub>2</sub><sup>+</sup>, the number of electrons in the  $\sigma_{2p}$  molecular orbital is :-

[JEE-MAINS-2018 (Online)]

- (1) 3      (2) 1      (3) 0      (4) 2

CB0116

40. Xenon hexafluoride on partial hydrolysis produces compounds 'X' and 'Y' Compounds 'X' and 'Y' and the oxidation state of Xe are respectively :

[JEE-MAINS-2018 (Online)]

- (1) XeO<sub>2</sub>F<sub>2</sub>(+6) and XeO<sub>2</sub>(+4)      (2) XeOF<sub>4</sub>(+6) and XeO<sub>2</sub>F<sub>2</sub>(+6)  
(3) XeOF<sub>4</sub>(+6) and XeO<sub>3</sub>(+6)      (4) XeO<sub>2</sub>(+4) and XeO<sub>3</sub>(+6)

CB0117

41. Which of the following is a lewis acid ?

[JEE-MAINS-2018 (Online)]

- (1) NaH      (2) NF<sub>3</sub>      (3) PH<sub>3</sub>      (4) B(CH<sub>3</sub>)<sub>3</sub>

CB0118

42. A group 13 element 'X' reacts with chlorine gas to produce a compound XCl<sub>3</sub>. XCl<sub>3</sub> is electron deficient and easily reacts with NH<sub>3</sub> to form Cl<sub>3</sub>X ← NH<sub>3</sub> adduct; however, XCl<sub>3</sub> does not dimerize. X is :-

[JEE-MAINS-2018 (Online)]

- (1) Ga      (2) Al      (3) In      (4) B

CB0119

43. Which of the following conversions involves change in both shape and hybridisation ?

[JEE-MAINS-2018 (Online)]

- (1) BF<sub>3</sub> → BF<sub>4</sub><sup>-</sup>      (2) H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup>      (3) CH<sub>4</sub> → C<sub>2</sub>H<sub>6</sub>      (4) NH<sub>3</sub> → NH<sub>4</sub><sup>+</sup>

CB0120

## EXERCISE # J-ADVANCE

1. The molecules that will have dipole moment are : [IIT-1992]  
 (A) 2, 2-dimethylpropane (B) trans-pent-2-ene  
 (C) cis-hex-3-ene (D) 2, 2, 3, 3-tetramethylbutane  
CB0121
2. Which of the following have identical bond order ? [IIT-1992]  
 (A)  $\text{CN}^-$  (B)  $\text{O}_2^-$  (C)  $\text{NO}^+$  (D)  $\text{CN}^+$   
CB0122
3. Among the following the one that is polar and has the central atom with  $\text{sp}^2$  hybridisation is : [IIT-1997]  
 (A)  $\text{H}_2\text{CO}_3$  (B)  $\text{SiF}_4$  (C)  $\text{BF}_3$  (D)  $\text{HClO}_2$   
CB0123
4. Which of the following is soluble in water ? [IIT 98]  
 (A)  $\text{CS}_2$  (B)  $\text{C}_2\text{H}_5\text{OH}$  (C)  $\text{CCl}_4$  (D)  $\text{CHCl}_3$   
CB0124
5. The correct order of hybridization of the central atom in the following species  $\text{NH}_3$ ,  $[\text{PtCl}_4]^{2-}$ ,  $\text{PCl}_5$  and  $\text{BCl}_3$  is : [IIT 2001]  
 (A)  $\text{dsp}^2$ ,  $\text{sp}^3\text{d}$ ,  $\text{sp}^2$  and  $\text{sp}^3$  (B)  $\text{sp}^3$ ,  $\text{dsp}^2$ ,  $\text{sp}^3\text{d}$ ,  $\text{sp}^2$   
 (C)  $\text{dsp}^2$ ,  $\text{sp}^2$ ,  $\text{sp}^3$ ,  $\text{sp}^3\text{d}$  (D)  $\text{dsp}^2$ ,  $\text{sp}^3$ ,  $\text{sp}^2$ ,  $\text{sp}^3\text{d}$   
CB0125
6. The common features among the species  $\text{CN}^-$ ,  $\text{CO}$  and  $\text{NO}^+$  are : [IIT 2001]  
 (A) bond order three and isoelectronic (B) bond order three and weak field ligands  
 (C) bond order two and  $\pi$  - acceptors (D) isoelectronic and weak field ligands  
CB0126
7. Which of the following molecular specie has unpaired electron(s) ? [JEE 2002]  
 (A)  $\text{N}_2$  (B)  $\text{F}_2$  (C)  $\text{O}_2^-$  (D)  $\text{O}_2^{2-}$   
CB0127
8. According to molecular orbital theory which of the following statement about the magnetic character and bond order is correct regarding  $\text{O}_2^+$  [JEE 2004]  
 (A) Paramagnetic and Bond order  $< \text{O}_2$  (B) Paramagnetic and Bond order  $> \text{O}_2$   
 (C) Diamagnetic and Bond order  $< \text{O}_2$  (D) Diamagnetic and Bond order  $> \text{O}_2$   
CB0128
9. Among the following, the paramagnetic compound is [JEE 2007]  
 (A)  $\text{Na}_2\text{O}_2$  (B)  $\text{O}_3$  (C)  $\text{N}_2\text{O}$  (D)  $\text{KO}_2$   
CB0129
10. The species having bond order different from that in  $\text{CO}$  is [JEE 2007]  
 (A)  $\text{NO}^-$  (B)  $\text{NO}^+$  (C)  $\text{CN}^-$  (D)  $\text{N}_2$   
CB0130



11. **Statement-1** : In water, orthoboric acid behaves as a weak monobasic acid. [JEE 2007]

**Statement-2** : In water, orthoboric, acid acts as a proton donor.

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.

CB0131

12. **Statement-1** :  $Pb^{+4}$  compounds are stronger oxidizing agents than  $Sn^{+4}$  compounds [JEE 2008]

**Statement-2** : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect' .

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.

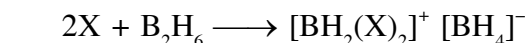
CB0132

13. Match each of the diatomic molecules/ions in Column I with its property / properties in Column II. [JEE 2009]

Column I	Column II
(A) $B_2$	(P) Paramagnetic
(B) $N_2$	(Q) undergoes oxidation
(C) $O_2^-$	(R) Undergoes reduction
(D) $O_2$	(S) Bond order $\geq 2$
	(T) Mixing of 's' and 'p' orbitals

CB0133

14. In the reaction



the amine(s) X is (are)

- (A)  $NH_3$  (B)  $CH_3NH_2$  (C)  $(CH_3)_2NH$  (D)  $(CH_3)_3N$

[JEE 2009]

CB0134

15. The species having pyramidal shape is

- (A)  $SO_3$  (B)  $BrF_3$  (C)  $SiO_3^{2-}$  (D)  $OSF_2$

[JEE 2010]

CB0135

16. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule  $B_2$  is [JEE 2010]

- (A) 1 and diamagnetic (B) 0 and diamagnetic (C) 1 and paramagnetic (D) 0 and paramagnetic

CB0136

### Subjective

17. The value of n in the molecular formula  $Be_nAl_2Si_6O_{18}$  is [JEE 2010]

CB0137

18. The total number of diprotic acids among the following is [JEE 2010]

$H_3PO_4$	$H_2SO_4$	$H_3PO_3$	$H_2CO_3$	$H_2S_2O_7$
$H_3BO_3$	$H_3PO_2$	$H_2CrO_4$	$H_2SO_3$	

CB0138

19. Among the following, the number of elements showing only one non-zero oxidation state is [JEE 2010]

O, Cl, F, N, P, Sn, Tl, Na, Ti

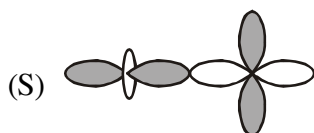
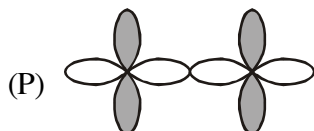
CB0139

20. Assuming 2s-2p mixing is NOT operative, the paramagnetic species among the following is :  
[JEE Adv. 2014]
- (A)  $\text{Be}_2$  (B)  $\text{B}_2$  (C)  $\text{C}_2$  (D)  $\text{N}_2$

CB0140

21. Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists.  
[JEE Adv. 2014]

## List-I



## List-II

(1) p - d  $\pi$  antibonding(2) d - d  $\sigma$  bonding(3) p - d  $\pi$  bonding(4) d - d  $\sigma$  antibonding

Code :

	P	Q	R	S
(A)	2	1	3	4
(C)	2	3	1	4

	P	Q	R	S
(B)	4	3	1	2
(D)	4	1	3	2

CB0141

22. Three moles of  $\text{B}_2\text{H}_6$  are completely reacted with methanol. The number of moles of boron containing product formed is -  
[JEE Adv. 2015]

CB0142

23. When  $\text{O}_2$  is adsorbed on a metallic surface, electron transfer occurs from the metal to  $\text{O}_2$ . The TRUE, statement (s) regarding this adsorption is (are)  
[JEE Adv. 2015]

- (A)  $\text{O}_2$  is physisorbed  
(B) heat is released  
(C) occupancy of  $\pi_{2p}^*$  of  $\text{O}_2$  is increased  
(D) bond length of  $\text{O}_2$  is increased

CB0143

24. According to Molecular Orbital Theory,  
[JEE Adv. 2016]

- (A)  $\text{C}_2^{2-}$  is expected to be diamagnetic  
(B)  $\text{O}_2^{2+}$  is expected to have a longer bond length than  $\text{O}_2$   
(C)  $\text{N}_2^+$  and  $\text{N}_2^-$  have the same bond order  
(D)  $\text{He}_2^+$  has the same energy as two isolated He atoms

CB0144

25. The colour of the  $X_2$  molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to - [JEE Adv. 2017]  
 (A) the physical state of  $X_2$  at room temperature changes from gas to solid down the group  
 (B) decrease in HOMO-LUMO gap down the group  
 (C) decrease in  $\pi^*-\sigma^*$  gap down the group  
 (D) decrease in ionization energy down the group  
**CB0145**
26. Among  $H_2$ ,  $He_2^+$ ,  $Li_2$ ,  $Be_2$ ,  $B_2$ ,  $C_2$ ,  $N_2$ ,  $O_2^-$ , and  $F_2$ , the number of diamagnetic species is - (Atomic number) : H = 1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8, f = 9) [JEE Adv. 2017]  
**CB0146**
27. The sum of the number of lone pairs of electrons on each central atom in the following species is. [JEE Adv. 2017]  
 $[TeBr_6]^{2-}$ ,  $[BrF_2]^+$ ,  $SNF_3$  and  $[XeF_3]^-$   
 [Atomic number : N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54]  
**CB0147**
28. The option(s) with only amphoteric oxides is (are): [JEE Adv. 2017]  
 (A)  $Cr_2O_3$ , CrO, SnO, PbO (B) NO,  $B_2O_3$ , PbO,  $SnO_2$   
 (C)  $Cr_2O_3$ , BeO, SnO,  $SnO_2$  (D) ZnO,  $Al_2O_3$ , PbO,  $PbO_2$   
**CB0148**
29. Among the following, the correct statement(s) is are [JEE Adv. 2017]  
 (A)  $Al(CH_3)_3$  has the three-centre two-electron bonds in its dimeric structure  
 (B)  $AlCl_3$  has the three-centre two-electron bonds in its dimeric structure  
 (C)  $BH_3$  has the three-centre two-electron bonds in its dimeric structure  
 (D) The Lewis acidity of  $BCl_3$  is greater than that of  $AlCl_3$   
**CB0149**
30. Based on the compounds of group 15 elements, the correct statement(s) is (are) [JEE Adv. 2018]  
 (A)  $Bi_2O_5$  is more basic than  $N_2O_5$   
 (B)  $NF_3$  is more covalent than  $BiF_3$   
 (C)  $PH_3$  boils at lower temperature than  $NH_3$   
 (D) The N-N single bond is stronger than the P-P single bond  
**CB0150**
31. Each of the following options contains a set of four molecules. Identify the option(s) where all four molecules possess permanent dipole moment at room temperature. [JEE Adv. 2019]  
 (1)  $BeCl_2$ ,  $CO_2$ ,  $BCl_3$ ,  $CHCl_3$  (2)  $SO_2$ ,  $C_6H_5Cl$ ,  $H_2Se$ ,  $BrF_5$   
 (3)  $BF_3$ ,  $O_3$ ,  $SF_6$ ,  $XeF_6$  (4)  $NO_2$ ,  $NH_3$ ,  $POCl_3$ ,  $CH_3Cl$   
**CB0151**
32. Among  $B_2H_6$ ,  $B_3N_3H_6$ ,  $N_2O$ ,  $N_2O_4$ ,  $H_2S_2O_3$  and  $H_2S_2O_8$ , the total number of molecules containing covalent bond between two atoms of the same kind is \_\_\_\_\_ [JEE Adv. 2019]  
**CB0152**

**ANSWERS KEY****EXERCISE # (O-1)**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A	D	D	B	A	D	D	A	D	D
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	D	C	A	A	B	D	B	A	A	A
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	B	D	C	C	A	C	C	B	A	D
Que.	31	32	33							
Ans.	A	A	B							

**EXERCISE (O-2)**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A, B, C	A, B, C	A, C	A, B, C	B, C	A, B, C	B, C, D	B, C, D	B, C	B, C, D
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	C, D	A, C	A, C	A, D	A, B, D	B, C, D	A, B, C	A, B, C	A, B, D	B, D
Que.	21	22	23	24	25	26				
Ans.	A, B, C, D	A, B	A, B, C	A, B, D	A, B, C	B, C, D				

**EXERCISE (S-1)**

Que.	1	2	3	4	5	6	7
Ans.	8	4	2	105	4	3	4

**EXERCISE (S-2)**

Que.	1	2	3	4	5	6	7	8	9	10	
Ans.	D	A	B	A	D	A	B	B	B	D	
Que.	11	12	13	14				15			
Ans.	C	B	C	(A)-Q,R,S (B)-P,Q,S (C)-S (D)-P,Q				(A)-P,S (B)-Q,T (C)-R (D)-P,S			
Que.	16					17	18	19			
Ans.	(A)-P,R,T (B)-Q (C)-Q (D)-Q,T					B	C	D			

## EXERCISE # J-MAINS

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	2	3	4	2	3	4	1	4	1	4
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	1	1	3	1	2	3	2	3	3	3
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	4	2	2	2	4	2	4	1 & 3	4	1
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	4	3	1	3	3	2	1	1	2	2
Que.	41	42	43							
Ans.	4	4	1							

## EXERCISE # J-ADVANCE

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	B, C	A, C	A	B	B	A	C	B	D	A
Que.	11	12	13					14	15	16
Ans.	C	C	(A)-P,Q,R,T(B)-Q,R,S,T(C)-P,Q,R(D)-P,Q,R,S					B, C	D	A
Que.	17	18	19	20	21	22	23	24	25	26
Ans.	3	6	2	C	C	6	B,C,D	A,C	B, C	5 or 6
Que.	27	28	29	30	31	32				
Ans.	6	C, D	A, C, D	A, B, C	2,4	4.00				

## CO-ORDINATION CHEMISTRY

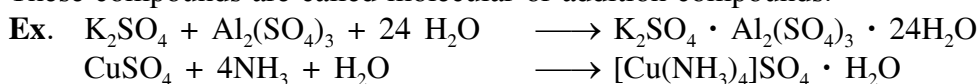
### □ INTRODUCTION :

- (a) The concept of co-ordination compounds arises from the complex formation tendency of transition elements.
- (b) These compounds play a vital role in our lives, as chlorophyll of plants, vitamin B<sub>12</sub> and haemoglobin of animal blood are the co-ordination compounds of Mg, Co and Fe respectively.
- (c) The co-ordination compounds play important role in analytical chemistry, polymerisation reactions, metallurgy and refining of metals, photography, water purification etc.
- (d) Co-ordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

### □ ADDITION COMPOUNDS :

When solutions containing two or more salts in simple molecular proportion are evaporated, crystals of new compound separate out.

These compounds are called molecular or addition compounds.



These addition compounds can be divided into two classes :

#### (A) DOUBLE SALTS :

**Those which lose their identity in solution**

In solutions these compounds break down into simpler ions. Such addition compounds which lose their identity in solutions are called **double salts**.

**Example :**

Potash alum  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  when dissolved in water breaks down into  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Al}^{+3}$  ions and therefore is an example of **double salt**.

#### (B) COORDINATION COMPOUNDS :

**Those which retain their identity in solution.**

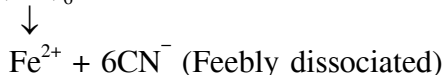
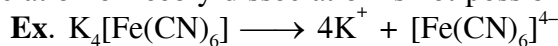
In aqueous solution, these addition compounds do not furnish all simple ions but instead give more complex ions having complicated structure.

**Example :**

Potassium ferrocyanide  $\text{K}_4[\text{Fe}(\text{CN})_6]$  does not furnish simple  $\text{K}^+$ ,  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions but gives  $\text{K}^+$  ions and complex ferrocyanide ions,  $[\text{Fe}(\text{CN})_6]^{4-}$ . These types of compounds are called **complex compounds or co-ordination compounds**.

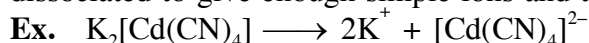
On the basis of stability of complex ion, complex ions are further divided as follows –

- (i) **Perfect complexes :** The compounds in which complex ion is fairly stable and further dissociation or feebly dissociation is not possible in solution state.



The ferrocyanide ion  $[\text{Fe}(\text{CN})_6]^{4-}$  is so insignificantly dissociated that it can be considered as practically undissociated and does not give the qualitative test of  $\text{Fe}^{2+}$  or  $\text{CN}^-$  ions..

- (ii) **Imperfect complexes :** Those complexes in which complex ion is less stable and is reversibly dissociated to give enough simple ions and thus respond to their usual qualitative test.



## DEFINITIONS OF TERMS USED IN CO-ORDINATION COMPOUNDS

- (a) **Co-ordination or complex compound** : Co-ordination compounds are those molecular compounds which retain their identity even when dissolved in water or any other solvent and their properties are completely different from those of the constituent ions.
- (b) **Central ion** : The cation to which one or more neutral molecules or ions are attached is called the atom / ion. Since, the central ion acts as an acceptor and thus has to accommodate electron pairs donated by the donor atoms of neutral molecules or ions, it must have empty orbitals of appropriate energy.
- (c) **Complex ion** : A complex ion may be defined as an electrically charged radical which is formed by the combination of a simple cation with one/more neutral molecules or one/more simple.
- (d) **Co-ordination number** : The total number of co-ordinate covalent bond formed by central metal in complex is called the co-ordination number of the central metal ion .

Some common co-ordination number of important metals are as given below.

Metal	Coordination Number	Metal	Coordination Number
Cu <sup>+</sup>	2, 4	Ni <sup>2+</sup>	4, 6
Ag <sup>+</sup>	2	Fe <sup>2+</sup>	4, 6
Au <sup>+</sup>	2, 4	Fe <sup>3+</sup>	6
Hg <sub>2</sub> <sup>2+</sup>	2	Co <sup>2+</sup>	4, 6
Cu <sup>2+</sup>	4, 6	Co <sup>3+</sup>	6
Ag <sup>2+</sup>	4	Al <sup>3+</sup>	6
Pt <sup>2+</sup>	4	Sc <sup>3+</sup>	6
Pd <sup>2+</sup>	4	Pt <sup>4+</sup>	6
Mg <sup>2+</sup>	6	Pd <sup>4+</sup>	6

**Example.** Coordination number of the central metal ions in

- (i) [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> is four      (ii) [Fe(EDTA)]<sup>-</sup> is six

- (e) **Co-ordination sphere** : The part of the complex enclosed in square bracket is known as co-ordination sphere. It is actually combination of central metal and ligands.
- (f) **Ligands** :
- (a) The ions or neutral molecules which combine with central metal ion to form complex are called ligands.
- (b) They act as electron pair donor (i.e. Lewis bases) though certain ligands also accept electron from central metal and such ligands are known as  $\pi$  - acid ligands.

## ❖ CLASSIFICATION OF LIGANDS

## (A) Based on charge

(i) Neutral ligands :  $\text{H}_2\text{O}$ ,  $\text{NO}$ ,  $\text{CO}$ ,  $\text{C}_6\text{H}_6$  etc.(ii) Positive ligands :  $\text{NO}^+$ ,  $\text{N}_2\text{H}_5^+$ (iii) Negative ligands :  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{CN}^-$ ,  $\text{OH}^-$ 

## (B) Based on denticity

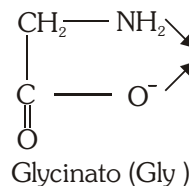
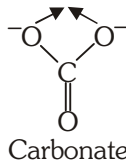
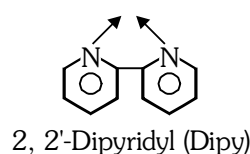
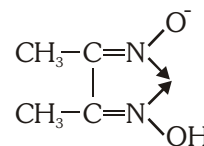
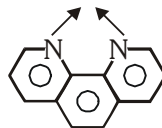
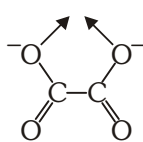
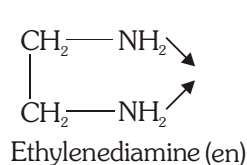
The number of electron pairs donated to central metal by a particular ligand is known as DENTICITY. Depending on number of electron pairs donated, these are classified in following categories.

## (a) Unidentate/monodentate ligands

Ligands which donate one pair of electron to the central metal are called unidentate ligands.  $\text{X}^-$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_3$ , Pyridine,  $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_3^{2-}$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{OH}^-$ ,  $\text{O}^{2-}$ ,  $(\text{C}_6\text{H}_5)_3\text{P}$  etc.

## (b) Bidentate ligands

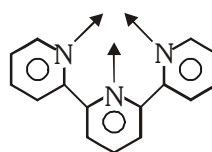
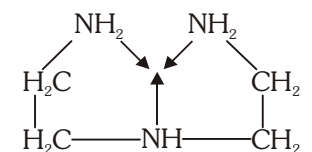
Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands.



## (c) Tridentate ligands

The ligands which donate three pairs of electrons to the central metal are called tridentate ligands

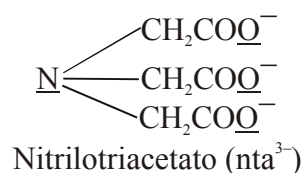
*Example.*



## (d) Tetradentate ligands

Those ligands which can donate four electron pairs to the central metal are known as tetradentate ligands,

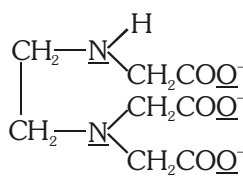
*Example :* (Underline atoms are donating atom)





- (e) **Pentadentate ligands** : Those ligands which can five electron pairs to the central metal are known as pentadentate ligands.

*Example* : Ethylenediamine triacetate ion. (Underline atoms are donating atom)

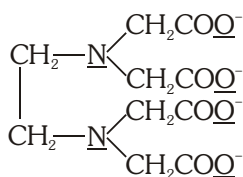


(EDTA)<sup>-3</sup>

Ethylenediaminetriacetate ion

- (f) **Hexadentate ligands** : Those ligands which can donate six electron pairs to the central metal are known as hexadentate ligands.

*Example* : (Underline atoms are donating atom)

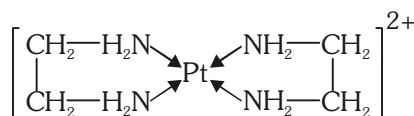


Ethylenediaminetetraacetate ion (EDTA)<sup>-4</sup>

- (g) **Chelating ligands**

Polydentate ligands whose structures permit the attachment of two or more donor site to metal ion simultaneously, thus resulting in cyclic structure are called chelating ligands and compound formed is known as **chelate compound**.

*Example* :



- (h) **Ambidentate ligands**

Ligands which can ligate through two different atoms present in it are called ambidentate ligands. At a time only one atom can donate.



*Example* :

CN<sup>-</sup> can coordinate through either the nitrogen or the carbon atom to central metal ion.

- (i) **Flexidentate ligands**

Ligands which sometimes do not use all the donor sites to get coordinated with central metal ion are known as flexidentate ligands.

**Ex.** SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup> etc.

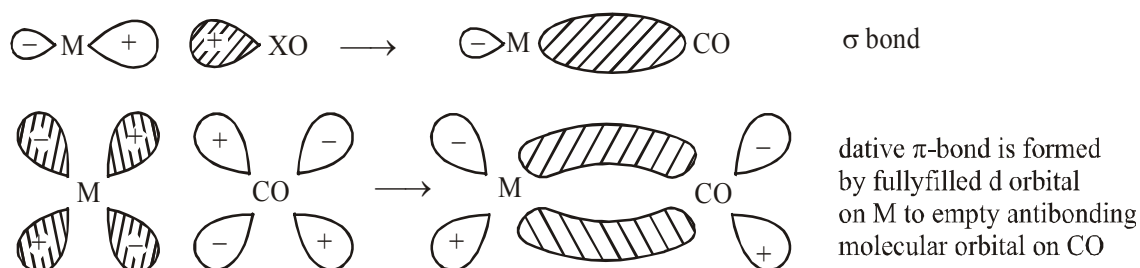
- (C) Based upon bonding interaction between the ligand and the central atom.

(i) **Classical or simple ligand** : These ligand only donate the lone pair of electrons to the central atom.

eg. : O<sup>2-</sup>, OH<sup>-</sup>, F<sup>-</sup> etc.

(ii) **Non classical or π-acid or π-acceptor ligand** : These ligand not only donate the lone pair of electrons to central metal but also accept the electron cloud from central atom

eg. : CO, CN<sup>-</sup>, NO<sup>+</sup>, PF<sub>3</sub>, PR<sub>3</sub> etc.

**BONDING IN METAL CARBONYL :** Ex.  $[\text{Fe}(\text{CO})_5]$  ;  $[\text{Ni}(\text{CO})_4]$  ;  $[\text{Cr}(\text{CO})_6]$ 


Schematic diagram of orbital overlaps in metal carbonyls.

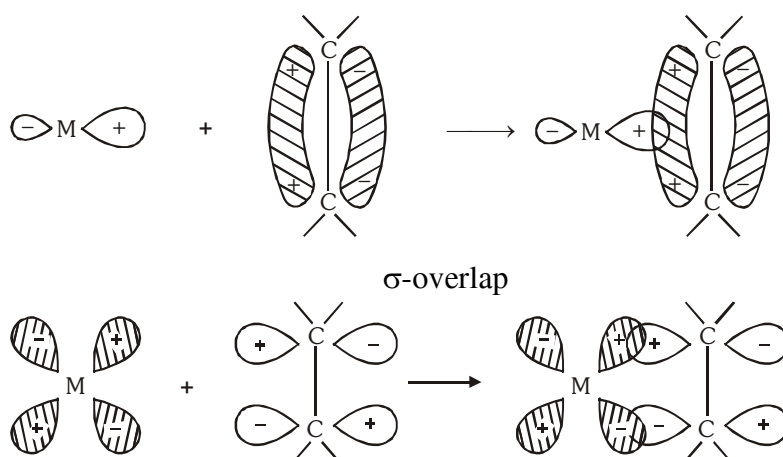
- (a) The metal-carbon bond in metal carbonyls may be represented as the donation of an electron pair from carbon to vacant orbital of metal & form  $\sigma$  bond ( $\text{M} \leftarrow \text{CO}$ ).
- (b) A second bond is formed by back bonding sometimes called dative  $\pi$ -bonding. This arises from side ways overlap of a full orbital on the metal with the empty antibonding  $\pi^*p_y/\pi^*p_z$  (if x-axis is molecular axis) molecular orbital of the carbon monoxide, thus forming a  $\pi \text{ M} \xrightarrow{d\pi-p\pi} \text{CO}$  bond ( $d\pi-p\pi$  back bond).
- (c) The filling or partial filling, of the antibonding orbital on CO reduces the bond order of C–O bond from the triple bond in CO towards a double bond. This shown by the increase in C–O bond length from 1.128 Å in CO to about 1.15 Å in many carbonyls.
- (d) Since CO accept the back donated electrons from the metal atom in to its vacant  $\pi^*$  orbital, CO is called  $\pi$ -acid or  $\pi$ -acceptor ligand or  $\pi$ -bonding ligand. Other such  $\pi$ -acid ligands are–  $\text{CN}^-$ ,  $\text{RCN}$ ,  $\overset{+}{\text{N}}\text{O}$ .

**Note:-**  $\pi$ -acid ligands like  $\text{PF}_3$ ,  $\text{PPh}_3$ ,  $\text{AsCl}_3$  etc. accept the back donated electrons from the metal atom in to its vacant d-orbital of central atom.

**Bonding in  $\pi$ -bonded organo metallic compound.** Like zeises salt  $\text{K} [\text{PtCl}_3(\pi\text{-C}_2\text{H}_4)]$

The bonding of alkenes to a transition metal to form complexes has two components. First, the  $\pi$ -electron density of the alkene overlaps with a  $\sigma$ -type vacant orbital of the metal atom.

Second is the  $\pi$  back bond formed by the flow of electron density from a filled d-orbital on the metal into the vacant  $\pi^*$ -antibonding molecular orbital on the alkene molecule as shown below :



## □ IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

The main rules of naming of complexes are –

- (a) Like simple salts, the positive part of the coordination compound is named first.

**Ex.**  $K_4[Fe(CN)_6]$  the naming of this complex starts with potassium.

$[Cr(NH_3)_6]Cl_3$  the naming of this complex starts with name of complex ion.

- (b) Naming of coordination sphere :- The names of ligands along with their numerical prefixes (to represent their no) are written first, followed by the name of central metal.

- (c) The ligands can be neutral, anionic or cationic.

- (i) The neutral ligands are named as the molecule **Ex.**  $C_5H_5N$  pyridine,  $(C_6H_5)_3P$  Triphenyl phosphine.

$H_2N-CH_2-CH_2-NH_2$  ethylene diamine.

The neutral ligands which are not named as the molecule are CO carbonyl, NO nitrosyl,  $H_2O$  Aqua,  $NH_3$  ammine.

- (ii) Anionic ligands ending with 'ide' are named by replacing the 'ide' with suffix 'O'.

Symbol	Name as ligand	Symbol	Name as ligand
$Cl^-$	Chloro/Chlorido	$N^{3-}$	Nitrido
$Br^-$	Bromo/Bromido	$O_2^{2-}$	Peroxo/Peroxido
$CN^-$	Cyano/Cyanido	$O_2H^-$	Perhydroxo/Perhydroxido
$O^{2-}$	Oxo/Oxido	$S^{2-}$	Sulphido
$OH^-$	Hydroxo/Hydroxido	$NH^{2-}$	Imido
$H^-$	Hydrido/Hydrido	$NH_2^-$	Amido

Ligands whose names end in 'ite' or 'ate' become 'ito' i.e., by replacing the ending 'e' with 'o' as follows.

Symbol	Name as ligand	Symbol	Name as ligand
$CO_3^{2-}$	Carbonato	$SO_3^{2-}$	Sulphito
$C_2O_4^{2-}$	Oxalato	$CH_3COO^-$	Acetato
$SO_4^{2-}$	Sulphato	$ONO^-$	(bonded through oxygen) nitrito
$NO_3^-$	Nitrato	$NO_2^-$	(bonded through nitrogen) nitro
$S_2O_3^{-2}$	Thiosulphato		

- (iii) Positive ligands naming ends in 'ium'  $NH_2-NH_3^+$  Hydrazinium,  $NO^+$  nitrosonium/nitrosylium.

- (d) If ligands are present more than once, then their number is indicated by prefixes like di, tri, tetra etc.

- (e) If words like di, tri, tetra are already used in the naming of ligand, or if it is polydentate ligand or organic ligand, the prefixes bis-, tris-, tetrakis-, pentakis- etc. are used to specify their number.

**Example :**  $[Pt(en)_2Cl_2]Cl_2$  : Dichlorobis(ethylenediamine)platinum(IV) chloride.

- (f) When more than one type of ligands are present in the complex, then the ligands are named in the alphabetical order.
- (g) After naming of ligands the central metal ion is to be named followed by its oxidation state in Roman numbers in brackets. (as per IUPAC)

If the complex is neutral or provides a cationic complex ion, then the central metal ion is to be named as it is.

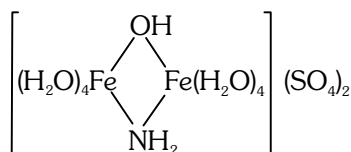
If the complex provides anionic complex ion then the name of central metal ion ends with 'ate'

**Example :**  $(\text{NH}_4)_2[\text{CuCl}_4]$  : Ammonium tetrachloridocuprate(II)

- (h) After the naming of central metal ion, anion which is in the outer sphere is to be named. The naming of some of the complexes is done as follows – (as per IUPAC)

Complex Compounds	IUPAC Name
(i) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (anionic complex) so suffix 'ate' is added with metal name	Potassium hexacyanoferrate(II)
(ii) $\text{K}_2[\text{PtCl}_6]$	Potassium hexachloridoplatinate(IV)
(iii) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (Cationic complex) so metal is without any suffix	Hexamminecobalt(III) chloride
(iv) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$	Tetraaquadichloridochromium(III) chloride
(v) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	Diamminetetrachloridoplatinum(IV)
(vi) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (Neutral complex) So no suffix is used with metal ion	Triamminetrichloridocobalt(III)
(vii) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$	Potassium hexanitrocobaltate(III)
(viii) $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NO}]$	Sodium pentacyanonitrosylferrate(II)
(ix) $[\text{NiCl}_4]^{2-}$	Tetrachloridonickelate(II) ion
(x) $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{+2}$	Pentamminechloridoruthenium(III) ion
(xi) $[\text{Fe}(\text{en})_3]\text{Cl}_3$	Tris(ethylenediamine)iron(III) chloride
(xii) $[\text{Ni}(\text{Gly})_2]$	Bis(glycinato)nickel(II)

- (i) If a complex ion has two metal atoms then it is termed polynuclear. The ligand which connects the two metal ions is called as **Bridging ligand or Bridge group**.  
A prefix of Greek letter  $\mu$ , is repeated before the name of each different kind of bridging group.



Tetraaquairon(III)- $\mu$ -amido- $\mu$ -hydroxotetraaquairon(III) sulphate

## FORMATION OF CO-ORDINATION COMPOUNDS

It can be explained by number of theories.

- (A) Werner's co-ordination theory
- (B) Sidwick theory or Effective Atomic Number Theory (EAN)
- (C) Valence bond theory
- (D) Crystal field theory

### (A) WERNER'S CO-ORDINATION THEORY :

Werner's co-ordination theory was the first attempt to explain the bonding in co-ordination compounds. The main postulates of this theory are :

- (a) Metals possess two types of valencies - Primary valency and secondary valency.
- (b) Primary valencies are normally ionisable and are exhibited by a metal in the formation of its simple salts such as  $\text{CoCl}_3$ ,  $\text{CuSO}_4$  and  $\text{AgCl}$ . In these salts the primary valencies of Co, Cu and Ag are 3, 2, 1 respectively. Primary valencies are referred to as oxidation state of their metal ion.
- (c) Secondary valencies are non-ionisable and are exhibited by a metal in the formation of its complex ions such as  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Ag}(\text{NH}_3)_2]^+$ . In these complex, the secondary valencies of  $\text{Co}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$  are 6, 4 and 2 respectively. These are referred to as co-ordination number (C.N.) of the metal cation.
- (d) Primary linkages (valencies) are satisfied by negative ions while secondary valencies are satisfied by neutral molecules, negative ions or in some cases positive ions also.
- (e) Every metal atom or ion has a fixed number of secondary valencies. In other words, the co-ordination number of the metal atom is usually fixed.
- (f) Every metal has tendency to satisfy both its primary and secondary valencies.
- (g) The ligands satisfying secondary valency are always directed towards fixed positions in space about the central metal atom or ion. Thus, the co-ordination compounds have a definite geometry. Werner deduced that in  $\text{CoCl}_3 \cdot 5\text{NH}_3$  only two of the three chlorine atoms are ionic and 5  $\text{NH}_3$  and one Cl form co-ordinate bonds to  $\text{Co}^{3+}$  ion.

Formula of some cobalt complexes.

#### Example :

	Old	New	No. of $\text{Cl}^-$ ions precipitated	Total No. of ions
(i)	$\text{CoCl}_3 \cdot 6 \text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	3	4
(ii)	$\text{CoCl}_5 \cdot 5 \text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	2	3
(iii)	$\text{CoCl}_3 \cdot 4 \text{NH}_3$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	1	2

Complex	Modern formula	No. of Cl <sup>-</sup> ions precipitated	Total number of ions
PtCl <sub>4</sub> · 6NH <sub>3</sub>	[Pt(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>4</sub>	4	5
PtCl <sub>4</sub> · 5NH <sub>3</sub>	[Pt(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>3</sub>	3	4
PtCl <sub>4</sub> · 4NH <sub>3</sub>	[Pt(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl <sub>2</sub>	2	3
PtCl <sub>4</sub> · 3NH <sub>3</sub>	[Pt(NH <sub>3</sub> ) <sub>3</sub> Cl <sub>3</sub> ]Cl	1	2
PtCl <sub>4</sub> · 2NH <sub>3</sub>	[Pt(NH <sub>3</sub> ) <sub>2</sub> Cl <sub>4</sub> ]	0	0 (non-electrolyte)

### ❖ WERNER'S REPRESENTATION OF COMPLEXES

(i)	Fe(NH <sub>3</sub> ) <sub>6</sub> Cl <sub>3</sub>		[Fe(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub> Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.
(ii)	Fe(NH <sub>3</sub> ) <sub>5</sub> Cl <sub>3</sub>		[Fe(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>2</sub> In this complex two 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also.
(iii)	Fe(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>3</sub>		[Fe(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl In this complex one 'Cl' group act as primary valency and two of the 'Cl' groups act as secondary valencies also.

### (B) SIDWICK THEORY OR EFFECTIVE ATOMIC NUMBER CONCEPT (EAN)

Sidwick proposed effective atomic number theory to explain the stability of the complexes. Total number of electrons on central metal including those transferred from ligands is known as EAN. The EAN generally coincides with the atomic number of next inert gas except in some cases.

EAN can be calculated by the following relation :

**EAN = (atomic number of the metal – oxidation state of central metal with sign) + number of electrons gained from the donor atoms of the ligands.**

**Example** Effective atomic number of the metal atom in the following :

- (a) K<sub>3</sub>[Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] is 33      (b) K<sub>4</sub>[Fe(CN)<sub>6</sub>] is 36

(C) VALENCE BOND THEORY

The main features of this theory are -

- (a) Every metal ion when it forms a complex compound undergoes formation of coordinate covalent bond.
- (b) During this bond formation, the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals.
- (c) The number of vacant orbitals provided is equal to the coordination number of metal ion.

**Example :** In the formation of  $[\text{Fe}(\text{NH}_3)_6]^{3+}$ ,  $\text{Fe}^{+3}$  ion provides six vacant orbitals.

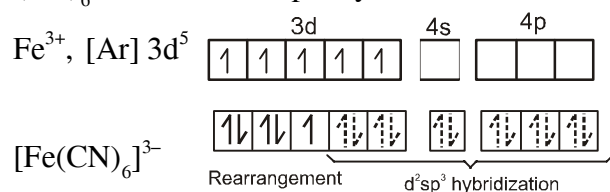
In  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $\text{Cu}^{+2}$  ion provides four vacant orbitals.

- (d) The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.
- (e) The vacant hybrid orbitals of metal ion get overlapped by orbitals of ligands containing lone pair of electrons.
- (f) The number of such overlappings is equal to the coordination number of metal ion.
- (g) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and accordingly complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively.
- (h) In certain complexes pairing of electrons takes place in ligand field, resulting in decrease in spin only magnetic moment, such complexes are known as Low spin complexes
- (i) Bohr magneton =  $\frac{eh}{4\pi mc}$
- (j) Paramagnetism is represented in the term of spin only magnetic moment.

$$\mu = \sqrt{n(n+2)} \text{ B.M.} \quad n = \text{Number of unpaired electron}$$

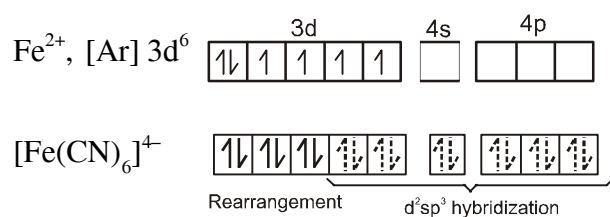
**Example**  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic while  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic.

**Sol.**  $[\text{Fe}(\text{CN})_6]^{3-}$  involves  $d^2sp^3$  hybridization.



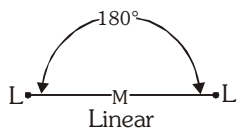
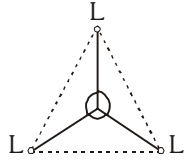
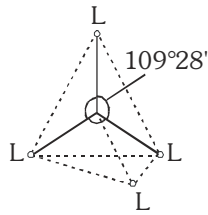
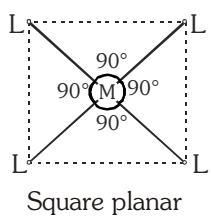
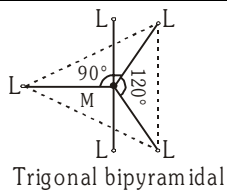
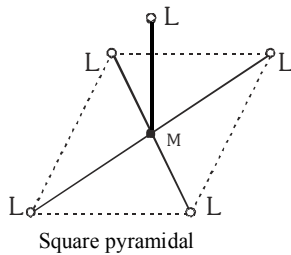
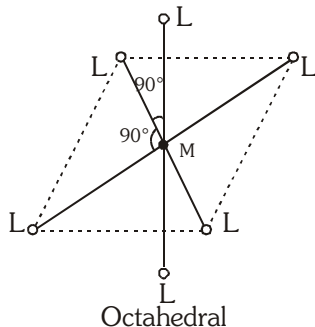
One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[\text{Fe}(\text{CN})_6]^{4-}$  also involves  $d^2sp^3$  hybridization but it has  $\text{Fe}^{2+}$  ion as central ion.



All electrons are paired, hence it is diamagnetic in nature.

## Some Example :

Coordination Number	Hybridised orbitals	Geometrical shape of the Complex	Examples of Complex
2	$sp$		$[\text{Ag}(\text{NH}_3)_2]^+$ $[\text{Ag}(\text{CN})_2]^-$
3	$sp^2$		$[\text{HgI}_3]^-$
4	$sp^3$		$[\text{CuCl}_4]^{2-}$ $[\text{ZnCl}_4]^{2-}$ $[\text{FeCl}_4]^-$ $[\text{Ni}(\text{CO})_4]$ $[\text{Zn}(\text{NH}_3)_4]^{+2}$
4	$dsp^2$ ( $d = d_{x^2-y^2}$ )		$[\text{PdCl}_4]^{2-}$ $[\text{Ni}(\text{CN})_4]^{2-}$ $[\text{Pt}(\text{NH}_3)_4]^{+2}$ $[\text{Cu}(\text{NH}_3)_4]^{+2}$ $[\text{PtCl}_4]^{2-}$
5	$sp^3d$ ( $d = d_{z^2}$ ) or $dsp^3$ ( $d = d_{z^2}$ )		$[\text{Fe}(\text{CO})_5]$ $[\text{CuCl}_5]^{3-}$
5	$sp^3d$ ( $d = d_{x^2-y^2}$ ) or $dsp^3$ ( $d = d_{x^2-y^2}$ )		$[\text{Ni}(\text{CN})_5]^{3-}$
6	$d^2sp^3$ (inner orbital complex) or $sp^3d^2$ (outer orbital complex) in both case d-orbitals are $d_{z^2}$ & $d_{x^2-y^2}$ .		$[\text{Cr}(\text{NH}_3)_6]^{+3}$ $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ $[\text{Fe}(\text{CN})_6]^{3-}$ $[\text{Co}(\text{NH}_3)_6]^{+3}$ $[\text{PtCl}_6]^{2-}, [\text{CoF}_6]^{3-}$



♦ **Drawback of valence bond theory :**

- It describes bonding in co-ordination compounds only qualitatively but not account for the relative stabilities for different co-ordination complexes.
- It does not offer any explanation for optical absorption spectra (coloration) of complexes
- It does not describe the detailed magnetic properties of co-ordination compounds.

**(D) CRYSTAL FIELD THEORY :** The drawbacks of VBT of coordination compounds are, to a considerable extent, removed by the Crystal Field Theory.

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five d-orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of polar molecules like  $\text{NH}_3$  and  $\text{H}_2\text{O}$ ) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lost. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field.

**(a) Crystal field splitting in octahedral coordination entities :**

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in d orbitals of metal and the electrons (or negative charges) of the ligands. Such a repulsion is more when the d orbitals of metal are directed towards the ligand than when it is away from the ligand.

Thus, the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals (axial orbitals) which point towards the axis along the direction of the ligand will experience more repulsion and will be raised in energy ; and the  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals (non-axial) orbitals which are directed between the axis will be lowered in energy relative to the average energy in the spherical crystal field.

Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy,  $t_{2g}$  set and two orbitals of higher energy,  $e_g$  set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by  $\Delta_0$  (the subscript o is for octahedral). Thus, the energy of the two  $e_g$  orbitals will increase by  $(3/5)\Delta_0$  and that of the three  $t_{2g}$  will decrease by  $(2/5)\Delta_0$ .

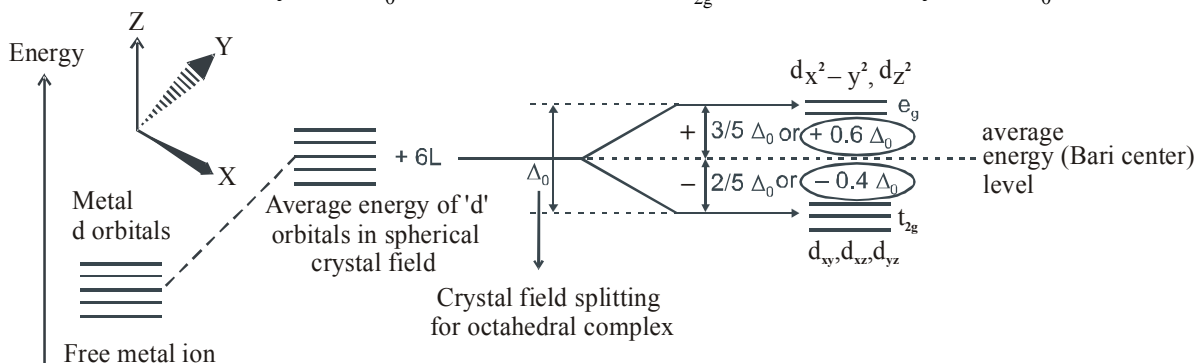
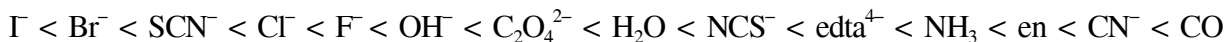


Figure showing crystal field splitting in octahedral complex.

The crystal field splitting,  $\Delta_0$ , depends upon the fields produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below :



**Note :** In  $\text{SCN}^-$ , S is donating atom and in  $\text{NCS}^-$ , N is donating atom.

Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands. For  $d^4$  configuration, the fourth electron will singly occupy  $e_g$  orbital (according to Hund's rule) or will undergo pairing in  $t_{2g}$  orbital, which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting,  $\Delta_0$  and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two possibilities are :

- (i) If  $\Delta_0 < P$ , the fourth electron enters in one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$ . Ligands for which  $\Delta_0 < P$  are known as weak field ligands and form high spin complexes.
- (ii) If  $\Delta_0 > P$ , it becomes more energetically favourable for the fourth electron to occupy a  $t_{2g}$  orbital with configuration  $t_{2g}^4 e_g^0$ . Ligands which produce this effect are known as strong field ligands and form low spin complexes.

### Crystal Field stabilising energy in Octahedral field :

$$\text{Formula : CFSE} = [-0.4 n_{t_{2g}} + 0.6 n_{e_g}] \Delta_0 + xP.$$

Where  $n_{t_{2g}}$  &  $n_{e_g}$  are number of electron(s) in  $t_{2g}$  &  $e_g$  orbitals respectively and  $\Delta_0$  crystal field splitting energy for octahedral complex. "x" represents the number of electron pairs and P is mean pairing energy.

### (b) Crystal field splitting in tetrahedral coordination entities :

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that  $\Delta_t = (4/9)\Delta_0$ . This may be attributed to the following two reasons.

- (i) There are only four ligands instead of six, so the ligand field is only two thirds the size ; as the ligand field splitting is also two thirds the size and (ii) the direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly further two thirds. So  $\Delta_t = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9} \Delta_0$ .

Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

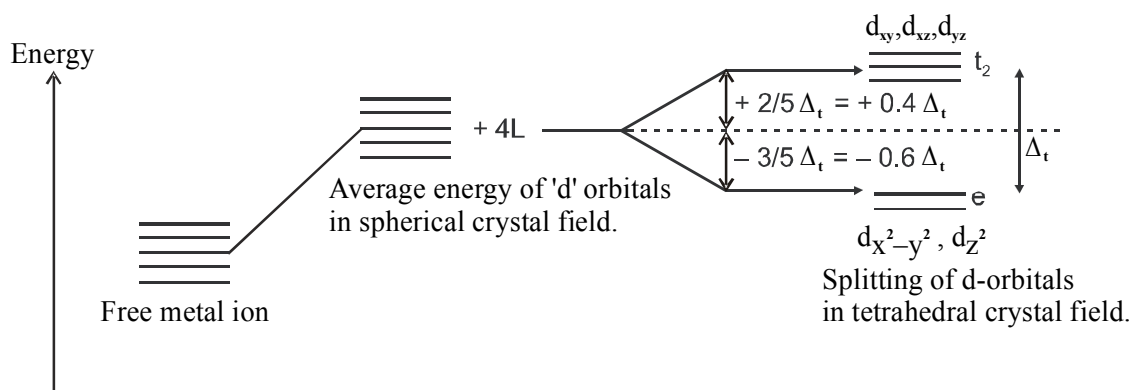


Figure showing crystal field splitting in tetrahedral complex.

Since  $\Delta_t < \Delta_o$  crystal field splitting favours the formation of octahedral complexes.

### Crystal Field stabilising energy in Tetrahedral field :

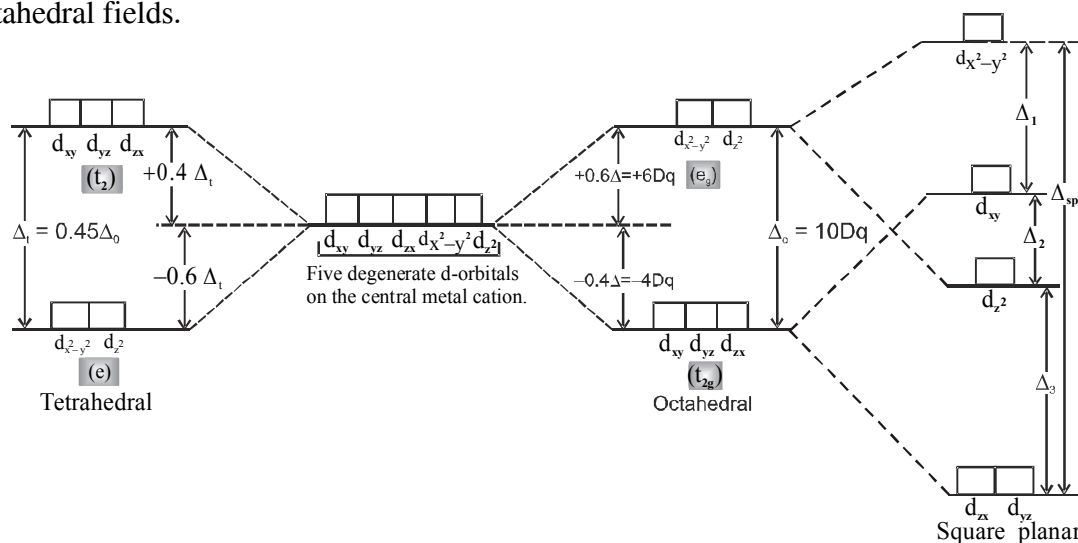
**Formula :**  $CFSE = [-0.6 n_e + 0.4 n_{t_2}] \Delta_t + xP$ .

where  $n_{t_2}$  &  $n_e$  are number of electron(s) in  $t_2$  &  $e$  orbitals respectively and  $\Delta_t$  crystal field splitting energy for tetrahedral complex. "x" represents the number of electron pairs and P is mean pairing energy.

### (c) Crystal field splitting in square planar co-ordination entities :

The square planar arrangement of ligands may be considered to be one derived from the octahedral field by removing two trans-ligands located along the Z-axis. In the process, the  $e_g$  and  $t_{2g}$  sets of orbitals is lifted i.e., these orbitals will no longer be degenerate.

The four ligands in square planar arrangement around the central metal ion are shown in Fig. As the ligands approach through the x and y axis, they would have greatest influence on  $d_{x^2-y^2}$  orbital, so the energy of this orbital, will be raised most. The  $d_{xy}$  orbital, lying in the same plane, but between the ligands will also have a greater energy though the effect will be less than that on the  $d_{x^2-y^2}$  orbitals. On the other hand, due to absence of ligands along Z-axis, the  $d_{z^2}$  orbital becomes more stable and has energy lower than that of  $d_{xy}$  orbital. Similarly  $d_{yz}$  and  $d_{zx}$  become more stable. The energy level diagram may be represented as shown in figure along with tetrahedral and octahedral fields.



The value of  $\Delta_{sp}$  has been found larger than  $\Delta_o$  because of the reason that  $d_{xz}$  and  $d_{yz}$  orbitals interact with only two ligands in the square planar complexes, while in octahedral complexes the interaction takes place only with four ligands.  $\Delta_{sp}$  has been found equal to  $1.3\Delta_o$ . Thus.

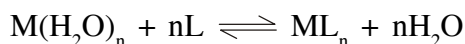
$$\Delta_{sp} = (\Delta_1 + \Delta_2 + \Delta_3) > \Delta_o \quad \text{and} \quad \Delta_{sp} = 1.3 \Delta_o.$$

**(E). STABILITY OF COORDINATION COMPOUNDS :**

The stability of a coordination compound  $[ML_n]$  is measured in terms of the stability constant (equilibrium constant) given by the expression,

$$\beta_n = [ML_n]/[M(H_2O)_n][L]^n$$

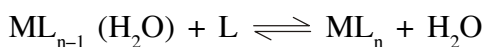
for the overall reaction :



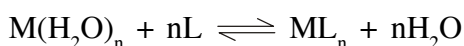
By convention, the water displaced is ignored, as its concentration remains essentially constant. The above overall reaction takes place in steps, with a stability (formation) constant,  $K_1$ ,  $K_2$ ,  $K_3$ , .....  $K_n$  for each step as represented below :



$$K_1 = [ML(H_2O)_{n-1}] / \{[M(H_2O)_n][L]\}$$



$$K_n = [ML_n] / \{[ML_{n-1}(H_2O)][L]\}$$



$$\beta_n = K_1 \times K_2 \times K_3 \times \dots \times K_n$$

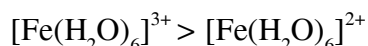
$\beta_n$ , the stability constant, is related to thermodynamic stability when the system has reached equilibrium. Most of the measurements have been made from aqueous solutions, which implies that the complex is formed by the ligand displacing, water from the aqua complex of the metal ion. Ignoring the charge and taking L as an unidentate ligand, the stepwise formation of the complex is represented as shown above.

$K_1$ ,  $K_2$ ,  $K_3$  .....  $K_n$  representing the stepwise stability (or formation) constants.

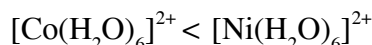
The above is thermodynamic stability criteria, there can be another kind of stability called kinetic stability, which measures the rate of ligand replacement.

**(F). FACTORS INFLUENCING THE MAGNITUDE OF C.F.S.E. :**

- 1. Different charges on the cation of the same metal :** The cation with a higher oxidation state has a larger value of CFSE than that with lower oxidation state e.g.,



- 2. Same charges on the cation but the number of d-electrons is different :** The metal cation the magnitude of CFSE with the increase of the number of d-electrons, e.g.,



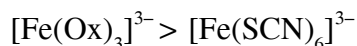
- 3. Quantum number (n) of the d-orbitals of the central metal ion :** As 'n' increase CFSE increases.



- 4. Types of Hybridisation :**

$$\Delta_t = \frac{4}{9} \Delta_0$$

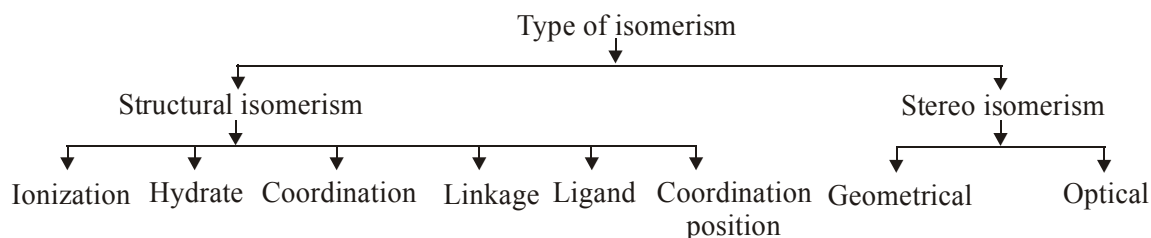
- 5. Presence of chelating ligand increases CFSE :**



## □ ISOMERISM IN COMPLEXES

- (a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as **Isomers**.
- (b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.

## ❖ CLASSIFICATION OF ISOMERISM



### (A) Structural isomerism

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

#### (a) Ionisation isomerism

The type of isomerism which is due to the exchange of groups or ions between the coordination sphere and the ionisation sphere.

*Example.* (i)  $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{SO}_4$  can be represented as  
 $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{SO}_4$  (red violet) and  $[\text{Co}(\text{NH}_3)_4\text{SO}_4]\text{Br}_2$  (red)  
 These complexes give sulphate ion and bromide ion respectively

(ii)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$  and  $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$

(iii)  $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_4\text{SO}_4](\text{NO}_3)_2$

#### (b) Hydrate isomerism

This type of isomerism is due to presence of different number of water molecules inside a coordination sphere.

*Example.*  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$  has four possible structures

(i)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  violet

(ii)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  green

(iii)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  dark green.

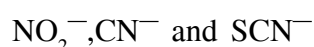
(iv)  $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$  dark green.

These complexes differ from one another with respect to the number of water molecules acting as ligands. Other hydrate isomers are

$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$

#### (c) Linkage isomerism

(i) This type of isomerism arises due to presence of ambidentate ligands like



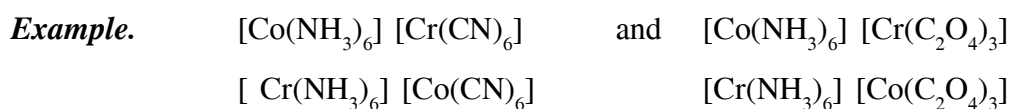
(ii) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.

(iii) Such type of isomers are distinguished by infra red (I.R.) spectroscopy.

- Example.**
- $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$
  - In  $\text{NO}_2^-$  ligand, The coordinating sites are nitrogen (i.e.,  $\text{NO}_2^-$  Nitro ligand) or through oxygen (i.e. ONO Nitrito ligand)
  - The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

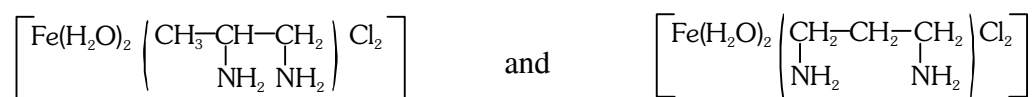
(d) **Coordination isomerism**

- (i) This type of isomerism is exhibited when the complex has two complex ions in it - 'cationic and anionic'.
- (ii) This type of isomerism is caused by the interchange of ligands between the two complex ions of the same complex.

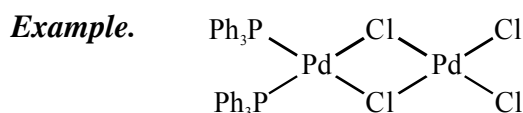
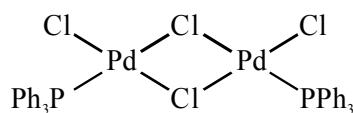
(e) **Ligand isomerism**

- (i) Ligands with  $\text{C}_3\text{H}_6(\text{NH}_2)_2$  have two different structures i.e. 1, 3-diamino propane and 1, 2-diaminopropane(propylene diamine).
- (ii) Those complexes which have same molecular formula, but differ with respect to their ligands are called as **Ligand isomers**.

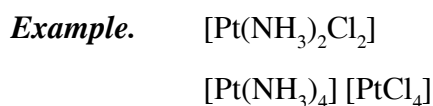
**Example.**  $[\text{Fe}(\text{H}_2\text{O})_2 \text{C}_3\text{H}_6(\text{NH}_2)_2\text{Cl}_2]$  has two different structures

(f) **Co-ordination Position Isomerisation :**

It is shown by polynuclear complexes, due interchange of ligands between the different metal nuclei.

(g) **Polymerization Isomerism :**

This is not true isomerism because it occurs between compounds having the same empirical formula, but different molecular weights.



**(B) Stereo isomerism**

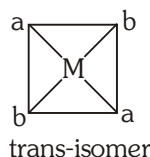
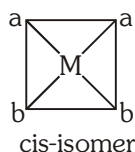
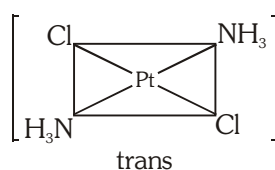
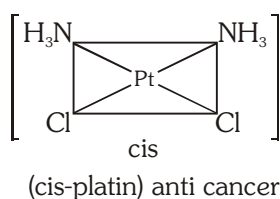
They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion. The two stereo isomers which are possible Geometrical and Optical.

**(a) Geometrical isomerism**

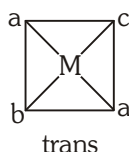
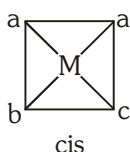
- (i) The ligands occupy different positions around the central metal ion.
- (ii) When two identical ligands are co-ordinated to the metal ion from same side then it is **cis isomer**. (Latin, cis means same).
- (iii) If the two identical ligands are co-ordinated to the metal ion from opposite side then it is **trans isomer** (in Latin, trans means across).

**Geometrical isomers with co-ordination number = 4 (Square planar complexes)**

- (i) Complexes with general formula,  $\text{Ma}_2\text{b}_2$  (where both a and b are monodentate) can have cis-and trans isomers.

**Example. [Pt (NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]**

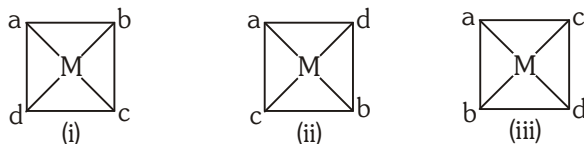
- (ii) Complexes with general formula  $\text{Ma}_2\text{bc}$  can have cis - and trans-isomers.



**Example.**  $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]$



(iii) Complexes with general formula,  $\text{Mabcd}$  can have three isomers.



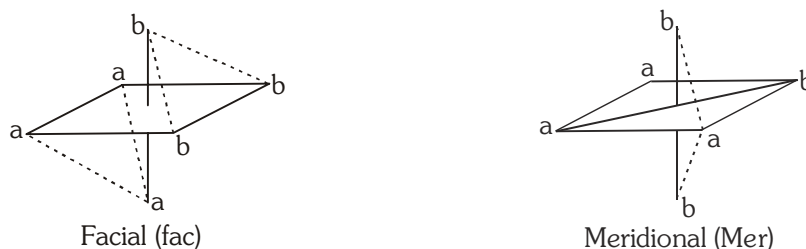
**Geometrical isomers with Co-ordination number = 6**

(i) Complexes with general formula  $\text{Ma}_4\text{b}_2$  can have cis - and trans-isomers.

**Example.**  $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]$



(iii) **Facial and Meridional isomerism ( $\text{Ma}_3\text{b}_3$ )**



Other 6-Coordinated geometrical isomers are

Note :	General formula	Total No. of geometrical isomers
	$\text{Mabcdef}$	15
	$\text{Ma}_2\text{bcde}$	9
	$\text{Ma}_2\text{b}_2\text{cd}$	6
	$\text{Ma}_2\text{b}_2\text{c}_2$	5
	$\text{Ma}_3\text{bcd}$	4
	$\text{Ma}_3\text{b}_2\text{c}$	3
	$\text{Ma}_3\text{b}_3$	2
	$\text{Ma}_4\text{bc}$	2
	$\text{Ma}_4\text{b}_2$	2
	$\text{Ma}_5\text{b}$	Not possible
	$\text{Ma}_6$	Not possible

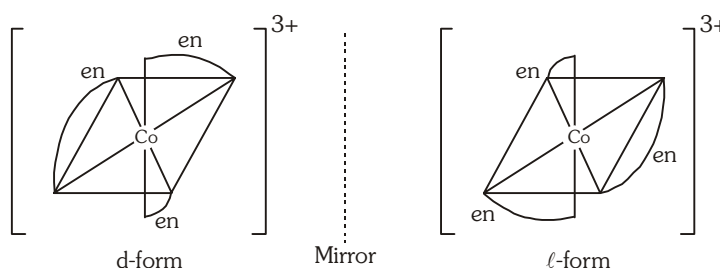
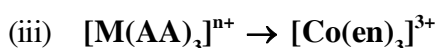
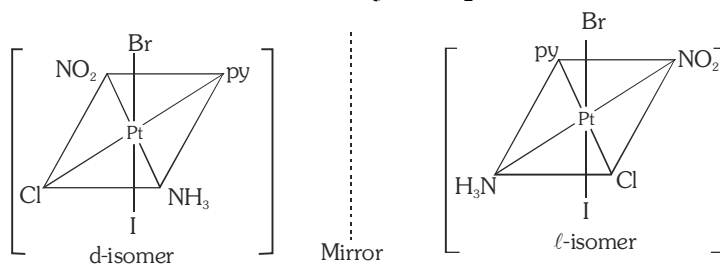
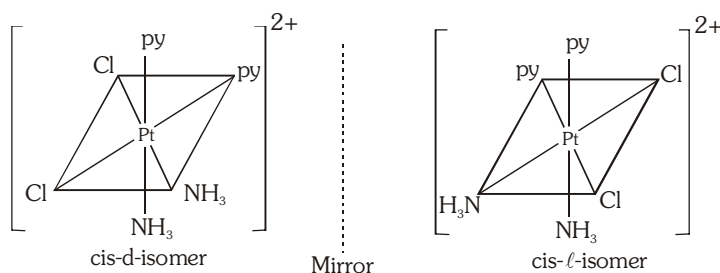
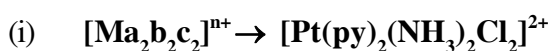
Here M = central atom a, b, c, d, e, f = Monodentate ligands



(b) **Optical isomers**

- (i) Optically active complexes are those which are nonsuperimposable over the mirror image structure.
- (ii) An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.
- (iii) The complex which rotates plane polarised light to left hand side is **laevo rotatory** i.e. '*l*' or '-' and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory** '*d*' or '+'.  
 (iv) Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.
- (v) The '*d*' and '*l*' isomers of a compound are called as **Enantiomers or Enantiomorphs**.
- (vi) Optical isomerism is expected in tetrahedral complexes of the type  $Mabcd$ .

**Optical isomers with Co-ordination number = 6**



## NUMBER OF POSSIBLE ISOMERS FOR SPECIFIC COMPLEXES

Formula	Number of stereoisomers	Pairs of Enantiomers
$M_{a_4b_2}$	2	0
$M_{a_3b_3}$	2	0
$M_{a_4bc}$	2	0
$M_{a_3bcd}$	5	1
$M_{a_2bcde}$	15	6
$M_{abcdef}$	30	15
$M_{a_2b_2c_2}$	6	1
$M_{a_2b_2cd}$	8	2
$M_{a_3b_2c}$	3	0
$M(AA)(BC)de$	10	5
$M(AB)(AB)cd$	11	5
$M(AB)(CD)ef$	20	10
$M(AB)_3$	4	2

*Note : Uppercase letters represent chelating ligands and lowercase letters represent monodentate ligands.*

## EXERCISE : O-1

**SINGLE OPTION CORRECT :***Double salt and complex compound*

1. Some salts although containing two different metallic elements give test for one of them in solution. Such salts are
- (A) complex salt (B) double salt  
(C) normal salt (D) none of these

CC0001

2. Aqueous solution of  $\text{FeSO}_4$  gives tests for both  $\text{Fe}^{2+}$  and  $\text{SO}_4^{2-}$  but after addition of excess of KCN, solution ceases to give test for  $\text{Fe}^{2+}$ . This is due to the formation of
- (A) the double salt  $\text{FeSO}_4 \cdot 2\text{KCN} \cdot 6\text{H}_2\text{O}$   
(B)  $\text{Fe}(\text{CN})_3$   
(C) the complex ion  $[\text{Fe}(\text{CN})_6]^{4-}$   
(D) the complex ion  $[\text{Fe}(\text{CN})_6]^{3-}$

CC0002

*Werner theory*

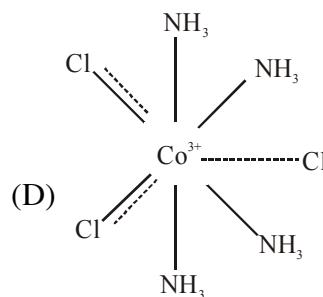
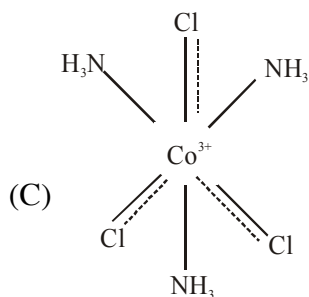
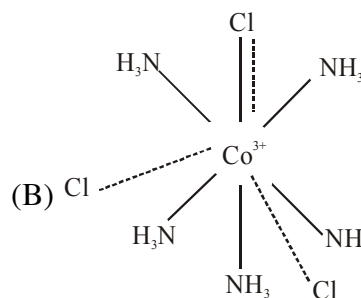
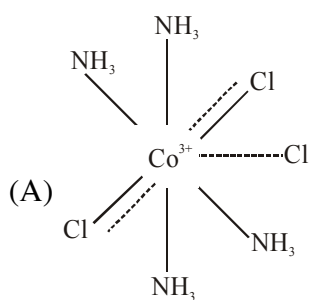
3. Consider the following statements:  
According to the Werner's theory.
- (a) Ligands are connected to the metal ions by covalent bonds.  
(b) Secondary valencies have directional properties  
(c) Secondary valencies are non-ionisable
- Of these statements:
- (A) a, b and c are correct (B) b and c are correct  
(C) a and c are correct (D) a and b are correct

CC0003

4. A complex of platinum, ammonia and chloride produces four ions per molecule in the solution. The structure consistent with the observation is:
- (A)  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_4$  (B)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$   
(C)  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$  (D)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$

CC0004

5. Which of the following Werner's complex has least electrical conductivity ?



CC0005

### Classification of ligand

6. How many EDTA<sup>4-</sup> molecules are required to make an octahedral complex with a Ca<sup>2+</sup> ion ?

(A) Six (B) Three (C) One (D) Two

CC0006

7.  $\pi$ -bonding is not involved in :

(A) ferrocene (B) dibenzene chromium (C) Zeise's salt (D) Grignard reagent

CC0007

8. Which of the following is not considered as an organometallic compound ?

(A) Ferrocene (B) Cis-platin (C) Ziese's salt (D) Grignard reagent

CC0008

9. Diethylene triamine is:

(A) Chelating agent (B) Polydentate ligand  
(C) Tridentate ligand (D) All of these

CC0009

10. Which of the following species is not expected to be a ligand

(A) NO<sup>+</sup> (B) NH<sub>4</sub><sup>+</sup> (C) NH<sub>2</sub>-NH<sub>3</sub><sup>+</sup> (D) CO

CC0010

11. The disodium salt of ethylene diamine tetraacetic acid can be used to estimate the following ion(s) in the aqueous solution

(A) Mg<sup>2+</sup> ion (B) Ca<sup>2+</sup> ion (C) Na<sup>+</sup> ion (D) both Mg<sup>2+</sup> and Ca<sup>2+</sup>

CC0011



20. How many  $\pi$  electrons are donated by  $C_5H_5^-$  ligand -  
 (A) 2 (B) 4 (C) 5 (D) 6 CC0020
21. Effective atomic number of  $Co(CO)_4$  is 35, hence it is less stable. It attains stability by  
 (A) Oxidation of Co (B) Reduction of Co  
 (C) Dimerization (D) Both (B) & (C) CC0021
22. In the complex  $Fe(CO)_x$ , the value of x is:  
 (A) 3 (B) 4 (C) 5 (D) 6 CC0022
23. The EAN of platinum in potassium hexachloroplatinate (IV) is:  
 (A) 46 (B) 86 (C) 36 (D) 84 CC0023
24. The EAN of metal atoms in  $Fe(CO)_2(NO)_2$  and  $Co_2(CO)_8$  respectively are  
 (A) 34, 35 (B) 34, 36 (C) 36, 36 (D) 36, 35 CC0024

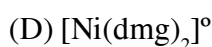
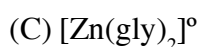
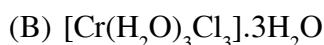
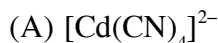
*Naming of complex compound*

25. The IUPAC name for the coordination compound  $Ba[BrF_4]_2$  is  
 (A) Barium tetrafluorobromate (V) (B) Barium tetrafluorobromate (III)  
 (C) Barium bis (tetrafluorobromate) (III) (D) none of these CC0025
26. The number of ions formed, when bis (ethane-1,2-diamine) copper (II) sulphate is dissolved in water will be  
 (A) 1 (B) 2 (C) 3 (D) 4 CC0026
27. The IUPAC name of the Wilkinson's catalyst  $[Rh Cl (P Ph_3)_3]$  is  
 (A) Chloridotris(triphenylphosphine)rhodium(I)  
 (B) Chloridotris(triphenylphosphine)rhodium(IV)  
 (C) Chloridotris(triphenylphosphine)rhodium(0)  
 (D) Chloridotris(triphenylphosphine)rhodium(VI) CC0027
28. The formula for the compound tris (ethane-1, 2-diamine)cobalt (III) sulphate is  
 (A)  $[Co(en)_3]SO_4$  (B)  $[Co(SO_4)(en)_3]$   
 (C)  $[Co(en)_3](SO_4)_2$  (D)  $[Co(en)_3]_2(SO_4)_3$  CC0028



## Stereoisomerism

34. Which of the following complex shows optical isomerism -



CC0034

35. How many coordination isomers of  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$  show geometrical isomerism.

(A) All

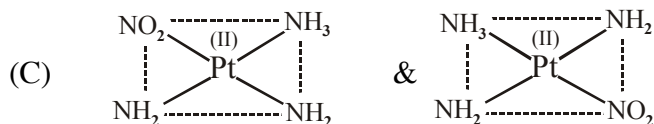
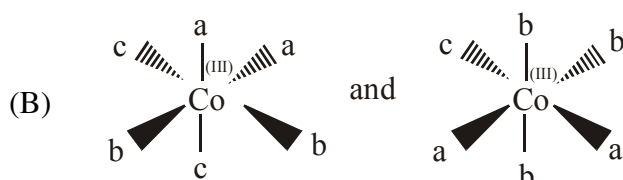
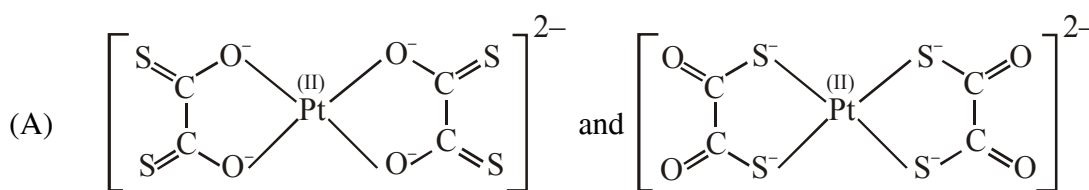
(B) One

(C) Two

(D) None

CC0035

36. Identify the pair of complex which are stereoisomer of each other -



(D) All of the above

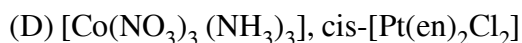
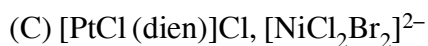
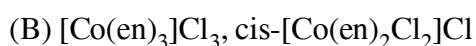
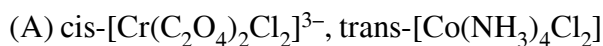
CC0036

37. Find complex which have maximum number of stereoisomers -



CC0037

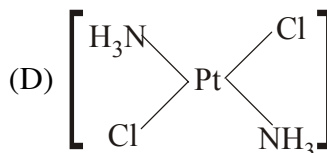
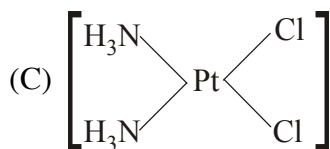
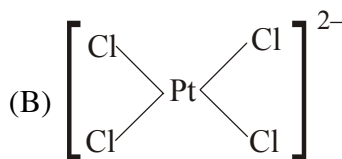
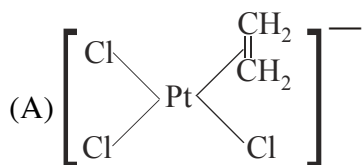
38. In which of the following pairs both the complexes show optical isomerism ?



CC0038

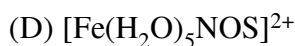
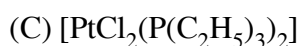


39. Which of the following is considered to be an anticancer species ?



CC0039

40. Which of the following can exhibit geometrical isomerism ?



CC0040

41. The oxidation state of Mo in its oxo-complex species  $[\text{Mo}_2\text{O}_4(\text{C}_2\text{H}_4)_2(\text{H}_2\text{O})_2]^{2-}$  is:

(A) +2

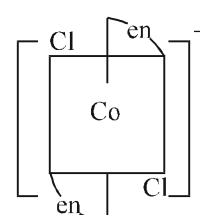
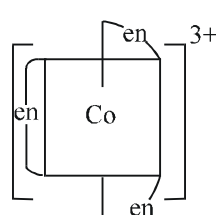
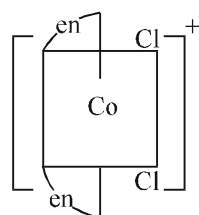
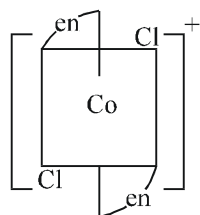
(B) +3

(C) +4

(D) +5

CC0041

42. Which of the following ions are optically active?



(A) I only

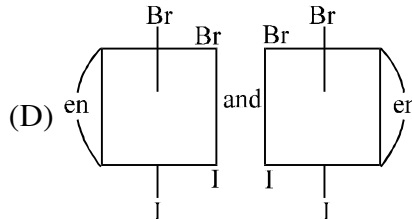
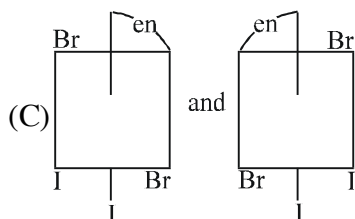
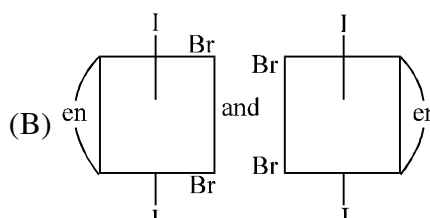
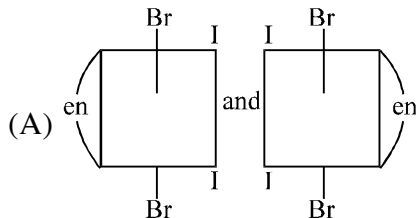
(B) II only

(C) II and III

(D) IV only

CC0042

43. The complex ion has two optical isomers. Their **CORRECT** configurations are:



CC0043

## V.B.T/CFT

44. Which of the following complex is coloured and diamagnetic -  
 (A)  $\text{MnO}_4^{2-}$  (B)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  (C)  $[\text{CrCl}_6]^{3-}$  (D)  $\text{CrO}_4^{2-}$  CC0044
45. What is the hybridisation of Fe in  $[\text{Fe}(\text{CO})_4]^{-2}$   
 (A)  $d^2sp^3$  (B)  $sp^3d^2$  (C)  $sp^3d$  (D)  $sp^3$  CC0045
46. One unknown complex has the spin only magnetic moment is of 1.73 BM. As per the C. F. T., complex is.  
 (A)  $d^7$ , Oh-field, with Strong Field Legend (B)  $d^9$ , sq.planar-field, with Strong Field Legend  
 (C)  $d^9$ , Td,field with Weak Field Legend (D) All of these CC0046
47. Identify tetrahedral species which has maximum magnetic moment value :  
 (A)  $[\text{CuCl}_4]^{2-}$  (B)  $[\text{CoCl}_4]^{2-}$  (C)  $[\text{FeCl}_4]^{2-}$  (D)  $[\text{AlCl}_4]^-$  CC0047
48. In the co-ordination compound  $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$  oxidation state of Fe is -  
 (A) +1 (B) +2 (C) +3 (D) +4 CC0048
49. Which one of the following complex is an outer orbital complex -  
 (A)  $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$  (B)  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$   
 (C)  $[\text{Fe}(\text{NH}_3)_6]^{+2}$  (D) All of these CC0049
50. Which of the following is diamagnetic and  $sp^3$  hybridised -  
 (A)  $[\text{NiCl}_4]^{2-}$  (B)  $[\text{Ni}(\text{CN})_4]^{4-}$  (C)  $[\text{Ni}(\text{CN})_4]^{2-}$  (D)  $[\text{NiCl}_2(\text{PPh}_3)_2]$  CC0050
51.  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (atomic number of Cr = 24) has a magnetic moment of 3.83 B.M. The CORRECT distribution of 3d electrons in the chromium present in the complex is:  
 (A)  $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$  (B)  $3d_{xy}^1, 3d_{yz}^1, 3d_{z^2}^1$   
 (C)  $3d_{(x^2-y^2)}^1, 3d_{z^2}^1, 3d_{xz}^1$  (D)  $3d_{xy}^1, 3d_{(x^2-y^2)}^1, 3d_{yz}^1$  CC0051
52.  $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$  has Crystal Field Splitting Energy value  $10,400 \text{ cm}^{-1}$  and pairing energy value  $17,600 \text{ cm}^{-1}$  then it is :  
 (A) Low spin complex (B) Paramagnetic in nature  
 (C) Diamagnetic in nature (D) None of these CC0052

53. In which of the following coordination entities, the magnitude of  $\Delta_0$  [CFSE in octahedral field] will be maximum? :
- (A)  $[\text{Co}(\text{CN})_6]^{3-}$  (B)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$   
 (C)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  (D)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- CC0053**
54. The number of unpaired electrons calculated in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{CoF}_6]^{3-}$  are :
- (A) 4 and 4 (B) 0 and 2 (C) 2 and 4 (D) 0 and 4
- CC0054**
55. An ion  $\text{M}^{2+}$ , forms the complexes  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{M}(\text{en})_3]^{2+}$  and  $[\text{MBr}_6]^{4-}$ , match the complex with the appropriate colour.
- (A) Green, blue and red (B) Blue, red and green  
 (C) Green, red and blue (D) Red, blue and green
- CC0055**
56. Formula of ferrocene is:
- (A)  $[\text{Fe}(\text{CN})_6]^{4-}$  (B)  $[\text{Fe}(\text{CN})_6]^{3+}$  (C)  $[\text{Fe}(\text{CO})_5]$  (D)  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$
- CC0056**
57.  $\text{Ni}(\text{CO})_4$  and  $[\text{Ni}(\text{NH}_3)_4]^{2+}$  do not differ in
- (A) magnetic moment (B) oxidation number of Ni  
 (C) geometry (D) EAN
- CC0057**
58. A complex of certain metal has the magnetic moment of 4.91 BM whereas another complex of the same metal with same oxidation state has zero magnetic moment. The metal ion could be
- (A)  $\text{Co}^{2+}$  (B)  $\text{Mn}^{2+}$  (C)  $\text{Fe}^{2+}$  (D)  $\text{Fe}^{3+}$
- CC0058**
59. The tetrahedral  $[\text{CoI}_4]^{2-}$  and square planar  $[\text{PdBr}_4]^{2-}$  complex ions are respectively
- (A) low spin, high spin (B) high spin, low spin  
 (C) both low spin (D) both high spin
- CC0059**
60. Which one of the following species does not represent cationic species of vanadium formed in aqueous solution
- (A)  $\text{VO}_2^+$  (B)  $\text{VO}^{2+}$  (C)  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  (D)  $\text{VO}_2^{2+}$
- CC0060**

61. On treatment of  $[\text{Ni}(\text{NH}_3)_4]^{2+}$  with concentrated HCl, two compounds I and II having the same formula,  $[\text{NiCl}_2(\text{NH}_3)_2]$  are obtained, I can be converted into II by boiling with dilute HCl. A solution of I reacts with oxalic acid to form  $[\text{Ni}(\text{C}_2\text{O}_4)(\text{NH}_3)_2]$  whereas II does not react. Point out the correct statement of the following
- (A) I cis, II trans; both tetrahedral (B) I cis, II trans; both square planar  
(C) I trans, II cis; both tetrahedral (D) I trans, II cis; both square planar
- CC0061**
62. Among the following, the compound that is both paramagnetic and coloured is
- (A)  $\text{K}_2\text{Cr}_2\text{O}_7$  (B)  $(\text{NH}_4)_2[\text{TiCl}_6]$  (C)  $\text{VOSO}_4$  (D)  $\text{K}_3[\text{Cu}(\text{CN})_4]$
- CC0062**
63. The magnetic moment of  $[\text{NiX}_4]^{2-}$  ion is found to be zero. Then the metal of the complex ion is (X = monodentate anionic ligand).
- (A)  $\text{sp}^3$  hybridised (B)  $\text{sp}^2$  hybridised (C)  $\text{dsp}^2$  hybridised (D)  $\text{d}^2\text{sp}$  hybridised
- CC0063**
64. For which of the following types of  $\text{d}^n$  configuration, the number of unpaired electrons in octahedral complexes remains same irrespective of the ligand field strength.
- (A)  $\text{d}^3$  (B)  $\text{d}^4$  (C)  $\text{d}^5$  (D)  $\text{d}^6$
- CC0064**
65. Which of the following electronic arrangement gives the highest value of the magnetic moment?
- (A)  $\text{d}^6$ , strong field (B)  $\text{d}^7$ , high spin (C)  $\text{d}^4$ , weak field (D)  $\text{d}^2$ , strong field
- CC0065**
66. Select appropriate ligand for given complex
- $[\text{Co}(\dots)_6]^{+x}$ ;  $\mu = 0 \text{ BM}$
- (A)  $\text{C}_2\text{O}_4^{2-}$  (B) en (C)  $\text{H}_2\text{O}$  (D)  $\text{F}^-$
- CC0066**
67. According to C.F.T., ligands are treated as -
- (A) Point charges (B) Lewis acids (C) Proton donor (D) All of the above
- CC0067**
68. Which of the following is correct electronic configuration of 3d orbital in excited state of central metal ion, when  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  absorbed yellow-green light.
- (A) 3d 

			1	
--	--	--	---	--

 (B)  $t_{2g}^1, e_g^0$   
(C)  $t_{2g}^1, e_g^1$  (D)  $t_{2g}^0, e_g^1$
- CC0068**
69. If  $\lambda_{\text{absorbed}}$  for d-d transition is in order  $[\text{Ti}(\text{X})_6]^{3+} > [\text{Ti}(\text{Y})_6]^{3+} > [\text{Ti}(\text{Z})_6]^{3+}$ .  
Select correct order of strength of ligands (X, Y, Z are monodentate ligand)-
- (A)  $\text{Z} > \text{Y} > \text{X}$  (B)  $\text{X} > \text{Y} > \text{Z}$   
(C)  $\text{Z} > \text{X} > \text{Y}$  (D) Not predictable
- CC0069**

## EXERCISE : O-2

MORE THAN ONE MAY BE CORRECT

1. Which of the following exhibit geometrical isomerism (M stands for a metal, and a and b are achiral ligands)?

(A)  $\text{Ma}_2\text{b}_2$  (Sq. Pl.) (B)  $\text{Ma}_4\text{b}_2$  (C)  $\text{Ma}_5\text{b}$  (D)  $\text{Ma}_6$

CC0070

2. Which of the following statement(s) is (are) **CORRECT** ?

(A) The oxidation state of iron in sodium nitroprusside  $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$  is +II.

(B)  $[\text{Ag}(\text{CN})_2]^-$  is linear in shape.

(C) In  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , Fe is  $d^2sp^3$  hybridized.

(D) In  $\text{Ni}(\text{CO})_4$ , the oxidation state of Ni is zero.

CC0071

3. Which of the following compound(s) show(s) optical isomerism.

(A)  $[\text{Pt}(\text{bn})_2]^{2+}$  (B)  $[\text{CrCl}_2(\text{en})_2]^+$  (C)  $[\text{Co}(\text{en})_3]$  (D)  $[\text{Zn}(\text{gly})_2]$

CC0072

4. Select **INCORRECT** statement(s) for  $[\text{Cu}(\text{CN})_4]^{3-}$ ,  $[\text{Cd}(\text{CN})_4]^{2-}$  and  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  complex ion.

(A) Both  $[\text{Cd}(\text{CN})_4]^{2-}$  and  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  have square planar geometry

(B)  $[\text{Cu}(\text{CN})_4]^{3-}$  and  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  have equal no. of unpaired electron

(C)  $[\text{Cu}(\text{CN})_4]^{3-}$  and  $[\text{Cd}(\text{CN})_4]^{2-}$  can be separated from the mixture on passing  $\text{H}_2\text{S}$  gas.

(D) All the three complexes have magnetic moment equal to zero.

CC0073

5. Which of the following will have two stereoisomeric forms?

(A)  $[\text{Cr}(\text{NO}_3)_3(\text{NH}_3)_3]$

(B)  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$

(C)  $[\text{CoCl}_2(\text{en})_2]^+$

(D)  $[\text{CoBrCl}(\text{Ox})_2]^{3-}$

CC0074

6. Which is / are **NOT** correctly matched.

**Complex compounds****IUPAC name**

(A)  $\text{K}[\text{CrF}_4\text{O}]$

Potassium tetrafluoridooxidochromate(V)

(B)  $\text{Na}[\text{BH}(\text{OCH}_3)_3]$

Sodium hydridotrimethoxyborate(III)

(C)  $[\text{Be}(\text{CH}_3-\text{CO}-\text{CH}_2-\text{CO}-\text{C}_6\text{H}_5)_2]^\circ$

Bis(benzoylacetato)beryllium(III)

(D)  $\text{H}[\text{AuCl}_4]$

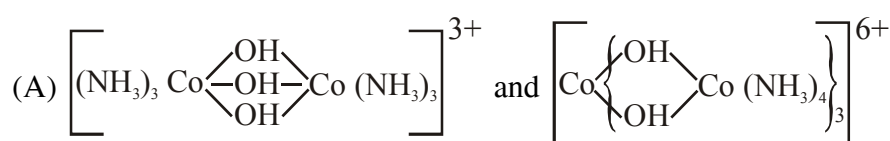
Hydrogen tetrachloroaurate(III)

CC0075

7. Which of the following statement(s) is/are **INCORRECT**
- (A) In  $[\text{CoBrCl}(\text{en})_2]^+$  geometrical isomerism exists, while optical isomerism does not exist
- (B) Potassium aquadicyanidosuperoxidoperoxidochromate(III) is IUPAC name for  $\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O}_2)(\text{H}_2\text{O})]$
- (C) There are 3 geometrical isomers and 15 stereoisomers possible for  $[\text{Pt}(\text{NO}_2)(\text{NH}_3)(\text{NH}_2\text{OH})(\text{py})]^+$  and  $[\text{PtBrCl}(\text{NO}_2)(\text{NH}_3)(\text{py})]$  respectively
- (D) cis and trans forms are not diastereomers of each other

CC0076

8. Which of the following complexes are polymerisation isomers :



- (B)  $[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_3)_4] [\text{Pt}(\text{NH}_3)\text{Cl}_3]_2$
- (C)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2 [\text{PtCl}_4]$
- (D)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$  and  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

CC0077

9. Which of the following is **CORRECT** about Tetraamminedithiocyanato-Scobalt(III) tris(oxalato)cobaltate(III)
- (A) formula of the complex is  $[\text{Co}(\text{SCN})_2(\text{NH}_3)_4][\text{Co}(\text{ox})_3]$
- (B) It is a chelating complex and show linkage isomerism.
- (C) It shows optical isomerism.
- (D) It shows geometrical isomerism.

CC0078

10. Which is **CORRECT** statement(s)?
- (A)  $[\text{Ag}(\text{NH}_3)_2]^+$  is linear with  $sp$  hybridised  $\text{Ag}^+$  ion
- (B)  $\text{NiCl}_4^{2-}$ ,  $\text{VO}_4^{3-}$  and  $\text{MnO}_4^-$  have tetrahedral geometry
- (C)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  &  $[\text{Ni}(\text{CN})_4]^{2-}$  have  $dsp^2$  hybridisation of the metal ion
- (D)  $\text{Fe}(\text{CO})_5$  has trigonal bipyramidal structure with  $d_{z^2}sp^3$  hybridised iron.

CC0079

11. In which of the following complex(s) spin only magnetic moment is independent, from the nature of ligand. (L = monodentate ligand) -

- (A)  $[\text{NiL}_4]^{II}$                       (B)  $[\text{NiL}_6]^{II}$                       (C)  $[\text{FeL}_6]^{III}$                       (D)  $[\text{CrL}_6]^{III}$

CC0080

12. Which of the following compound(s) can show optical isomerism ?

- (A)  $[\text{PtCl}_4]^{2-}$                       (B)  $[\text{PtCl}_2(\text{NH}_3)_2]$                       (C)  $[\text{Fe}(\text{EDTA})]^-$                       (D)  $[\text{Fe}(\text{en})_3]^{3+}$

CC0081

13. Which of the following compounds are resolvable into d or *l*-forms?

- (A)  $[\text{ZnCl}_2(\text{en})]$                       (B)  $[\text{Be}(\text{acac})_2]$                       (C)  $[\text{Co}(\text{gly})_3]$                       (D)  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

CC0082

14. Which of the following ion is/are diamagnetic and non planar ?

- (A)  $[\text{Ni}(\text{CN})_4]^{2-}$                       (B)  $\text{MnO}_4^-$                       (C)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$                       (D)  $\text{CrO}_4^{2-}$

CC0083

## EXERCISE : S-1

**INTEGER TYPE**

- Find number of ligands which is / are stronger ligand as compared to  $\text{NH}_3$   
 $\text{NO}_2^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{C}_2\text{O}_4^{2-}$ , en,  $\text{Cl}^-$ ,  $\bar{\text{CN}}$  CC0084
- If crystal field stabilization energy of  $[\text{ML}_6]^{+n}$  is  $-0.8 \Delta_{\text{O}}$ .  
 Find minimum number of electrons in  $t_{2g}$  orbitals of metal ion ? CC0085
- Find number of Co–N linkage in,  
**Pentaamminecobalt(III)– $\mu$ –amidodiamminetriaquacobalt(III) chloride.** CC0086
- Find the EAN value of central atom of  $[\text{Fe}(\pi\text{-C}_4\text{H}_4)(\text{CO})_3]$  CC0087
- Find the maximum number of atoms lying in one plane for  $[\text{Cr}(\text{CN})_6]^{3-}$  CC0088
- Select complex in which metal–carbon linkage(s) is / are present :  
 $[\text{Fe}^{\text{III}}(\text{EDTA})]^-$ ,  $\text{K}[\text{PtCl}_3(\pi\text{-C}_2\text{H}_4)]$ ,  $[\text{Cr}(\text{acac})_3]^0$ ,  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Co}(\text{C}_2\text{H}_5\text{O})_6]^{3-}$ ,  $[\text{Ni}(\text{dmg})_2]$  CC0089
- Find out the total number of geometrical isomers of  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3]$ . CC0090
- Find the value of E.A.N of  $[\text{Pd}(\text{CO})_4]^{+2}$  (atomic number = 46) : CC0091
- A co-ordination compound have magnetic moment 5.92 B.M. Find out the number of unpaired electron(s) in the compound. CC0092
- Find the number of optically active isomers for  $[\text{Pd}(\text{en})_2(\text{NH}_3)(\text{H}_2\text{O})]^{4+}$  cation. CC0093



## EXERCISE : S-2

MATCH THE COLUMN :

1. Match the complexes in column-I with the EAN of central atom in column-II:

Column-I	Column-II
(A) $[\text{Fe}(\text{CO})_4]^{2-}$	(P) 34
(B) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	(Q) 35
(C) $\text{K}_2[\text{Ni}(\text{CN})_4]$	(R) 36
(D) $[\text{Cu}(\text{NH}_3)_4]^{2+}$	(S) 37

CC0094

2. Match the complexes in column-I with their properties in column-II:

Column - I	Column - II
(A) $\text{Na}_2 [\text{Fe}(\text{CN})_5 \text{NO}]$	(P) $\mu = 0$ B.M.
(B) $[\text{Fe}(\text{H}_2\text{O})_5 \text{NO}] \text{SO}_4$	(Q) octahedral
(C) $[\text{Ag}(\text{CN})_2]^-$	(R) $\mu = \sqrt{15}$ B.M.
(D) $\text{K}_4[\text{Fe}(\text{CN})_6]$	(S) $\text{NO}^+$ ligand

CC0095

3. Match the complexes in column I with their stereoproperties in column II:

Column I	Column II
(A) $[\text{CoCl}_3(\text{NH}_3)_3]$	(P) Has a facial isomer
(B) $[\text{Cr}(\text{ox})_3]^{3-}$	(Q) Cis form is optically active
(C) $[\text{CrCl}_2(\text{ox})_2]$	(R) Trans form is optically inactive
(D) $[\text{RhCl}_3(\text{Py})_3]$	(S) Has a meridional form
	(T) Two optically active isomer

CC0096

4. Match each coordination compound in List-I with co-ordination number of central metal/ion from List-II and select the correct answer using the code given below the lists.

List-I	List-II
(P) $[\text{Co}(\text{en})_3]^{3+}$	(1) 6
(Q) $[\text{Ca}(\text{EDTA})]^{2-}$	(2) 4
(R) $[\text{Ni}(\text{CO})_4]$	(3) 2
(S) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	(4) 5

Code :

	P	Q	R	S
(A)	2	1	2	3
(B)	1	1	2	3
(C)	1	4	2	3
(D)	1	1	3	2

CC0097

5. Match the List-I with List-II :

**List-I**

- (P) Ferrocene  
 (Q)  $\text{Mn}_2(\text{CO})_{10}$   
 (R) Vitamine  $\text{B}_{12}$   
 (S) Haemoglobin

**List-II**

- (1) Iron present  
 (2) Cobalt  
 (3) Metal-Metal bonding  
 (4) Sandwich structure

Code :

	P	Q	R	S
(A)	4	3	1	2
(B)	1	3	1	2
(C)	1,4	3	2	1
(D)	1	3	4	2

CC0098

6. Match the List-I with List-II :

**List-I**

- (P)  $\text{EDTA}^{4-}$   
 (Q) en  
 (R) gly<sup>-</sup>  
 (S) amide

**List-II**

- (1) N-donor atom  
 (2) Chelate ligand with same donor site  
 (3) Bidentate with different donor atom  
 (4) Hexadentate

Code :

	P	Q	R	S
(A)	4	2	1	3
(B)	2	1	3	4
(C)	4	1	2	3
(D)	4	2	3	1

CC0099

**Assertion Reason :**

7. **Statement-1:** Complexes containing three bidentate groups such as  $[\text{Cr}(\text{ox})_3]^{3-}$  and  $[\text{Co}(\text{en})_3]^{3+}$  do not show optical activity.  
**Statement-2:** Octahedral complex,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  shows geometrical isomerism.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CC0100

8. **Statement-1:** After splitting of d-orbitals during complex formation, the orbitals form two sets of orbitals  $t_{2g}$  and  $e_g$  in an octahedral field.  
**Statement-2:** Splitting of d-orbitals occur only in the case of strong field ligands such as  $CN^-$ .  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CC0101

9. **Statement-1:**  $[Ti(H_2O)_6]^{3+}$  is coloured while  $[Sc(H_2O)_6]^{3+}$  is colourless.  
**Statement-2:** d-d transition is not possible in  $[Sc(H_2O)_6]^{3+}$  because no d-electron is present while possible for  $Ti^{3+}$  having  $d^1$  system.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

CC0102

**Comprehension (10 to 12)**

Ligands are neutral or ionic species capable of donating at least one electron pair to central metal. Hence ligands can be of different denticities.

10. For a given metal  $M^{3+}$  coordination number is six, then for which set of ligands, complex will be most stable-  
 (A)  $6H_2O$  (B)  $6F^-$  (C)  $EDTA^{4-}$  (D)  $2H_2O$  and  $2C_2O_4^{2-}$
11.  $[Mn(CO)_5]$  can attain more stability by :  
 (A) Oxidation of itself (B) Reduction of itself  
 (C) Dimerization (D) Both (B) and (C)
12. The metal cation that has least tendency to accept electron pair from  $NH_3$  is  
 (A)  $Fe^{3+}$  (B)  $Rh^{3+}$  (C)  $Zn^{2+}$  (D)  $Ba^{++}$

CC0103

CC0104

CC0105

**Comprehension (13 to 15)**

Complex compounds are molecular compounds which retain their identities even when dissolved in water. They do not give all the simple ions in solution but instead furnish complex ions with complicated structures. The complex compounds are often called coordination compounds because certain groups called ligands are attached to the central metal ion by coordinate or dative bonds. Coordination compounds exhibit isomerism, both structural and stereoisomerism. The structure, magnetic property, colour and electrical properties of complexes are explained by various theories.

13. Arrange the following compounds in order of their Molar conductance:

- (I)  $K[Co(NO_2)_4(NH_3)_2]$  (II)  $[Cr(ONO)_3(NH_3)_3]$   
 (III)  $[Cr(NO_2)(NH_3)_5]_3 [Co(NO_2)_6]_2$  (IV)  $Mg[Cr(NO_2)_5(NH_3)]$   
 (A) II < I < IV < III (B) I < II < III < IV  
 (C) II < I < III < IV (D) IV < III < II < I

CC0106

14. The oxidation number and coordination number of chromium in the following complex is  $[Cr(C_2O_4)_2(NH_3)_2]^{1-}$

- (A) O.N. = +4, C.N. = 4 (B) O.N. = +3, C.N. = 4  
 (C) O.N. = -1, C.N. = 4 (D) O.N. = +3, C.N. = 6

CC0107

15. In which of the following pairs, both the complexes have the same geometry but different hybridisation

- (A)  $[NiCl_4]^{2-}$ ,  $[Ni(CN)_4]^{2-}$  (B)  $[CoF_6]^{3-}$ ,  $[Co(NH_3)_6]^{3+}$   
 (C)  $[Ni(CO)_4]$ ,  $[Ni(CN)_4]^{2-}$  (D)  $[Cu(NH_3)_4]^{2+}$ ,  $[Ni(NH_3)_6]^{2+}$

CC0108

**Matching list type 1 × 3Q. (Three list type Question)**

The following column I, II, III represent the different type of observations based on CFT in complex compounds.

Answer the questions that follow

**Column-I - Crystal field stabilization energy (CFSE) (neglecting PE in all cases)**

**Column-II - Electronic configuration**

**Column-III - Type of complex**

Column - I CFSE (neglecting PE in all cases)	Column - II Electronic Configuration	Column - III Type of Complex
(I) $-0.4 \Delta_o$	(i) $t_{2g}^5, e_g^0$	(P) High spin & Paramagnetic
(II) $-2.0 \Delta_o$	(ii) $t_{2g}^4, e_g^0$	(Q) Low spin & Paramagnetic
(III) $-2.4 \Delta_o$	(iii) $t_{2g}^6, e_g^0$	(R) High spin & Diamagnetic
(IV) $-1.2 \Delta_o$	(iv) $t_{2g}^4, e_g^2$	(S) Low spin & Diamagnetic

16. For sodium nitroprusside complex the only **CORRECT** combination is

- (A) (III), (iv), (Q) (B) (III), (iii), (S) (C) (III), (iii), (R) (D) (II), (iii), (Q)

CC0109

17. For  $[Co(H_2O)_3F_3]$  complex the only **CORRECT** combination is.

- (A) (I), (iv), (Q) (B) (II), (iv), (S) (C) (III), (ii), (R) (D) (I), (iv), (P)

CC0110

18. For  $[Mn(CN)_6]^{4-}$  complex the only **CORRECT** combination is.

- (A) (IV), (i), (S) (B) (II), (i), (R) (C) (I), (i), (S) (D) (II), (i), (Q)

CC0111

## EXERCISE : JEE-MAIN

1. In  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ , the isomerism shown is - [AIEEE-2002]  
 (1) Ligand (2) Optical (3) Geometrical (4) Ionization  
 CC0112
2. In the complexes  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{SCN})_6]^{3-}$ ,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  and  $[\text{FeCl}_6]^{3-}$ , more stability is shown by - [AIEEE-2002]  
 (1)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  (2)  $[\text{Fe}(\text{SCN})_6]^{3-}$  (3)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  (4)  $[\text{FeCl}_6]^{3-}$   
 CC0113
3. One mole of the complex compound  $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ , gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of  $\text{AgNO}_3$  solution to yield two moles of  $\text{AgCl}(\text{s})$ . The structure of the complex is - [AIEEE-2003]  
 (1)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \cdot 2\text{NH}_3$  (2)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$   
 (3)  $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2 \cdot \text{NH}_3$  (4)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$   
 CC0114
4. In the coordination compound  $\text{K}_4[\text{Ni}(\text{CN})_4]$ , the oxidation state of nickel is - [AIEEE-2003]  
 (1) 0 (2) +1 (3) +2 (4) -1  
 CC0115
5. The number of 3d-electrons remained in  $\text{Fe}^{2+}$  (At.no. of Fe = 26) ion is - [AIEEE-2003]  
 (1) 4 (2) 5 (3) 6 (4) 3  
 CC0116
6. Ammonia forms the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with copper ions in alkaline solutions but not in acidic solution. What is the reason for it :- [AIEEE-2003]  
 (1) In acidic solutions hydration protects copper ions  
 (2) In acidic solutions protons coordinate with ammonia molecules forming  $\text{NH}_4^+$  ions and  $\text{NH}_3$  molecules are not available  
 (3) In alkaline solutions insoluble  $\text{Cu}(\text{OH})_2$  is precipitated which is soluble in excess of any alkali  
 (4) Copper hydroxide is an amphoteric substance  
 CC0117
7. Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by  $\text{CN}^-$  ion towards metal species is :- [AIEEE-2004]  
 (1) c, a (2) b, c (3) a, b (4) a, b, c  
 CC0118
8. The coordination number of a central metal atom in a complex is determined by :- [AIEEE-2004]  
 (1) The number of ligands around a metal ion bonded by sigma and pi-bonds both  
 (2) The number of ligands around a metal ion bonded by pi-bonds  
 (3) The number of ligands around a metal ion bonded by sigma bonds  
 (4) The number of only anionic ligands bonded to the metal ion  
 CC0119

9. Which one of the following complexes is an outer orbital complex :- [AIEEE-2004]  
 (1)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (2)  $[\text{Mn}(\text{CN})_6]^{4-}$  (3)  $[\text{Fe}(\text{CN})_6]^{4-}$  (4)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$   
 (Atomic nos.: Mn=25 ; Fe=26 ; Co=27 ; Ni = 28) CC0120
10. Coordination compounds have great importance in biological systems. In this context which of the following statements is **INCORRECT** ? [AIEEE-2004]  
 (1) Cyanocobalamin is vitamin B<sub>12</sub> and contains cobalt  
 (2) Haemoglobin is the red pigment of blood and contains iron  
 (3) Chlorophylls are green pigments in plants and contain calcium  
 (4) Carboxypeptidase - A is an enzyme and contains zinc CC0121
11. The **CORRECT** order of magnetic moments (spin only values in B.M.) among is :- [AIEEE-2004]  
 (1)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-}$  (2)  $[\text{MnCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-}$   
 (3)  $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$  (4)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$   
 (Atomic nos. : Mn = 25, Fe = 26, Co = 27) CC0122
12. For octahedral complex, the value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The **CORRECT** one is [AIEEE-2005]  
 (1)  $d^4$  (in strong ligand field) (2)  $d^4$  (in weak ligand field)  
 (3)  $d^3$  (in weak as well as in strong field) (4)  $d^5$  (in strong ligand field) CC0123
13. The IUPAC name for the complex  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$  is - [AIEEE-2006]  
 (1) pentaammine nitrito-N- cobalt (II) chloride  
 (2) pentaammine nitrito-N- cobalt (III) chloride  
 (3) nitrito-N- pentaamminecobalt (III) chloride  
 (4) nitrito-N- pentaamminecobalt (II) chloride CC0124
14. Nickel ( $Z=28$ ) combines with a uninegative monodentate ligand  $X^-$  to form a paramagnetic complex  $[\text{NiX}_4]^{2-}$ . The number of unpaired electrons in the nickel and geometry of this complex ion are, respectively. [AIEEE-2006]  
 (1) one, square planar (2) two, square planar (3) one, tetrahedral (4) two, tetrahedral CC0125
15. In  $\text{Fe}(\text{CO})_5$ , the Fe-C bond possesses [AIEEE-2006]  
 (1) ionic character (2)  $\sigma$  - character only (3)  $\pi$  -character only (4) both  $\sigma$  and  $\pi$  character CC0126
16. How many EDTA (ethylenediaminetetraacetate) molecules are required to make an octahedral complex with a  $\text{Ca}^{2+}$  ion ? [AIEEE-2006]  
 (1) One (2) Two (3) Six (4) Three CC0127

17. The "spin-only" magnetic moment [in units of Bohr magneton, ( $\mu_B$ )] of  $\text{Ni}^{2+}$  in aqueous solution would be (At. No. Ni = 28)- [AIEEE-2006]  
 (1) 0 (2) 1.73 (3) 2.84 (4) 4.90  
 CC0128
18. Which one of the following has a square planar geometry :- (Co = 27, Ni = 28, Fe = 26, Pt = 78) [AIEEE-2007]  
 (1)  $[\text{CoCl}_4]^{2-}$  (2)  $[\text{FeCl}_4]^{2-}$  (3)  $[\text{NiCl}_4]^{2-}$  (4)  $[\text{PtCl}_4]^{2-}$   
 CC0129
19. The coordination number and the oxidation state of the element 'E' in the complex  $[\text{E}(\text{en})_2(\text{C}_2\text{O}_4^{2-})] \text{NO}_2^{\ominus}$  (where (en) is ethylene diamine) are, respectively - [AIEEE-2008]  
 (1) 6 and 2 (2) 4 and 2 (3) 4 and 3 (4) 6 and 3  
 CC0130
20. In which of the following octahedral complexes of Co (at. no. 27), will the magnitude of  $\Delta_0$  be the highest ? [AIEEE-2008]  
 (1)  $[\text{Co}(\text{CN})_6]^{3-}$  (2)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  (3)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  (4)  $[\text{Co}(\text{NH}_3)_6]^{3+}$   
 CC0131
21. Which of the following pairs represent linkage isomers ? [AIEEE-2009]  
 (1)  $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$   
 (2)  $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$  and  $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$   
 (3)  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$   
 (4)  $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$  and  $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$   
 CC0132
22. Which of the following has an optical isomer? [AIEEE-2009]  
 (1)  $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$  (2)  $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$   
 (3)  $[\text{Co}(\text{NH}_3)_3\text{Cl}]^+$  (4)  $[\text{Co}(\text{en})(\text{NH}_3)_2]^{2+}$   
 CC0133
23. Which one of the following has an optical isomer ? [AIEEE-2010]  
 (1)  $[\text{Zn}(\text{en})_2]^{2+}$  (2)  $[\text{Zn}(\text{en})(\text{NH}_3)_2]^{2+}$   
 (3)  $[\text{Co}(\text{en})_3]^{3+}$  (4)  $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$   
 (en = ethylenediamine)  
 CC0134
24. A solution containing 2.675 g of  $\text{CoCl}_3 \cdot 6\text{NH}_3$  (molar mass = 267.5 g mol<sup>-1</sup>) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of  $\text{AgNO}_3$  to give 4.78 g of  $\text{AgCl}$  (molar mass = 143.5 g mol<sup>-1</sup>). The formula of the complex is :- [AIEEE-2010]  
 (At. mass of Ag = 108 u)  
 (1)  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$  (2)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$   
 (3)  $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$  (4)  $[\text{CoCl}_3(\text{NH}_3)_3]$   
 CC0135

25. Which of the following facts about the complex  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  is **wrong** ? [AIEEE-2011]  
 (1) The complex is an outer orbital complex  
 (2) The complex gives white precipitate with silver nitrate solution  
 (3) The complex involves  $d^2sp^3$  hybridisation and is octahedral in shape  
 (4) The complex is paramagnetic  
 CC0136
26. The magnetic moment (spin only) of  $[\text{NiCl}_4]^{2-}$  is :- [AIEEE-2011]  
 (1) 2.82 BM (2) 1.41 BM (3) 1.82 BM (4) 5.46 BM  
 CC0137
27. Among the ligands  $\text{NH}_3$ , en,  $\text{CN}^-$  and CO the **CORRECT** order of their increasing field strength, is :- [AIEEE-2011]  
 (1)  $\text{CO} < \text{NH}_3 < \text{en} < \text{CN}^-$  (2)  $\text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$   
 (3)  $\text{CN}^- < \text{NH}_3 < \text{CO} < \text{en}$  (4)  $\text{en} < \text{CN}^- < \text{NH}_3 < \text{CO}$   
 CC0138
28. Which one of the following complex ions has geometrical isomers ? [AIEEE-2011]  
 (1)  $[\text{Co}(\text{en})_3]^{3+}$  (2)  $[\text{Ni}(\text{NH}_3)_5\text{Br}]^+$  (3)  $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$  (4)  $[\text{Cr}(\text{NH}_3)_4(\text{en})]^{3+}$   
 CC0139
29. Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide ? [AIEEE-2012]  
 (1)  $[\text{Cr}(\text{en})\text{Br}_2]\text{Br}$  (2)  $[\text{Cr}(\text{en})_3]\text{Br}_3$  (3)  $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$  (4)  $[\text{Cr}(\text{en})\text{Br}_4]^-$   
 CC0140
30. The complex ion  $[\text{Pt}(\text{NO}_2)(\text{Py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+$  will give :- [J-MAIN-2012, Online]  
 (1) 4 isomers (Geometrical) (2) 2 isomers (Geometrical)  
 (3) 3 isomers (Geometrical) (4) 6 isomers (Geometrical)  
 CC0141
31. Which of the following complex ions will exhibit optical isomerism? [J-MAIN-2012, Online]  
 (en = 1, 2-diamine ethane)  
 (1)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  (2)  $[\text{Zn}(\text{en})_2]^{2+}$  (3)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  (4)  $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2]^+$   
 CC0142
32. Which of the following complex species is **NOT** expected to exhibit optical isomerism ? [J-MAIN-2013]  
 (1)  $[\text{Co}(\text{en})_3]^{3+}$  (2)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$   
 (3)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (4)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$   
 CC0143
33. Type of isomerism which exists between  $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{SCN})_2]$  and  $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{NCS})_2]$  is : [J-MAIN-2013, Online]  
 (1) Solvate isomerism (2) Ionisation isomerism  
 (3) Linkage isomerism (4) Coordination isomerism  
 CC0144



34. Which of the following is diamagnetic ? [J-MAIN-2013, Online]  
 (1)  $[\text{CoF}_6]^{3-}$  (2)  $[\text{FeF}_6]^{3-}$  (3)  $[\text{Fe}(\text{CN})_6]^{3-}$  (4)  $[\text{Co}(\text{Ox})_3]^{3-}$   
 CC0145
35. The magnetic moment of the complex anion  $[\text{Cr}(\text{NO})(\text{NH}_3)(\text{CN})_4]^{2-}$  is : [J-MAIN-2013, Online]  
 (1) 2.82 BM (2) 5.91 BM (3) 1.73 BM (4) 3.87 BM  
 CC0146
36. The octahedral complex of a metal ion  $\text{M}^{3+}$  with four monodentate ligands  $\text{L}_1, \text{L}_2, \text{L}_3$  and  $\text{L}_4$  absorb wavelength in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is: [J-MAIN-2014]  
 (1)  $\text{L}_3 < \text{L}_2 < \text{L}_4 < \text{L}_1$  (2)  $\text{L}_1 < \text{L}_2 < \text{L}_4 < \text{L}_3$  (3)  $\text{L}_4 < \text{L}_3 < \text{L}_2 < \text{L}_1$  (4)  $\text{L}_1 < \text{L}_3 < \text{L}_2 < \text{L}_4$   
 CC0147
37. The equation which is balanced and represents the **CORRECT** product (s) is : [J-MAIN-2014]  
 (1)  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} + (\text{EDTA})^{4-} \xrightarrow{\text{excess NaOH}} [\text{Mg}(\text{EDTA})]^{2-} + 6\text{H}_2\text{O}$   
 (2)  $\text{CuSO}_4 + 4\text{KCN} \rightarrow \text{K}_2[\text{Cu}(\text{CN})_4] + \text{K}_2\text{SO}_4$   
 (3)  $\text{Li}_2\text{O} + 2\text{KCl} \rightarrow 2\text{LiCl} + \text{K}_2\text{O}$   
 (4)  $[\text{CoCl}(\text{NH}_3)_5]^+ + 5\text{H}^+ \rightarrow \text{Co}^{2+} + 5\text{NH}_4^+ + \text{Cl}^-$   
 CC0148
38. The **CORRECT** statement about the magnetic properties of  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{FeF}_6]^{3-}$  is : ( $Z = 26$ ). [J-MAIN-2014, Online]  
 (1)  $[\text{Fe}(\text{CN})_6]^{3-}$  is paramagnetic,  $[\text{FeF}_6]^{3-}$  is diamagnetic.  
 (2) both are diamagnetic.  
 (3)  $[\text{Fe}(\text{CN})_6]^{3-}$  is diamagnetic,  $[\text{FeF}_6]^{3-}$  is paramagnetic.  
 (4) both are paramagnetic  
 CC0149
39. An octahedral complex of  $\text{Co}^{3+}$  is diamagnetic. The hybridisation involved in the formation of the complex is : [J-MAIN-2014]  
 (1)  $d^2sp^3$  (2)  $dsp^3d$  (3)  $dsp^2$  (4)  $sp^3d^2$   
 CC0150
40. Which of the following name formula combinations is **NOT CORRECT**? [J-MAIN-2014, Online]
- | Formula   | Name   |
|---|--|
| (1) $\text{K}[\text{Cr}(\text{NH}_3)_2\text{Cl}_4]$                     | Potassium diammine Tetrachlorochromate (III) |
| (2) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}]\text{SO}_4$ | Tetraammine aquaiodo cobalt (III) sulphate   |
| (3) $[\text{Mn}(\text{CN})_5]^{2-}$                                     | Pentacyanomagnate (II) ion                   |
| (4) $\text{K}_2[\text{Pt}(\text{CN})_4]$                                | Potassium tetracyanoplatinate(II)            |
- CC0151

41. Consider the coordination compound,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ . In the formation of this complex, the species which acts as the Lewis acid is : [J-MAIN-2014, Online]
- (1)  $[\text{Co}(\text{NH}_3)_6]^{3+}$       (2)  $\text{NH}_3$       (3)  $\text{Co}^{3+}$       (4)  $\text{Cl}^-$
- CC0152**
42. Among the following species the one which causes the highest CFSE,  $\Delta_0$  as a ligand is :- [J-MAIN-2014, Online]
- (1)  $\text{CN}^-$       (2)  $\text{NH}_3$       (3)  $\text{CO}$       (4)  $\text{F}^-$
- CC0153**
43. Which one of the following complexes will most likely absorb visible light ? [J-MAIN-2014, Online]
- (At nos. Sc = 21, Ti = 22, V = 23, Zn = 30) :-
- (1)  $[\text{Ti}(\text{NH}_3)_6]^{4+}$       (2)  $[\text{V}(\text{NH}_3)_6]^{3+}$       (3)  $[\text{Zn}(\text{NH}_3)_6]^{2+}$       (4)  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$
- CC0154**
44. Nickel (Z = 28) combines with a uninegative monodentate ligand to form a diamagnetic complex  $[\text{NiL}_4]^{2-}$ . The hybridisation involved and the number of unpaired electrons present in the complex are respectively : [J-MAIN-2014, Online]
- (1)  $\text{sp}^3$ , zero      (2)  $\text{sp}^3$ , two      (3)  $\text{dsp}^2$ , one      (4)  $\text{dsp}^2$ , zero
- CC0155**
45. The number of geometrical isomers that can exist for square planar  $[\text{Pt}(\text{Cl})(\text{py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+$  is (py = pyridine) : [J-MAIN-2015]
- (1) 4      (2) 6      (3) 2      (4) 3
- CC0156**
46. The color of  $\text{KMnO}_4$  is due to : [J-MAIN-2015]
- (1)  $\text{L} \rightarrow \text{M}$  charge transfer transition      (2)  $\sigma - \sigma^*$  transition  
(3)  $\text{M} \rightarrow \text{L}$  charge transfer transition      (4)  $\text{d} - \text{d}$  transition
- CC0157**
47. Which of the following complex ions has electrons that are symmetrically filled in both  $t_{2g}$  and  $e_{g}$  orbitals ? [J-MAIN-2015, Online]
- (1)  $[\text{CoF}_6]^{3-}$       (2)  $[\text{Mn}(\text{CN})_6]^{4-}$       (3)  $[\text{FeF}_6]^{3-}$       (4)  $[\text{Co}(\text{NH}_3)_6]^{2+}$
- CC0158**
48. When concentrated  $\text{HCl}$  is added to an aqueous solution of  $\text{CoCl}_2$ , its colour changes from reddish pink to deep blue. Which complex ion gives blue colour in this reaction ?:- [J-MAIN-2015, Online]
- (1)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$       (2)  $[\text{CoCl}_6]^{3-}$       (3)  $[\text{CoCl}_4]^{2-}$       (4)  $[\text{CoCl}_6]^{4-}$
- CC0159**

49. The **CORRECT** statement on the isomerism associated with the following complex ions, [J-MAIN-2015, Online]
- (a)  $[\text{Ni}(\text{H}_2\text{O})_5\text{NH}_3]^{2+}$   
 (b)  $[\text{Ni}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+}$  and  
 (c)  $[\text{Ni}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{2+}$  is :
- (1) (a) and (b) show geometrical and optical isomerism  
 (2) (b) and (c) show geometrical and optical isomerism  
 (3) (a) and (b) show only geometrical Isomerism  
 (4) (b) and (c) show only geometrical Isomerism
- CC0160
50. Which one of the following complexes shows optical isomerism :- [J-MAIN-2016]
- (1)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (2)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$   
 (3)  $\text{cis}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  (4)  $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$   
 (en = ethylenediamine)
- CC0161
51. The pair having the same magnetic moment is:- [J-MAIN-2016]
- [At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]
- (1)  $[\text{CoCl}_4]^{2-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (2)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{CoCl}_4]^{2-}$   
 (3)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (4)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
- CC0162
52. Which one of the following complexes will consume more equivalents of aqueous solution of  $\text{Ag}(\text{NO}_3)$  ? [J-MAIN-2016, Online]
- (1)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (2)  $\text{Na}_2[\text{CrCl}_5(\text{H}_2\text{O})]$  (3)  $\text{Na}_3[\text{CrCl}_6]$  (4)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$
- CC0163
53. Identify the **CORRECT** trend given below : [J-MAIN-2016, Online]
- (Atomic No. = Ti : 22, Cr : 24 and Mo : 42)
- (1)  $\Delta_0$  of  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} < [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$  and  $\Delta_0$  of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} < [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$   
 (2)  $\Delta_0$  of  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} < [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$  and  $\Delta_0$  of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} > [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$   
 (3)  $\Delta_0$  of  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$  and  $\Delta_0$  of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} > [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$   
 (4)  $\Delta_0$  of  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$  and  $\Delta_0$  of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} < [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
- CC0164
54.  $[\text{Co}_2(\text{CO})_8]$  displays:- [J-MAIN-2017, Online]
- (1) no Co-Co bond, four terminal CO and four bridging CO  
 (2) one Co-Co bond, six terminal CO and two bridging CO  
 (3) no Co-Co bond, six terminal CO and two bridging CO  
 (4) one Co-Co bond, four terminal CO and four bridging CO
- CC0165

55. On treatment of 100 mL of 0.1 M solution of  $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$  with excess  $\text{AgNO}_3$ ;  $1.2 \times 10^{22}$  ions are precipitated. The complex is :- **[J-MAIN-2017, Offline]**
- (1)  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  (2)  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$   
 (3)  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$  (4)  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
- CC0166**
56. The pair of compounds having metal in their highest oxidation state is : **[J-MAIN-2017, Online]**
- (1)  $[\text{NiCl}_4]^{2-}$  and  $[\text{CoCl}_4]^{2-}$  (2)  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Cu}(\text{CN})_4]^{2-}$   
 (3)  $[\text{FeCl}_4]^-$  and  $\text{Co}_2\text{O}_3$  (4)  $\text{MnO}_2$  and  $\text{CrO}_2\text{Cl}_2$
- CC0167**
57. The oxidation states of Cr in  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ ,  $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ , and  $\text{K}_2[\text{Cr}(\text{CN})_2(\text{O})_2(\text{O}_2)(\text{NH}_3)]$  respectively are : **[J-MAIN-2018, Offline]**
- (1) +3, +2, and +4 (2) +3, 0, and +6  
 (3) +3, 0, and +4 (4) +3, +4, and +6
- CC0168**
58. Consider the following reaction and statements : **[J-MAIN-2018, Offline]**  
 $[\text{Co}(\text{NH}_3)_4\text{Br}_2]^+ + \text{Br}^- \rightarrow [\text{Co}(\text{NH}_3)_3\text{Br}_3] + \text{NH}_3$
- (I) Two isomers are produced if the reactant complex ion is a *cis*-isomer.  
 (II) Two isomers are produced if the reactant complex ion is a *trans*-isomer.  
 (III) Only one isomer is produced if the reactant complex ion is a *trans*-isomer.  
 (IV) Only one isomer is produced if the reactant complex ion is a *cis*-isomer.
- The correct statements are :
- (1) (I) and (III) (2) (III) and (IV) (3) (II) and (IV) (4) (I) and (II)
- CC0169**
59. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point ? **[J-MAIN-2018, Offline]**
- (1)  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (2)  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$   
 (3)  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$  (4)  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$
- CC0170**
60. The total number of possible isomers for square-planar  $[\text{Pt}(\text{Cl})(\text{NO}_2)(\text{NO}_3)(\text{SCN})]^{2-}$  is :- **[J-MAIN-2018, Online]**
- (1) 16 (2) 8 (3) 24 (4) 12
- CC0171**
61. The correct order of spin-only magnetic moments among the following is : **[J-MAIN-2018, Online]**  
 (Atomic number : Mn = 25, Co = 27, Ni = 28, Zn = 30)
- (1)  $[\text{ZnCl}_4]^{2-} > [\text{NiCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$   
 (2)  $[\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-} > [\text{NiCl}_4]^{2-} > [\text{ZnCl}_4]^{2-}$   
 (3)  $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{NiCl}_4]^{2-} > [\text{ZnCl}_4]^{2-}$   
 (4)  $[\text{NiCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-} > [\text{ZnCl}_4]^{2-}$
- CC0172**

62. The correct combination is

[J-MAIN-2018, Online]

- (1)  $[\text{Ni}(\text{CN})_4]^{2-}$  – tetrahedral;  
 $[\text{Ni}(\text{CO})_4]$  – paramagnetic
- (2)  $[\text{NiCl}_4]^{2-}$  – paramagnetic;  
 $[\text{Ni}(\text{CO})_4]$  – tetrahedral
- (3)  $[\text{NiCl}_4]^{2-}$  – diamagnetic;  
 $[\text{Ni}(\text{CO})_4]$  – square-planar
- (4)  $[\text{NiCl}_4]^{2-}$  – square-planar;  
 $[\text{Ni}(\text{CN})_4]^{2-}$  – paramagnetic

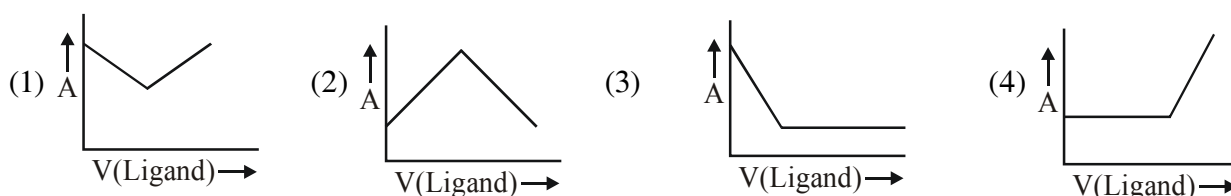
CC0173

63. Which of the following complexes will show geometrical isomerism ? [J-MAIN-2018, Online]

- (1) Potassium amminetrichloroplatinate(II)
- (2) Aquachlorobis (ethylenediamine) cobalt(II) chloride
- (3) Potassium tris(oxalato) chromate(III)
- (4) Pentaquachlorochromium(III) chloride

CC0174

64. In a complexometric titration of metal ion with ligand  $\text{M}(\text{Metal ion}) + \text{L}(\text{Ligand}) \rightarrow \text{C}(\text{Complex})$  end point is estimated spectrophotometrically (through light absorption). If 'M' and 'C' do not absorb light and only 'L' absorbs, then the titration plot between absorbed light (A) versus volume of ligand 'L' (v) would look like :-  
 [J-MAIN-2018, Online]



CC0175

65. In Wilkinson's catalyst, the hybridization of central metal ion and its shape are respectively

[J-MAIN-2018, Online]

- (1)  $\text{dsp}^2$ , square planar
- (2)  $\text{sp}^3\text{d}$ , trigonal bipyramidal
- (3)  $\text{sp}^3$ , tetrahedral
- (4)  $\text{d}^2\text{sp}^3$ , octahedral

CC0176

## EXERCISE : JEE-ADVANCED

1. The complex ion which has no 'd' electrons in the central metal atom is : [JEE 2001]  
[ At No. Cr = 24, Mn = 25, Fe = 26, Co = 27 ]  
(A)  $[\text{MnO}_4]^-$  (B)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (C)  $[\text{Fe}(\text{CN})_6]^{3-}$  (D)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$   
CC0177
2. The **CORRECT** order of hybridisation of the central atom in the following species. [JEE 2001]  
 $\text{NH}_3$ ,  $[\text{PtCl}_4]^{2-}$ ,  $\text{PCl}_5$  and  $\text{BCl}_3$  is [At No. Pt = 78]  
(A)  $\text{dsp}^2, \text{sp}^3\text{d}, \text{sp}^2$  and  $\text{sp}^3$  (B)  $\text{sp}^3, \text{dsp}^2, \text{sp}^3\text{d}, \text{sp}^2$   
(C)  $\text{dsp}^2, \text{sp}^2, \text{sp}^3$  and  $\text{sp}^3\text{d}$  (D)  $\text{dsp}^2, \text{sp}^3, \text{sp}^2$  and  $\text{sp}^3\text{d}$   
CC0178
3. The species having tetrahedral shape is : [JEE 2004]  
(A)  $[\text{PdCl}_4]^{2-}$  (B)  $[\text{Ni}(\text{CN})_4]^{2-}$  (C)  $[\text{Pd}(\text{CN})_4]^{2-}$  (D)  $[\text{NiCl}_4]^{2-}$   
CC0179
4. The pair of compounds having metals in their highest oxidation state is [JEE 2004]  
(A)  $\text{MnO}_2, \text{FeCl}_3$  (B)  $[\text{MnO}_4]^-$ ,  $\text{CrO}_2\text{Cl}_2$   
(C)  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Co}(\text{CN})_3]$  (D)  $[\text{NiCl}_4]^{2-}$ ,  $[\text{CoCl}_4]^-$   
CC0180
5. Spin only magnetic moment of the compound  $\text{Hg}[\text{Co}(\text{SCN})_4]$  is [JEE 2004]  
(A)  $\sqrt{3}$  (B)  $\sqrt{15}$  (C)  $\sqrt{24}$  (D)  $\sqrt{8}$   
CC0181
6. Which of the following pair is expected to exhibit same colour in solution? [JEE 2005]  
(A)  $\text{VOCl}_2$ ;  $\text{FeCl}_2$  (B)  $\text{CuCl}_2$ ;  $\text{VOCl}_2$  (C)  $\text{MnCl}_2$ ;  $\text{FeCl}_2$  (D)  $\text{FeCl}_2$ ;  $\text{CuCl}_2$   
CC0182
7. Which type of isomerism is shown by  $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{Cl}$ ? [JEE 2005]  
(A) Geometrical and Ionisation (B) Optical and Ionisation  
(C) Geometrical and Optical (D) Geometrical only  
CC0183

**Question No. 8 to 10 (3 questions)**

[JEE 2006]

The coordination number of  $\text{Ni}^{2+}$  is 4. $\text{NiCl}_2 + \text{KCN}$  (excess)  $\rightarrow$  A (cyano complex) $\text{NiCl}_2 + \text{KCl}$  (excess)  $\rightarrow$  B (chloro complex)

8. The IUPAC name of A and B are  
(A) Potassium tetracyanonickelate (II), potassium tetrachloridonickelate (II)  
(B) Tetracyanidopotassiumnickelate (II), tetrachloridopotassiumnickelate (II)  
(C) Tetracyanonickel (II), tetrachloridonickel (II)  
(D) Potassium tetracyanonickel (II), potassium tetrachloridonickel (II)

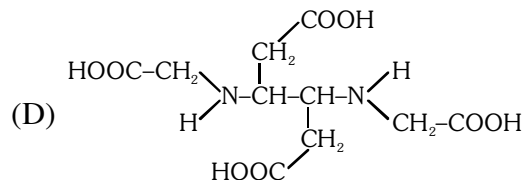
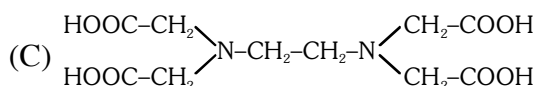
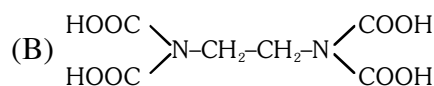
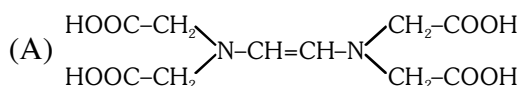
CC0184

9. Predict the magnetic nature of A and B.  
 (A) Both are diamagnetic.  
 (B) A is diamagnetic and B is paramagnetic with one unpaired electron.  
 (C) A is diamagnetic and B is paramagnetic with two unpaired electrons.  
 (D) Both are paramagnetic. CC0185
10. The hybridization of A and B are  
 (A)  $dsp^2, sp^3$                       (B)  $sp^3, sp^3$                       (C)  $dsp^2, dsp^2$                       (D)  $sp^3d^2, d^2sp^3$  CC0186
11. If the bond length of CO bond in carbon monoxide is  $1.128\text{\AA}$ , then what is the value of CO bond length in  $Fe(CO)_5$ ? [JEE 2006]  
 (A)  $1.15\text{\AA}$                       (B)  $1.128\text{\AA}$                       (C)  $1.72\text{\AA}$                       (D)  $1.118\text{\AA}$  CC0187
12. Among the following metal carbonyls, the C–O bond order is lowest in [JEE 2007]  
 (A)  $[Mn(CO)_6]^+$                       (B)  $[Fe(CO)_5]$                       (C)  $[Cr(CO)_6]$                       (D)  $[V(CO)_6]^-$  CC0188
13. Match the complexes in Column I with their properties listed in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS. [JEE 2007]
- | Column I                       | Column II                             |
|--------------------------------|---------------------------------------|
| (A) $[Co(NH_3)_4(H_2O)_2]Cl_2$ | (P) Geometrical isomers               |
| (B) $[Pt(NH_3)_2Cl_2]$         | (Q) Paramagnetic                      |
| (C) $[Co(H_2O)_5Cl]Cl$         | (R) Diamagnetic                       |
| (D) $[Ni(H_2O)_6]Cl_2$         | (S) Metal ion with 2+ oxidation state |
- CC0189
14. Among the following, the coloured compound is [JEE 2008]  
 (A) CuCl                      (B)  $K_3 [Cu (CN)_4]$                       (C)  $CuF_2$                       (D)  $[Cu(CH_3CN)_4] BF_4$  CC0190
15. The IUPAC name of  $[Ni(NH_3)_4] [NiCl_4]$  is [JEE 2008]  
 (A) Tetrachloronickel (II)-tetraamminenickel (II)  
 (B) Tetraamminenickel (II)-tetrachloronickel (II)  
 (C) Tetraamminenickel (II)-tetrachloronickelate (II)  
 (D) Tetrachloronickel (II)-tetraamminenickelate (0) CC0191

16. Both  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic. The hybridisations of nickel in these complexes, respectively, are [JEE 2008]  
 (A)  $sp^3, sp^3$  (B)  $sp^3, dsp^2$  (C)  $dsp^2, sp^3$  (D)  $dsp^2, dsp^2$   
CC0192
17. Statement-1 : The geometrical isomers of the complex  $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$  are optically inactive.  
 Statement-2 : Both geometrical isomers of the complex  $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$  possess axis of symmetry.  
 (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1  
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1  
 (C) Statement-1 is True, Statement-2 is False  
 (D) Statement-1 is False, Statement-2 is True [JEE 2008]  
CC0193
18. Statement-1 :  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$  is paramagnetic [JEE 2008]  
 Statement-2 : The Fe in  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$  has three unpaired electrons.  
 (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1  
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1  
 (C) Statement-1 is True, Statement-2 is False  
 (D) Statement-1 is False, Statement-2 is True CC0194
19. The spin only magnetic moment value (in Bohr magneton units) of  $\text{Cr}(\text{CO})_6$  is [JEE 2009]  
 (A) 0 (B) 2.84 (C) 4.90 (D) 5.92  
CC0195
20. The compound(s) that exhibit(s) geometrical isomerism is (are) : [JEE 2009]  
 (A)  $[\text{Pt}(\text{en})\text{Cl}_2]$  (B)  $[\text{Pt}(\text{en})_2]\text{Cl}_2$  (C)  $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$  (D)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$   
CC0196
21. The number of water molecule(s) directly bonded to the metal centre in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is. [JEE 2009]  
CC0197
22. The ionization isomer of  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$  is – [JEE 2010]  
 (A)  $[\text{Cr}(\text{H}_2\text{O})_4(\text{O}_2\text{N})]\text{Cl}_2$  (B)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$   
 (C)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$  (D)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)] \cdot \text{H}_2\text{O}$   
CC0198
23. Total number of geometrical isomers for the complex  $[\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{NH}_3)]$  is. [JEE 2010]  
CC0199



24. The correct structure of ethylenediaminetetraacetic acid (EDTA) is – [JEE 2010]



CC0200

25. Geometrical shapes of the complexes formed by the reaction of  $\text{Ni}^{2+}$  with  $\text{Cl}^-$ ,  $\text{CN}^-$  and  $\text{H}_2\text{O}$  respectively, are - [JEE 2011]

- (A) octahedral, tetrahedral and square planar (B) tetrahedral, square planar and octahedral  
(C) square planar, tetrahedral and octahedral (D) octahedral, square planar and octahedral

CC0201

26. Among the following complexes (K-P) [JEE 2011]

$\text{K}_3[\text{Fe}(\text{CN})_6]$  (K),  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (L),  $\text{Na}_3[\text{Co}(\text{oxalate})_3]$  (M),  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$  (N),  
 $\text{K}_2[\text{Pt}(\text{CN})_4]$  (O) and  $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$  (P)

The diamagnetic complex are -

- (A) K, L, M, N (B) K, M, O, P (C) L, M, O, P (D) L, M, N, O

CC0202

27. The volume (in mL) of 0.1M  $\text{AgNO}_3$  required for complete precipitation of chloride ions present in 30 mL of 0.01M solution of  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ , as silver chloride is close to. [JEE 2011]

CC0203

28. As per IUPAC nomenclature, the name of the complex  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$  is : [JEE 2012]

- (A) Tetraaquadiaminecobalt(III) chloride (B) Tetraaquadiammincobalt(III) chloride  
(C) Diaminetetraaquacobalt(III) chloride (D) Diamminetetraaquacobalt(III) chloride

CC0204

29. The colour of light absorbed by an aqueous solution of  $\text{CuSO}_4$  is - [JEE 2012]

- (A) orange-red (B) blue-green (C) yellow (D) violet

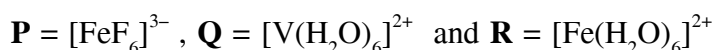
CC0205

30.  $\text{NiCl}_2\{\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\}_2$  exhibits temperature dependent magnetic behavior (paramagnetic/diamagnetic). The coordination geometries of  $\text{Ni}^{2+}$  in the paramagnetic and diamagnetic states are respectively : [JEE 2012]

- (A) tetrahedral and tetrahedral (B) square planar and square planar  
(C) tetrahedral and square planar (D) square planar and tetrahedral

CC0206

31. Consider the following complex ions P, Q and R ,



The **CORRECT** order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is - [JEE 2013]

- (A)  $R < Q < P$       (B)  $Q < R < P$       (C)  $R < P < Q$       (D)  $Q < P < R$

CC0207

32. EDTA<sup>4-</sup> is ethylenediaminetetraacetate ion. The total number of N–Co–O bond angles in [Co(EDTA)]<sup>-1</sup> complex ion is [JEE 2013]

CC0208

33. The pair(s) of coordination complex/ion exhibiting the same kind of isomerism is(are) - [JEE 2013]

- (A)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$       (B)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$   
 (C)  $[\text{CoBr}_2\text{Cl}_2]^{2-}$  and  $[\text{PtBr}_2\text{Cl}_2]^{2-}$       (D)  $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$

CC0209

34. Match each coordination compound in List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists. [JEE Adv. 2014]

{en = H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> ' atomic numbers ; Ti = 22 ; Cr = 24 ; Co = 27 ; Pt = 78 }

**List-I**

- (P)  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
 (Q)  $[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}](\text{NO}_3)_2$   
 (R)  $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]\text{NO}_3$   
 (S)  $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{NO}_3$

**List-II**

- (1) Paramagnetic and exhibits ionisation isomerism  
 (2) Dimagnetic and exhibits *cis-trans* isomerism  
 (3) Paramagnetic and exhibits *cis-trans* isomerism  
 (4) Dimagnetic and exhibits ionisation isomerism

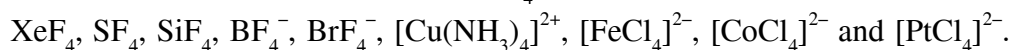
**Code :**

- |     | <b>P</b> | <b>Q</b> | <b>R</b> | <b>S</b> |
|-----|----------|----------|----------|----------|
| (A) | 4        | 2        | 3        | 1        |
| (C) | 2        | 1        | 3        | 4        |

- |     | <b>P</b> | <b>Q</b> | <b>R</b> | <b>S</b> |
|-----|----------|----------|----------|----------|
| (B) | 3        | 1        | 4        | 2        |
| (D) | 1        | 3        | 4        | 2        |

CC0210

35. A list of species having the formula XZ<sub>4</sub> is given below : [JEE Adv. 2014]



Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

CC0211

**Subjective**

36. Draw the structures of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$ . Write the hybridisation of atomic orbitals of the transition metal in each case. [JEE 2000]

CC0212

37. A metal complex having composition  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$  has been isolated in two forms A and B. The form A reacts with  $\text{AgNO}_3$  to give a white precipitate readily soluble in dilute aqueous ammonia, whereas B gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of A and B and state the hybridisation of chromium in each. Calculate their magnetic moments (spin-only value). [JEE 2001]  
CC0213
38. Deduce the structures of  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species. [JEE 2002]  
CC0214
39. Write the IUPAC name of the compound  $\text{K}_2[\text{Cr}(\text{NO})(\text{CN})_4(\text{NH}_3)]$ . Spin magnetic moment of the complex  $\mu = 1.73$  BM. Give the structure of anion. [JEE 2003]  
CC0215
40.  $\text{NiCl}_2$  in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of  $\text{NH}_4\text{OH}$ , giving a bright red colour. [JEE 2004]  
(a) Draw its structure and show H-bonding  
(b) Give oxidation state of Ni and its hybridisation  
(c) Predict whether it is paramagnetic or diamagnetic  
CC0216
41. For the octahedral complexes of  $\text{Fe}^{3+}$  in  $\text{SCN}^-$  (thiocyanato-S) and in  $\text{CN}^-$  ligand environments, the difference between the spin only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is : [Atomic number of Fe = 26] [JEE Ad. 2015]  
CC0217
42. In the complex acetylbromidodicarbonylbis(triethylphosphine)iron(II), the number of Fe–C bond(s) is- [JEE Ad. 2015]  
CC0218
43. Among the complex ions,  $[\text{Co}(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2)_2\text{Cl}_2]^+$ ,  $[\text{CrCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ ,  $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$ ,  $[\text{Co}(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2)_2(\text{NH}_3)\text{Cl}]^{2+}$  and  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ , the number of complex ion(s) that show(s) *cis-trans* isomerism is - [JEE Ad. 2015]  
CC0219
44. Among  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{NiCl}_4]^{2-}$ ,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ ,  $\text{Na}_3[\text{CoF}_6]$ ,  $\text{Na}_2\text{O}_2$  and  $\text{CsO}_2$ , the total number of paramagnetic compounds is - [JEE Ad. 2016]  
(A) 2 (B) 3 (C) 4 (D) 5  
CC0220

45. The number of geometric isomers possible for the complex  $[\text{CoL}_2\text{Cl}_2]^-$  ( $\text{L} = \text{H}_2\text{NCH}_2\text{CH}_2\text{O}^-$ ) is  
[JEE Ad. 2016]  
CC0221
46. The geometries of the ammonia complexes of  $\text{Ni}^{2+}$ ,  $\text{Pt}^{2+}$  and  $\text{Zn}^{2+}$ , respectively, are :  
(A) octahedral, square planar and tetrahedral [JEE Ad. 2016]  
(B) square planar, octahedral and tetrahedral  
(C) tetrahedral, square planar and octahedral  
(D) octahedral, tetrahedral and square planar  
CC0222
47. Addition of excess aqueous ammonia to a pink coloured aqueous solution of  $\text{MCl}_2 \cdot 6\text{H}_2\text{O}$  (X) and  $\text{NH}_4\text{Cl}$  gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1 : 3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y. [JEE Ad. 2017]  
Among the following options, which statements is(are) **CORRECT** ?  
(A) The hybridization of the central metal ion in Y is  $d^2sp^3$   
(B) Z is tetrahedral complex  
(C) Addition of silver nitrate to Y gives only two equivalents of silver chloride  
(D) When X and Z are in equilibrium at  $0^\circ\text{C}$ , the colour of the solution is pink  
CC0223
48. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are)  
(Atomic numbers : Fe = 26, Ni = 28) [JEE Ad. 2018]  
(A) Total number of valence shell electrons at metal centre in  $\text{Fe}(\text{CO})_5$  or  $\text{Ni}(\text{CO})_4$  is 16  
(B) These are predominantly low spin in nature  
(C) Metal - carbon bond strengthens when the oxidation state of the metal is lowered  
(D) The carbonyl C–O bond weakens when the oxidation state of the metal is increased  
CC0224
49. The correct option(s) regarding the complex  $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$  :- [JEE Ad. 2018]  
(en =  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ) is (are)  
(A) It has two geometrical isomers  
(B) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands  
(C) It is paramagnetic  
(D) It absorbs light at longer wavelength as compared to  $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$   
CC0225

50. Match each set of hybrid orbitals from LIST-I with complex (es) given in LIST-II.

## LIST-I

P.  $dsp^2$ Q.  $sp^3$ R.  $sp^3d^2$ S.  $d^2sp^3$ 

## LIST-II

1.  $[FeF_6]^{4-}$ 2.  $[Ti(H_2O)_3Cl_3]$ 3.  $[Cr(NH_3)_6]^{3+}$ 4.  $[FeCl_4]^{2-}$ 5.  $Ni(CO)_4$ 6.  $[Ni(CN)_4]^{2-}$ 

[JEE Ad. 2018]

The correct option is

(A) P  $\rightarrow$  5; Q  $\rightarrow$  4,6; R  $\rightarrow$  2,3; S  $\rightarrow$  1(B) P  $\rightarrow$  5,6; Q  $\rightarrow$  4; R  $\rightarrow$  3; S  $\rightarrow$  1,2(C) P  $\rightarrow$  6; Q  $\rightarrow$  4,5; R  $\rightarrow$  1; S  $\rightarrow$  2,3(D) P  $\rightarrow$  4,6; Q  $\rightarrow$  5,6; R  $\rightarrow$  1,2; S  $\rightarrow$  3

CC0226

51. Among the species given below, the total number of diamagnetic species is\_\_\_\_\_.

H atom,  $NO_2$  monomer,  $O_2^-$  (superoxide), dimeric sulphur in vapour phase, [JEE Ad. 2018]

$Mn_3O_4$ ,  $(NH_4)_2[FeCl_4]$ ,  $(NH_4)_2[NiCl_4]$ ,  $K_2MnO_4$ ,  $K_2CrO_4$

CC0227

52. Total number of *cis* N–Mn–Cl bond angles (that is, Mn–N and Mn–Cl bonds in *cis* positions) present in a molecule of *cis*- $[Mn(en)_2Cl_2]$  complex is \_\_\_\_ (*en* =  $NH_2CH_2CH_2NH_2$ ) [JEE Ad. 2019]

CC0228

## ANSWERS KEY

## EXERCISE : O-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A	C	B	C	C	C	D	B	D	B
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	D	B	A	B	A	C	C	D	A	D
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	D	C	B	C	B	B	A	D	A	B
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	D	D	B	C	D	C	C	B	C	C
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	B	C	D	D	D	D	C	B	D	B
Que.	51	52	53	54	55	56	57	58	59	60
Ans.	A	B	A	D	B	D	A	C	B	D
Que.	61	62	63	64	65	66	67	68	69	
Ans.	B	C	C	A	C	C	A	D	A	

## EXERCISE : O-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A,B	A,B,D	A,B,C,D	A,B,D	A,B	B,C,D	A,B,C,D	A,B,C	B,C,D	A,B,C,D
Que.	11	12	13	14						
Ans.	B,D	C,D	C,D	B,D						

## EXERCISE : S-1

- |        |         |        |         |
|--------|---------|--------|---------|
| 1. (3) | 2. (2)  | 3. (9) | 4. (36) |
| 5. (9) | 6. (2)  | 7. (2) | 8. (52) |
| 9. (5) | 10. (2) |        |         |

## EXERCISE : S-2

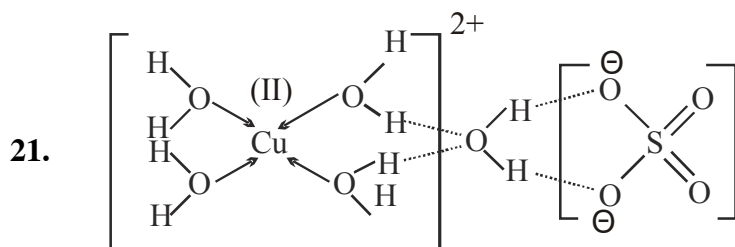
Que.	1				2					
Ans.	(A)-R,	(B)-R	(C)-P	(D)-Q	(A)-P,Q,S	(B)-Q,R,S	(C)-P	(D)-P,Q		
Que.	3									
Ans.	(A)-P,S	(B)-T	(C)-Q,R,T	(D)-P,S						
Que.	4	5	6	7	8	9	10	11	12	13
Ans.	B	C	D	D	C	A	C	D	D	A
Que.	14	15	16	17	18					
Ans.	D	B	B	D	D					

EXERCISE : J-MAIN

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	2	3	4	1	3	2	1	3	4	3
Que.	11	12	13	14	15	16	17	18	19	20
	3	1	2	4	4	1	3	4	4	1
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	4	2	3	2	1	1	2	3	3	3
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	1	3	3	4	3	4	4	4	1	3
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	3	3	2	4	4	1	3	3	4	3
Que.	51	52	53	54	55	56	57	58	59	60
Ans.	3	1	2	2	1	2	2	1	3	4
Que.	61	62	63	64	65					
Ans.	3	2	2	4	1					

EXERCISE : J-ADVANCED

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A	B	D	B	B	B	A	A	C	A
Que.	11	12	13				14	15	16	17
Ans.	A	D	(A)-P,Q,S ; (B)-PR,S ; (C)-Q,S ; (D)-Q,S				C	C	B	B
Que.	18	19	20							
Ans.	A	A	C, D							



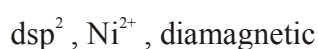
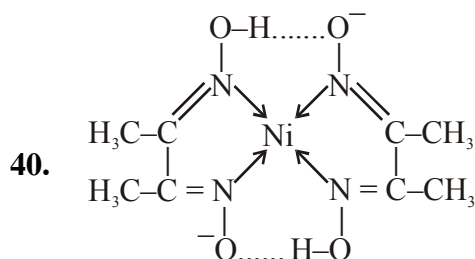
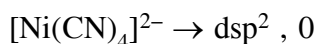
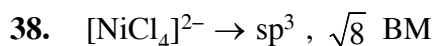
Que.	22	23	24	25	26	27	28	29	30	31
Ans.	B	3	C	B	C	6	D	A	C	B
Que.	32	33	34	35						
Ans.	8	B, D	B	4						

36.  $d^2sp^3$ ,  $dsp^2$  and  $sp^3$

37. A  $\rightarrow$   $[\text{Cr}(\text{NH}_3)_4\text{ClBr}]\text{Cl}$

B  $\rightarrow$   $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$

In both Cr is  $d^2 sp^3$  hybridised and magnetic moment is  $\sqrt{15}$  BM



41. Ans. (4)

42. Ans. (3)

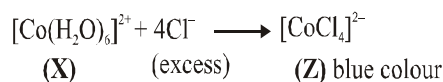
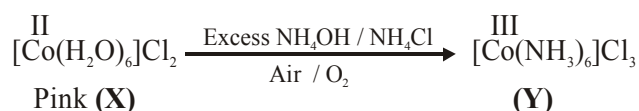
43. Ans. (6)

44. Ans. (B)

45. Ans. (5)

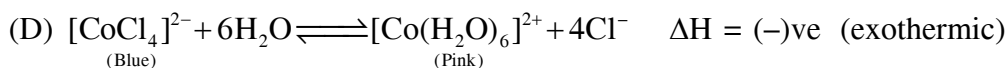
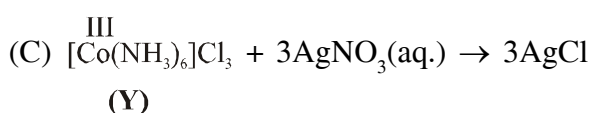
46. Ans. (A)

47. Ans. (A,B,D)



(A) Hybridisation of (Y) is  $d^2sp^3$  as  $\text{NH}_3$  is strong field ligand

(B)  $[\text{CoCl}_4]^{2-}$  have  $sp^3$  hybridisation as  $\text{Cl}^-$  is weak field ligand



When ice is added to the solution the equilibrium shifts right hence pink colour will remain predominant

So, correct answer is (A,B& D)

48. Ans. (B,C)

49. Ans. (A,B,D)

50. Ans. (C)

51. Ans.(1)

52. Ans.(6.00)





### Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.

### Physical Properties

- Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point.
- Rest of the members are soft metals with low melting point and high electrical conductivity.
- It is worth while to note that gallium with unusually low melting point (303K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures.
- Density of the elements increases down the group from boron to thallium.

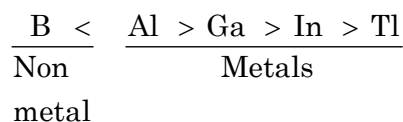
### Melting and Boiling points order

**M.P.**  $B > Al > Tl > In > Ga$

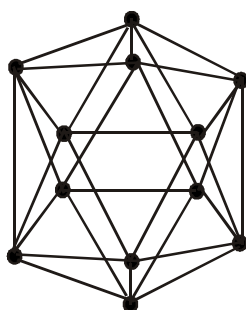
**B.P.**  $B > Al > Ga > In > Tl$

### Electropositive Character

Due to high IE they are less electropositive on moving down the group metallic character increases due to decrease in IE [  $\therefore$  B is nonmetals and other elements are metals.]



**Note :** Boron exists in many allotropic forms. All the allotropes have basic building  $B_{12}$  icosahedral units made up of polyhedron having 20 faces and 12 corners. For example one is the simplest form  $\alpha$  - rhombohedral boron.



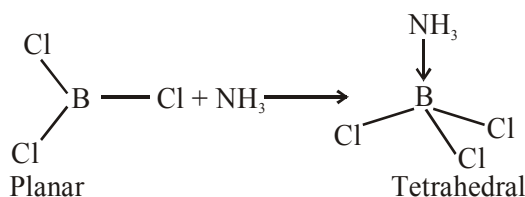
But Al, In & Tl all have close packed metal structure.

### Chemical Properties

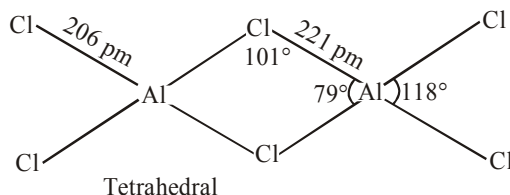
#### *Oxidation state and trends in chemical reactivity*

- Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form  $Al^{3+}$  ions. In fact, aluminium is a highly electropositive metal.

- (ii) However, down the group, due to poor shielding effect of intervening d and f orbitals, the increased effective nuclear charge holds ns electrons tightly (responsible for inert pair effect) and thereby, restricting their participation in bonding. As a result of this, only p-orbital electrons may be involved in bonding. In fact in Ga, In and Tl, both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements:  $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$ . In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidising in character.
- (iii) The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.
- (iv) In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in  $\text{BF}_3$ ) will be only six. Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group.  $\text{BCl}_3$  easily accepts a lone pair of electrons from ammonia to form  $\text{BCl}_3 \cdot \text{NH}_3$ .



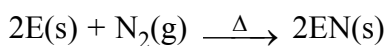
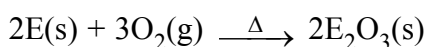
$\text{AlCl}_3$  achieves stability by forming a dimer



- (v) In trivalent state most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hydrolysis in water form tetrahedral  $[\text{M}(\text{OH})_4]^-$  species; the hybridisation state of element M is  $sp^3$ . Aluminium chloride in acidified aqueous solution forms octahedral  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ion. In this complex ion, the 3d orbitals of Al are involved and the hybridisation state of Al is  $sp^3d^2$

#### REACTIVITY TOWARDS AIR :

- (i) Boron is unreactive in crystalline form.
- (ii) Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack.
- (iii) Amorphous boron and aluminium metal on heating in air form  $\text{B}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  respectively. With dinitrogen at high temperature they form nitrides.



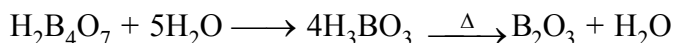
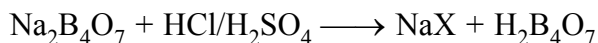
(E = element)

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

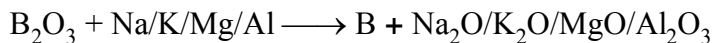


**Preparation of Boron :**

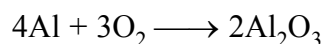
- (i) Preparation of
- $B_2O_3$
- from Borax or Colemanite



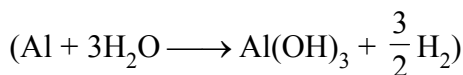
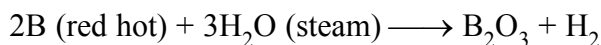
- (ii) Reduction of
- $B_2O_3$

**Chemical Properties :**

- (i) Burning in air:
- $4B + 3O_2 \longrightarrow 2B_2O_3$

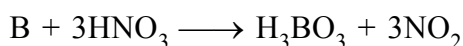
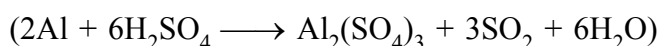
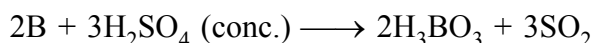
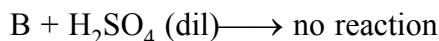


- (ii) Reaction with water

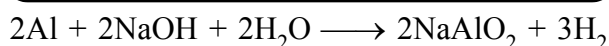


(red hot)

- (iii)
- $B + HCl \longrightarrow$
- no reaction

[ $Al + HNO_3(80\%) \longrightarrow Al_2O_3$  (passive layer) and does not react further.]

- (iv)
- $2B + 2NaOH + 2H_2O \xrightarrow{\Delta} 2NaBO_2 + 3H_2$



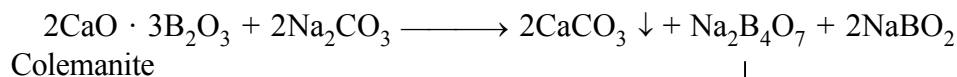
- (v)
- $2B + N_2 \longrightarrow 2BN$
- (
- $2Al + N_2 \longrightarrow 2AlN$
- )



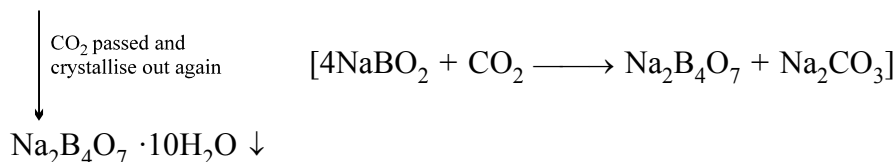
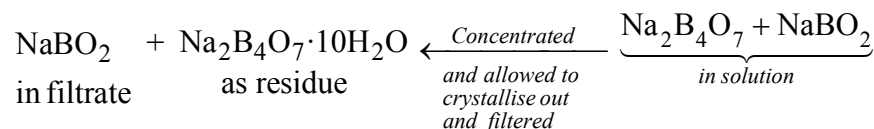
- (vi)
- $3Mg + 2B \longrightarrow Mg_3B_2$

**SOME IMPORTANT COMPOUNDS OF BORON**

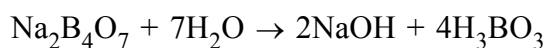
Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly study their chemistry.

**Preparation of Borax :****Borax**

↓  
Filtered  
- CaCO<sub>3</sub>(as residue)

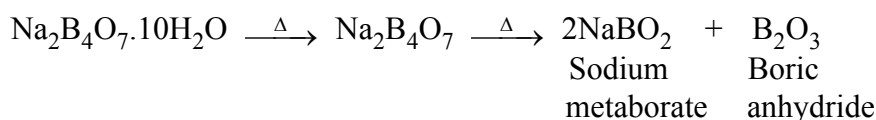
**Properties :**

- (i) It is a white crystalline solid of formula Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O. In fact it contains the tetranuclear units [B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub>]<sup>2-</sup> and correct formula, therefore, is Na<sub>2</sub>[B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub>]·8H<sub>2</sub>O.
- (ii) Borax dissolves in water to give an alkaline solution.



Orthoboric acid

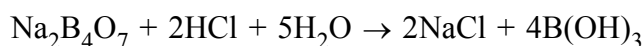
- (iii) On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.



The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured Co(BO<sub>2</sub>)<sub>2</sub> bead is formed.

**Orthoboric acid :****Preparation :**

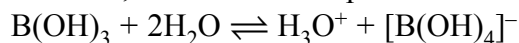
- (i) It can be prepared by acidifying an aqueous solution of borax.



- (ii) It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.)

**Property :**

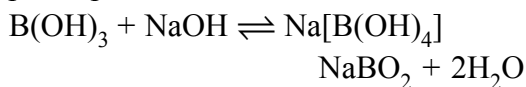
- (i) Orthoboric acid, H<sub>3</sub>BO<sub>3</sub> is a white crystalline solid, with soapy touch.
- (ii) It is sparingly soluble in water but highly soluble in hot water.
- (iii) H<sub>3</sub>BO<sub>3</sub> is soluble in water and behaves as weak monobasic acid. It does not donate protons like most the acids, but rather it accepts OH<sup>-</sup>. It therefore is Lewis acid (B(OH)<sub>3</sub>)



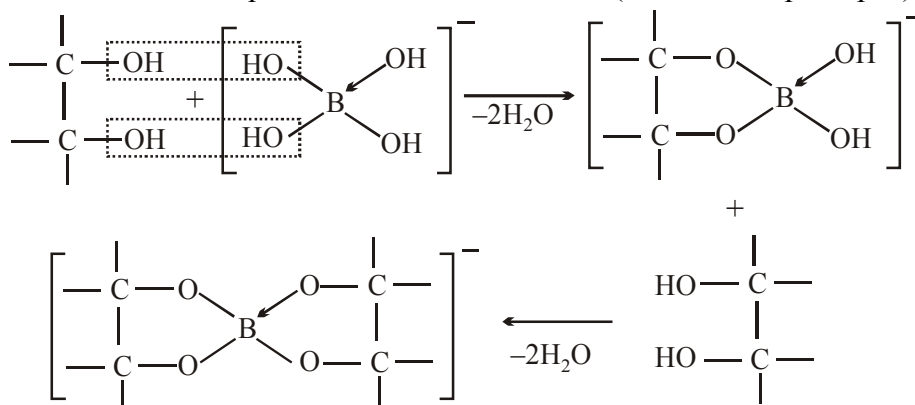
or



Since  $B(OH)_3$  only partially reacts with water to form  $H_3O^+$  and  $[B(OH)_4]^-$  it behaves as a weak acid. Thus it cannot be titrated satisfactorily with  $NaOH$  as a sharp end point is not obtained. If certain polyhydroxy compounds such as glycerol, mannitol or sugar are added to the titration mixture then  $B(OH)_3$  behaves as a strong monobasic acid, and hence can now be titrated with  $NaOH$  and end point is diluted using phenolphthalein as indicator.

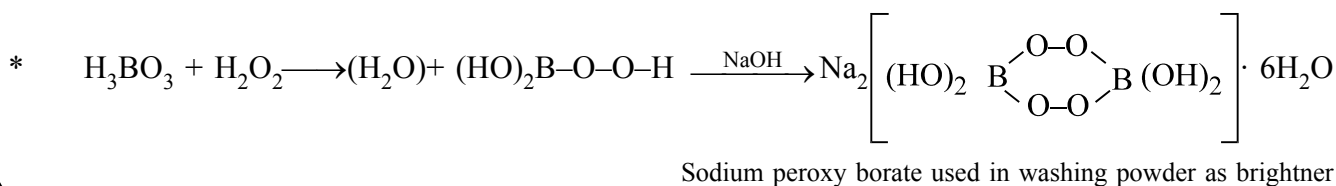
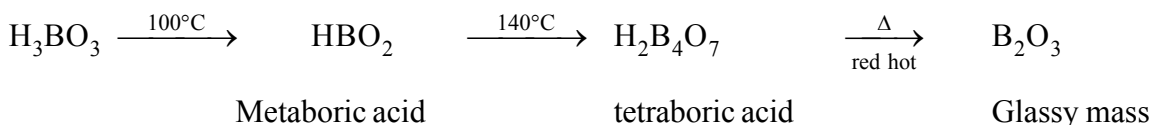


The added compound must be a cis diol to enhance the acidic properties in this way the cis-diol forms very stable complexes with  $[B(OH)_4]^-$  formed in forward direction above, thus effectively removing it from solution. Hence reaction proceeds in forward direction (Le-Chatelier principle.)



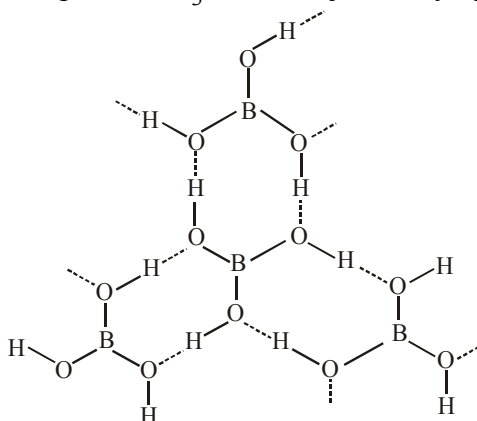
On heating, orthoboric acid above 370K forms metaboric acid,  $HBO_2$  which on further heating yields boric oxide,  $B_2O_3$ .

□ **Heating of boric acid :**



**STRUCTURE**

It has a layer structure in which planar  $BO_3$  units are joined by hydrogen bonds as shown in figure.



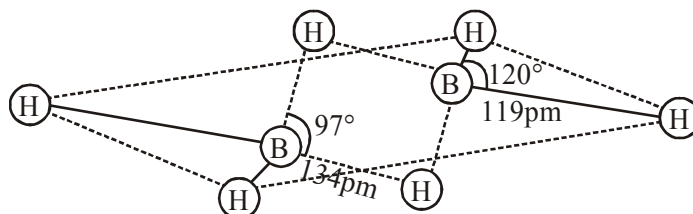
Structure of boric acid; the dotted lines represent hydrogen bonds



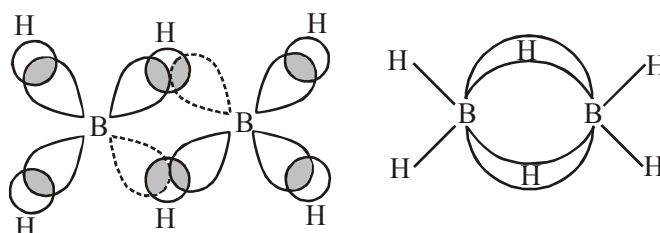


**Structure & bonding in diborane :**

The structure of diborane is shown in figure. The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B–H bonds are regular two centre-two electron bonds while the two bridge (B–H–B) bonds are different and can be described in terms of three centre–two electron bonds shown in figure.



The structure of diborane,  $B_2H_6$



**Figure:** Bonding in diborane.

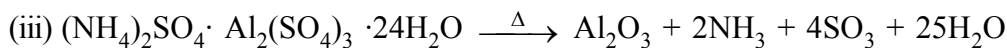
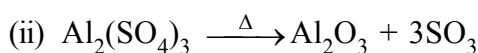
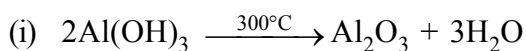
Each B atom uses  $sp^3$  hybrid orbitals for bonding. Out of the four  $sp^3$  hybrid orbital on each B atom, one is without an electron shown in broken lines. The terminal B–H bonds are normal 2-centre-2-electron bonds but the two bridge bonds are 3-centre-2-electron bonds. The 3-centre-2-electron bridge bonds are also referred to as banana bonds.

**Note: Metal hydrido borates :** Boron also forms a series of hydridoborates; the most important one is the tetrahedral  $[BH_4]^-$  ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetrahydridoborates, also known as borohydrides, are prepared by the reaction of metal hydrides with  $B_2H_6$  in diethyl ether.



Both  $LiBH_4$  and  $NaBH_4$  are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

□  **$Al_2O_3$  preparation :**



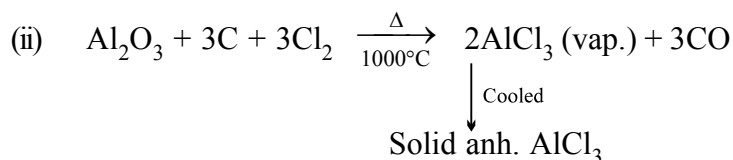
**Uses:** (i) In making refractory bricks

(ii) as an abrasive

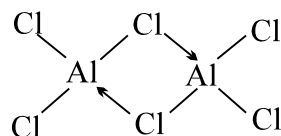
(iii) To make high alumina cement

□  **$AlCl_3$  preparation :**

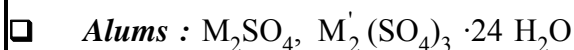


**Properties :**

- (i) Its anhydrous form is deliquescent and fumes in air.
- (ii) It sublimes at  $180^\circ C$ .
- (iii) It is covalent and exists in the form of dimer even if in non polar solvents e.g. alcohol, ether, benzene, where it is soluble in fair extent.



- Uses:** (i) Friedel-Craft reaction  
 (ii) Dyeing, drug & perfumes etc.

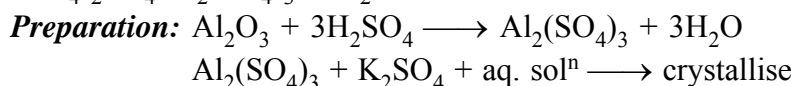


**Properties:** Swelling characteristics

where  $M = Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, NH_4^+$  (except  $Li^+$ )

$M' = Al^{+3}, Cr^{+3}, Fe^{+3}, Mn^{+3}, Co^{+3}$

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Potash alum
$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Ammonium alum
$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$	Chrome alum
$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$	Ferric alum



- Uses:** (i) Act as coagulant  
 (ii) Purification of water  
 (iii) Tanning of leather  
 (iv) Mordant in dyeing  
 (v) Antiseptic

## USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

**Boron :**

- (i) Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications.
- (ii) Boron fibres are used in making bullet-proof vest and light composite material for aircraft.
- (iii) The boron-10 ( $^{10}B$ ) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods.
- (iv) The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses (e.g., Pyrex), glass-wool and fibreglass.
- (v) Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as constituent of medicinal soaps.
- (vi) An aqueous solution of orthoboric acid is generally used as a mild antiseptic.



❑ **Melting and Boiling Points**

M.P. : C > Si > Ge > Pb > Sn

B.P. : Si > Ge > Sn > Pb

❑ **Electronegativity**

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

❑ **Physical Properties**

All group 14 members are solids. Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

❑ **Chemical Properties**

*Oxidation states and trends in chemical reactivity*

- (i) The group 14 elements have four electrons in outermost shell.
- (ii) The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature.
- (iii) In heavier members the tendency to show +2 oxidation state increases in the sequence  $\text{Ge} < \text{Sn} < \text{Pb}$ . It is due to the inability of  $ns^2$  electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group.
- (iv) Carbon and silicon mostly show +4 oxidation state.
- (v) Germanium forms stable compounds in +4 state and only few compounds in +2 state.
- (vi) Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent).
- (vii) Lead compounds in +2 state are stable and in +4 state are strong oxidising agents.
- (viii) In tetravalent state the number of electrons around the central atom in a molecule (*e.g.*, carbon in  $\text{CCl}_4$ ) is eight. Being *electron precise* molecules, they are normally not expected to act as electron acceptor or electron donor species. Although carbon cannot exceed its covalence more than 4, other elements of the group can do so. It is because of the presence of *d* orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like,  $\text{SiF}_6^{2-}$ ,  $[\text{GeCl}_6]^{2-}$ ,  $[\text{Sn}(\text{OH})_6]^{2-}$  exist where the hybridisation of the central atom is  $sp^3d^2$ .

❑ **Reactivity towards oxygen**

All members when heated in oxygen form oxides. There are mainly two types of oxides, *i.e.*, monoxide and dioxide of formula MO and  $\text{MO}_2$  respectively. SiO only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states. The dioxides —  $\text{CO}_2$ ,  $\text{SiO}_2$  and  $\text{GeO}_2$  are acidic, whereas  $\text{SnO}_2$  and  $\text{PbO}_2$  are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

### □ Reactivity towards water

Carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and dihydrogen gas.

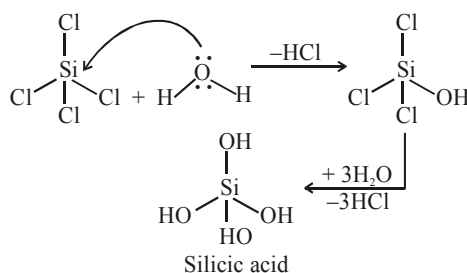


Lead is unaffected by water, probably because of a protective oxide film formation.

### □ Reactivity towards halogen

- (i) These elements can form halides of formula  $\text{MX}_2$  and  $\text{MX}_4$  (where  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ). Except carbon, all other members react directly with halogen under suitable condition to make halides.
- (ii) Most of the  $\text{MX}_4$  are covalent in nature. The central metal atom in these halides undergoes  $sp^3$  hybridisation and the molecule is tetrahedral in shape. Exceptions are  $\text{SnF}_4$  and  $\text{PbF}_4$ , which are ionic in nature.
- (iii)  $\text{PbI}_4$  does not exist because  $\text{Pb}-\text{I}$  bond initially formed during the reaction does not release enough energy to unpair  $6s^2$  electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom.
- (iv) Heavier members Ge to Pb are able to make halides of formula  $\text{MX}_2$ .
- (v) Stability of dihalides increases down the group. Considering the thermal and chemical stability,  $\text{GeX}_4$  is more stable than  $\text{GeX}_2$ , whereas  $\text{PbX}_2$  is more than  $\text{PbX}_4$ .
- (vi) Except  $\text{CCl}_4$ , other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in  $d$  orbital.

Hydrolysis can be understood by taking the example of  $\text{SiCl}_4$ . It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in  $d$  orbitals of Si, finally leading to the formation of  $\text{Si}(\text{OH})_4$  as shown below :



### IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy unavailability of  $d$  orbitals. In carbon, only  $s$  and  $p$  orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of  $d$  orbitals.

Carbon also has unique ability to form  $p_\pi-p_\pi$  multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are:  $\text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$ ,  $\text{C}=\text{O}$ ,  $\text{C}=\text{S}$  and  $\text{C}\equiv\text{N}$ . Heavier elements do not form  $p_\pi-p_\pi$  bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

### Catenation Property

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called **catenation**. This is because C—C bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is  $C \gg Si > Ge \approx Sn$ . Lead does not show catenation.

Bond	Bond enthalpy / $\text{kJ mol}^{-1}$
C—C	348
Si—Si	297
Ge—Ge	260
Sn—Sn	240

Due to property of catenation and  $p_{\pi}-p_{\pi}$  bond formation, carbon is able to show allotropic forms.

### ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as **fullerenes** was discovered by H.W. Kroto, E. Smalley and R.F. Curl. For this discovery they were awarded the Nobel Prize in 1996.

### SOME IMPORTANT COMPOUNDS OF CARBON AND SILICON

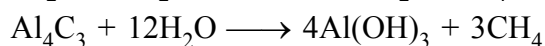
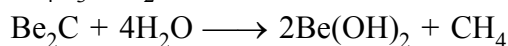
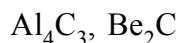
#### Types of Carbide

(i) Ionic and salt like:

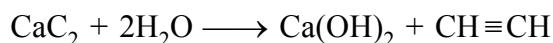
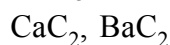
Classification on basis of  
no. of carbon atoms  
present in hydrocarbon  
found on their hydrolysis

- (a)  $C_1$  unit  
(b)  $C_2$  unit  
(c)  $C_3$  unit

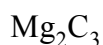
**$C_1$  unit:**



**$C_2$  unit:**



**$C_3$  unit:**

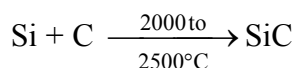
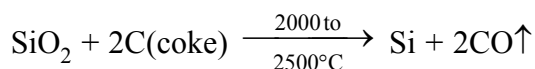


(ii) Covalent carbide : SiC &  $B_4C$

(iii) Interstitial carbide :

(Transition element or inner transitional elements forms this kind of carbide)

Interstitial carbide formation doesn't affect the metallic lusture and electrical conductivity. ( $\because$  no chemical bond is present, no change in property)

SiC (Carborundum)**Preparation**

Note :

(i) SiC has diamond like or wurtzite structure

(ii) SiC is often dark purple, black or dark green due to traces of Fe and other impurities but pure sample are pale yellow to colourless.

**Properties**

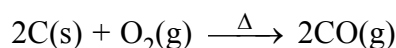
(i) It is very hard and is used in cutting tools and abrasive powder (polishing material)

(ii) It is very much inert

(iii) It is not being affected by any acid except  $\text{H}_3\text{PO}_4$

**Carbon Monoxide****Preparation :**

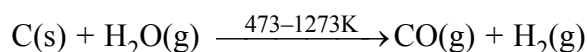
(i) Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.



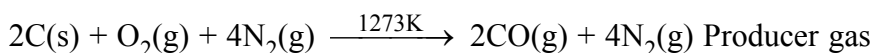
(ii) On small scale pure CO is prepared by dehydration of formic acid with concentrated  $\text{H}_2\text{SO}_4$  at 373 K



(iii) On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and  $\text{H}_2$  thus produced is known as **water gas** or **synthesis gas**.

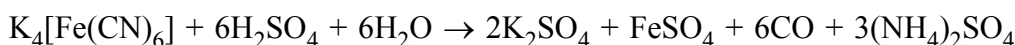
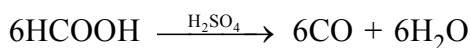
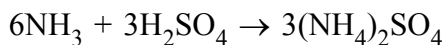
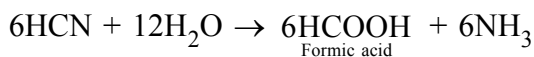
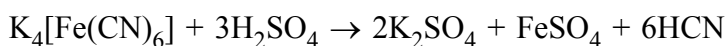


When air is used instead of steam, a mixture of CO and  $\text{N}_2$  is produced, which is called **producer gas**.



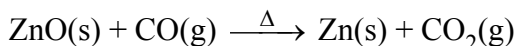
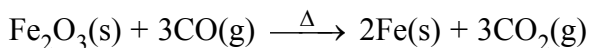
Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

**(iv) By heating potassium ferrocyanide with conc.  $\text{H}_2\text{SO}_4$  :** When potassium ferrocyanide in powdered state is heated with concentrated  $\text{H}_2\text{SO}_4$ , CO is evolved. Dilute  $\text{H}_2\text{SO}_4$  should never be used because it shall evolve highly poisonous gas HCN.



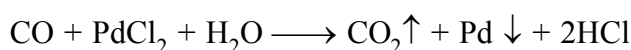
**Properties :**

- (i) Carbon monoxide is a colourless, odourless and almost water insoluble gas.
- (ii) It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of CO is used in the extraction of many metals from their oxides ores.

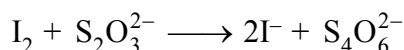
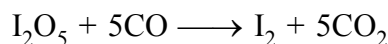
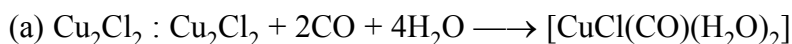
**DETECTION**

(a) burns with blue flame

(b) CO is passed through PdCl<sub>2</sub> solution giving rise to black ppt.



Black metallic  
deposition

**ESTIMATION****ABSORBERS****□ Bonding in CO mole**

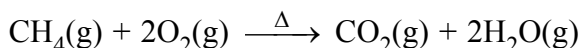
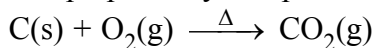
In CO molecule, there are one sigma and two π bonds between carbon and oxygen. Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form **metal carbonyls**.

**□ Poisonous nature of CO**

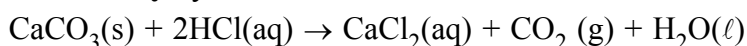
The highly poisonous nature of CO arises because of its ability to form a **complex with haemoglobin**, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

**□ Carbon Dioxide****Preparation :**

- (i) It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.



- (ii) **Laboratory** by the action of dilute HCl on calcium carbonate.

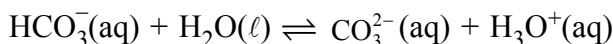
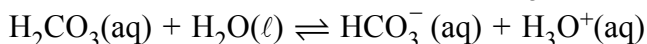


- (iii) Commercial scale by heating limestone.



**Properties :**

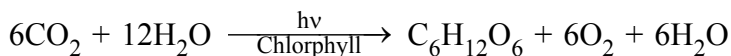
- (i) It is a colourless and odourless gas.
- (ii) Its low solubility in water makes it of immense biochemical and geo-chemical importance.
- (iii) With water, it forms carbonic acid,  $\text{H}_2\text{CO}_3$  which is a weak dibasic acid and dissociates in two steps:



$\text{H}_2\text{CO}_3/\text{HCO}_3^-$  buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalies to form metal carbonates.

**Use of  $\text{CO}_2$** 

Carbon dioxide, which is normally present to the extent of  $\sim 0.03\%$  by volume in the atmosphere, is removed from it by the process known as **photosynthesis**. It is the process by which green plants convert atmospheric  $\text{CO}_2$  into carbohydrates such as glucose. The overall chemical change can be expressed as:

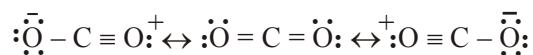


By this process plants make food for themselves as well as for animals and human beings.

**Harmful effect of  $\text{CO}_2$** 

Unlike CO, it is not poisonous. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the  $\text{CO}_2$  content of the atmosphere. This may lead to increase in **green house effect** and thus, raise the temperature of the atmosphere which might have serious consequences.

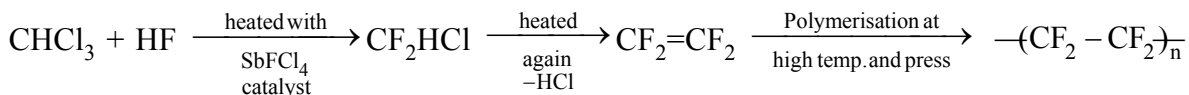
- (i) Carbon dioxide can be obtained as a solid in the form of **dry ice** by allowing the liquified  $\text{CO}_2$  to expand rapidly and dry ice is used as a refrigerant for ice-cream and frozen food.
- (ii) Gaseous  $\text{CO}_2$  is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher.
- (iii) A substantial amount of  $\text{CO}_2$  is used to manufacture urea. In  $\text{CO}_2$  molecule carbon atom undergoes *sp* hybridisation. Two *sp* hybridised orbitals of carbon atom overlap with two *p* orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in  $p_\pi-p_\pi$  bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment. The resonance structures are shown below:



Resonating structures of carbon dioxide

**Note :** Carbongene has 95% O<sub>2</sub> and 5% CO<sub>2</sub> and is used as an antidote for poisoning of CO.

**Teflon**  $-(CF_2 - CF_2)_n$



### Purpose

Temperature with standing capacity upto 300°C (1<sup>st</sup> organic compound withstand this kind of high temperature)

## SILICON (Si)

### Occurrence

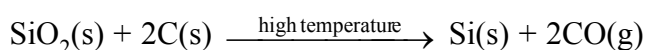
Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron. Aluminium silicate is however the most common constituent of rocks and clays.

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

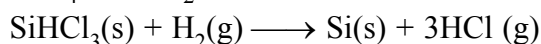
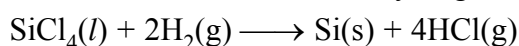
- (i) Feldspar – K<sub>2</sub>O. Al<sub>2</sub>O<sub>3</sub>. 6SiO<sub>2</sub>
- (ii) Kaolinite – Al<sub>2</sub>O<sub>3</sub>. 2SiO<sub>2</sub>. 2H<sub>2</sub>O
- (iii) Asbestos – CaO. 3MgO. 4SiO<sub>2</sub>

### Preparation

- (i) From silica (sand): Elemental silicon is obtained by the reduction of silica (SiO<sub>2</sub>) with high purity coke in an electric furnace.



- (ii) From silicon tetrachloride (SiCl<sub>4</sub>) or silicon chloroform (SiHCl<sub>3</sub>) : Silicon of very high purity required for making semiconductors is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen followed by purification by zone refining.



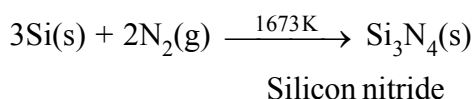
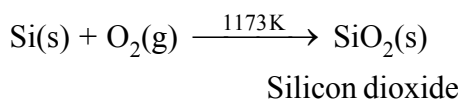
### Physical Properties :

- (i) Elemental silicon is very hard having diamond like structure.
- (ii) It has shining luster with a melting point of 1793 K and boiling point of about 3550 K.
- (iii) Silicon exists in three isotopes, i.e.  $^{28}_{14}Si$ ,  $^{29}_{14}Si$  and  $^{30}_{14}Si$  but  $^{28}_{14}Si$  is the most common isotope.

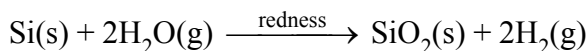
### Chemical Properties :

Silicon is particularly unreactive at room temperature towards most of the elements except fluorine. Some important chemical reactions of silicon are discussed below.

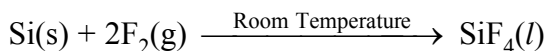
- (i) **Action of air :** Silicon reacts with oxygen of air at 1173 K to form silicon dioxide and with nitrogen of air at 1673 K to form silicon nitride,.



(ii) **Action of steam** : It is slowly attacked by steam when heated to redness liberating dihydrogen gas.

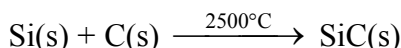


(iii) **Reaction with halogens**: It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride (SiF<sub>4</sub>).



However, with other halogens, it combines at high temperatures forming tetrahalides.

(iv) **Reaction with carbon** : Silicon combines with carbon at 2500 °C forming silicon carbide (SiC) known as carborundum.



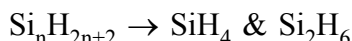
Carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

**Uses :**

- (i) Silicon is added to steel as such or more usually in form of ferrosilicon (an alloy of Fe and Si) to make it acid-resistant.
- (ii) High purity silicon is used as semiconductors in electronic devices such as transistors.
- (iii) It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

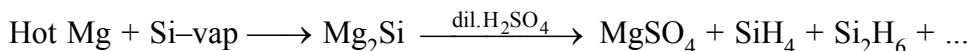
**Compounds of Silicon :**

**Silane :**



Only these two are found

Higher molecules are not formed. ∴ Si can't show catenation property

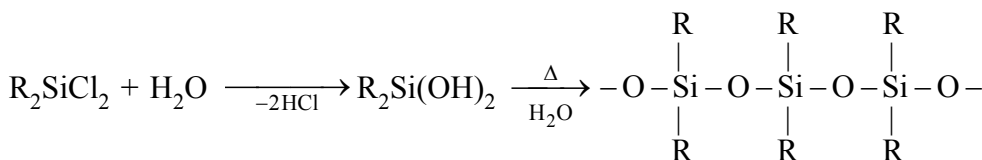


**Silicones**

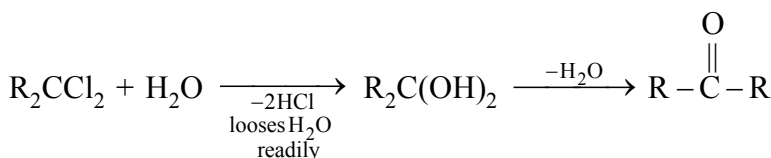
It is an organosilicon polymer

**TYPES OF SILICONES :**

**(i) Linear silicones**



**Linear silicone**





### SILICA (SiO<sub>2</sub>)

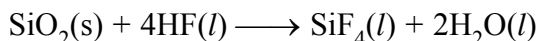
#### Occurrence :

Silica or silicon dioxide occurs in nature in the free state as sand, quartz and flint and in the combined state as silicates like, Feldspar : K<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.6SiO<sub>2</sub>, Kaolinite : Al<sub>2</sub>O<sub>3</sub>. 2SiO<sub>2</sub>. 2H<sub>2</sub>O etc.

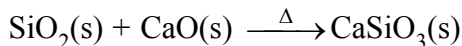
#### Properties :

(i) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.

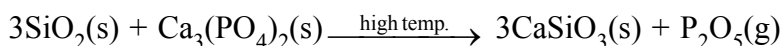
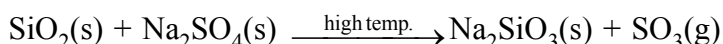
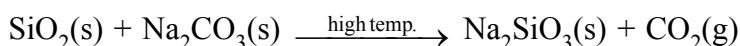
(ii) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.



(iii) It also combines with metallic oxides at high temperature giving silicates e.g.



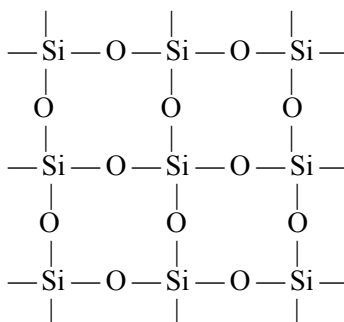
(iv) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.



The first two examples quoted here are important in glass making.

#### Structures of Silica :

Silica has a three-dimensional network structure. In silica, silicon is sp<sup>3</sup>-hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure. This three-dimensional network structure imparts stability to SiO<sub>2</sub> crystal and hence a large amount of energy is required to break the crystal resulting in high melting point.



#### Uses :

(i) Sand is used in large quantities to make mortar and cement.

(ii) Being transparent to ultraviolet light, large crystal of quartz are used for making lenses for optical instruments and for controlling the frequency of radio-transmitters.

(iii) Powdered quartz is used for making silica bricks.

(iv) Silica gel (SiO<sub>2</sub>.xH<sub>2</sub>O) is used as a desiccant (for absorbing moisture) and as an adsorbent in chromatography.

**Quartz**

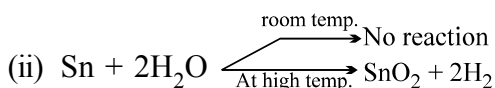
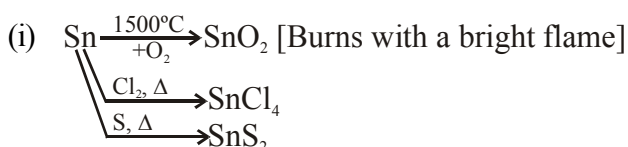
Quartz is extensively used as a piezoelectric material; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.

**Silicates**

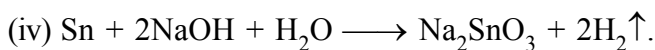
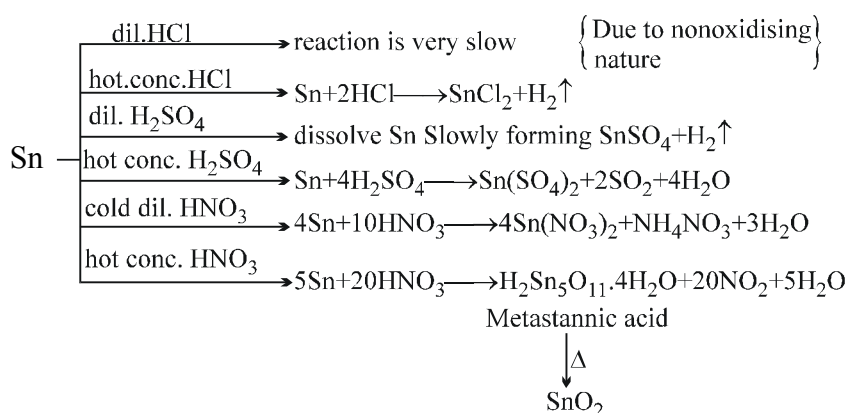
A large number of silicates minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. Two important man-made silicates are glass and cement.

**Zeolites**

If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Ca}^{2+}$  balance the negative charge. Examples are feldspar and zeolites. Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of "hard" water.

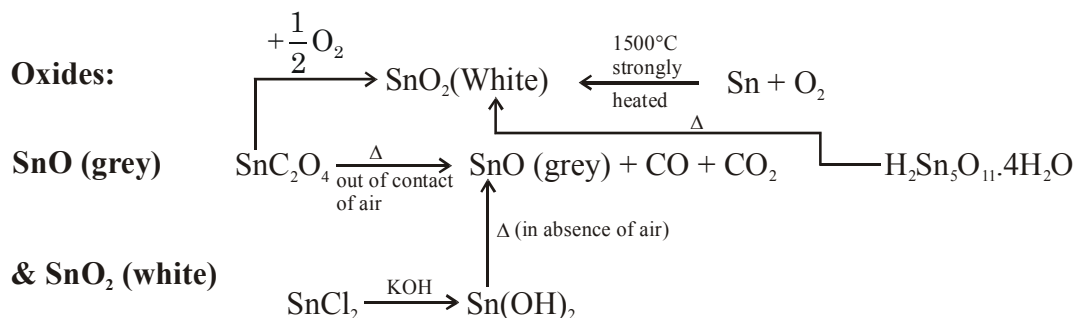
**TIN & ITS COMPOUND**

(iii) Reaction with acid.

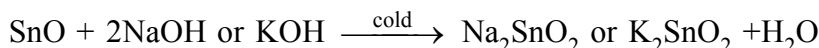
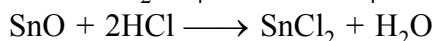
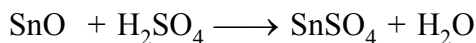


or

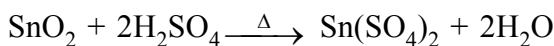
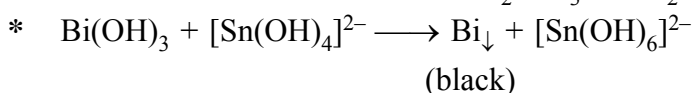
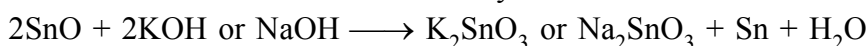
KOH [In absence of air  $\text{K}_2\text{SnO}_2$  forms and in contact with air it readily converts into  $\text{K}_2\text{SnO}_3$ ]



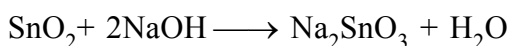
Both are amphoteric in nature :



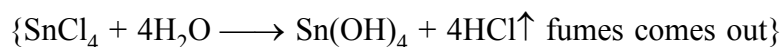
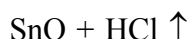
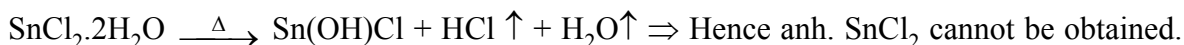
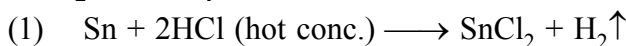
But conc. hot alkali behaves differently.



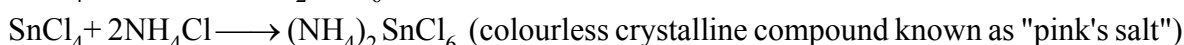
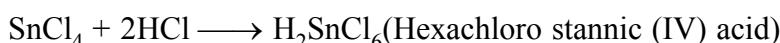
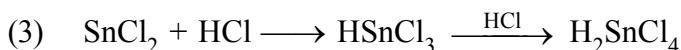
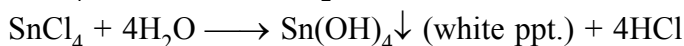
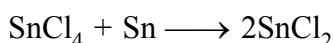
(Soluble only in hot conc.  $H_2SO_4$ )



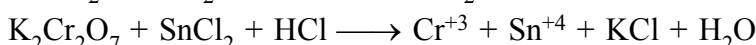
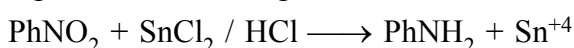
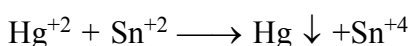
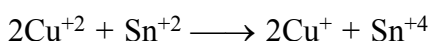
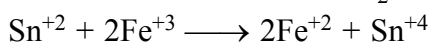
**$SnCl_2$  &  $SnCl_4$  :**



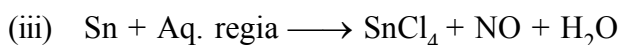
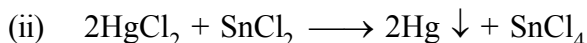
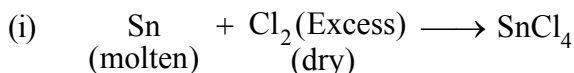
(2) A piece of Sn is always added to preserve a solution of  $SnCl_2$ . Explain.



(4) Reducing Properties of  $SnCl_2$  :



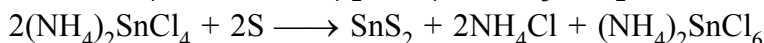
(5) Readily combines with  $I_2 \Rightarrow SnCl_2I_2 \Rightarrow$  This reaction is used to estimate tin.

**Formation of SnCl<sub>4</sub> :**

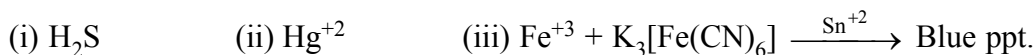
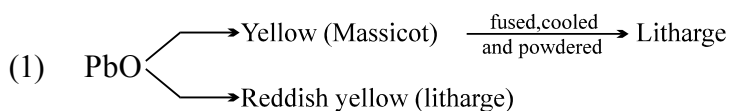
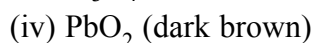
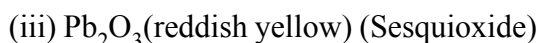
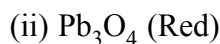
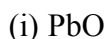
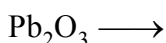
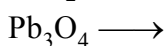
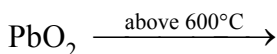
\*  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  is known as butter of tin  $\Rightarrow$  used as mordant.

$(\text{NH}_4)_2\text{SnCl}_6$  is known as 'pink's salt'  $\Rightarrow$  used in calico printing.

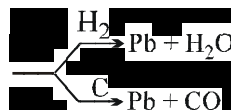
**Mosaic gold** :  $\text{SnS}_2$  yellow crystalline substance :



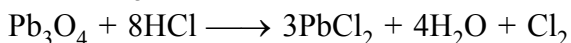
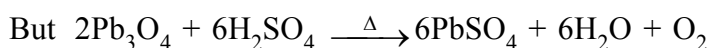
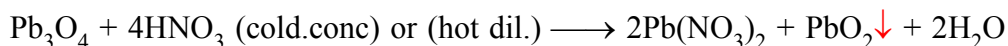
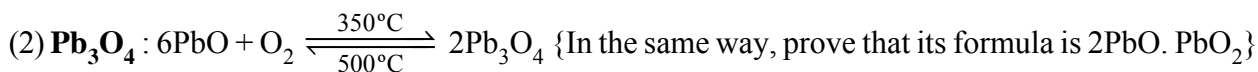
**Note** : Mosaic gold used for filling purpose (in joining gold pieces)

**Distinction of Sn<sup>+2</sup> / Sn<sup>+4</sup> :****COMPOUNDS OF LEAD****Oxides of lead :****Laboratory Prep<sup>n</sup>. :**

} PbO, hot oxide easily reduced to Pb by H<sub>2</sub> or C.

**Preparation of Pb<sub>2</sub>O<sub>3</sub> :**

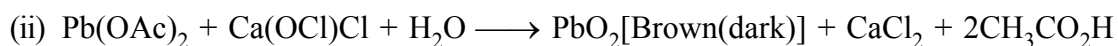
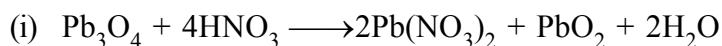
This reaction suggests that Pb<sub>2</sub>O<sub>3</sub> contains PbO<sub>2</sub>.





(3) **PbO<sub>2</sub>** : Insoluble in water :

HNO<sub>3</sub>, But reacts with HCl and H<sub>2</sub>SO<sub>4</sub>(hot conc.) but does not react with HNO<sub>3</sub> and soluble in hot NaOH / KOH.

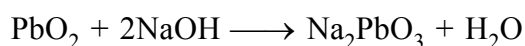
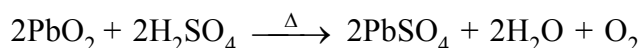
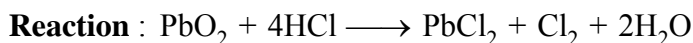


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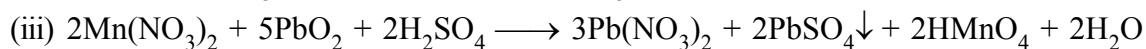
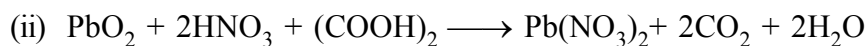
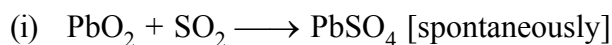
Excess bleaching powder

is being removed by stirring with

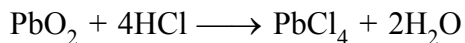
HNO<sub>3</sub>



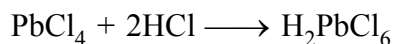
**PbO<sub>2</sub>** : Powerful oxidising agent :



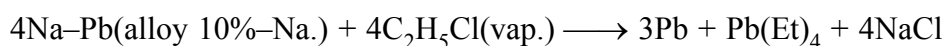
**PbCl<sub>4</sub>** : Exists as H<sub>2</sub>[PbCl<sub>6</sub>]



{ice cold conc. saturated with Cl<sub>2</sub>}



**TetraEthyl lead :**



It is antiknocking agent.

## NITROGEN FAMILY

## GROUP-15 ELEMENTS (N, P, As, Sb, Bi)

- (i) As we go down the group, there is a shift from non-metallic to metallic through metalloidal character.
- (ii) Nitrogen and phosphorus are **non-metals**, arsenic and antimony **metalloids** and bismuth is a **typical metal**.

**Occurrence :**

**Nitrogen :** Molecular nitrogen comprises 78% by volume of the atmosphere. It is 33<sup>rd</sup> most abundant element in the earth's crust. In the earth's crust, it occurs as sodium nitrate,  $\text{NaNO}_3$  (called Chile saltpetre) and potassium nitrate (Indian saltpetre). It is found in the form of proteins and nucleic acid in plants and animals.

**Phosphorus :**

- (i) It is eleventh most abundant element in earth's crust occurs in minerals of the apatite family,  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaX}_2$  ( $X = \text{F}, \text{Cl}$  or  $\text{OH}$ ) (e.g., fluorapatite  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaF}_2$ ) and also found as chlorapatite  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaCl}_2$ .
- (ii) It is also present in nucleic acid (in DNA and RNA) which are the main components of phosphate rocks.
- (iii) Arsenic, antimony and bismuth are found mainly as sulphide minerals.

**Electronic Configuration :**

The valence shell electronic configuration of these elements is  $ns^2np^3$ .

**Atomic and Ionic Radii :**

Covalent radius :  $\text{N} < \text{P} < \text{As} < \text{Sb} < \text{Bi}$

**Explanation :**

Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and/or f orbitals in heavier members.

**Ionisation Enthalpy :**

$\text{N} > \text{P} > \text{As} > \text{Sb} > \text{Bi}$  ( $\text{IE}_1$  values)

**Explanation :**

Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled p orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is  $\Delta_1 H_1 < \Delta_1 H_2 < \Delta_1 H_3$  (See above table).

**Electronegativity :**

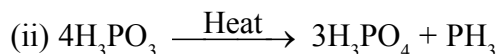
$\text{N} > \text{P} > \text{As} > \text{Sb} = \text{Bi}$   
(1.9) (1.9)



- (iv) The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group.
- (v) Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxoacids.
- (vi) In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,



- (vii) Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid.



- (viii) +3 oxidation state in case of arsenic, antimony and bismuth becomes increasingly stable with respect to disproportionation.
- (ix) Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.
- (x) The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalency as in  $\text{PF}_6^-$ .

### Anomalous properties of nitrogen

- (i) Nitrogen has unique ability to form  $p_\pi - p_\pi$  multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O).
- (ii) Heavier elements of this group do not form  $p_\pi - p_\pi$  bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.
- (iii) Nitrogen exists as a diatomic molecule with a triple bond (one  $\sigma$  and two  $\pi$ ) between the two atoms.  $\text{N}_2$  bond enthalpy ( $941.4 \text{ kJ mol}^{-1}$ ) is very high.
- (iv) Phosphorus, arsenic and antimony form single bonds as P-P, As-As and Sb-Sb while bismuth forms metallic bonds in elemental state.
- (v) The single N-N bond is weaker than the single P-P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen.
- (vi) Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form  $d_\pi - p_\pi$  bond as the heavier elements can e.g.,  $\text{R}_3\text{P}=\text{O}$  or  $\text{R}_3\text{P}=\text{CH}_2$  (R=alkyl group).
- (vii) Phosphorus and arsenic can form  $d_\pi - d_\pi$  bond also with transition metals when their compounds like  $\text{P}(\text{C}_2\text{H}_5)_3$  and  $\text{As}(\text{C}_6\text{H}_5)_3$  act as ligands.

**(i) Reactivity towards hydrogen:**

All the elements of Group 15 form hydrides of the type  $\text{EH}_3$  where  $\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}$  or  $\text{Bi}$ . Some of the properties of these hydrides are shown in Table. The hydrides show regular gradation in their properties. The stability of hydrides decreases from  $\text{NH}_3$  to  $\text{BiH}_3$  which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while  $\text{BiH}_3$  is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 \geq \text{BiH}_3$ .

**Table :** Properties of Hydrides of Group 15 Elements

Property	$\text{NH}_3$	$\text{PH}_3$	$\text{AsH}_3$	$\text{SbH}_3$	$\text{BiH}_3$
Melting point/K	195.2	139.5	156.7	185	—
Boiling point/K	238.5	185.5	210.6	254.6	290
(E–H) distance/pm	101.7	141.9	151.9	170.7	—
HEH angle ( $^\circ$ )	107.8	93.6	91.8	91.3	—
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	–46.1	13.4	66.4	145.1	278
$\Delta_{\text{diss}} H^\ominus (\text{E} - \text{H}) / \text{kJ mol}^{-1}$	389	322	297	255	—

- (ii) Reactivity towards oxygen:** All these elements form two types of oxides:  $\text{E}_2\text{O}_3$  and  $\text{E}_2\text{O}_5$ . The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type  $\text{E}_2\text{O}_3$  of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.
- (iii) Reactivity towards halogens:** These elements react to form two series of halides:  $\text{EX}_3$  and  $\text{EX}_5$ . Nitrogen does not form pentahalide due to non-availability of the d orbitals in its valence shell. Pentahalides are more covalent than trihalides. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only  $\text{NF}_3$  is known to be stable. Trihalides except  $\text{BiF}_3$  are predominantly covalent in nature.
- (iv) Reactivity towards metals:** All these elements react with metals to form their binary compounds exhibiting –3 oxidation state, such as,  $\text{Ca}_3\text{N}_2$  (calcium nitride)  $\text{Ca}_3\text{P}_2$  (calcium phosphide),  $\text{Na}_3\text{As}$  (sodium arsenide),  $\text{Zn}_3\text{Sb}_2$  (zinc antimonide) and  $\text{Mg}_3\text{Bi}_2$  (magnesium bismuthide).

**DINITROGEN****Preparation :****(a) Commercial preparation :**

Dinitrogen is produced **commercially** by the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K).

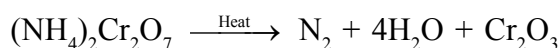
**(b) Laboratory preparation :**

(i) Dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

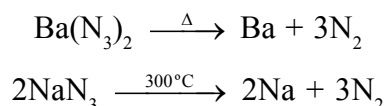


Small amounts of  $\text{NO}$  and  $\text{HNO}_3$  are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.

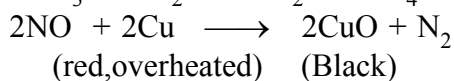
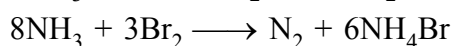
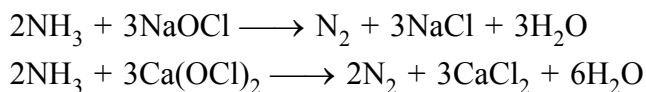
(ii) Dinitrogen can also be obtained by the thermal decomposition of ammonium dichromate.



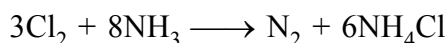
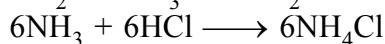
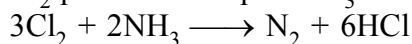
**Note :** Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.



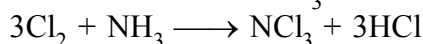
**(c) Other preparation**



$\text{Cl}_2$  passed into liquid  $\text{NH}_3$



In this method conc. of  $\text{NH}_3$  should not be lowered down beyond a particular limit.



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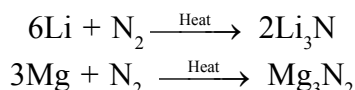
(Tremendously explosive)

**Physical properties :**

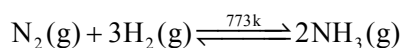
- (i) Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.
- (ii) Nitrogen atom has two stable isotopes:  $^{14}\text{N}$  and  $^{15}\text{N}$ .
- (iii) It has a very low solubility in water (23.2  $\text{cm}^3$  per litre of water at 273 K and 1 bar pressure)
- (iv) Dinitrogen has low freezing and boiling points.

**Chemical properties**

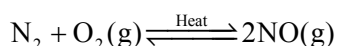
**Reaction with metal :** At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:



**Reaction with metal :** It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:

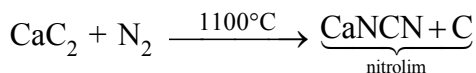


Dinitrogen combines with dioxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO.

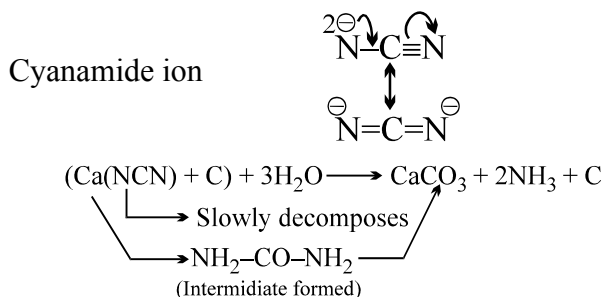


**Absorption on calcium carbide**

$N_2$  can be absorbed by calcium carbide at the temperature around  $1000^\circ C$ .



It is a very good fertiliser.

**Qus. Why dinitrogen is inert at room temperature ?**

**Ans.** Dinitrogen is inert at room temperature because of the high bond enthalpy of  $N \equiv N$  bond. Reactivity, however, increases rapidly with rise in temperature.

**TYPES OF NITRIDE :**

Salt like or ionic :  $Li_3N$ ,  $Na_3N$ ,  $K_3N$ ,  $Ca_3N_2$ ,  $Mg_3N_2$ ,  $Be_3N_2$

Covalent :  $AlN$ ,  $BN$ ,  $Si_3N_4$ ,  $Ge_3N_4$ ,  $Sn_3N_4$

Interstitial :  $MN$  ( $M = Sc, Ti, Zr, Hf, La$ )  
HCP or FCC

No of metal atom per unit cell is equal to no of octahedral voids per unit cell.

All the octahedral voids are occupied by nitrogen atoms. Hence the formula is  $MN$ .

HCP : Hexagonal closed packing

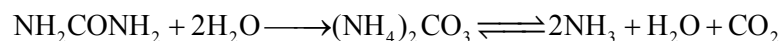
FCC : Face centred cubic

**Uses :**

- The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen, (e.g., calcium cyanamide).
- It also finds use where an inert atmosphere is required (e.g., in iron and steel industry, inert diluent for reactive chemicals).
- Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

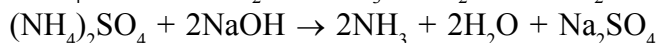
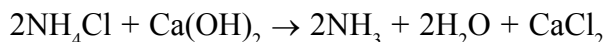
**AMMONIA****Preparation :**

- Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.

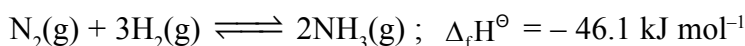


- Small scale preparation

By the decomposition of ammonium salts when treated with caustic soda or calcium hydroxide.

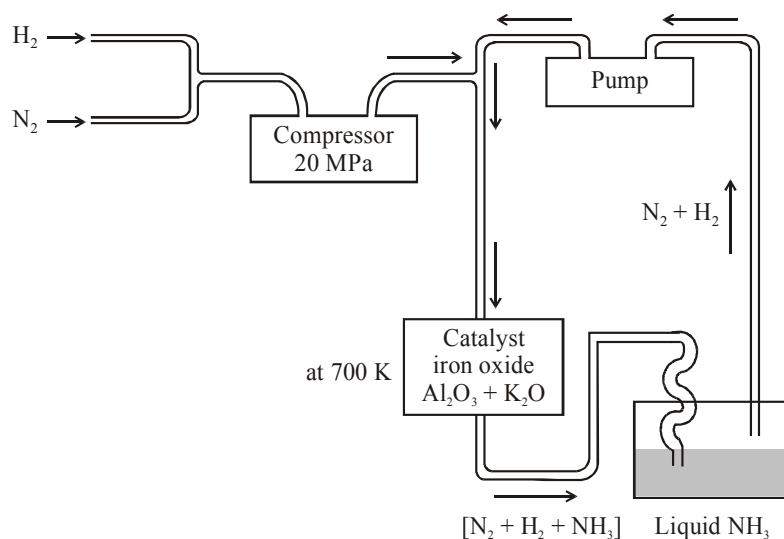


- Large scale manufacturing (Haber's Process)



- \* According to Le Chatelier's principle, high pressure and low temperature would favour the formation of ammonia.

- \* The optimum conditions for the production of ammonia are a pressure of  $200 \times 10^5$  Pa (about 200 atm), a temperature of  $\sim 700$  K.
- \* Use of a catalyst such as iron oxide with small amounts of  $K_2O$  and  $Al_2O_3$  to increase the rate of attainment of equilibrium.
- \* The flow chart for the production of ammonia is shown in figure. Earlier, iron was used as a catalyst with molybdenum as a promoter.



Flow chart for the manufacture of ammonia

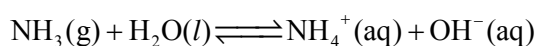
**Other preparation :**

- (i) Nitrate or nitrite reduction :  $NO_3^- / NO_2^- + Zn \text{ or } Al + NaOH \longrightarrow NH_3 + [Zn(OH)_4]^{2-}$   
or  $[Al(OH)_4]^-$
- (ii) Metal nitride hydrolysis :  $N^{3-} + 3H_2O \longrightarrow NH_3 \uparrow + 3 OH^-$

**Properties :**

- Ammonia is a colourless gas with a pungent odour.
- Its freezing and boiling points are 198.4 and 239.7 K respectively.
- In the solid and liquid states, it is associated through hydrogen bonds as in the case of water and that accounts for its higher melting and boiling points than expected on the basis of its molecular mass.
- Ammonia gas is highly soluble in water.
- Basic character :**

Its aqueous solution is weakly basic due to the formation of  $OH^-$  ions.

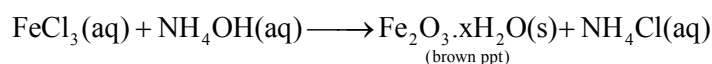
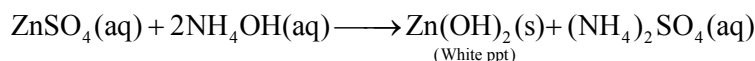


It forms ammonium salts with acids, e.g.,  $NH_4Cl$ ,  $(NH_4)_2SO_4$ , etc.

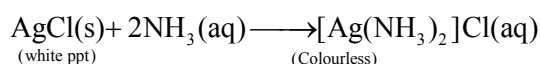
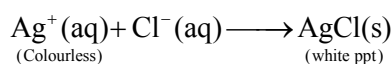
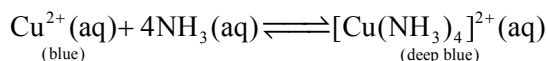
As a weak base, it precipitates the hydroxides (hydrated oxides in case of some metals) of many metals from their salt solutions.



For example,

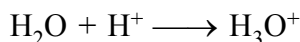
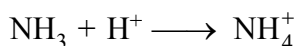
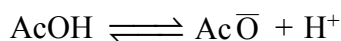


In ammonia molecule the presence of a lone pair of electrons on the nitrogen atom of the makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ :



### Other reactions

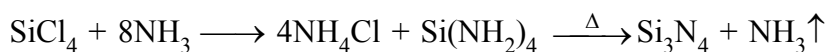
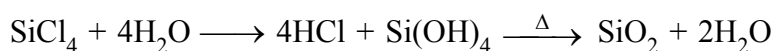
**$\text{CH}_3\text{COOH}$  is strong acid in liq.  $\text{NH}_3$  while in water is weak acid.**



Basicity order  $\text{NH}_3 > \text{H}_2\text{O}$

more solvation of  $\text{H}^+$  in  $\text{NH}_3$ .

**Hydrolysis and Ammonolysis occurs in a same way.**



Rate of hydrolysis and Ammonolysis will be affected by the presence of  $\text{HCl}$  vapour &  $\text{NH}_4\text{Cl}$  vapour respectively.

**Uses :**

- (i) Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate).
- (ii) In the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid.
- (iii) Liquid ammonia is also used as a refrigerant.

### BONDING IN AMMONIA :

The ammonia molecule is trigonal pyramidal with the nitrogen atom at the apex. It has three bond pairs and one lone pair of electrons.

**OXIDES OF NITROGEN :**

Nitrogen forms a number of oxides in different oxidation states. The names, formulas, preparation and physical appearance of these oxides are given in Table.

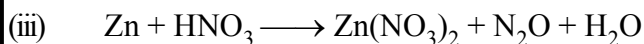
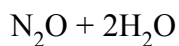
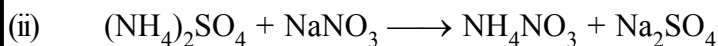
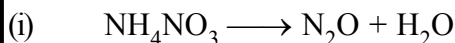
Oxides of Nitrogen				
Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen oxide]	N <sub>2</sub> O	+1	NH <sub>4</sub> NO <sub>3</sub> $\xrightarrow{\text{Heat}}$ N <sub>2</sub> O + 2H <sub>2</sub> O	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+2	2NaNO <sub>2</sub> + 2FeSO <sub>4</sub> + 3H <sub>2</sub> SO <sub>4</sub> → Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 2NaHSO <sub>4</sub> + 2H <sub>2</sub> O + 2NO	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen (III) oxide]	N <sub>2</sub> O <sub>3</sub>	+3	2NO + N <sub>2</sub> O <sub>4</sub> $\xrightarrow{-30^\circ\text{C}}$ 2N <sub>2</sub> O <sub>3</sub>	Pale Blue solid (MP = -100.1°C), acidic, Intense blue liquid (-30°C)
Nitrogen dioxide [Nitrogen (IV) oxide]	NO <sub>2</sub>	+4	2Pb(NO <sub>3</sub> ) <sub>2</sub> $\xrightarrow{673\text{K}}$ 4NO <sub>2</sub> + 2PbO + O <sub>2</sub>	brown gas, acidic
Dinitrogen tetroxide [Nitrogen (IV) oxide]	N <sub>2</sub> O <sub>4</sub>	+4	2NO <sub>2</sub> $\xrightleftharpoons[\text{Heat}]{\text{Cool}}$ N <sub>2</sub> O <sub>4</sub>	Colourless solid/liquid, acidic
Dinitrogen pentaoxide [Nitrogen(V) oxide]	N <sub>2</sub> O <sub>5</sub>	+5	4HNO <sub>3</sub> + P <sub>4</sub> O <sub>10</sub> → 4HPO <sub>3</sub> + 2N <sub>2</sub> O <sub>5</sub>	colourless solid, acidic

**Structure of Oxides of Nitrogen**

Formula	Resonance structures	Bond Parameters
N <sub>2</sub> O	$\ddot{\text{N}} = \text{N} = \ddot{\text{O}} \leftrightarrow \text{:N} \equiv \text{N} - \ddot{\text{O}}\text{:}$	N—N—O 113 pm 119 pm Linear
NO	$\text{:N} = \ddot{\text{O}} \leftrightarrow \text{:}\ddot{\text{N}} = \ddot{\text{O}}\text{:}$	N—O 115 pm Linear
N <sub>2</sub> O <sub>3</sub>	$\begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array} - \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array} \leftrightarrow \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array} - \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array}$	 114 pm 105° 186 pm 117° 130° 121 pm
NO <sub>2</sub>	$\begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array} \leftrightarrow \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array}$	 N 120 pm O 134° O Angular
N <sub>2</sub> O <sub>4</sub>	$\begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array} - \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array} \leftrightarrow \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array} - \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array}$	 O 135° N 175 pm N 121 pm O Planar
N <sub>2</sub> O <sub>5</sub>	$\begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array} - \ddot{\text{O}} - \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array} \leftrightarrow \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array} - \ddot{\text{O}} - \begin{array}{c} \ddot{\text{O}} \\ \parallel \\ \text{N} \\ \parallel \\ \ddot{\text{O}} \end{array}$	 O 151 pm O 119 pm N 112° N 134° O Planar

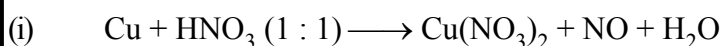
**Preparation:**

1. **N<sub>2</sub>O**

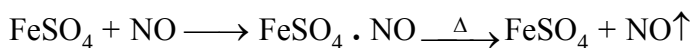
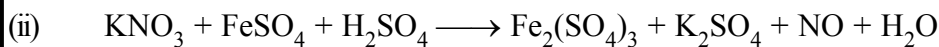


(dil. & cold)

2. **NO**

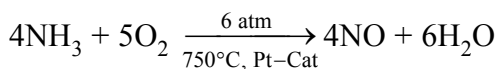


hot

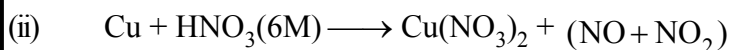
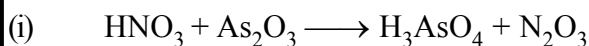


(iii) Oswald process—Restricted oxidation of NH<sub>3</sub>.

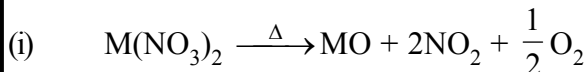
Industrial process.



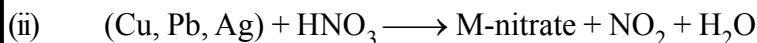
3. **N<sub>2</sub>O<sub>3</sub>**



4. **NO<sub>2</sub>**

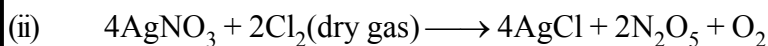
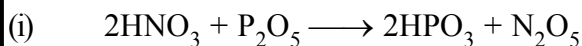


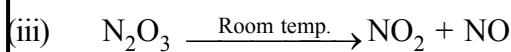
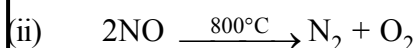
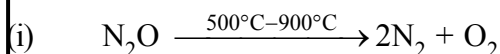
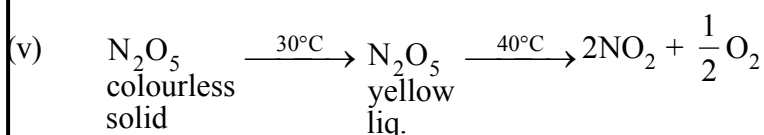
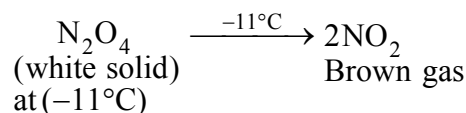
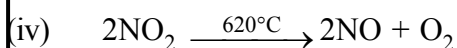
M = Pb, Cu, Ba, Ca



(hot & conc.)

5. **N<sub>2</sub>O<sub>5</sub>**

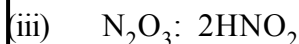
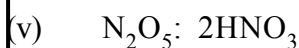
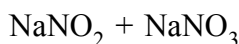
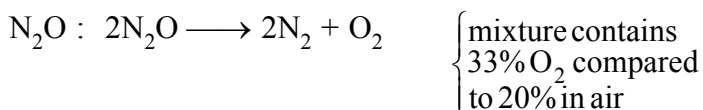


**Properties:****(I) Decomposition Behaviour**(Blue liq.) at  $(-30^\circ\text{C})$ **(II) Reaction with H<sub>2</sub>O & NaOH**(i) N<sub>2</sub>O : Fairly soluble in water and produces neutral solution

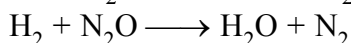
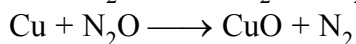
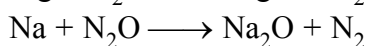
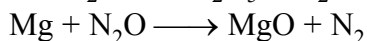
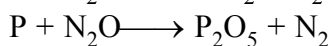
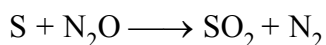
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(ii) NO : Sparingly soluble in water and produces neutral sol<sup>n</sup>.

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Hence it is known as anhydride of HNO<sub>2</sub>(iv) NO<sub>2</sub>: HNO<sub>2</sub> + HNO<sub>3</sub> called as mixed anhydridecalled as anhydride of HNO<sub>3</sub>**Other properties:**

Hence, it is a better supporter for combustion.



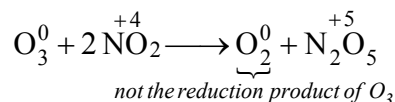
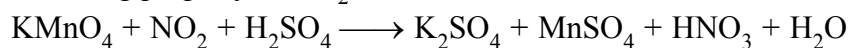
- NO : (i) It burns :  $\text{NO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{NO}_2$
- (ii) It supports combustion also for molten sulphur and hot phosphorous.  
 $\text{S} + 2\text{NO} \longrightarrow \text{SO}_2 + \text{N}_2$   
 $2\text{P} + 5\text{NO} \longrightarrow \text{P}_2\text{O}_5 + \frac{5}{2} \text{N}_2$
- (iii) It is being absorbed by  $\text{FeSO}_4$  solution.
- (iv) It is having reducing property.  
 $\text{KMnO}_4 + \text{NO} + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{HNO}_3 + \text{H}_2\text{O}$   
 $\text{HOCl} + \text{NO} + \text{H}_2\text{O} \longrightarrow \text{HNO}_3 + \text{HCl}$
- (v) NO shows oxidising property also.  
 $\text{SO}_2 + 2\text{NO} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + \text{N}_2\text{O}$   
 $\text{H}_2\text{S} + 2\text{NO} \longrightarrow \text{H}_2\text{O} + \text{S}\downarrow + \text{N}_2\text{O}$   
 $3\text{SnCl}_2 + 2\text{NO} + 6\text{HCl} \longrightarrow 3\text{SnCl}_4 + 2\text{NH}_2\text{OH}$   
 (Used for  $\text{NH}_2\text{OH}$  preparation)
- (vi) NO combines with  $\text{X}_2$  ( $\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{F}_2$ ) to produce NO X  
 $2\text{NO} + \text{X}_2 \longrightarrow 2\text{NOX}$

$\text{N}_2\text{O}_3$  : No more properties.

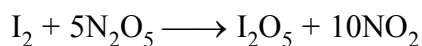
- $\text{NO}_2$  : (1) It is having oxidising property.  
 $\text{S} + \text{NO}_2 \longrightarrow \text{SO}_2 + \text{NO}$   
 $\text{P} + \text{NO}_2 \longrightarrow \text{P}_2\text{O}_5 + \text{NO}$   
 $\text{C} + \text{NO}_2 \longrightarrow \text{CO}_2 + \text{NO}$   
 $\text{SO}_2 + \text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + \text{NO}$   
 $\text{H}_2\text{S} + \text{NO}_2 \longrightarrow \text{H}_2\text{O} + \text{S}\downarrow + \text{NO}$   
 $\text{CO} + \text{NO}_2 \longrightarrow \text{CO}_2 + \text{NO}$

NO not formed :  $2\text{KI} + 2\text{NO}_2 \longrightarrow \text{I}_2 + 2\text{KNO}_2$

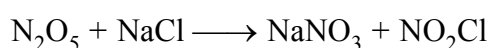
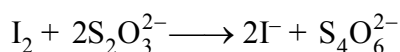
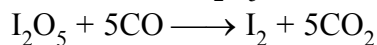
- (2) Reducing property of  $\text{NO}_2$ .



$\text{N}_2\text{O}_5$  :



$\text{I}_2\text{O}_5$  is used for the estimation of CO



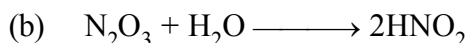
This proves that  $\text{N}_2\text{O}_5$  is consisting of ion pair of  $\text{NO}_2^+$  &  $\text{NO}_3^-$

## OXOACIDS OF NITROGEN

$\text{H}_2\text{N}_2\text{O}_2$  (hyponitrous acid),  $\text{HNO}_2$  (nitrous acid) and  $\text{HNO}_3$  (nitric acid). Amongst them  $\text{HNO}_3$  is the most important.

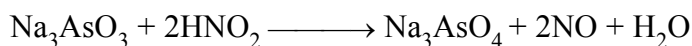
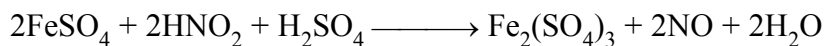
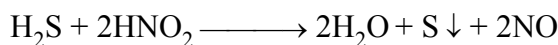
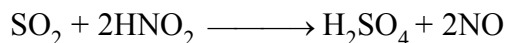
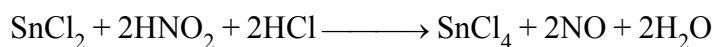
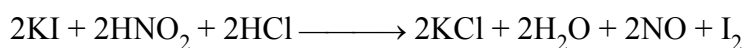
NITROUS ACID ( $\text{HNO}_2$ )

## Preparation

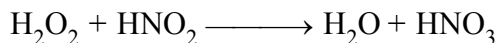
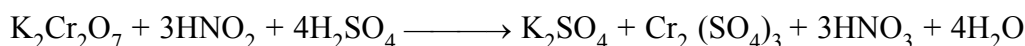
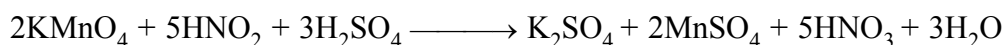
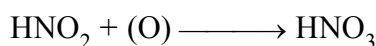


## Properties

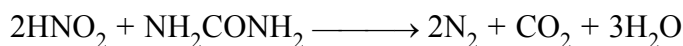
- (a) **Oxidising property** : Because of its easy oxidation to liberate nascent oxygen, it acts as a strong oxidant
- $$2\text{HNO}_2 \longrightarrow \text{H}_2\text{O} + 2\text{NO} + (\text{O})$$



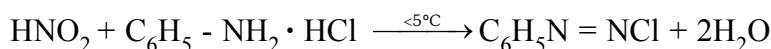
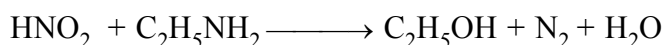
- (b) **Reducing property** : Nitrous acid also acts as a reducing agent as it can be oxidised into nitric acid.



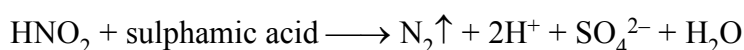
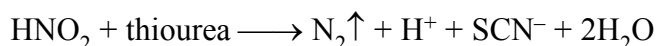
- (c) **Reaction with  $\text{NH}_3$  /  $-\text{NH}_2$  compounds** :



Urea

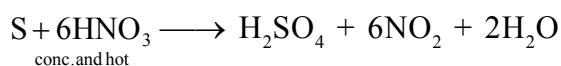


Benzene diazonium chloride





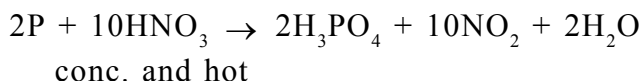
(1) Sulphur is oxidised to sulphuric acid



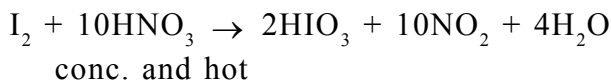
(2) Carbon is oxidised to carbonic acid



(3) Phosphorus is oxidised to orthophosphoric acid.



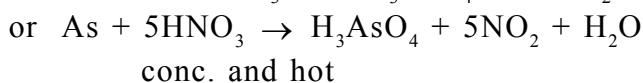
(4) Iodine is oxidised to iodic acid



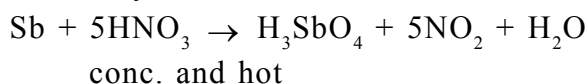
**(ii) Oxidation of metalloids**

Metalloids like non-metals also form oxyacids of highest oxidation state.

(1) Arsenic is oxidised to arsenic acid



(2) Antimony is oxidised to antimonic acid

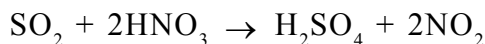


(3) Tin is oxidised to meta-stannic acid.

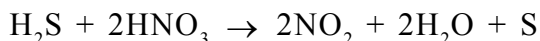


**(iii) Oxidation of Compounds:**

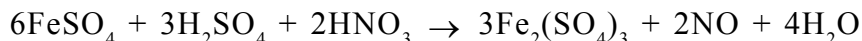
(1) Sulphur dioxide is oxidised to sulphuric acid



(2) Hydrogen sulphide is oxidised to sulphur



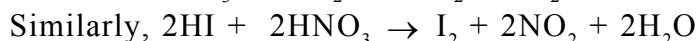
(3) Ferrous sulphate is oxidised to ferric sulphate in presence of  $\text{H}_2\text{SO}_4$



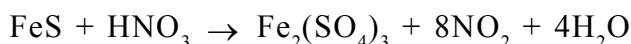
(4) Iodine is liberated from KI.



(5) HBr, HI are oxidised to  $\text{Br}_2$  and  $\text{I}_2$ , respectively.



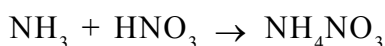
(6) Ferrous sulphide is oxidised to ferric sulphate



(7) Stannous chloride is oxidised to stannic chloride in presence of HCl.



Hydroxylamine





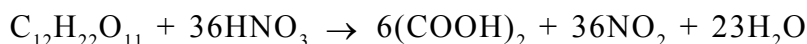
## (8) Oxidation of organic compounds .

Sawdust catches fire when nitric acid is poured on it.

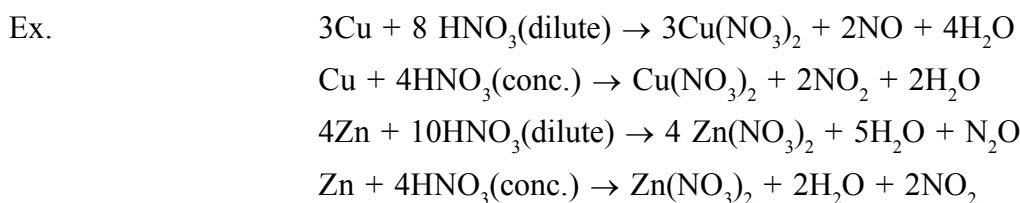
Turpentine oil bursts into flames when treated with fuming nitric acid.

Toluene is oxidised to benzoic acid with dil.  $\text{HNO}_3$ .

Cane sugar is oxidised to oxalic acid.

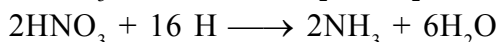
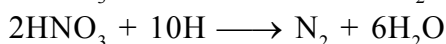
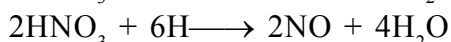
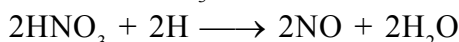
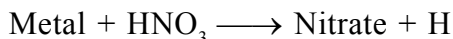


(ii) **Reaction with metal** concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. Au & Pt dissolve in aqua regia a mixture of 25% conc.  $\text{HNO}_3$  & 75% conc. HCl. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.



Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Armstrong postulated that primary action of nitric acid is to produce hydrogen in the nascent form. Before this hydrogen is allowed to escape, it reduces the nitric acid into number of products like  $\text{NO}_2$ , NO,  $\text{N}_2\text{O}$ ,  $\text{N}_2$  or  $\text{NH}_3$  according to the following reactions:



The progress of the reaction is controlled by a number of factors :

- the nature of the metal,
- the concentration of the acid,
- the temperature of the reaction,
- the presence of other impurities.

Concentration of nitric acid	Metal	Main Products
Very dilute $\text{HNO}_3$ (6%)	Mg, Mn	$\text{H}_2$ + Metal nitrate
	Fe, Zn, Sn	$\text{NH}_4\text{NO}_3$ + metal nitrate + $\text{H}_2\text{O}$
	Pb, Cu, Ag, Hg	NO + metal nitrate + $\text{H}_2\text{O}$

Dilute  $\text{HNO}_3$  (20%) Fe, Zn  $\text{N}_2\text{O} + \text{metal nitrate} + \text{H}_2\text{O}$

-----  
Sn  $\text{NH}_4\text{NO}_3 + \text{Sn}(\text{NO}_3)_2$

-----  
Conc.  $\text{HNO}_3$  (70%) Zn, Fe, Pb, Cu, Ag  $\text{NO}_2 + \text{metal nitrate} + \text{H}_2\text{O}$

-----  
Sn  $\text{NO}_2 + \text{H}_2\text{SnO}_3$   
Metastannic acid

#### Action on Proteins :

Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow. This property is utilized for the test of proteins.

**Uses :** The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the **pickling of stainless steel**, etching of metals and as an oxidiser in rocket fuels.

**Pickling** is a metal surface treatment used to remove impurities, such as stains, inorganic contaminants, rust or scale from ferrous metals, copper, precious metals and aluminium alloys. A solution called pickle liquor, which contains strong acids, is used to remove surface impurities.

### ALLOTROPIC FORMS OF PHOSPHORUS

#### Comparison between White and Red Phosphorus

Property	White phosphorus	Red phosphorus
Physical state	Soft waxy solid.	Brittle powder.
Colour	White when pure. Attains yellow colour on standing.	Red.
Odour	Garlic	Odourless.
Solubility in water	Insoluble.	insoluble
Solubility in $\text{CS}_2$	Soluble.	Insoluble.
Physiological action	Poisonous.	Non-poisonous.
Chemical activity	Very active.	Less active.
Stability	Unstable.	Stable.
Phosphorescence	Glow in dark	Does not glow in dark.
Molecular formula	$\text{P}_4$	Complex polymer.

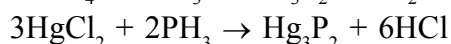
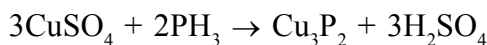


**Physical Properties :**

- (i) It is a colourless gas with rotten fish smell and is highly poisonous.
- (ii) It explodes in contact with traces of oxidising agents like  $\text{HNO}_3$ ,  $\text{Cl}_2$  and  $\text{Br}_2$  vapours.
- (iii) It is slightly soluble in water but soluble in  $\text{CS}_2$ . The solution of  $\text{PH}_3$  in water decomposes in presence of light giving red phosphorus and  $\text{H}_2$ .

**Chemical Properties :**

- (i) It absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.



Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,



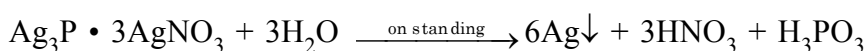
- (ii)  $\text{PH}_3 + \text{O}_2 \xrightarrow{150^\circ} \text{P}_2\text{O}_5 + \text{H}_2\text{O}$

- (iii)  $\text{PH}_3 + 3\text{Cl}_2 \longrightarrow \text{PCl}_3 + 3\text{HCl}$

- (iv)  $\text{PH}_3 + 4\text{N}_2\text{O} \xrightarrow[\text{sparking}]{\text{electrical}} \text{H}_3\text{PO}_4 + 4\text{N}_2$

- (v)  $\text{PH}_3 + 6\text{AgNO}_3 \longrightarrow [\text{Ag}_3\text{P} \cdot 3\text{AgNO}_3\downarrow] + 3\text{HNO}_3$

yellow ppt.



Black ppt.

- (vi)  $\text{PH}_3 + 4\text{HCHO} + \text{HCl} \longrightarrow [\text{P}(\text{CH}_2\text{OH})_4]^+\text{Cl}^-$

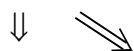
white/colourless solid

which is used for making

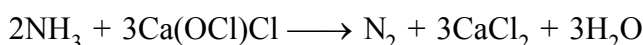
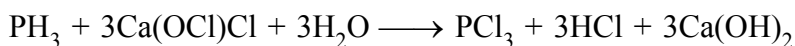
fire-proof cotton fabrics

**Note :**

Like  $\text{NH}_3$ ,  $\text{PH}_3$  also can form addition product.



$\text{PH}_3$  can be absorbed by  $\text{Ca}(\text{OCl})\text{Cl}$ .

**Uses :**

(i) The spontaneous combustion of phosphine is technically used in Holme's signals. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.

(ii) It is also used in smoke screens.

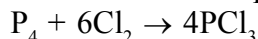
### PHOSPHORUS HALIDES

Phosphorus forms two types of halides,  $PX_3$  ( $X = F, Cl, Br, I$ ) and  $PX_5$  ( $X = F, Cl, Br$ ).

#### PHOSPHORUS TRICHLORIDE

##### Preparation

- (i) By passing dry chlorine over heated white phosphorus.



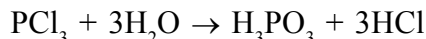
- (ii) By the action of thionyl chloride with white phosphorus.



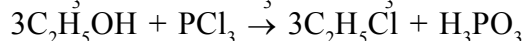
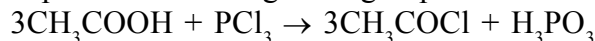
##### Properties

- (i) It is a colourless oily liquid

- (ii) Hydrolyses in the presence of moisture.



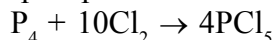
- (iii) It reacts with organic compounds containing  $-OH$  group such as  $CH_3COOH$ ,  $C_2H_5OH$ .



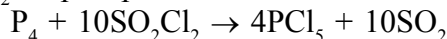
#### PHOSPHORUS PENTACHLORIDE

##### Preparation

- (i) By the reaction of white phosphorus with excess of dry chlorine.



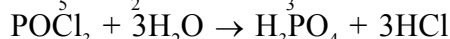
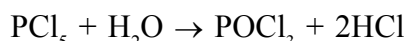
- (ii) By the action of  $SO_2Cl_2$  on phosphorus.



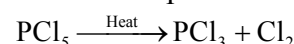
##### Properties :

- (i)  $PCl_5$  is a yellowish white powder

- (ii) It hydrolyses in moist air to  $POCl_3$  and finally gets converted to phosphoric acid.



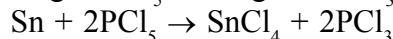
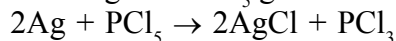
- (iii) When heated, it sublimes but decomposes on stronger heating.



- (iv) It reacts with organic compounds containing  $-OH$  group converting them to chloro derivatives.



- (v) Finely divided metals on heating with  $PCl_5$  give corresponding chlorides.

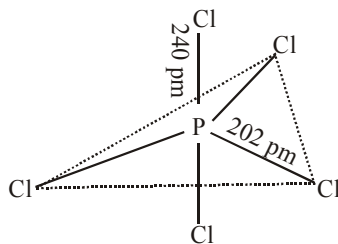


##### Uses :

It is used in the synthesis of some organic compounds, e.g.,  $C_2H_5Cl$ ,  $CH_3COCl$ .

##### Note :

In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown. The three equatorial P-Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.



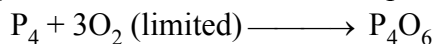
In the solid state it exists as an ionic solid,  $[PCl_4]^+[PCl_6]^-$  in which the cation,  $[PCl_4]^+$  is tetrahedral and the anion,  $[PCl_6]^-$  is octahedral.

**OXIDES OF PHOSPHORUS**

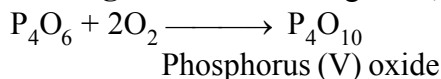
It forms two important oxides which exist in dimeric forms.

**PHOSPHORUS TRIOXIDE (P<sub>4</sub>O<sub>6</sub>)****Preparation**

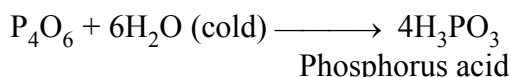
Phosphorus trioxides is formed when phosphorus is burnt in a limited supply of air and inert atmosphere.

**Properties**

(a) **Heating in air :** On heating in air, it forms phosphorus pentoxide.



(b) **Action of water :** It dissolves in cold water to give phosphorus acid.



It is, therefore, considered as anhydride of phosphorus acid.

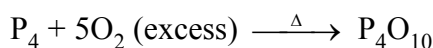
**Note:** With hot water, it gives phosphoric acid and inflammable phosphine.

**Structure**

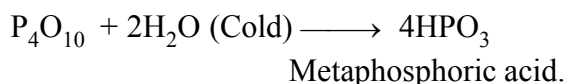
- Each atom of phosphorus in P<sub>4</sub>O<sub>6</sub> is present at the corner of a tetrahedron
- Each phosphorus atom is covalently bonded to three oxygen atoms and each oxygen atom is bonded to two phosphorus atoms.
- It is clear from the structure that the six oxygen atoms lie along the edges of the tetrahedron of P atoms.

**PHOSPHORUS (V) OXIDE (P<sub>4</sub>O<sub>10</sub>)**

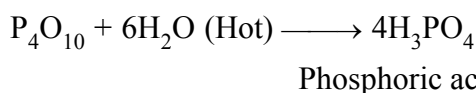
**Preparation :** It is prepared by heating white phosphorus in excess of air.

**Properties**

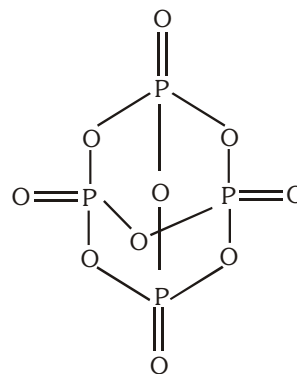
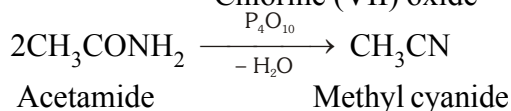
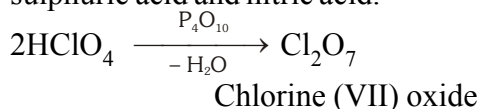
- It is snowy white solid.
- Action with water :** It readily dissolves in cold water forming metaphosphoric acid.



With hot water it gives phosphoric acid.



- Dehydrating nature :** Phosphorus pentoxide has strong affinity for water and, therefore, acts as a powerful dehydrating agent. It extracts water from many inorganic and organic compounds.
- P<sub>4</sub>O<sub>10</sub> is a very strong dehydrating agent and extracts water from many compounds including sulphuric acid and nitric acid.



**Structure**

- (a) Its structure is similar to that of  $P_4O_6$ .
- (b) In addition, each phosphorus atom forms a double bond with oxygen atom as shown in figure.

**OXOACIDS OF PHOSPHORUS :**

The important oxoacids of phosphorus with their formulae, methods of preparation and the presence of some characteristic bonds in their structures are given in a table.

**Oxoacids of Phosphorus**

Name	Formula	Oxidation state of Phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorus (Phosphinic)	$H_3PO_2$	+ 1	One P — OH Two P — H One P = O	white $P_4$ + alkali
Orthophosphorous (Phosphonic)	$H_3PO_3$	+ 3	Two P — OH One P — H One P = O	$P_2O_3$ + $H_2O$
Pyrophosphorous	$H_4P_2O_5$	+ 3	Two P — OH Two P — H Two P = O	$PCl_3$ + $H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+ 4	Four P — OH Two P = O One P — P	red $P_4$ + alkali
Orthophosphoric	$H_3PO_4$	+ 5	Three P — OH One P = O	$P_4O_{10}$ + $H_2O$
Pyrophosphoric	$H_4P_2O_7$	+ 5	Four P — OH Two P = O One P — O — P	heat phosphoric acid
Metaphosphoric*	$(HPO_3)_n$	+ 5	Three P — OH Three P = O Three P — O — P	phosphorous acid + $Br_2$ , heat in a sealed tube

**STRUCTURE OF OXOACID :**

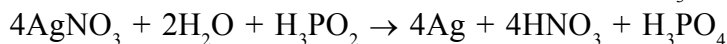
In oxoacids phosphorus is tetrahedrally surrounded by other atoms. All these acids contain at least one P=O bond and one P—OH bond. The oxoacids in which phosphorus has lower oxidation state (less than +5) contain, in addition to P=O and P—OH bonds, either P—P (e.g., in  $H_4P_2O_6$ ) or P—H (e.g., in  $H_3PO_2$ ) bonds but not both.  $H_3PO_3$  and  $H_3PO_2$  are diacidic and monobasic respectively.

**Note :-**

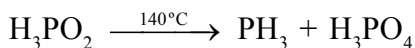
(i) These acids in +3 oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states. For example, phosphorous acid on heating disproportionates to give orthophosphoric acid (or phosphoric acid) and phosphine.



(ii) The acids which contain P–H bond have strong reducing properties. Thus, hypophosphorous acid is a good reducing agent as it contains two P–H bonds and reduces,  $\text{AgNO}_3$  to metallic silver.

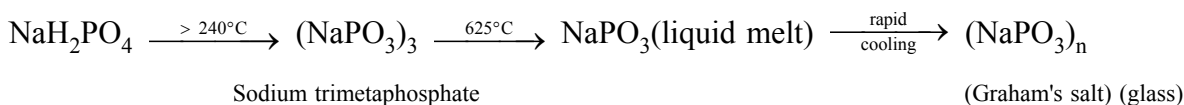


### Heating Effect :



### Graham salt

Graham's salt is the best known of these long chain polyphosphates, and is formed by quenching molten  $\text{NaPO}_3$ . Graham's salt is soluble in water. These solutions give precipitates with metal ions such as  $\text{Pb}^{2+}$  and  $\text{Ag}^+$  but not with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Graham's salt is sold commercially under the trade name Calgon. In industry it is incorrectly called sodium hexametaphosphate crystallizing. It is widely used for softening water.







### ❑ Physical Properties

- (i) Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal.
- (ii) Polonium is radioactive and is short lived (Half-life 13.8 days).
- (iii) All these elements exhibit allotropy.
- (iv) The melting and boiling points increase with an increase in atomic number down the group. The large difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exists as diatomic molecule ( $O_2$ ) whereas sulphur exists as polyatomic molecule ( $S_8$ ).

### ❑ Chemical Properties

#### Oxidation states and trends in chemical reactivity :

- (i) The stability of -2 oxidation state decreases down the group. Polonium hardly shows -2 oxidation state.
- (ii) Electronegativity of oxygen is very high, it shows only negative oxidation state as -2 except Oxygen shows oxidation states of +2 and +1 in oxygen fluorides  $OF_2$  and  $O_2F_2$  respectively.
- (iii) Elements of the group exhibit +2, +4, +6 oxidation states but +4 and +6 are more common.
- (iv) Sulphur, selenium and tellurium usually show +4 oxidation state in their compounds with oxygen and +6 with fluorine.
- (v) The stability of +6 oxidation state decreases down the group and stability of +4 oxidation state increases (inert pair effect).
- (vi) Bonding in +4 and +6 oxidation states is primarily covalent.

### ❑ Anomalous behaviour of oxygen

The anomalous behaviour of oxygen, like other members of p-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in  $H_2O$  which is not found in  $H_2S$ . The absence of d orbitals in oxygen limits its covalency to four and in practice, rarely exceeds two. On the other hand, in case of other elements of the group, the valence shells can be expanded and covalency exceeds four.

### (I) Reactivity with hydrogen:

- (i) All the elements of Group 16 form hydrides of the type  $H_2E$  ( $E = O, S, Se, Te, Po$ ).
- (ii) Their acidic character increases from  $H_2O$  to  $H_2Te$ . The increase in acidic character can be explained in terms of decrease in bond enthalpy for the dissociation of H-E bond down the group. Owing to the decrease in enthalpy for the dissociation of H-E bond down the group, the thermal stability of hydrides also decreases from  $H_2O$  to  $H_2Po$ .
- (iii) All the hydrides except water possess reducing property and this character increases from  $H_2S$  to  $H_2Te$ .

## Properties of Hydrides of Group 16 Elements

Property	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te
m.p./K	273	188	208	222
b.p./K	373	213	232	269
H—E distance /pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H / \text{kJ mol}^{-1}$	-286	-20	73	100
$\Delta_{\text{diss}} H (\text{H} - \text{E}) / \text{kJ mol}^{-1}$	463	347	276	238
Dissociation constant <sup>a</sup>	$1.8 \times 10^{-16}$	$1.3 \times 10^{-7}$	$1.3 \times 10^{-4}$	$2.3 \times 10^{-3}$

**(II) Reactivity with oxygen:**

- All these elements form oxides of the EO<sub>2</sub> and EO<sub>3</sub> types where E = S, Se, Te or Po.
- Ozone (O<sub>3</sub>) and sulphur dioxide (SO<sub>2</sub>) are gases while selenium dioxide (SeO<sub>2</sub>) is solid.
- Reducing property of dioxide decreases from SO<sub>2</sub> to TeO<sub>2</sub>; SO<sub>2</sub> is reducing while TeO<sub>2</sub> is an oxidising agent.
- Besides EO<sub>2</sub> type, sulphur, selenium and tellurium also form EO<sub>3</sub> type oxides (SO<sub>3</sub>, SeO<sub>3</sub>, TeO<sub>3</sub>). Both types of oxides are acidic in nature.

**(III) Reactivity towards the halogens:**

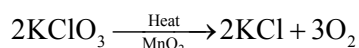
- Elements of Group 16 form a large number of halides of the type, EX<sub>6</sub>, EX<sub>4</sub> and EX<sub>2</sub> where E is an element of the group and X is a halogen.
- The stability of the halides decreases in the order F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>.
- Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride, SF<sub>6</sub> is exceptionally stable for steric reasons.

Amongst tetrafluorides, SF<sub>4</sub> is a gas, SeF<sub>4</sub> a liquid and TeF<sub>4</sub> a solid. These fluorides have *sp*<sup>3</sup>*d* hybridisation and thus, have trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as see-saw geometry. All elements except oxygen form dichlorides and dibromides (because they form oxides). These dihalides are formed by *sp*<sup>3</sup> hybridisation and thus, have tetrahedral structure. The well known monohalides are dimeric in nature. Examples are S<sub>2</sub>F<sub>2</sub>, S<sub>2</sub>Cl<sub>2</sub>, S<sub>2</sub>Br<sub>2</sub>, Se<sub>2</sub>Cl<sub>2</sub> and Se<sub>2</sub>Br<sub>2</sub>. These dimeric halides undergo disproportionation as given below :  $2\text{Se}_2\text{Cl}_2 \rightarrow \text{SeCl}_4 + 3\text{Se}$

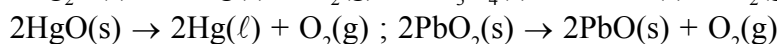
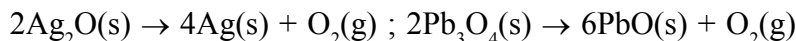
## DIOXYGEN

## (a) Laboratory method

(i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.



(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.



(iii) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.

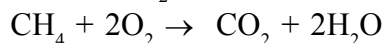
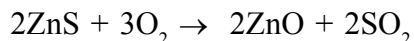
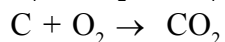
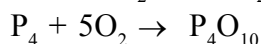
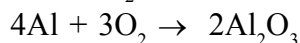
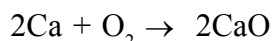


(b) **Large scale preparation** : It can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

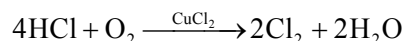
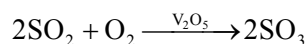
(c) **Industrially method** : Dioxygen is obtained from air by first removing carbon dioxide and water vapour and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

**Properties**

- (i) Dioxygen is a colourless and odourless gas.
- (ii) Its solubility in water is to the extent of  $3.08 \text{ cm}^3$  in  $100 \text{ cm}^3$  water at 293 K which is just sufficient for the vital support of marine and aquatic life.
- (iii) It liquefies at 90 K and freezes at 55 K.
- (iv) Oxygen atom has three stable isotopes:  $^{16}\text{O}$ ,  $^{17}\text{O}$  and  $^{18}\text{O}$ . Molecular oxygen,  $\text{O}_2$  is unique in being paramagnetic inspite of having even number of electrons.
- (v) Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases. Its combination with other elements is often strongly exothermic which helps in sustaining the reaction. However, to initiate the reaction, some external heating is required as bond dissociation enthalpy of oxygen-oxygen double bond is high ( $493.4 \text{ kJ mol}^{-1}$ ). Some of the reactions of dioxygen with metals, non-metals and other compounds are as follows :



Some compounds are catalytically oxidised. For example,



**Uses:** (i) It's importance in normal respiration and combustion processes, oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel.

(ii) Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering.

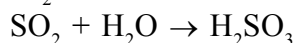
(iii) The combustion of fuels, e.g., hydrazines in liquid oxygen, provides tremendous thrust in rockets.

## SIMPLE OXIDES

A binary compound of oxygen with another element is called oxide. In many cases one element forms two or more oxides. The oxides vary widely in their nature and properties. Oxides can be simple (e.g., MgO, Al<sub>2</sub>O<sub>3</sub>) or mixed (Pb<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>).

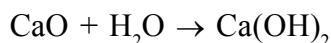
**Types of simple oxide :** Simple oxides can be classified on the basis of their acidic, basic or amphoteric character.

**Acidic oxide :** An oxide that combines with water to give an acid is termed acidic oxide (e.g., SO<sub>2</sub>, Cl<sub>2</sub>O<sub>7</sub>, CO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>). For example, SO<sub>2</sub> combines with water to give H<sub>2</sub>SO<sub>3</sub>, an acid.

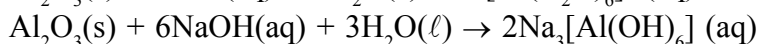
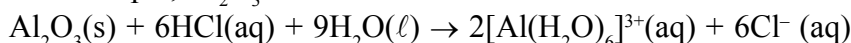


As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g., Mn<sub>2</sub>O<sub>7</sub>, CrO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>).

**Basic oxide :** The oxides which give a base with water are known as basic oxides (e.g., Na<sub>2</sub>O, CaO, BaO). In general, metallic oxides are basic. For example, CaO combines with water to give Ca(OH)<sub>2</sub>, a base.

**Amphoteric oxide :**

Some metallic oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides. They react with acids as well as alkalies. For example, Al<sub>2</sub>O<sub>3</sub> reacts with acids as well as alkalies.

**Neutral oxide:**

There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N<sub>2</sub>O.

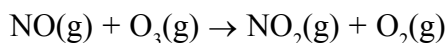
**OZONE**

(i) Ozone is an allotropic form of oxygen and is diamagnetic.

(ii) It is too reactive to remain for long in the atmosphere at sea level. At a height of about 20 kilometres, it is formed from atmospheric oxygen in the presence of sunlight. This ozone layer protects the earth's surface from an excessive concentration of ultraviolet (UV) radiations.

**Threats to ozone layer**

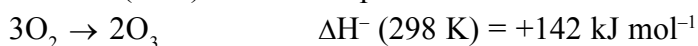
(i) Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.



(ii) Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

**Preparation**

When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonised oxygen.

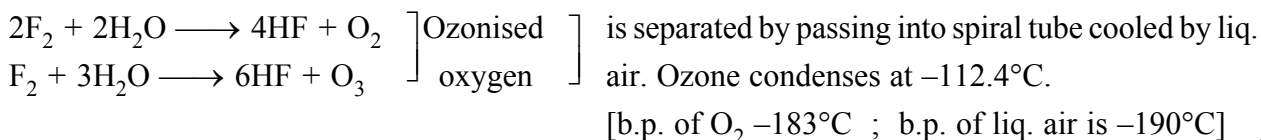


Since the formation of ozone from oxygen is an **endothermic** process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition. If concentration of ozone greater than 10 percent is required, a battery of ozonisers can be used, and pure ozone (b.p. -112.4°C) can be condensed in a vessel surrounded by liquid oxygen.

**Ques.** Ozone is thermodynamically unstable with respect to oxygen. Explain ?

**Sol.** Because its decomposition into oxygen results in the liberation of heat ( $\Delta H$  is negative) and an increase in entropy ( $\Delta S$  is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change ( $\Delta G$ ) for its conversion into oxygen.

**Note :**



**Properties**

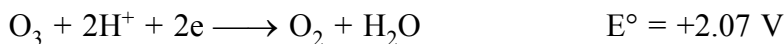
- (i) Pure ozone is a pale blue gas, dark blue liquid and violet-black solid.
- (ii) Ozone has a characteristic fishy smell and in small concentrations it is harmless.

**Toxic effect :**

- (a) Toxic enough (more toxic than KCN). It's intense blue colour is due to the absorption of red light.
- (b) However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

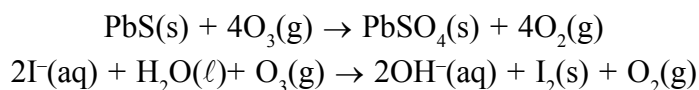
**Oxidizing properties**

It is one of best oxidising agent, in acid solution, its standard, reduction potential value is 2.07 V.

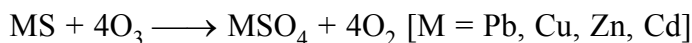


It is next to  $F_2$ . [above 2.07 V, only  $F_2$ ,  $F_2O$  are there]

It is not really surprising, therefore, high concentrations of ozone can be dangerously explosive. Due to the ease with which it liberates atoms of nascent oxygen ( $O_3 \rightarrow O_2 + O$ ), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.

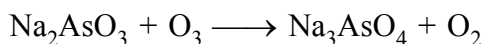
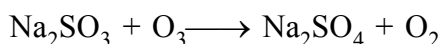


- (i) Metal Sulphides to Sulphates.

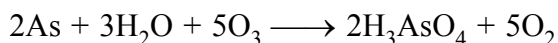
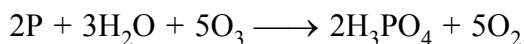
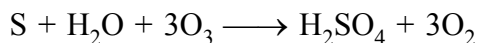


- (ii)  $2HX + O_3 \longrightarrow X_2 + H_2O + O_2 \quad [X = Cl, Br, I]$

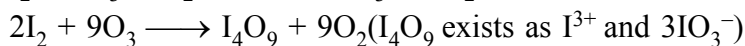
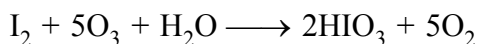
- (iii)  $NaNO_2 + O_3 \longrightarrow NaNO_3 + O_2$

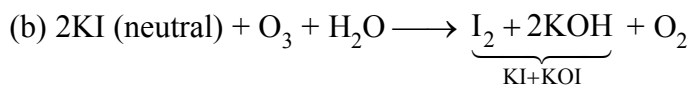
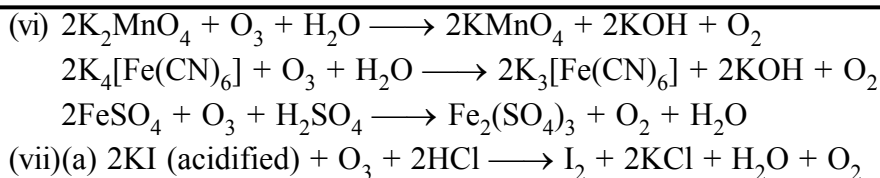


- (iv) Moist S, P, As +  $O_3 \Rightarrow$

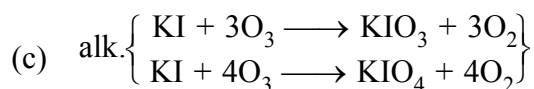
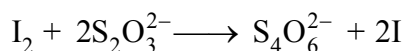
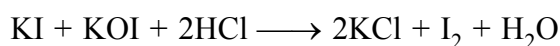


- (v) Moist  $I_2 \longrightarrow HIO_3$  whereas dry iodine  $\longrightarrow I_4O_9$  (yellow)

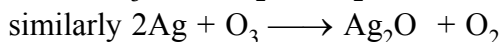
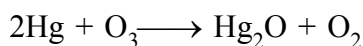




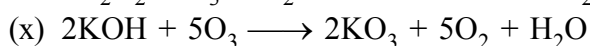
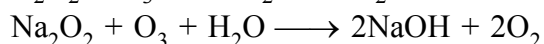
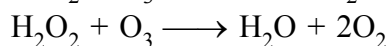
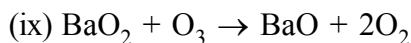
}  $\text{O}_3$  is estimated by this reaction



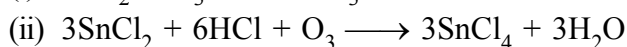
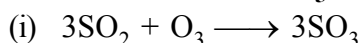
(viii) Hg loses its fluidity (tailing of Hg)



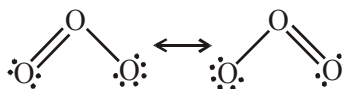
Brown



**In all above reaction  $\text{O}_3$  gives up  $\text{O}_2$  but some reactions are there which consumes all O-atom.**



**Bonding in ozone :** In ozone the two oxygen-oxygen bond lengths in the ozone molecule are identical (128 pm) and the molecule is angular as expected with a bond angle of about  $117^\circ$ . It is a resonance hybrid of two main forms given below:



**Absorbent :** (i) Turpentine oil (ii) Oil of cinnamon

**Quantitative method for the estimating on Ozone :** Ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate.

**Uses :** (i) Sterilising water

(ii) Detection of position of the double bond in the unsaturated compound.

(iii) It is used as a germicide, disinfectant and for sterilising water.

(iv) It is also used for bleaching oils, ivory, flour, starch, etc.

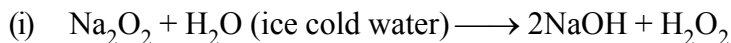
(v) It acts as an oxidising agent in the manufacture of potassium permanganate.

## □ HYDROGEN PEROXIDE (H<sub>2</sub>O<sub>2</sub>)

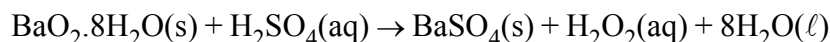
Hydrogen peroxide is an important chemical used in pollution control treatment of domestic and industrial effluents.

### Preparation

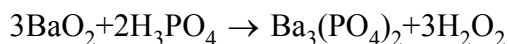
It can be prepared by the following methods.



(ii) Acidifying barium peroxide and removing excess water by evaporation under reduced pressure gives hydrogen peroxide.

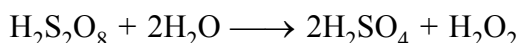
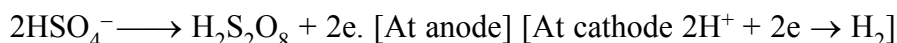
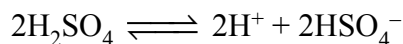


Instead of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> is added now-a-days because H<sub>2</sub>SO<sub>4</sub> catalyses the decomposition of H<sub>2</sub>O<sub>2</sub> whereas H<sub>3</sub>PO<sub>4</sub> favours to restore it.

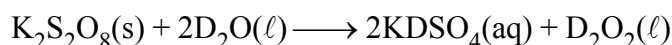


and  $\text{Ba}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{BaSO}_4 + 2\text{H}_3\text{PO}_4$  (reused again)

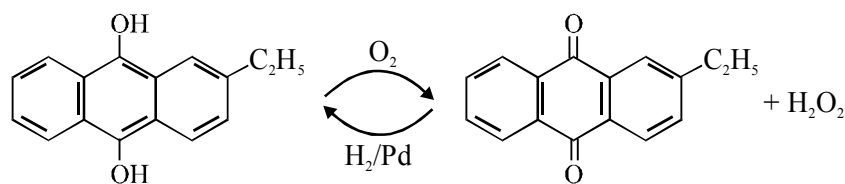
(iii) Peroxodisulphate, obtained by electrolytic oxidation of acidified sulphate solutions at high current density, on hydrolysis yields hydrogen peroxide.



This method is now used for the laboratory preparation of D<sub>2</sub>O<sub>2</sub>.



(iii) Industrially it is prepared by the autooxidation of 2-alkylanthraquinols.



2-ethylanthraquinol

2-ethylanthraquinone

In this case 1% H<sub>2</sub>O<sub>2</sub> is formed. It is extracted with water and concentrated to ~30% (by mass) by distillation under reduced pressure. It can be further concentrated to ~85% by careful distillation under low pressure. The remaining water can be frozen out to obtain pure H<sub>2</sub>O<sub>2</sub>.

### ◆ Physical Properties

In the pure state H<sub>2</sub>O<sub>2</sub> is an almost colourless (very pale blue) liquid. Its important physical properties are given in Table. H<sub>2</sub>O<sub>2</sub> is miscible with water in all proportions and forms a hydrate H<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O (mp 221K). A 30% solution of H<sub>2</sub>O<sub>2</sub> is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30% H<sub>2</sub>O<sub>2</sub> solution will give 100 mL of oxygen at STP. Commercially marketed sample is 10 V, which means that the sample contains 3% H<sub>2</sub>O<sub>2</sub>.

30% (w/v) or "100 V" H<sub>2</sub>O<sub>2</sub> solution is called **per hydrol**.

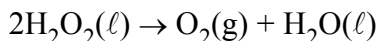


**Problem**

Calculate the strength of 10 volume solution of hydrogen peroxide.

**Solution**

10 volume solution of  $\text{H}_2\text{O}_2$  means that 1L of this  $\text{H}_2\text{O}_2$  solution will give 10 L of oxygen at STP



On the basis of above equation 22.7 L of  $\text{O}_2$  is produced from 68 g  $\text{H}_2\text{O}_2$  at STP 10 L of  $\text{O}_2$  at STP is produced from

$$\frac{68 \times 10}{22.7} \text{ g} = 29.9 \text{ g} \quad 30 \text{ g } \text{H}_2\text{O}_2$$

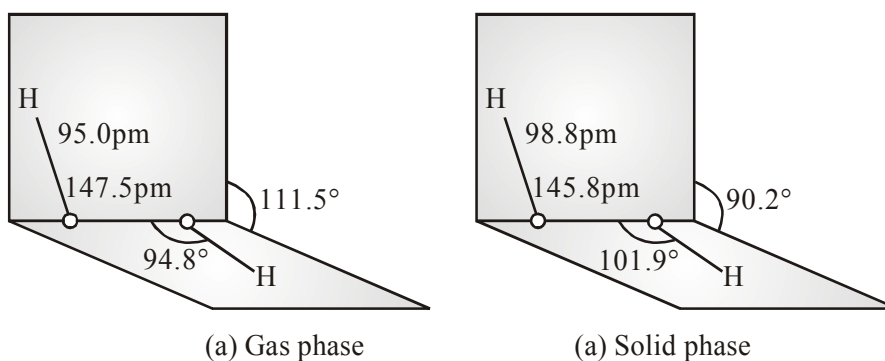
Therefore, strength of  $\text{H}_2\text{O}_2$  in 10 volume  $\text{H}_2\text{O}_2$  solution = 30 g/L = 3%  $\text{H}_2\text{O}_2$  solution

**Physical Properties of Hydrogen Peroxide**

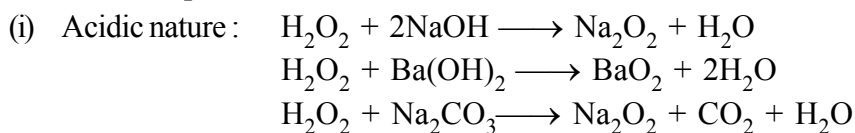
Melting point/K	272.4	Density (liquid at 298K)/g cm <sup>-3</sup>	1.44
Boiling point (extrapolated)/K	423	Viscosity (290 K)/centipoise	1.25
Vapour pressure (298K) mmHg	1.9	Dielectric constant (298K)/C <sup>2</sup> /N m <sup>2</sup>	70.7
Density (solid at 268.5K)/g cm <sup>-3</sup>	1.64	Electrical conductivity (298K)/Ω <sup>-1</sup> cm <sup>-1</sup>	$5.1 \times 10^{-8}$

**Structure**

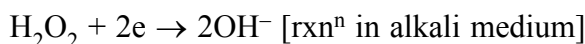
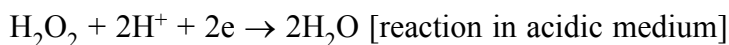
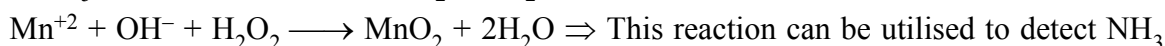
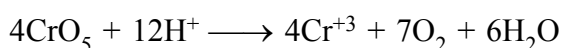
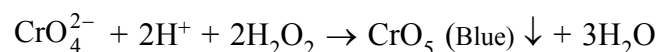
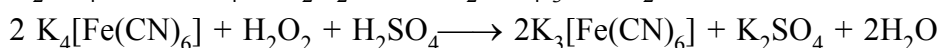
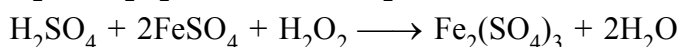
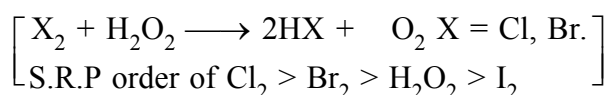
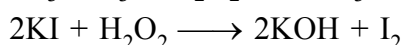
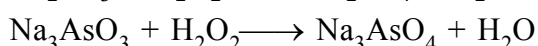
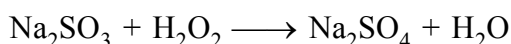
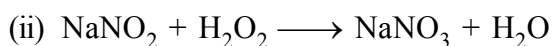
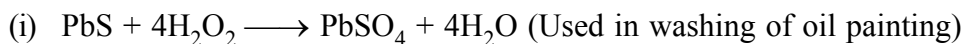
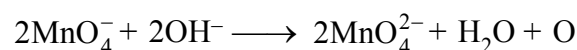
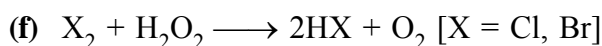
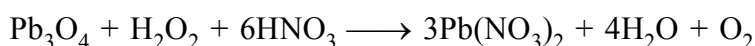
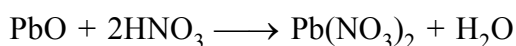
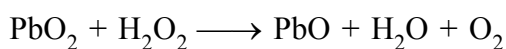
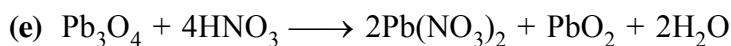
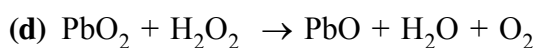
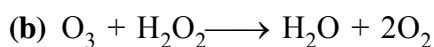
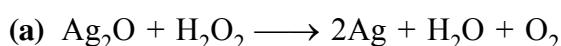
Hydrogen peroxide has a non-planar structure. The molecular dimensions in the gas phase and solid phase are shown in Fig.



**Fig.** (a)  $\text{H}_2\text{O}_2$  structure in gas phase, dihedral angle is  $111.5^\circ$ . (b)  $\text{H}_2\text{O}_2$  structure in solid phase at 110K, dihedral angle is  $90.2^\circ$ .

**Chemical Properties:**

(ii) It is oxidant as well as reductant.

**Oxidising Properties:****Reducing properties:**



- (ii) It is used to manufacture chemicals like sodium perborate and per-carbonate, which are used in high quality detergents.
- (iii) It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.
- (iv) It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.
- (v) As a rocket propellant:  

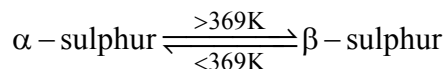
$$\text{NH}_2\text{-NH}_2 + 2\text{H}_2\text{O}_2 \longrightarrow \text{N}_2 + 4\text{H}_2\text{O}$$
 [highly exothermic and large increase in volume]
- (vi) In detection of  $\text{Cr}^{+3}$ ,  $\text{Ti}^{+4}$  etc.  

$$\text{Ti}(\text{SO}_4)_2 + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow \text{H}_2\text{TiO}_4 + 2\text{H}_2\text{SO}_4$$

Yellow or orange  
Pertitanic acid
- (vii) Nowadays it is also used in Environmental (Green) Chemistry. For example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.

### ALLOTROPIC FORMS OF SULPHUR

Sulphur forms numerous allotropes of which the yellow rhombic ( $\alpha$ -sulphur) and monoclinic ( $\beta$ -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.



At 369 K both the forms are stable. This temperature is called transition temperature.

#### Note: Viscosity of 'S' with temperature :

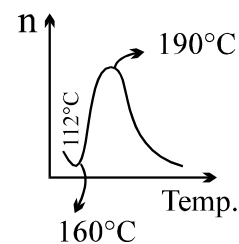
m.p. of 'S'  $\longrightarrow$  112.8°C.

$> 112.8^\circ\text{C}$  to  $160^\circ\text{C} \Rightarrow$  slow decreases due to

$\text{S}_8$  rings slip and roll over one another easily.

$> 160^\circ\text{C}$ , increases sharply due to breaking of

$\text{S}_8$  rings into chains and polymerises into large size chain.



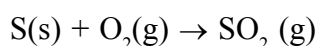
#### Amorphous forms are

- (i) Plastic sulphur      (ii) Milk of sulphur      (iii) Colloidal sulphur

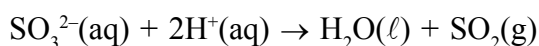
### SULPHUR DIOXIDE

#### Preparation

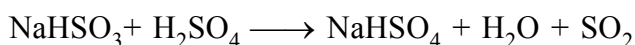
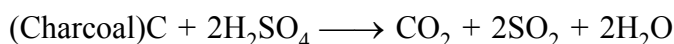
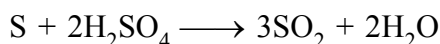
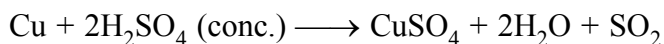
Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:



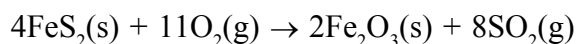
**laboratory method** by treating a sulphite with dilute sulphuric acid.



**other preparation :**



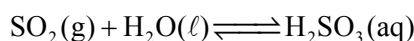
**Industrial method**, by-product of the roasting of sulphide ores.



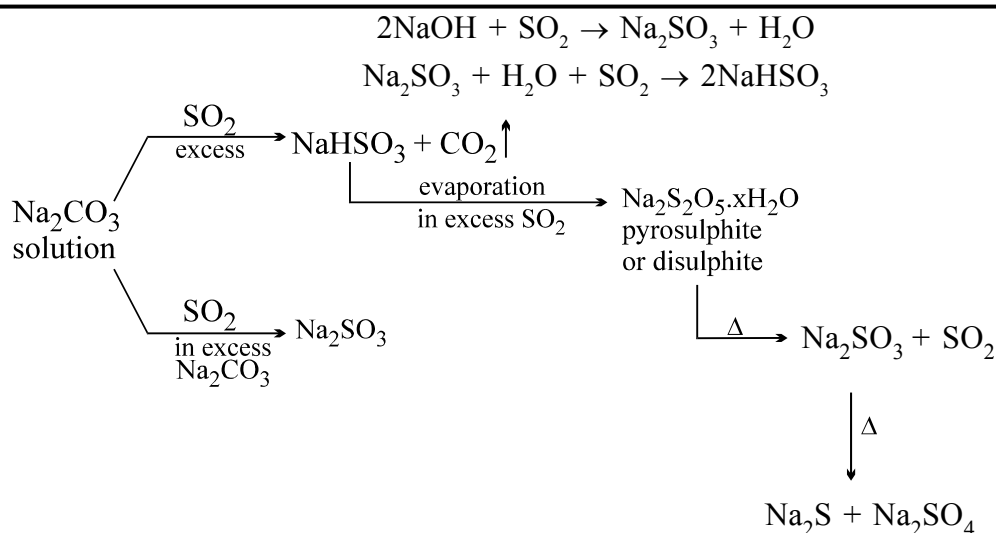
The gas after drying is liquefied under pressure and stored in steel cylinders.

### Properties

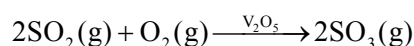
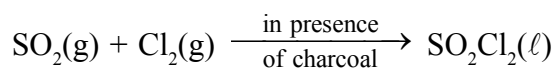
- (i) Sulphur dioxide is a colourless gas with pungent smell.
- (ii) It is highly soluble in water.
- (iii) It liquefies at room temperature under a pressure of two atmospheres and boils at 263 K.
- (iv) **Acidic character:** sulphur dioxide, when passed through water, forms a solution of sulphurous acid.



It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

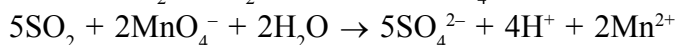
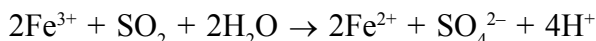


In its reaction with water and alkalis, the behaviour of sulphur dioxide is very similar to that of carbon dioxide. Sulphur dioxide reacts with chlorine in the presence of charcoal (which acts as a catalyst) to give sulphuryl chloride,  $\text{SO}_2\text{Cl}_2$ . It is oxidised to sulphur trioxide by oxygen in the presence of vanadium(V) oxide catalyst.

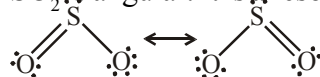


### Reducing properties

When moist, sulphur dioxide behaves as a reducing agent. For example, it converts iron(III) ions to iron(II) ions and decolourises acidified potassium permanganate(VII) solution; the latter reaction is a convenient test for the gas.



**Bonding in  $\text{SO}_2$** : The molecule of  $\text{SO}_2$  is angular. It is a resonance hybrid of the two canonical forms:



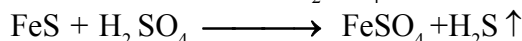
**Uses:**

- It is used refining petroleum and sugar
- It is used in bleaching wool and silk
- It is used as an anti-chlor, disinfectant and preservative. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide. Liquid  $\text{SO}_2$  is used as a solvent to dissolve a number of organic and inorganic chemicals.

### HYDROGEN SULPHIDE ( $\text{H}_2\text{S}$ ) SULPHURATED HYDROGEN

#### Preparation

By the action of dil.  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  on iron pyrites.

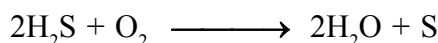


Note: **Drying agent for this gas : fused  $\text{CaCl}_2$ ,  $\text{Al}_2\text{O}_3$  (dehydrated)  $\text{P}_2\text{O}_5$  etc. But not  $\text{H}_2\text{SO}_4$ , because  $\text{H}_2\text{SO}_4 + \text{H}_2\text{S} \longrightarrow 2\text{H}_2\text{O} + \text{SO}_2 + \text{S}$**

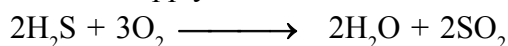
#### Properties

It is a colourless gas having an offensive smell of rotten eggs.

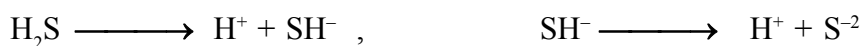
- (a) It burn in air with blue flame



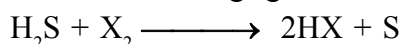
If the air supply is in excess



- (b) It is a mild acid.



- (c) It act as a reducing agent. It reduces halogen into corresponding hydroacid.



#### Tests of $\text{H}_2\text{S}$

- Unpleasant odour resembling that of rotten eggs.
- It turns lead acetate into paper black  
 $(\text{CH}_3\text{COO})_2\text{Pb} + \text{H}_2\text{S} \longrightarrow \text{PbS} \downarrow (\text{Black}) + 2\text{CH}_3\text{COOH}$
- It gives a violet colouration with a alkaline solution of sodium nitroprusside.

#### Structure of $\text{H}_2\text{S}$

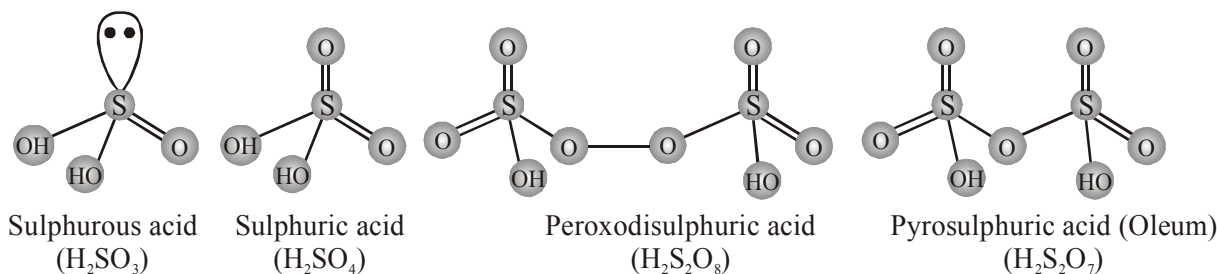
- (a) Similar to structure of water molecule i.e. V-shaped structure with bond length (H-S)  $1.35\text{\AA}$  and bond angle (H-S-H) is  $92.5^\circ$

#### Uses

- It is mainly employed in salt analysis for the detection of cation.
- Reducing agent for  $\text{H}_2\text{SO}_4$ ,  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{FeCl}_3$

## OXOACIDS OF SULPHUR

Sulphur forms a number of oxoacids such as  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{S}_2\text{O}_4$ ,  $\text{H}_2\text{S}_2\text{O}_5$ ,  $\text{H}_2\text{S}_x\text{O}_6$  ( $x = 2$  to  $5$ ),  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{S}_2\text{O}_7$ ,  $\text{H}_2\text{SO}_5$ ,  $\text{H}_2\text{S}_2\text{O}_8$ . Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the form of their salts. Structures of some important oxoacids are shown in Fig.



Structures of some important oxoacids of sulphur

## SULPHURIC ACID

Sulphuric acid is one of the most important industrial chemicals worldwide.

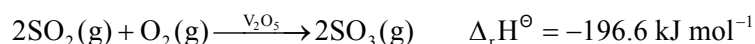
**Industrial Manufacturing** (Contact process)

Steps involved :

(i) **Burning of sulphur or sulphide ores in air to generate  $\text{SO}_2$ .**

(ii) **Conversion of  $\text{SO}_2$  to  $\text{SO}_3$  by the reaction with oxygen in the presence of a catalyst ( $\text{V}_2\text{O}_5$ ):**

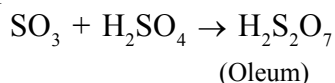
The  $\text{SO}_2$  produced is purified by removing dust and other impurities such as arsenic compounds. The key step in the manufacture of  $\text{H}_2\text{SO}_4$  is the catalytic oxidation of  $\text{SO}_2$  with  $\text{O}_2$  to give  $\text{SO}_3$  in the presence of  $\text{V}_2\text{O}_5$  (catalyst).

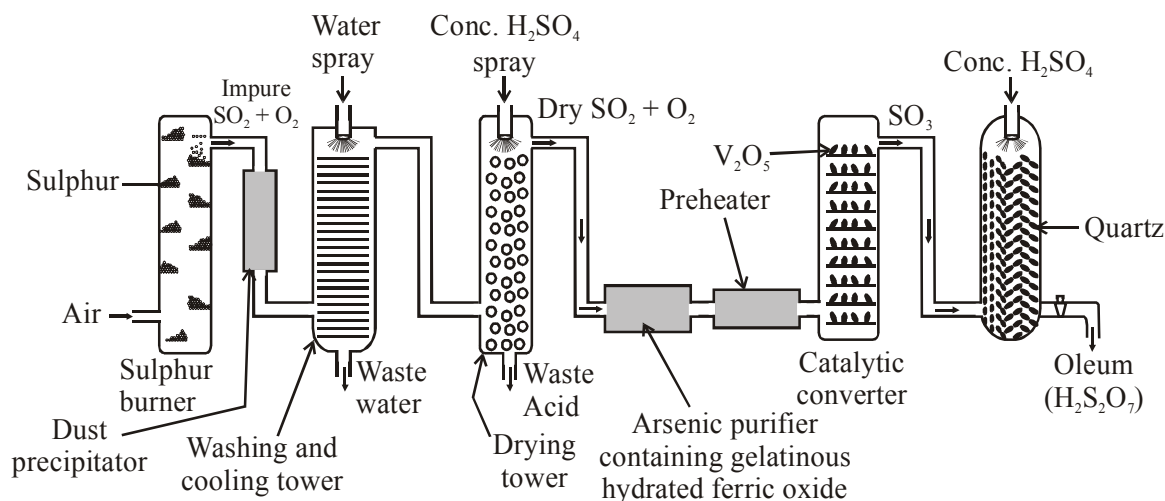


The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow. In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K.

(iii) **Absorption of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  to give Oleum ( $\text{H}_2\text{S}_2\text{O}_7$ ):**

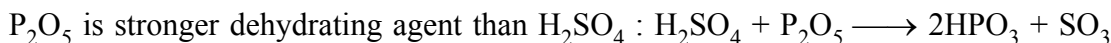
The  $\text{SO}_3$  gas from the catalytic converter is absorbed in concentrated  $\text{H}_2\text{SO}_4$  to produce oleum. Dilution of oleum with water gives  $\text{H}_2\text{SO}_4$  of the desired concentration. In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.





Flow diagram for the manufacture of sulphuric acid

The sulphuric acid obtained by Contact process is 96-98% pure.



### Properties

- Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K.
- The acid freezes at 283 K and boils at 611 K.
- It dissolves in water with the evolution of a large quantity of heat. Hence, care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into water with constant stirring.

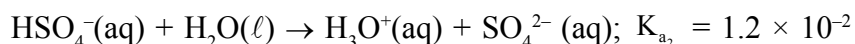
### Chemical properties

The chemical reactions of sulphuric acid are as a result of the following characteristics:

- |                                   |   |
|-----------------------------------|---|
| (a) low volatility                | (b) strong acidic character               |
| (c) strong affinity for water and | (d) ability to act as an oxidising agent. |

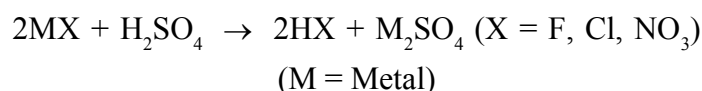
### Acidic character :

In aqueous solution, sulphuric acid ionises in two steps.



The larger value of  $K_{a_1}$  ( $K_{a_1} > 10$ ) means that  $\text{H}_2\text{SO}_4$  is largely dissociated into  $\text{H}^+$  and  $\text{HSO}_4^-$ . Greater the value of dissociation constant ( $K_a$ ), the stronger is the acid.

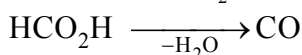
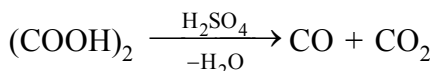
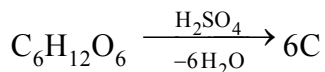
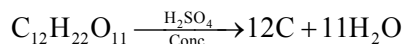
The acid forms two series of salts: normal sulphates (such as sodium sulphate and copper sulphate) and acid sulphates (e.g., sodium hydrogen sulphate). Sulphuric acid, because of its low volatility can be used to manufacture more volatile acids from their corresponding salts.



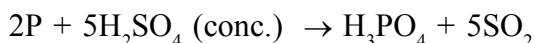
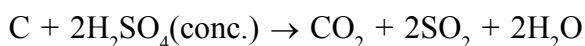
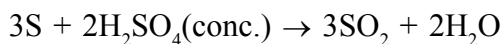
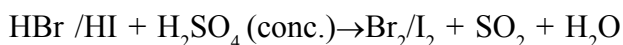
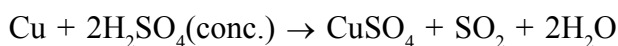
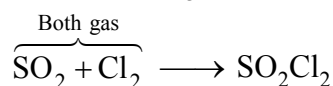


**Dehydrating Property :**

Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compounds; it is evident by its charring action on carbohydrates.

**Oxidizing Nature :**

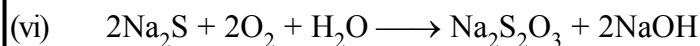
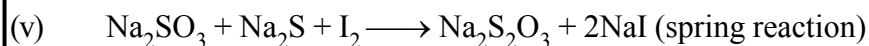
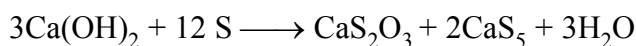
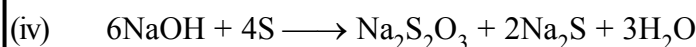
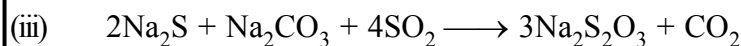
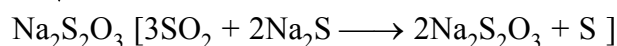
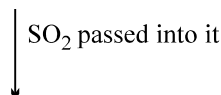
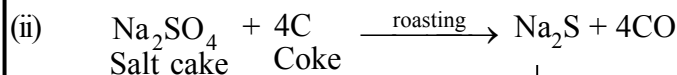
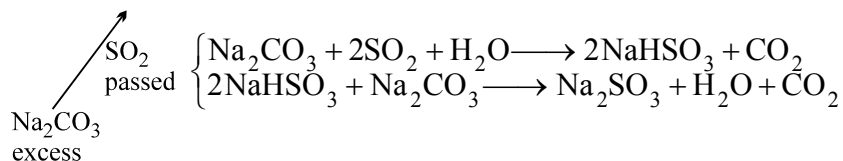
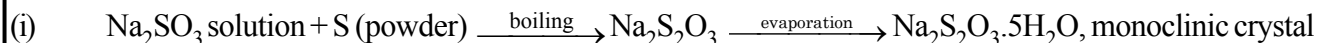
Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to  $SO_2$ .

 **$H_2SO_4$  &  $SO_3$  :**

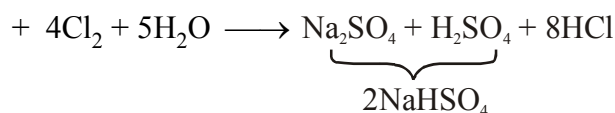
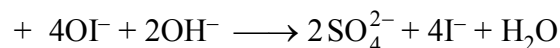
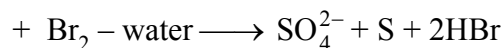
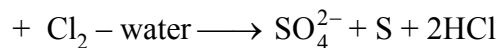
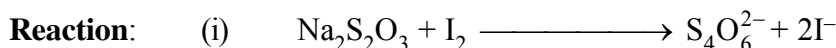
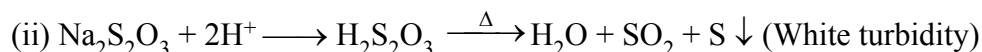
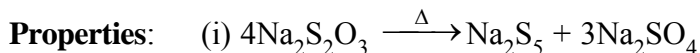
↓  
good chlorinating agent

**Uses:** Sulphuric acid is a very important industrial chemical. A nation's industrial strength can be judged by the quantity of sulphuric acid it produces and consumes. It is needed for the manufacture of hundreds of other compounds and also in many industrial processes. The bulk of sulphuric acid produced is used in the manufacture of fertilisers (e.g., ammonium sulphate, superphosphate). Other uses are in:

- (i) petroleum refining
- (ii) manufacture of pigments, paints and dyestuff intermediates
- (iii) detergent industry
- (iv) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanising)
- (v) storage batteries
- (vi) in the manufacture of nitrocellulose products and
- (vii) as a laboratory reagent.

SODIUM THIOSULPHATE**Preparation:**

[ $\text{Na}_2\text{S}$  is readily oxidised in air giving rise to  $\text{Na}_2\text{S}_2\text{O}_3$ ]



## HALOGEN FAMILY

### GROUP 17 ELEMENTS (F, Cl, Br, I, At)

These are collectively known as the halogens (Greek halo means salt and genes means born i.e., salt producers). Astatine is a radioactive element.

#### □ Occurrence

- (i) Fluorine and chlorine are fairly abundant while bromine and iodine less so.
- (ii) Fluorine is present mainly as insoluble fluorides (fluorspar  $\text{CaF}_2$ , cryolite  $\text{Na}_3\text{AlF}_6$  and fluoroapatite  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ ) and small quantities are present in soil, river water plants and bones and teeth of animals.
- (iii) Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly sodium chloride solution (2.5% by mass).
- (iv) The deposits of dried up seas contain these compounds, e.g., sodium chloride and carnallite,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Certain forms of marine life contain iodine in their systems; various seaweeds, for example, contain upto 0.5% of iodine and Chile saltpetre contains upto 0.2% of sodium iodate.

#### Electronic Configuration

The electronic configuration of outermost shell 17<sup>th</sup> group element is  $(\text{ns}^2\text{np}^5)$ .

□ **Atomic and ionic radii :**  $\text{F} < \text{Cl} < \text{Br} < \text{I}$

□ **Ionisation Enthalpy :**  $\text{F} > \text{Cl} > \text{Br} > \text{I}$

□ **Most Negative Electron Gain Enthalpy:**  $\text{Cl} > \text{F} > \text{Br} > \text{I}$

It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of fluorine and thus, the incoming electron does not experience much attraction.

□ **Electronegativity :**  $\text{F} > \text{Cl} > \text{Br} > \text{I}$

#### □ Physical Properties

- (i) Their melting and boiling points steadily increase with atomic number.
- (ii) All halogens are coloured. For example,  $\text{F}_2$  is a yellow gas,  $\text{Cl}_2$  greenish yellow gas,  $\text{Br}_2$  red liquid and  $\text{I}_2$  violet coloured solid. Reason : Decrease in HOMO-LUMO gap.
- (iii) Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.
- (iv) **Bond energy order ;**  $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$

A reason for this anomaly is the relatively large electron-electron repulsion among the lone pairs in  $\text{F}_2$  molecule where they are much closer to each other than in case of  $\text{Cl}_2$ .

## Chemical Properties

### Oxidation states :

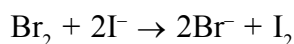
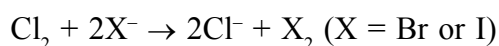
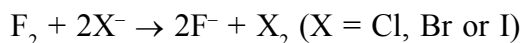
- (i) All the halogens exhibit  $-1$  oxidation state. However, chlorine, bromine and iodine exhibit  $+1$ ,  $+3$ ,  $+5$  and  $+7$  oxidation states also as explained below:

Halogen atom in ground state (other than fluorine)	ns	np	nd	
	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow$	$\square\square\square\square$	1 unpaired electron accounts for $-1$ or $+1$ oxidation states
First excited state	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\uparrow$	$\uparrow\square\square\square$	3 unpaired electron accounts for $+3$ oxidation states
Second excited state	$\uparrow\downarrow$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\square\square$	5 unpaired electron accounts for $+5$ oxidation states
Third excited state	$\uparrow$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\uparrow\square$	7 unpaired electron accounts for $+7$ oxidation states

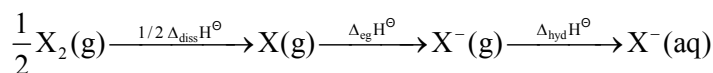
- (ii) The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides and oxoacids.
- (iii) The oxidation states of  $+4$  and  $+6$  occur in the oxides and oxoacids of chlorine and bromine.
- (iv) The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only  $-1$  oxidation state.

### Chemical reactivity

- (i) All the halogens are highly reactive.
- (ii) They react with metals and non-metals to form halides and the reactivity of the halogens decreases down the group. i.e. the order is  $F_2 > Cl_2 > Br_2 > I_2$
- (iii) The ready acceptance of an electron is the reason for the strong oxidising nature of halogens.  $F_2$  is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. In general, a halogen oxidises halide ions of higher atomic number.

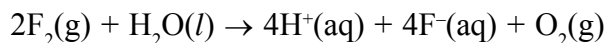


The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials, which are dependent on the parameters as follows :

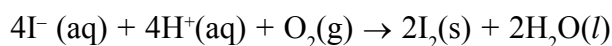


**(1) Reactivity towards water**

The relative oxidising power of halogens can further be illustrated by their reactions with water. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reaction of iodine with water is nonspontaneous. In fact, I<sup>-</sup> can be oxidised by oxygen in acidic medium; just the reverse of the reaction is observed with fluorine.



(where X = Cl or Br)

**Note : Anomalous behaviour of fluorine**

(i) Fluorine is anomalous in many properties. For example, ionisation enthalpy, electronegativity, and electrode potentials are all higher for fluorine than expected from the trends set by other halogens. Also, ionic and covalent radii, m.p. and b.p., enthalpy of bond dissociation and electron gain enthalpy are quite lower than expected.

(ii) Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements).

(iii) It forms only one oxoacid while other halogens form a number of oxoacids.

(iv) Hydrogen fluoride is a liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

**Reason for the anomalous behaviour of fluorine**

The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of d orbitals in valence shell.

Properties of Hydrogen Halides

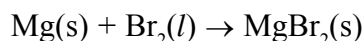
Property	HF	HCl	HBr	HI
Melting point/K	190	159	185	222
Boiling point/K	293	189	206	238
Bond length (H - X)/pm	91.7	127.4	141.4	160.9
$\Delta_{\text{diss}}\text{H}^\ominus/\text{kJ mol}^{-1}$	57.4	432	363	295
$\text{pK}_a$	3.2	-7.0	-9.5	-10.0

(2) **Reactivity towards hydrogen** : They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. Hydrogen halides dissolve in water to form hydrohalic acids. Some of the properties of hydrogen halides are :

- The acidic strength order :  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$
- The stability order of these halides :  $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$ .

**(3) Reactivity towards oxygen :**

- (i) Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides  $\text{OF}_2$  and  $\text{O}_2\text{F}_2$ . However, only  $\text{OF}_2$  is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents.  $\text{O}_2\text{F}_2$  oxidises plutonium to  $\text{PuF}_6$  and the reaction is used in removing plutonium as  $\text{PuF}_6$  from spent nuclear fuel.
- (ii) Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7.
- (iii) A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens,  $\text{I} > \text{Cl} > \text{Br}$ .
- (iv) The higher oxides of halogens tend to be more stable than the lower ones.
- (v) Chlorine oxides,  $\text{Cl}_2\text{O}$ ,  $\text{ClO}_2$ ,  $\text{Cl}_2\text{O}_6$  and  $\text{Cl}_2\text{O}_7$  are highly reactive oxidising agents and tend to explode.  $\text{ClO}_2$  is used as a bleaching agent for paper pulp and textiles and in water treatment.
- (vi) The bromine oxides,  $\text{Br}_2\text{O}$ ,  $\text{BrO}_2$ ,  $\text{BrO}_3$  are the least stable halogen oxides (middle row anomaly) and exist only at low temperatures. They are very powerful oxidising agents.
- (vii) The iodine oxides,  $\text{I}_2\text{O}_4$ ,  $\text{I}_2\text{O}_5$ ,  $\text{I}_2\text{O}_7$  are insoluble solids and decompose on heating.  $\text{I}_2\text{O}_5$  is a very good oxidising agent and is used in the estimation of carbon monoxide.

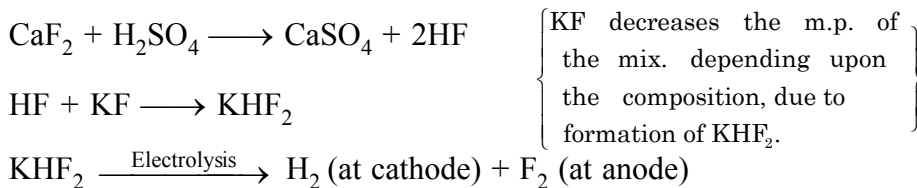
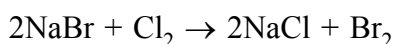
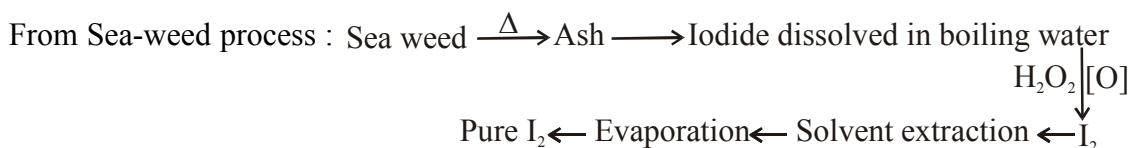
**(4) Reactivity towards metals :** Halogens react with metals to form metal halides. For example, bromine reacts with magnesium to give magnesium bromide.

The ionic character of the halides decreases in the order  $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$  where M is monovalent metal. If a metal exhibits more than one oxidation state, the halides in higher oxidation state will be more covalent than the one in lower oxidation state. For example,  $\text{SnCl}_4$ ,  $\text{PbCl}_4$ ,  $\text{SbCl}_5$  and  $\text{UF}_6$  are more covalent than  $\text{SnCl}_2$ ,  $\text{PbCl}_2$ ,  $\text{SbCl}_3$  and  $\text{UF}_4$  respectively.

**(5) Reactivity of halogens towards other halogens :** Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types  $\text{XX}'$ ,  $\text{XX}_3'$ ,  $\text{XX}_5'$  and  $\text{XX}_7'$  where X is a larger size halogen and X' is smaller size halogen.

**FLUORINE****Method of Preparation :**

**Moissan process :** [By electrolysis of  $\text{KHF}_2$  (which is obtained from  $\text{CaF}_2$ )]

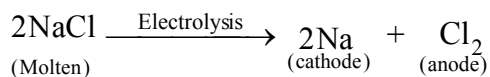
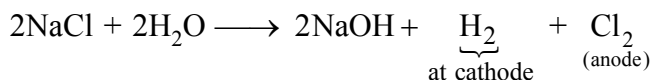
**BROMINE****IODINE****CHLORINE**

Chlorine was discovered in 1774 by Scheele by the action of  $\text{HCl}$  on  $\text{MnO}_2$ .

In 1810 Davy established its elementary nature and suggested the name chlorine on account of its colour (Greek, chloros = greenish yellow).

**Preparation**

(i) By electrolysis of aq.  $\text{NaCl}$  :



(ii) By heating manganese dioxide with concentrated hydrochloric acid.



However, a mixture of common salt and concentrated  $\text{H}_2\text{SO}_4$  is used in place of  $\text{HCl}$ .

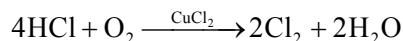


(iii) By the action of  $\text{HCl}$  on potassium permanganate.



### □ Manufacture of chlorine

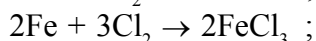
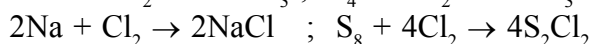
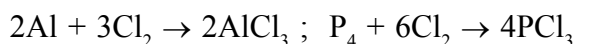
- (i) **Deacon's process** : By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of  $\text{CuCl}_2$  (catalyst) at 723 K.



- (ii) **Electrolytic process** : Chlorine is obtained by the electrolysis of brine (concentrated  $\text{NaCl}$  solution). Chlorine is liberated at anode. It is also obtained as a by-product in many chemical industries.

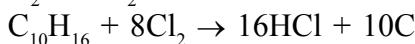
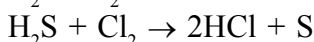
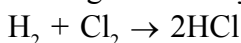
### Properties

- (i) It is a greenish yellow gas with pungent and suffocating odour.  
 (ii) It is about 2-5 times heavier than air.  
 (iii) It can be liquefied easily into greenish yellow liquid which boils at 239 K.  
 (iv) It is soluble in water. Chlorine reacts with a number of metals and non-metals to form chlorides.



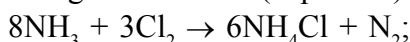
### Reaction with hydrogen

It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.

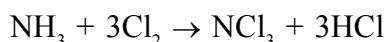


### Reaction with ammonia

With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.



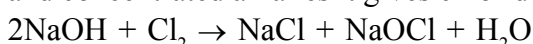
(excess)



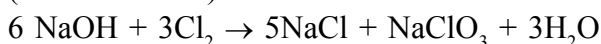
(excess)

### Reaction with alkalis

With cold and dilute alkalis chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalis it gives chloride and chlorate.

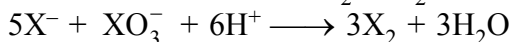
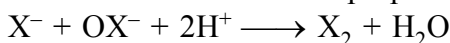


(cold and dilute)



(hot and conc.)

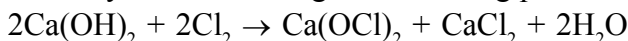
but on acidification the disproportionated product gives back the same element.



[X = Cl, Br, I]

### Reaction with slaked lime

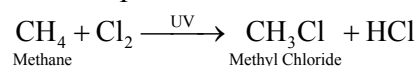
With dry slaked lime it gives bleaching powder.



The composition of bleaching powder is  $\text{Ca}(\text{OCl})_2 \cdot \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ .

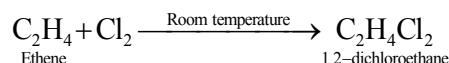
### Reaction with hydrocarbon

Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons. For example,



Methane

Methyl Chloride



Ethene

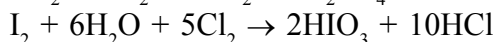
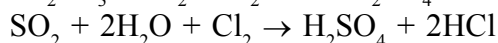
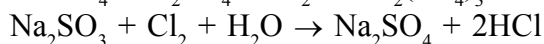
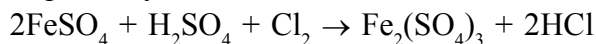
1,2-dichloroethane



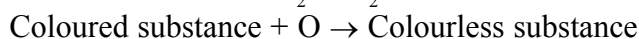
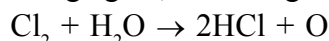
**Note :**

Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

- (i) It oxidises ferrous to ferric and sulphite to sulphate. Chlorine oxidises sulphur dioxide to sulphur trioxide and iodine to iodate. In the presence of water they form sulphuric acid and iodic acid respectively.



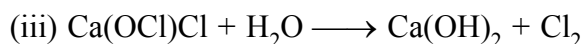
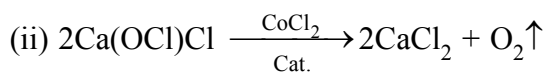
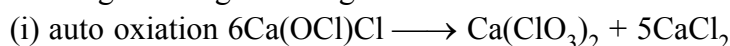
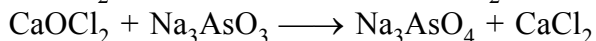
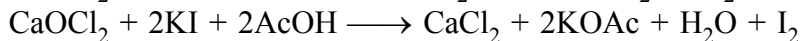
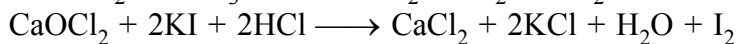
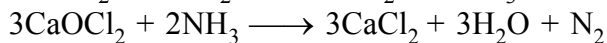
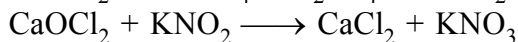
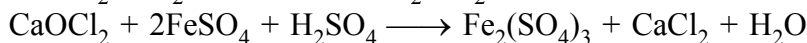
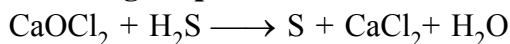
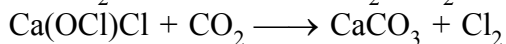
- (ii) It is a powerful bleaching agent; bleaching action is due to oxidation.



**Uses:** It is used (i) for bleaching woodpulp (required for the manufacture of paper and rayon), bleaching cotton and textiles, (ii) in the extraction of gold and platinum (iii) in the manufacture of dyes, drugs and organic compounds such as  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , DDT, refrigerants, etc. (iv) in sterilising drinking water and (v) preparation of poisonous gases such as phosgene ( $\text{COCl}_2$ ), tear gas ( $\text{CCl}_3\text{NO}_2$ ), mustard gas ( $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ ). (vi) It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.



- (a) On long standing it undergoes

**Oxidising Properties:****Reaction with acid:**

**Note:**  $\text{ClO}_2$  does not dimerise because odd electron undergoes delocalisation (in its own vacant 3d-orbital)

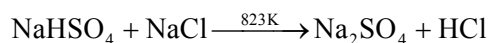
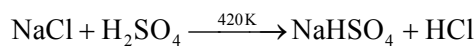
$\text{Cl}_2\text{O}_4$  ( $\text{Cl}.\text{ClO}_4$ ) is not the dimer of  $\text{ClO}_2$ . Actually it is Cl-perchlorate.

## HYDROGEN CHLORIDE

- (i) Glauber prepared this acid in 1648 by heating common salt with concentrated sulphuric acid.  
 (ii) Davy in 1810 showed that it is a compound of hydrogen and chlorine.

**Preparation**

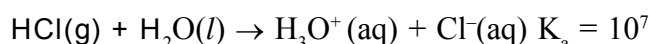
**Laboratory method** : it is prepared by heating sodium chloride with concentrated sulphuric acid.



HCl gas can be dried by passing through concentrated sulphuric acid.

**Properties**

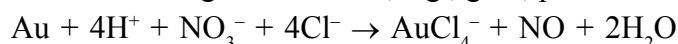
- (i) It is a colourless and pungent smelling gas. Due to strong affinity for water, conc. HCl pulls moisture of air towards self. The moisture forms droplets of water and hence, cloudy white fumes appear.  
 (ii) It is easily liquefied to a colourless liquid (b.p. 189 K) and freezes to a white crystalline solid (f.p. 159 K).  
 (iii) It is extremely soluble in water  
 (iv) **Acidic character** : It ionises as follows



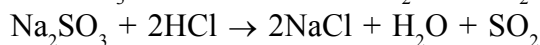
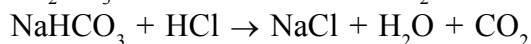
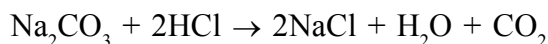
Its aqueous solution is called hydrochloric acid. High value of dissociation constant ( $K_a$ ) indicates that it is a strong acid in water. It reacts with  $\text{NH}_3$  and gives white fumes of  $\text{NH}_4\text{Cl}$ .

**Note : Aqua regia**

When three parts of concentrated HCl and one part of concentrated  $\text{HNO}_3$  are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

**Reaction with salts**

Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.

**Uses:**

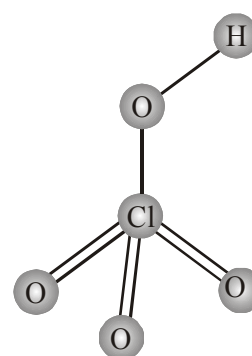
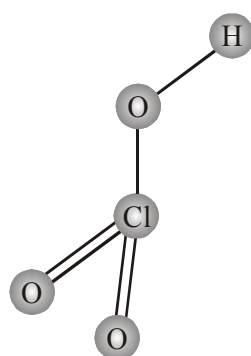
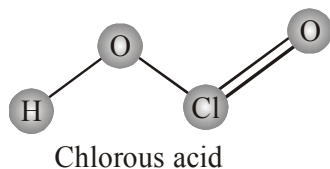
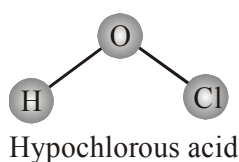
- (i) It is used in the manufacture of chlorine,  $\text{NH}_4\text{Cl}$  and glucose (from corn starch)  
 (ii) It is used for extracting glue from bones and purifying bone black  
 (iii) It is used in medicine and as a laboratory reagent.

**OXOACIDS OF HALOGENS**

- (i) Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid.  
 (ii) The other halogens form several oxoacids.  
 (iii) Most of them cannot be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts.

## Oxoacids of Halogens

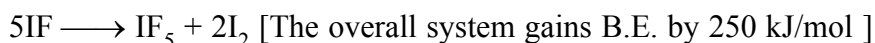
<b>Halic (I) acid</b> (Hypohalous acid)	<b>HOF</b> (Hypofluorous acid)	<b>HOCl</b> (Hypochlorous acid)	<b>HOBr</b> (Hypobromous acid)	<b>HOI</b> (Hypoiodous acid)
<b>Halic (III) acid</b> (Halous acid)	—	<b>HOClO</b> (Chlorous acid)	—	—
<b>Halic (V) acid</b> (Halic acid)	—	<b>HOClO<sub>2</sub></b> (Chloric acid)	<b>HOBrO<sub>2</sub></b> (Bromic acid)	<b>HOIO<sub>2</sub></b> (Iodic acid)
<b>Halic (VII) acid</b> (Perhalic acid)	—	<b>HOClO<sub>3</sub></b> (Perchloric acid)	<b>HOBrO<sub>3</sub></b> (Perbromic acid)	<b>HOIO<sub>3</sub></b> (Periodic acid)



The structures of oxoacids of chlorine

## INTERHALOGEN COMPOUNDS

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as  $XX'$ ,  $XX_3'$ ,  $XX_5'$  and  $XX_7'$  where X is halogen of larger size and  $X'$  of smaller size and X is more electropositive than  $X'$ . As the ratio between radii of X and  $X'$  increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum. That is why its formula is  $IF_7$  (having maximum number of atoms).



There are never more than two halogens in a molecule.

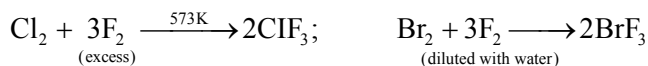
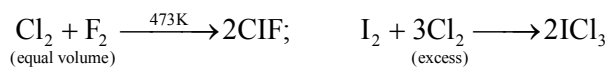
Bonds are essentially covalent and b.p. increases as the E.N. difference increases.

$AX_5$  &  $AX_7$  type formed by large atoms like Br & I to accommodate more atoms around it.

The interhalogens are generally more reactive than the halogens (except  $F_2$ ) due to weaker A–X bonds compared to X–X bond.

### Preparation

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions, For e.g.,



### Properties

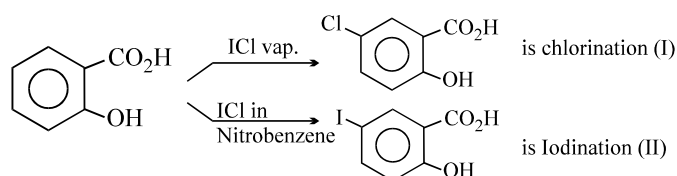
Some properties of interhalogen compounds are given in Table below

Some Properties of Interhalogen Compounds

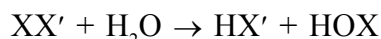
Type	Formula	Physical state and colour	Structure
XX' <sub>1</sub>	ClF	colourless gas	—
	BrF	pale brown gas	—
	IF <sup>a</sup>	Detected spectroscopically	—
	BrCl <sup>b</sup>	gas	—
	ICl	ruby red solid (α-form)	—
		brown red solid (β-form)	—
XX' <sub>3</sub>	IBr	black solid	—
	ClF <sub>3</sub>	colourless gas	Bent T-shaped
	BrF <sub>3</sub>	yellow green liquid	Bent T-shaped
	IF <sub>3</sub>	yellow powder	Bent T-shaped
XX' <sub>5</sub>	ICl <sub>3</sub> <sup>c</sup>	orange solid	Bent T-shaped
	IF <sub>5</sub>	colourless gas but solid below 77 K	square pyramidal
	BrF <sub>5</sub>	colourless liquid	square pyramidal
XX' <sub>7</sub>	ClF <sub>5</sub>	colourless liquid	square pyramidal
	IF <sub>7</sub>	colourless gas	pentagonal bipyramidal

<sup>a</sup>Very unstable; <sup>b</sup>The pure solid is known at room temperature; <sup>c</sup>Dimerises as Cl-bridged dimer (I<sub>2</sub>Cl<sub>6</sub>)

#### One peculiarity with ICl :



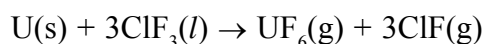
- (i) These are all covalent molecules and are diamagnetic in nature.
- (ii) They are volatile solids or liquids at 298 K except ClF which is a gas.
- (iii) Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.
- (iv) Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because X–X' bond in interhalogens is weaker than X–X bond in halogens except F–F bond.
- (v) All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX'), halite (when XX'<sub>3</sub>), halate (when XX'<sub>5</sub>) and perchalate (when XX'<sub>7</sub>) anion derived from the larger halogen.



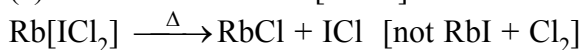
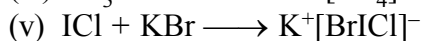
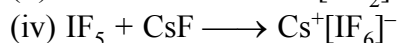
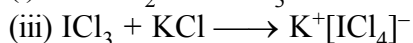
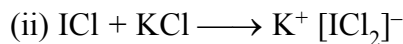
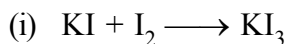
Their molecular structures are very interesting which can be explained on the basis of VSEPR theory. The XX<sub>3</sub> compounds have the bent 'T' shape, XX<sub>5</sub> compounds square pyramidal and IF<sub>7</sub> has pentagonal bipyramidal structures.

**Uses:** (i) These compounds can be used as non aqueous solvents.

(ii) Interhalogen compounds are very useful fluorinating agents. ClF<sub>3</sub> and BrF<sub>3</sub> are used for the production of UF<sub>6</sub> in the enrichment of <sup>235</sup>U.

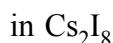
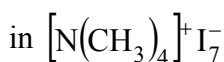
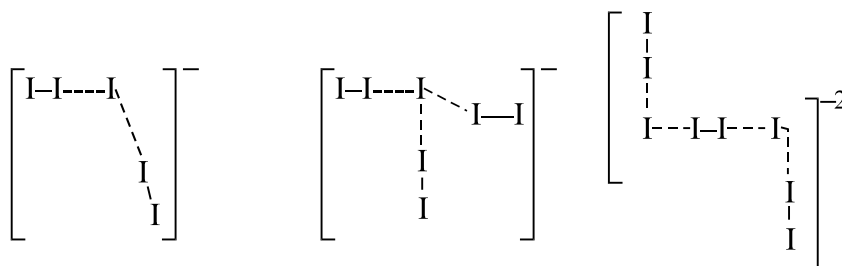


### POLYHALIDES



Here the products on heating depends on the lattice energy of the product halide. The lattice energy of alkali halide with smaller halogen is highest since the interatomic distance is least.

Structure of I<sub>5</sub><sup>-</sup>, I<sub>7</sub><sup>-</sup>, I<sub>8</sub><sup>-2</sup>



I<sub>3</sub><sup>-</sup>, Br<sub>3</sub><sup>-</sup>, Cl<sub>3</sub><sup>-</sup>, F<sub>3</sub><sup>-</sup> are known Cl<sub>3</sub><sup>-</sup> compounds are very less.

Stability order : I<sub>3</sub><sup>-</sup> > Br<sub>3</sub><sup>-</sup> > Cl<sub>3</sub><sup>-</sup> > F<sub>3</sub><sup>-</sup> depends upon the donating ability of X<sup>-</sup>.

### PSEUDO HALOGENS

There are univalent ion consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. E.g.

(i) Na-salts are soluble in water but Ag-salts are insoluble in water.

(ii) H-compounds are acids like HX.

(iii) Some anions can be oxidised to give molecules  $X_2$ .

**Anions :**

**Acids**

**Dimer**

$CN^-$

HCN

$(CN)_2$

$SCN^-$

HSCN(thiocyanic acid)

$(SCN)_2$

$SeCN^-$

$(SeCN)_2$

$OCN^-$

HOCN (cyanic acid)

$NCN^{2-}$ (Bivalent)

$H_2NCN$  (cyanamide)

$ONC^-$

HONC (Fulminic acid)

$N_3^-$

$HN_3$  (Hydrazoic acid)

$CN^\ominus$  shows maximum similarities with  $Cl^-$ ,  $Br^-$ ,  $I^-$

(i) forms HCN

(ii) forms  $(CN)_2$

(iii)  $AgCN$ ,  $Pb(CN)_2$ , are insoluble

(iv) Interpseudo halogen compounds  $ClCN$ ,  $BrCN$ ,  $ICN$  can be formed

(v)  $AgCN$  is insoluble in  $H_2O$  but soluble in  $NH_3$

(vi) forms large no. of complexes. e.g.  $[Cu(CN)_4]^{3-}$  &  $[CuCl_4]^{3-}$

### NOBLE GASES FAMILY

#### GROUP 18 ELEMENTS (He, Ne, Ar, Kr, Xe, Rn)

#### Occurrence

(i) All the noble gases except radon occur in the atmosphere.

Relative abundance : Ar is highest (Ne, Kr, He, Rn)

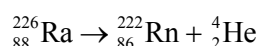
(ii) Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent.

(iii) Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite.

(iv) The main commercial source of helium is natural gas.

(v) Xenon and radon are the rarest elements of the group.

(vi) Radon is obtained as a decay product of  $^{226}Ra$ .



(vii) He liquid can exist in two forms. I-form when changes to II-form at  $\lambda$ -point temperature many physical properties change abruptly.

e.g.

(i) Sp. heat changes by a factor of 10

(ii) Thermal conductivity increases by  $10^6$  and it becomes 800 times faster than Cu

(iii) It shows zero resistance

(iv) It can flow up the sides of the vessel

**Qus. Why 18 group element are termed as noble gas ?**

**Ans.** All these are gases and chemically unreactive. They form very few compounds. Because of this they are termed noble gases.

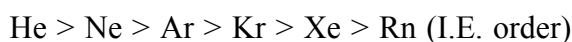
❑ **Electronic Configuration**

General electronic configuration of 18 group element is  $ns^2np^6$  except helium which has  $1s^2$ .

Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

❑ **Ionisation Enthalpy**

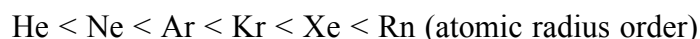
Ionisation energy decreases down the group with increase in atomic size.



Due to stable electronic configuration these gases exhibit very high ionisation enthalpy.

❑ **Atomic Radii**

Atomic radii increase down the group with increase in atomic number.



❑ **Electron Gain Enthalpy**

They have large positive values of electron gain enthalpy due to stable electronic configurations, and there for have no tendency to accept the electron

❑ **Melting point and boiling point**

$\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$  (Melting point order)

↓

( $-269^\circ\text{C}$ )

**B.P. order :**  $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$  (Boiling point order)

❑ **Density order :**



**Physical properties :**

(i) All the noble gases are monoatomic.

(ii) They are colourless, odourless and tasteless.

(iii) They are sparingly soluble in water.

(iv) They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.

(v) Helium has the lowest boiling point (4.2 K) of any known substance.

(vi) It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

### ❑ Chemical Properties

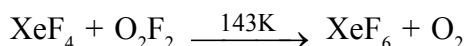
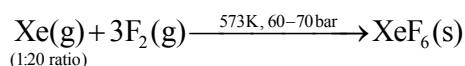
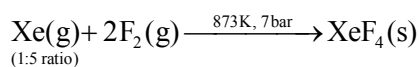
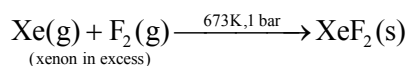
In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

- (i) The noble gases except helium ( $1s^2$ ) have completely filled  $ns^2np^6$  electronic configuration in their valence shell.
- (ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

**Note :** The reactivity of noble gases has been investigated occasionally, In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as  $O_2^+ PtF_6^-$ . He, then realised that the first ionisation enthalpy of molecular oxygen ( $1175 \text{ kJ mol}^{-1}$ ) was almost identical with that of xenon ( $1170 \text{ kJ mol}^{-1}$ ). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound  $Xe^+PtF_6^-$  by mixing  $PtF_6$  and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised. The compounds of krypton are fewer. Only the difluoride ( $KrF_2$ ) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g.,  $RnF_2$ ) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

### FLUORIDES OF XENON

#### Preparation

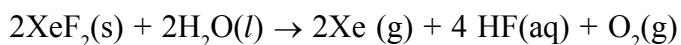


#### Physical properties

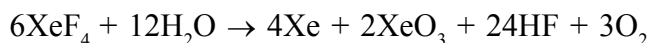
$\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  are colourless crystalline solids and sublime readily at 298 K.

#### Chemical properties

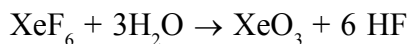
(i) **Hydrolysis :** They are readily hydrolysed even by traces of water. For example,  $\text{XeF}_2$  is hydrolysed to give Xe, HF and  $\text{O}_2$ .



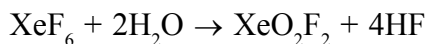
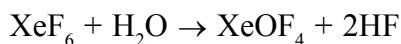
Hydrolysis of  $\text{XeF}_4$  and  $\text{XeF}_6$  with water gives  $\text{XeO}_3$ .



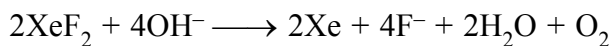




Partial hydrolysis of  $\text{XeF}_6$  gives oxyfluorides,  $\text{XeOF}_4$  and  $\text{XeO}_2\text{F}_2$ .



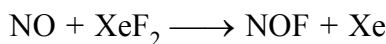
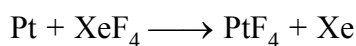
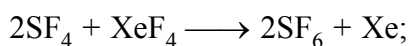
Note : **Hydrolysis in alkaline medium**



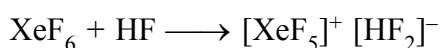
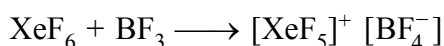
Xenate ion



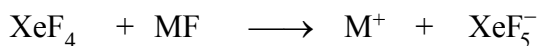
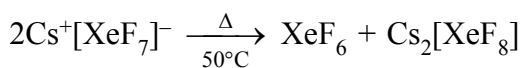
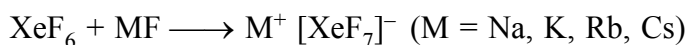
(ii) **As fluorinating agents** : They are powerful fluorinating agents.



(iii) **As fluoride donor**



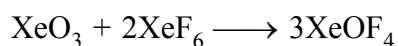
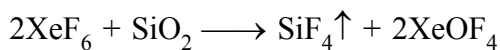
(iv) **As Fluoride acceptor**



(alkali metals fluoride)

(v) **Reaction with  $\text{SiO}_2$**

$\text{SiO}_2$  also converts  $\text{XeF}_6$  into  $\text{XeOF}_4$



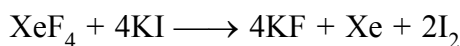
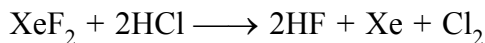
Similarly,  $\text{XeO}_3 + \text{XeOF}_4 \longrightarrow 2\text{XeO}_2\text{F}_2$

**(vi) Oxidizing properties**

$H_2$  reduces Xe – fluorides to Xe



Xe - fluorides oxidise  $Cl^-$  to  $Cl_2$  and  $I^-$  to  $I_2$

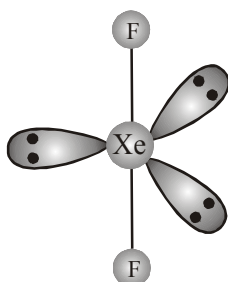


**Noble gas hydrate (clathrate compound)** : Ar, Kr, Xe can form clathrate compounds but He, Ne cannot due to their smaller size.

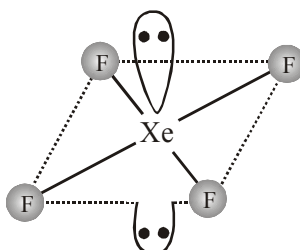
eg. $Xe \cdot 6H_2O$	} formed only when	
$Ar \cdot 6H_2O$		water freezes at high
$Kr \cdot 6H_2O$		pressure together with noble gas

**(a) Structure and bonding**

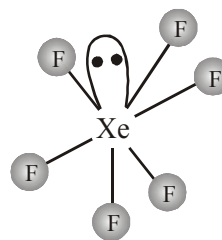
$XeF_2$  and  $XeF_4$  have linear and square planar structures respectively.  $XeF_6$  has seven electron pairs (6 bonding pairs and one lone pair) and would, thus, have a distorted octahedral structure as found experimentally in the gas phase. Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.



(a) Linear



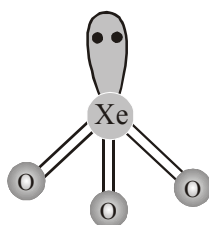
(b) Square planar



(c) Distorted octahedral

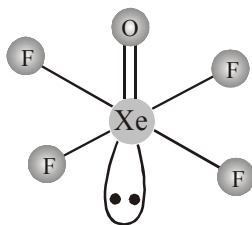
**(b) Xenon-oxygen compounds**

$XeO_3$  is a colourless, white hygroscopic explosive solid and has a pyramidal molecular structure.



Pyramidal

$XeOF_4$  is a colourless volatile liquid and has a square pyramidal molecular structure.



Square pyramidal

**Uses of helium :**

- (i) He is a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations.
- (ii) It is also used in gas-cooled nuclear reactors.
- (iii) It is used in cryoscopy to obtain the very low temperature required for superconductor and laser (b.p. 4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures.
- (iv) It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis.
- (v) It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood. He is used in preference to  $N_2$  to dil.  $O_2$  in the gas cylinders used by divers. This is because  $N_2$  is quite soluble in blood, so a sudden change in pressure causes degassing and gives bubbles of  $N_2$  in the blood. This causes the painful condition called bends. He is slightly soluble so the risk of bends is reduced.

**USES OF NEON :**

- (i) Ne is used in discharge tubes and fluorescent bulbs for advertisement display purposes.
- (ii) Neon bulbs are used in botanical gardens and in green houses.

**USES OF ARGON :**

- (i) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs.
- (ii) It is also used in the laboratory for handling substances that are air-sensitive.

**USES OF XENON AND KRYPTON :**

There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.

## SOLVED EXAMPLE

1. Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.

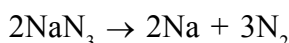
**Sol.** Nitrogen with  $n = 2$ , has s and p orbitals only. It does not have d orbitals to expand its covalency beyond four. That is why it does not form pentahalide.

2.  $\text{PH}_3$  has lower boiling point than  $\text{NH}_3$ . Why?

**Sol.** Unlike  $\text{NH}_3$ ,  $\text{PH}_3$  molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of  $\text{PH}_3$  is lower than  $\text{NH}_3$ .

3. Write the reaction of thermal decomposition of sodium azide.

**Sol.** Thermal decomposition of sodium azide gives dinitrogen gas.

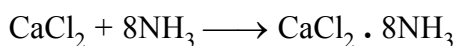
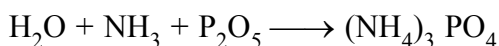


4. Why does  $\text{NH}_3$  act as a Lewis base ?

**Sol.** Nitrogen atom in  $\text{NH}_3$  has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base.

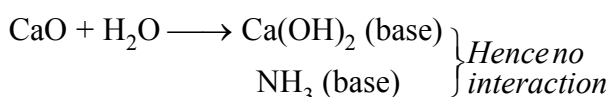
5.  $\text{NH}_3$  can't be dried by  $\text{H}_2\text{SO}_4$ ,  $\text{P}_2\text{O}_5$  and  $\text{anh. CaCl}_2$

**Sol.** because :  $2\text{NH}_3 + \text{H}_2\text{SO}_4 \longrightarrow (\text{NH}_4)_2 \text{SO}_4$



forms adduct

Quick lime is used for this purpose



$\text{NH}_3 \text{ (base)}$  } *Hence no interaction*

6. Why does  $\text{NO}_2$  dimerise ?

**Sol.**  $\text{NO}_2$  contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerisation, it is converted to stable  $\text{N}_2\text{O}_4$  molecule with even number of electrons.

7. In what way can it be proved that  $\text{PH}_3$  is basic in nature?

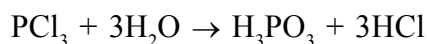
**Sol.**  $\text{PH}_3$  reacts with acids like HI to form  $\text{PH}_4\text{I}$  which shows that it is basic in nature.



Due to lone pair on phosphorus atom,  $\text{PH}_3$  is acting as a Lewis base in the above reaction.

8. Why does  $\text{PCl}_3$  fume in moisture ?

**Sol.**  $\text{PCl}_3$  hydrolyses in the presence of moisture giving fumes of HCl.



9. Are all the five bonds in  $\text{PCl}_5$  molecule equivalent? Justify your answer.

**Sol.**  $\text{PCl}_5$  has a trigonal bipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

10. How do you account for the reducing behaviour of  $\text{H}_3\text{PO}_2$  on the basis of its structure?

**Sol.** In  $\text{H}_3\text{PO}_2$ , two H atoms are bonded directly to P atom which imparts reducing character to the acid.

**11.** Elements of Group 16 generally show lower value of first ionisation enthalpy compared to the corresponding periods of group 15. Why?

**Sol.** Due to extra stable half-filled p orbitals electronic configurations of Group 15 elements, larger amount of energy is required to remove electrons compared to Group 16 elements.

**12.**  $\text{H}_2\text{S}$  is less acidic than  $\text{H}_2\text{Te}$ . Why?

**Sol.** Due to the decrease in bond (E–H) dissociation enthalpy down the group, acidic character increases.

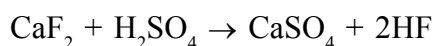
**13.** Which form of sulphur shows paramagnetic behaviour ?

**Sol.** In vapour state sulphur partly exists as  $\text{S}_2$  molecule which has two unpaired electrons in the antibonding  $\pi^*$  orbitals like  $\text{O}_2$  and, hence, exhibits paramagnetism.

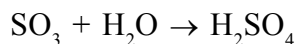
**14.** What happens when

- (i) Concentrated  $\text{H}_2\text{SO}_4$  is added to calcium fluoride
- (ii)  $\text{SO}_3$  is passed through water?

**Sol.** (i) It forms hydrogen fluoride



- (ii) It dissolves  $\text{SO}_3$  to give  $\text{H}_2\text{SO}_4$ .



**15.** Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?

**Sol.** Halogens have the smallest size in their respective periods and therefore high effective nuclear charge. As a consequence, they readily accept one electron to acquire noble gas electronic configuration.

**16.** Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?

**Sol.** It is due to

- (i) low enthalpy of dissociation of F–F bond
- (ii) high hydration enthalpy of  $\text{F}^-$

**17.** Fluorine exhibits only –1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation states also. Explain.

**Sol.** Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have d orbitals and therefore, can expand their octets and show +1, +3, +5 and +7 oxidation states also.

**18.** Write the balanced chemical equation for the reaction of  $\text{Cl}_2$  with hot and concentrated  $\text{NaOH}$ . Is this reaction a disproportionation reaction? Justify.

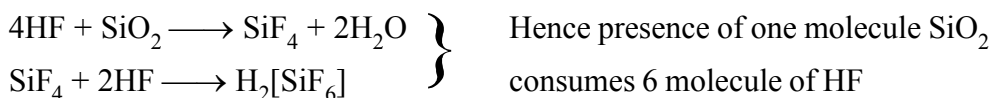
**Sol.**  $3\text{Cl}_2 + 6\text{NaOH} \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$

Yes, chlorine from zero oxidation state is changed to –1 and +5 oxidation states.

19.  $\text{CaF}_2$  used in HF prep<sup>n</sup>. must be free from  $\text{SiO}_2$ . Explain.

Ans.  $\text{CaF}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + \text{HF}$

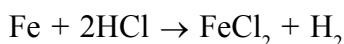
If  $\text{SiO}_2$  present as impurity



HF can not be stored in glass vessel due to same reason.

20. When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?

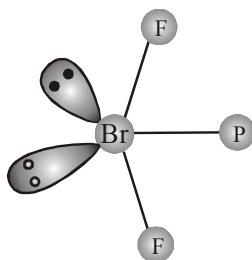
Sol. Its reaction with iron produces  $\text{H}_2$ .



Liberation of hydrogen prevents the formation of ferric chloride.

21. Discuss the molecular shape of  $\text{BrF}_3$  on the basis of VSEPR theory.

Sol. The central atom Br has seven electrons in the valence shell. Three of these will form electronpair bonds with three fluorine atoms leaving behind four electrons. Thus, there are three bond pairs and two lone pairs. According to VSEPR theory, these will occupy the corners of a trigonal bipyramid. The two lone pairs will occupy the equatorial positions to minimise lone pair-lone pair and the bond pair-lone pair repulsions which are greater than the bond pair-bond pair repulsions. In addition, the axial fluorine atoms will be bent towards the equatorial fluorine in order to minimise the lone-pair-lone pair repulsions. The shape would be that of a slightly bent 'T'.



22. Why are the elements of Group 18 known as noble gases ?

Sol. The elements present in Group 18 have their valence shell orbitals completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

23. Noble gases have very low boiling points. Why?

Sol. Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points.

24. Does the hydrolysis of  $\text{XeF}_6$  lead to a redox reaction?

Sol. No, the products of hydrolysis are  $\text{XeOF}_4$  and  $\text{XeO}_2\text{F}_2$  where the oxidation states of all the elements remain the same as it was in the reacting state.

25. Standard electrode potential values,  $E^\ominus$  for  $\text{Al}^{3+}/\text{Al}$  is  $-1.66\text{ V}$  and that of  $\text{Tl}^{3+}/\text{Tl}$  is  $+1.26\text{ V}$ . Predict about the formation of  $\text{M}^{3+}$  ion in solution and compare the electropositive character of the two metals.

**Sol.** Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to make  $\text{Al}^{3+}(\text{aq})$  ions, whereas  $\text{Tl}^{3+}$  is not only unstable in solution but is a powerful oxidising agent also. Thus  $\text{Tl}^+$  is more stable in solution than  $\text{Tl}^{3+}$ . Aluminium being able to form +3 ions easily, is more electropositive than thallium.

26. White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

**Sol.** Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate  $\text{HCl}$  gas. Moist  $\text{HCl}$  appears white in colour.

27. Boron is unable to form  $\text{BF}_6^{3-}$  ion. Explain.

**Sol.** Due to non-availability of d orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.

28. Why is boric acid considered as a weak acid ?

**Sol.** Because it is not able to release  $\text{H}^+$  ions on its own. It receives  $\text{OH}^-$  ions from water molecule to complete its octet and in turn releases  $\text{H}^+$  ions.

29. Select the member(s) of group 14 that (i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state, (iii) used as semiconductor.

**Sol.** (i) carbon (ii) lead (iii) silicon and germanium

30.  $[\text{SiF}_6]^{2-}$  is known whereas  $[\text{SiCl}_6]^{2-}$  not. Give possible reasons.

**Sol.** The main reasons are :

(i) six large chloride ions cannot be accommodated around  $\text{Si}^{4+}$  due to limitation of its size.

(ii) interaction between lone pair of chloride ion and  $\text{Si}^{4+}$  is not very strong.

31. Diamond is covalent, yet it has high melting point. Why ?

**Sol.** Diamond has a three-dimensional network involving strong  $\text{C}-\text{C}$  bonds, which are very difficult to break and, in turn has high melting point.

32.  $\text{SiH}_4$  is more reactive than  $\text{CH}_4$ . Explain

#### Reasons

(i)  $\text{Si}^{\delta+} - \text{H}^{\delta-}$  in  $\text{C}^{\delta-} - \text{H}^{\delta+}$

C - more electronegative than H

Si less electronegative than H

So bond polarity is reversed when  $\text{Nu}^-$  attacks, it faces repulsion in C but not in Si

(ii) Silicon is having vacant d orbital which is not in case of carbon

(iii) Silicon is larger in size compared to C. By which the incoming  $\text{Nu}^-$  doesn't face any steric hindrance to attack at Si whereas  $\text{CH}_4$  is tightly held from all sides.

## QUESTION BANK ON p-BLOCK ELEMENTS

## EXERCISE # I

Only one option is correct :

- PH<sub>3</sub>(Phosphine) when passed in aqueous solution of CuSO<sub>4</sub> it produce -

(A) Blue precipitate of Cu(OH)<sub>2</sub> (B) dark blue solution of [Cu(PH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>  
 (C) Black precipitate of Cu<sub>3</sub>P<sub>2</sub> (D) Colorless solution of [Cu(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup>
- H<sub>3</sub>PO<sub>2</sub>  $\xrightarrow{\Delta}$  (X) + PH<sub>3</sub> ; is

(A) Dehydration reaction (B) Oxidation reaction  
 (C) Disproportionation reaction (D) Dephosphorelation reaction
- Which of the following species is not a pseudohalide?

(A) CNO<sup>-</sup> (B) RCOO<sup>-</sup> (C) OCN<sup>-</sup> (D) N<sub>3</sub><sup>-</sup>
- An orange solid (X) on heating, gives a colourless gas (Y) and a only green residue (Z). Gas (Y) on treatment with Mg, produces a white solid substance .....

(A) Mg<sub>3</sub>N<sub>2</sub> (B) MgO (C) Mg<sub>2</sub>O<sub>3</sub> (D) MgCl<sub>2</sub>
- Conc. HNO<sub>3</sub> is yellow coloured liquid due to

(A) dissolution of NO in conc. HNO<sub>3</sub> (B) dissolution of NO<sub>2</sub> in conc. HNO<sub>3</sub>  
 (C) dissolution of N<sub>2</sub>O in conc. HNO<sub>3</sub> (D) dissolution of N<sub>2</sub>O<sub>3</sub> in conc. HNO<sub>3</sub>
- A gas at low temperature does not react with the most of compounds. It is almost inert and is used to create inert atmosphere in bulbs. The combustion of this gas is exceptionally an endothermic reaction. Based on the given information, we can conclude that the gas is

(A) oxygen (B) nitrogen  
 (C) carbon mono-oxide (D) hydrogen
- When chlorine gas is passed through an aqueous solution of a potassium halide in the presence of chloroform, a violet colouration is obtained. On passing more of chlorine water, the violet colour is disappeared and solution becomes colourless. This test confirms the presence of ..... in aqueous solution.

(A) chlorine (B) fluorine (C) bromine (D) iodine
- H<sub>3</sub>PO<sub>2</sub>  $\xrightarrow{140^\circ\text{C}}$  A  $\xrightarrow{220^\circ\text{C}}$  B  $\xrightarrow{320^\circ\text{C}}$  C  
 Compound (C) is

(A) H<sub>2</sub>PO<sub>3</sub> (B) H<sub>3</sub>PO<sub>3</sub> (C) (HPO<sub>3</sub>)<sub>n</sub> (D) H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>
- An explosive compound (A) reacts with water to produce NH<sub>4</sub>OH and HOCl. Then, the compound (A), is

(A) TNG (B) NCl<sub>3</sub> (C) PCl<sub>3</sub> (D) HNO<sub>3</sub>
- An inorganic compound (A) made of two most occurring elements into the earth crust, having a polymeric tetrahedral network structure. With carbon, compound (A) produces a poisonous gas (B) which is the most stable diatomic molecule. Compounds (A) and (B) will be

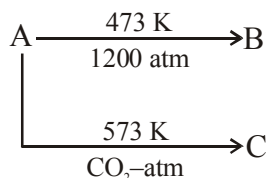
(A) SiO<sub>2</sub>, CO<sub>2</sub> (B) SiO<sub>2</sub>, CO (C) SiC, CO (D) SiO<sub>2</sub>, N<sub>2</sub>



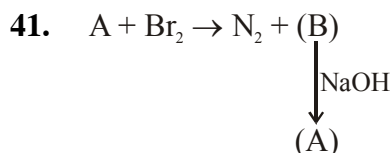
11. A sulphate of a metal (A) on heating evolves two gases (B) and (C) and an oxide (D). Gas (B) turns  $K_2Cr_2O_7$  paper green while gas (C) forms a trimer in which there is no S–S bond. Compound (D) with HCl, forms a Lewis acid (E) which exists as a dimer. Compounds (A), (B), (C), (D) and (E) are respectively  
 (A)  $FeSO_4$ ,  $SO_2$ ,  $SO_3$ ,  $Fe_2O_3$ ,  $FeCl_3$  (B)  $Al_2(SO_4)_3$ ,  $SO_2$ ,  $SO_3$ ,  $Al_2O_3$ ,  $FeCl_3$   
 (C)  $FeS$ ,  $SO_2$ ,  $SO_3$ ,  $FeSO_4$ ,  $FeCl_3$  (D)  $FeS$ ,  $SO_2$ ,  $SO_3$ ,  $Fe_2(PO_4)_3$ ,  $FeCl_2$
12. A tetra-atomic molecule (A) on reaction with nitrogen(I)oxide, produces two substances (B) and (C). (B) is a dehydrating agent while substance (C) is a diatomic gas which shows almost inert behaviour. The substances (A) and (B) and (C) respectively will be  
 (A)  $P_4$ ,  $P_4O_{10}$ ,  $N_2$  (B)  $P_4$ ,  $N_2O_5$ ,  $N_2$  (C)  $P_4$ ,  $P_2O_3$ , Ar (D)  $P_4$ ,  $P_2O_3$ ,  $H_2$
13. First compound of inert gases was prepared by scientist Neil Bartlett in 1962. This compound is  
 (A)  $XePtF_6$  (B)  $XeO_3$  (C)  $XeF_6$  (D)  $XeOF_4$
14. Carbongene has X% of  $CO_2$  and is used as an antidote for poisoning of Y. Then, X and Y are  
 (A) X = 95% and Y = lead poisoning (B) X = 5% and Y = CO poisoning  
 (C) X = 30% and Y =  $CO_2$  poisoning (D) X = 45% and Y = CO poisoning
15. The correct order of acidic strength of oxides of nitrogen is  
 (A)  $NO < NO_2 < N_2O < N_2O_3 < N_2O_5$  (B)  $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$   
 (C)  $NO < N_2O < N_2O_3 < N_2O_5 < N_2O_4$  (D)  $NO < N_2O < N_2O_5 < N_2O_3 < N_2O_4$
16.  $H_3BO_3 \xrightarrow{T_1} X \xrightarrow{T_2} Y \xrightarrow{\text{redhot}} B_2O_3$   
 if  $T_1 < T_2$  then X and Y respectively are  
 (A) X = Metaboric acid and Y = Tetraboric acid  
 (B) X = Tetraboric acid and Y = Metaboric acid  
 (C) X = Borax and Y = Metaboric acid  
 (D) X = Tetraboric acid and Y = Borax
17. When conc.  $H_2SO_4$  was treated with  $K_4[Fe(CN)_6]$ , CO gas was evolved. By mistake, somebody used dilute  $H_2SO_4$  instead of conc.  $H_2SO_4$  then the gas evolved was  
 (A) CO (B) HCN (C)  $N_2$  (D)  $CO_2$
18. An inorganic white crystalline compound (A) has a rock salt structure. (A) on reaction with conc.  $H_2SO_4$  and  $MnO_2$ , evolves a pungent smelling, greenish-yellow gas (B). Compound (A) gives white ppt. of (C) with  $AgNO_3$  solution. Compounds (A), (B) and (C) will be respectively  
 (A) NaCl,  $Cl_2$ , AgCl (B) NaBr,  $Br_2$ , NaBr  
 (C) NaCl,  $Cl_2$ ,  $Ag_2SO_4$  (D)  $Na_2CO_3$ ,  $CO_2$ ,  $Ag_2CO_3$
19.  $RCl \xrightarrow[Si]{Cu\text{-powder}} R_2SiCl_2 \xrightarrow{H_2O} R_2Si(OH)_2 \xrightarrow{\text{condensation}} A$   
 Compound (A) is  
 (A) a linear silicone (B) a chlorosilane (C) a linear silane (D) a network silane

20. When oxalic acid reacts with conc.  $\text{H}_2\text{SO}_4$ , two gases produced are of neutral and acidic in nature respectively. Potassium hydroxide absorbs one of the two gases. The product formed during this absorption and the gas which gets absorbed are respectively
- (A)  $\text{K}_2\text{CO}_3$  and  $\text{CO}_2$  (B)  $\text{KHCO}_3$  and  $\text{CO}_2$   
 (C)  $\text{K}_2\text{CO}_3$  and  $\text{CO}$  (D)  $\text{KHCO}_3$  and  $\text{CO}$
21. Conc.  $\text{H}_2\text{SO}_4$  cannot be used to prepare  $\text{HBr}$  from  $\text{NaBr}$  because it
- (A) reacts slowly with  $\text{NaBr}$  (B) oxidises  $\text{HBr}$   
 (C) reduces  $\text{HBr}$  (D) disproportionates  $\text{HBr}$
22. Ammonia can be dried by
- (A) conc.  $\text{H}_2\text{SO}_4$  (B)  $\text{P}_4\text{O}_{10}$  (C)  $\text{CaO}$  (D) anhydrous  $\text{CaCl}_2$
23. When chlorine reacts with a gas X, an explosive inorganic compound Y is formed. Then X and Y will be
- (A)  $\text{X} = \text{O}_2$  and  $\text{Y} = \text{NCl}_3$  (B)  $\text{X} = \text{NH}_3$  and  $\text{Y} = \text{NCl}_3$   
 (C)  $\text{X} = \text{O}_2$  and  $\text{Y} = \text{NH}_4\text{Cl}$  (D)  $\text{X} = \text{NH}_3$  and  $\text{Y} = \text{NH}_4\text{Cl}$
24.  $\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow \text{HPO}_3 + \text{A}$ ; the product A is
- (A)  $\text{N}_2\text{O}$  (B)  $\text{N}_2\text{O}_3$  (C)  $\text{NO}_2$  (D)  $\text{N}_2\text{O}_5$
25. Which of the following is the correct order of acidic strength?
- (A)  $\text{Cl}_2\text{O}_7 > \text{SO}_3 > \text{P}_4\text{O}_{10}$  (B)  $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$   
 (C)  $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$  (D)  $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$
26.  $\text{Ca} + \text{C}_2 \longrightarrow \text{CaC}_2 \xrightarrow{\text{N}_2} \text{A}$   
 Compound (A) is used as a/an
- (A) fertilizer (B) dehydrating agent (C) oxidising agent (D) reducing agent
27. A gas which exists in three allotropic forms  $\alpha$ ,  $\beta$  and  $\gamma$  is
- (A)  $\text{SO}_2$  (B)  $\text{SO}_3$  (C)  $\text{CO}_2$  (D)  $\text{NH}_3$
28. A red coloured mixed oxide (X) on treatment with conc.  $\text{HNO}_3$  gives a compound (Y). (Y) with  $\text{HCl}$ , produces a chloride compound (Z) which can also be produced by treating (X) with conc.  $\text{HCl}$ . Compounds (X), (Y), and (Z) will be
- (A)  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}_2$ ,  $\text{MnCl}_2$  (B)  $\text{Pb}_3\text{O}_4$ ,  $\text{PbO}_2$ ,  $\text{PbCl}_2$   
 (C)  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_2$  (D)  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_3$
29. One mole of calcium phosphide on reaction with excess of water gives
- (A) one mole of phosphine (B) two moles of phosphoric acid  
 (C) two moles of phosphine (D) one mole of phosphorus penta-oxide
30.  $\text{NaH}_2\text{PO}_4 \xrightarrow{> 240^\circ\text{C}} (\text{NaPO}_3)_3 \xrightarrow{625^\circ\text{C}} \text{NaPO}_3(\text{liquid melt}) \xrightarrow[\text{cooling}]{\text{rapid}} \text{D}(\text{glass})$   
 Sodium trimetaphosphate
- Compound (D) is known as
- (A) Microcosmic salt (B) Graham's salt (C) Fischer's salt (D) Switzer's Salt

31. Three allotropes (A), (B) and (C) of phosphorous in the following change are respectively



- (A) white,  $\beta$ -black, red (B)  $\beta$ -black, white, red  
 (C) red,  $\beta$ -black, white (D) red, violet,  $\beta$ -black
32. When an inorganic compound reacts with  $\text{SO}_2$  in aqueous medium, produces (A). (A) on reaction with  $\text{Na}_2\text{CO}_3$ , gives compound (B) which with sulphur, gives a substance (C) used in photography. Compound (C) is
- (A)  $\text{Na}_2\text{S}$  (B)  $\text{Na}_2\text{S}_2\text{O}_7$  (C)  $\text{Na}_2\text{SO}_4$  (D)  $\text{Na}_2\text{S}_2\text{O}_3$
33.  $\text{B(OH)}_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na[B(OH)}_4] + \text{H}_2\text{O}$   
 How can this reaction is made to proceed in forward direction?
- (A) addition of cis 1,2 diol (B) addititon of borax  
 (C) addition of trans 1,2 diol (D) addition of  $\text{Na}_2\text{HPO}_4$
34. Which is the compound responsible for the flickering light called **will-o-the-wisp**, some times seen in the Marsh.
- (A)  $\text{PH}_3$  (B)  $\text{P}_2\text{H}_4$  (C)  $\text{H}_2\text{S}$  (D)  $\text{PH}_3 + \text{H}_2\text{S}$
35. The gun powder is consisting of '\_\_\_\_\_' + sulphur + Charcoal what is the missing substance for gun powder
- (A)  $\text{LiNO}_3$  (B)  $\text{NH}_4\text{NO}_2$  (C)  $\text{KNO}_3$  (D) (A) and (B) mixture
36. An aqueous solution of borax is
- (A) Neutral (B) Amphoteric (C) Basic (D) Acidic
37. Boric acid is polymeric due to
- (A) Its acidic nature (B) The presence of hydrogen bonds  
 (C) Its monobasic nature (D) Its geometry
38. The type of hybridisation of boron in diborane is
- (A) sp (B)  $sp^2$  (C)  $sp^3$  (D)  $dsp^2$
39. Thermodynamically the most stable form of carbon is
- (A) Diamond (B) Graphite (C) Fullerenes (D) Coal
40. Elements of group 14
- (A) Exhibit oxidation state of +4 only (B) Exhibit oxidation state of +2 and +4 only  
 (C) Form  $\text{M}^{2-}$  and  $\text{M}^{4+}$  ions (D) Form  $\text{M}^{2+}$  and  $\text{M}^{4+}$  ions



if A is a basic gas then identified (A) and (B)

- (A)  $NH_3, NH_4Br$       (B)  $NH_3, N_2O$       (C)  $NH_3, N_2O_5$       (D) None of these

**Question No. 50 to 55 (6 questions)**

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

- (A) if both (A) and (R) are true and (R) is the correct explanation of (A)  
 (B) if both (A) and (R) are true but (R) is not correct explanation of (A)  
 (C) if (A) is true but (R) is false  
 (D) if (A) is false and (R) is true

42. **Assertion :** Borax bead test is applicable only to coloured salt.

**Reason :** In borax bead test, coloured salts are decomposed to give coloured metal meta borates.

43. **Assertion :** Aluminium and zinc metal evolve  $H_2$  gas from NaOH solution

**Reason :** Several non-metals such as P, S, Cl, etc. convert a hydride instead of producing  $H_2$  gas from NaOH.

44. **Assertion :** Conc.  $H_2SO_4$  can not be used to prepare pure HBr from NaBr

**Reason :** It reacts slowly with NaBr.

45. **Assertion :** Oxygen is more electronegative than sulphur, yet  $H_2S$  is acidic, while  $H_2O$  is neutral.

**Reason :** H–S bond is weaker than O–H bond.

46. **Assertion :** Chlorine gas disproportionates in hot & conc. NaOH solution.

**Reason :** NaCl and NaOCl are formed in the above reaction.

47. **Assertion :** Liquid  $IF_5$  conducts electricity.

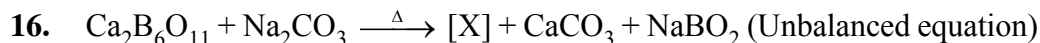
**Reason :** Liquid  $IF_5$  self ionizes as,  $2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$

## EXERCISE # II

One or more than one option may be correct :

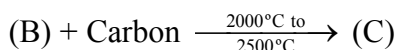
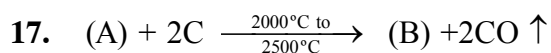
- When a compound X reacts with ozone in aqueous medium, a compound Y is produced. Ozone also reacts with Y and produces compound Z. Z acts as an oxidising agent, then X, Y and Z will be
  - X = HI, Y = I<sub>2</sub> and Z = HIO<sub>3</sub>
  - X = KI, Y = I<sub>2</sub> and Z = HIO<sub>3</sub>
  - X = KI, Y = I<sub>2</sub> and Z = HIO<sub>4</sub>
  - X = HI, Y = I<sub>2</sub> and Z = HIO<sub>4</sub>
- Which of the following statements is/are correct regarding B<sub>2</sub>H<sub>6</sub>?
  - banana bonds are longer but stronger than normal B–H bonds
  - B<sub>2</sub>H<sub>6</sub> is also known as 3c–2e compound
  - the hybrid state of B in B<sub>2</sub>H<sub>6</sub> is sp<sup>3</sup> while that of sp<sup>2</sup> in BH<sub>3</sub>
  - it cannot be prepared by reacting BF<sub>3</sub> with LiBH<sub>4</sub> in the presence of dry ether
- Which of the following statements is/are correct regarding inter-halogen compounds of AB<sub>x</sub> type?
  - x may be 1,3,5 and 7
  - A is a more electronegative halogen than B
  - FBr<sub>3</sub> cannot exist
  - The interhalogens are generally more reactive than the halogens (except F<sub>2</sub>) due to weaker A–X bonds compared to X–X bond.
- When an inorganic compound (X) having 3c–2e as well as 2c–2e bonds reacts with ammonia gas at a certain temperature, gives a compound (Y) iso-structural with benzene. Compound (X) with ammonia at a high temperature, produces a slippery substance (Z). Then
  - (X) is B<sub>2</sub>H<sub>6</sub>
  - (Z) is known as inorganic graphite
  - (Z) having structure similar to graphite
  - (Z) having structure similar to (X)
- Boric acid
  - exists in polymeric form due to inter-molecular hydrogen bonding.
  - is used in manufacturing of optical glasses.
  - is a tri-basic acid
  - with borax, it is used in the preparation of a buffer solution.

6. The correct statement(s) related to allotropes of carbon is/are
- (A) graphite is the thermodynamically most stable allotrope of carbon and having a two dimensional sheet like structure of hexagonal rings of carbon ( $sp^2$ )
- (B) diamond is the hardest allotrope of carbon and having a three dimensional network structure of  $C(sp^3)$
- (C) fullerene ( $C_{60}$ ) is recently discovered non-crystalline allotrope of carbon having a football-like structure.
- (D) Vander Waal's force of attraction acts between the layers of graphite  $6.14 \text{ \AA}$  away from each other
7.  $Al_2(SO_4)_3 + NH_4OH \longrightarrow X$ , then
- (A) X is a white coloured compound (B) X is insoluble in excess of  $NH_4OH$
- (C) X is soluble in NaOH (D) X cannot be used as an antacid
8. The species that undergo(es) disproportionation in an alkaline medium is/are
- (A)  $Cl_2$  (B)  $MnO_4^{2-}$  (C)  $P_4$  (D)  $ClO_4^-$
9. Select correct statement(s):
- (A) Borax is used as a buffer
- (B) 1 M borax solution reacts with equal volumes of 2 M HCl solution
- (C) Titration of borax can be made using methyl orange as the indicator
- (D) Coloured bead obtained in borax-bead test contains metaborate
10. Which of the following is / are correct for group 14 elements?
- (A) The stability of dihalides are in the order  $CX_2 < SiX_2 < GeX_2 < SnX_2 < PbX_2$
- (B) The ability to form  $p\pi-p\pi$  multiple bonds among themselves increases down the group
- (C) The tendency for catenation decreases down the group
- (D) They all form oxides with the formula  $MO_2$ .
11. Zeolite is used in which of the following cases :
- (A) Conversion of alcohols into gasoline (B) Cracking of hydrocarbon
- (C) Isomerisation of hydrocarbons (D) Softening of hard water
12. Which of the following oxides are mixed oxide ?
- (A)  $PbO_2$  (B)  $SnO_2$  (C)  $Pb_2O_3$  (D)  $Pb_3O_4$
13. Which of the following oxide(s) gives brown ppt on reaction with conc.  $HNO_3$  :
- (A)  $PbO$  (B)  $SnO$  (C)  $Pb_2O_3$  (D)  $Pb_3O_4$
14. Which of the following reaction produces  $PH_3$  :
- (A)  $Ca_3P_2 + H_2O \rightarrow$  (B)  $P_4 + NaOH \rightarrow$  (C)  $PH_4I + KOH \rightarrow$  (D)  $H_3PO_2 \xrightarrow{\Delta}$
15. Which of the following halides is least stable and has doubtful existence ?
- (A)  $CCl_4$  (B)  $GeI_4$  (C)  $SnI_4$  (D)  $PbI_4$



Correct statement for [X]

- (A) Structure of anion of crystalline (X) has one boron atom  $\text{sp}^3$  hybridised and other three boron atoms  $\text{sp}^2$  hybridised
- (B) (X) with  $\text{NaOH}(\text{aq.})$  gives a compound which on reaction with  $\text{H}_2\text{O}_2$  in alkaline medium yields a compound used as brightner in soaps
- (C) Hydrolysis of (X) with  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  yields a compound which on reaction with  $\text{HF}$  gives fluoroboric acid
- (D) [X] on heating with cobalt salt in oxidising flame gives blue coloured bead

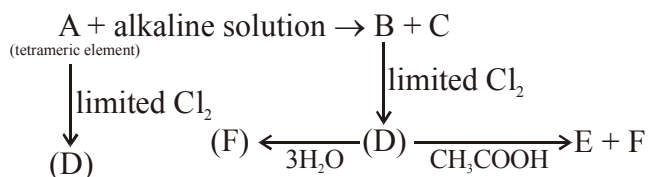


If A is an example of 3-d silicate then select the correct statements about (C)

- (A) Central atom of C is  $\text{sp}^3$  hybridised
- (B) (C) is non planar and all atoms are  $\text{sp}^3$  hybridised
- (C) (C) has diamond like structure, and it is coloured when impurity is present but pale yellow to colourless solid at room temperature
- (D) (C) is silicon carbide ( $\text{SiC}$ ) and it is not being affected by any acid except  $\text{H}_3\text{PO}_4$

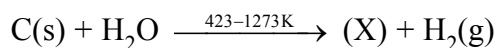
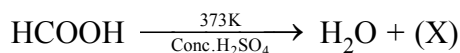
## EXERCISE # III

## Paragraph for Question No. 1 &amp; 2



- When D react with  $\text{C}_2\text{H}_5\text{OH}$  then product will be  
 (A)  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{H}_3\text{PO}_4$  (B)  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{H}_3\text{PO}_3$   
 (C)  $\text{CH}_3\text{COCl}$ ,  $\text{H}_3\text{PO}_3$  (D) Only  $\text{H}_3\text{PO}_3$
- B can be absorbed by :  
 (A)  $\text{Ca(OCl)Cl}$  (B)  $\text{H}_2\text{S}$  (C) Both (D) None

## Paragraph for Question No. 3 to 6



- Select the correct statement about (X)  
 (A) (X) is a colourless, odourless and almost water insoluble gas  
 (B) X is highly poisonous and burns with blue flame  
 (C) When (X) gas is passed through  $\text{PdCl}_2$  solution giving rise to black ppt  
 (D) All of these
- Mixture of (X) gas +  $\text{H}_2$  is called  
 (A) Water gas or synthesis gas (B) Producer gas  
 (C) Methane gas (D) None of these
- In second reaction when air is used instead of steam a mixture of (X) gas and  $\text{N}_2$  is produced which is called  
 (A) Water gas (B) Synthesis gas (C) Producer gas (D) Carbon dioxide gas
- Select the correct statement about (X)  
 (A) (X) gas is estimated by  $\text{I}_2\text{O}_5$  (B)  $\text{Cu}_2\text{Cl}_2$  is absorber of (X) gas  
 (C) (X) gas is the purifying agent for Ni (D) All of these

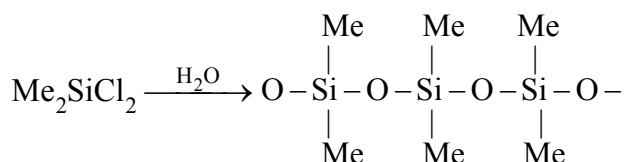
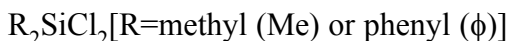


**Paragraph for Question No. 7 & 8**

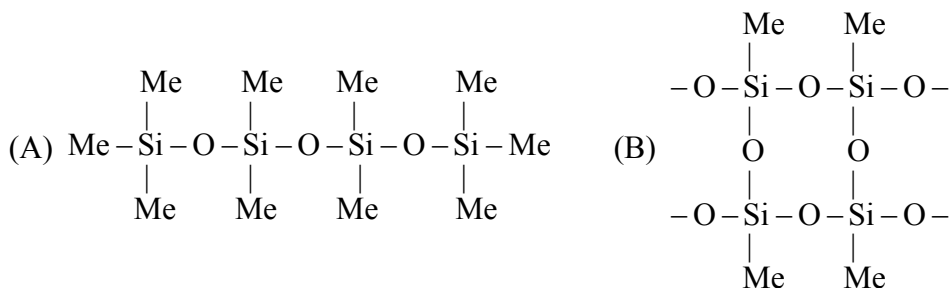
Read the following write-ups and answer the questions at the end of it.

Silicons are synthetic polymers containing repeated  $R_2SiO$  units. Since, the empirical formula is that of a ketone ( $R_2CO$ ), the name silicone has been given to these materials. Silicones can be made into oils, rubbery elastomers and resins. They find a variety of applications because of their chemical inertness, water repelling nature, heat-resistance and good electrical insulating property.

Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of

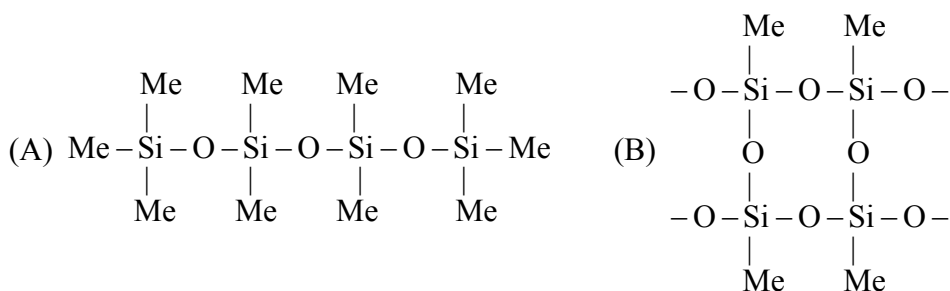


7. If we mix  $Me_3SiCl$  with  $Me_2SiCl_2$ , we get silicones of the type:



- (C) both of the above (D) none of the above

8. If we start with  $MeSiCl_3$  as the starting material, silicones formed is:



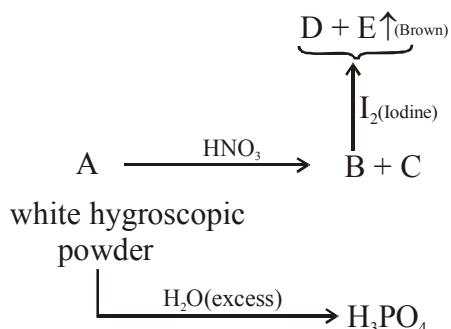
- (C) Both of the above (D) None of the above

**Paragraph for Question No. 9 & 10**

CO gas is absorbed by aqueous suspension of cuprous chloride forming the complex like  $[CuCl(CO)(H_2O)_2]$ .

9. Comment on the shape of the above complex.  
 (A) Tetrahedral (B) TBP (C) Square planar (D) Cannot be predicted
10. Choose the correct statement regarding the above molecule  
 (A) Cl-atom is separated by equal angle from both of the water molecule  
 (B) Magnetic moment of the above complex is 1.73 B.M.  
 (C) There are two stereo isomer for the above complex.  
 (D) Both (A) and (C)

## Paragraph for Question No. 11 to 12



11. Which of the following compound is not having +5 oxidation state on its central atom  
 (A) B (B) D (C) C (D) E
12. "A" on reacting with Acetamide yields a compound "F". The compound "F" contains  
 (A) 4  $\sigma$  bonds, 2  $\pi$  bonds  
 (B) 5  $\sigma$  bonds, 1  $\pi$  bonds  
 (C) 5  $\sigma$  bonds, 2  $\pi$  bonds  
 (D) 2  $\sigma$  bonds, 2  $\pi$  bonds
13. Match List-I with List-II

## List-I (Chemical reaction)

## List-II (Name of process)

- (I)  $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{800^\circ\text{C}/\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}$  (a) Contact process
- (II)  $4\text{HCl} + \text{O}_2 \xrightarrow{230^\circ\text{C}/\text{CuCl}_2} 2\text{Cl}_2 + 2\text{H}_2\text{O}$  (b) Ostwald's process
- (III)  $2\text{SO}_2 + \text{O}_2 \xrightarrow{450-500^\circ/\text{V}_2\text{O}_5} 2\text{SO}_3$  (c) Deacon's process
- (IV)  $2\text{N}_2 + 3\text{H}_2 \xrightarrow{\text{Fe+Mo}} 2\text{NH}_3$  (d) Haber's process
- (A) I-a, II-b, III-d, IV-c (B) I-b, II-c, III-a, IV-d  
 (C) I-a, II-d, III-c, IV-b (D) I-a, II-c, III-b, IV-d

## 14. Column-I

## Column-II

- (P) Dry ice (1) Used as antidote for CO-poisoning  
 (Q) Carbongene (2) Used as nonstick coating  
 (R) Carborundum (3) Used as refrigerant  
 (S) Teflon (4) Used as abrasive

## Code :

- |     |   |   |   |   |
|-----|---|---|---|---|
|     | P | Q | R | S |
| (A) | 4 | 1 | 3 | 2 |
| (C) | 3 | 1 | 4 | 2 |

- |     |   |   |   |   |
|-----|---|---|---|---|
|     | P | Q | R | S |
| (B) | 4 | 2 | 1 | 3 |
| (D) | 1 | 4 | 3 | 2 |

**15. Column-I  
Compound**

- (P)  $\text{SnCl}_2$
- (Q) Butter of tin
- (R) Mosaic gold
- (S) Pink's salt

**Code :**

- |     |   |   |   |   |
|-----|---|---|---|---|
|     | P | Q | R | S |
| (A) | 4 | 3 | 2 | 1 |
| (C) | 2 | 1 | 3 | 4 |

**Column-II  
Correct statement for compounds given**

- (1) Used in printing technology
- (2) Used for gilding purpose (in joining gold pieces)
- (3) Reducing agent
- (4) Mordant

- |     |   |   |   |   |
|-----|---|---|---|---|
|     | P | Q | R | S |
| (B) | 3 | 4 | 2 | 1 |
| (D) | 1 | 3 | 4 | 2 |

**16. Column-I (Metal)**

- (P) Fe
- (Q) Cu
- (R) Pb
- (S) Sn

**Code :**

- |     |      |      |      |         |
|-----|------|------|------|---------|
|     | P    | Q    | R    | S       |
| (A) | 2, 1 | 1    | 3, 4 | 2, 3    |
| (B) | 2, 3 | 1, 3 | 1, 3 | 2, 3, 4 |
| (C) | 1, 3 | 1, 2 | 3, 4 | 2       |
| (D) | 1, 4 | 2, 3 | 1, 3 | 1, 4    |

**Column-II (Correct statements)**

- (1) Produces NO with 20%  $\text{HNO}_3$
- (2) Produces  $\text{NH}_4\text{NO}_3$  with 6%  $\text{HNO}_3$
- (3) Produces  $\text{NO}_2$  with 70%  $\text{HNO}_3$
- (4) Produces  $\text{NH}_4\text{NO}_3$  with 20%  $\text{HNO}_3$

**17. Column-I (Reactions)**

- (P)  $\text{XeF}_2 + \text{PF}_5 \rightarrow$
- (Q)  $\text{XeF}_4 + \text{Pt} \rightarrow$
- (R)  $\text{XeF}_4 + \text{H}_2\text{O} \rightarrow$
- (S)  $\text{XeF}_6 + \text{CsF} \rightarrow$

**Code :**

- |     |   |   |   |   |
|-----|---|---|---|---|
|     | P | Q | R | S |
| (A) | 4 | 2 | 3 | 1 |
| (C) | 4 | 3 | 2 | 1 |

**Column-II (Correct statements)**

- (1) Fluoride of Xe acts as fluoride acceptor
- (2) Fluoride of Xe undergoes disproportion
- (3) Fluoride of Xe acts as fluorinating agent
- (4) Fluoride of Xe act as fluoride donor

- |     |   |   |   |   |
|-----|---|---|---|---|
|     | P | Q | R | S |
| (B) | 3 | 2 | 1 | 4 |
| (D) | 3 | 4 | 2 | 1 |

## 18. Column-I (Substances)

- (P)  $O_3$   
 (Q) Bleaching powder  
 (R)  $H_2O_2$   
 (S)  $HNO_3$

## Column-II (Can be prepared by)

- (1) Acidification of  $BaO_2$  with  $H_3PO_4$   
 (2) Birkeland Eyde process  
 (3) Dry  $O_2$  is passed through a silent electrical discharge  
 (4)  $Cl_2$  gas is passed through slaked lime

Code :

- P Q R S  
 (A) 3 4 1 2  
 (C) 2 1 3 4

- P Q R S  
 (B) 1 3 4 2  
 (D) 4 1 2 3

## MATCHING LIST TYPE 1 × 3 Q. (19 to 21)

For the following molecules in column-I, match the correct order of properties with column-II & column-III according to the questions asked.

Column - 1 Molecules	Column - 2 Properties	Column - 3 Correct order
(I) $NH_3, PH_3, AsH_3, SbH_3$	(i) Bond angle	(p) Increasing order
(II) $H_2O, H_2S, H_2Se, H_2Te$	(ii) Reducing character	(q) Decreasing order
(III) $HF, HCl, HBr, HI$	(iii) Intermolecular force	(r) All equal
(IV) $CH_4, SiH_4, GeH_4, SnH_4$	(iv) Boiling Point	(s) Irregular order

19. Which is the only **CORRECT** combination?

- (A) (I), (iv), (p)      (B) (II), (i), (p)      (C) (III), (iv), (q)      (D) (IV), (iii), (p)

20. Which is the only **INCORRECT** combination?

- (A) (I), (ii), (p)      (B) (IV), (i), (r)      (C) (III), (iii), (q)      (D) (II), (iv), (s)

21. In which combination, Drago's Rule plays an insignificant role in prediction of orders?

- (A) (I), (i), (q)      (B) (II), (iv), (s)      (C) (IV), (i), (r)      (D) (III), (ii), (p)

## MATCHING LIST TYPE 1 × 3 Q. (22 to 24)

Molecule	Hybridization of central atom(s)	Properties related to structure
(P) (HBNH) <sub>3</sub>	(I) sp <sup>2</sup>	(i) Cyclic structure
(Q) C <sub>3</sub> O <sub>2</sub>	(II) sp <sup>3</sup>	(ii) Has (X- $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}$ -X) linkage (X = central atom)
(R) P <sub>4</sub> O <sub>12</sub> <sup>4-</sup>	(III) sp <sup>3</sup> d	(iii) Planar
(S) N <sub>2</sub> O <sub>4</sub>	(IV) sp	(iv) Has (X - X) linkage

22. Identify **CORRECT** match

- (A) P, II, iii                      (B) P, I, i                      (C) P, IV, iii                      (D) Q, I, i

23. Identify **CORRECT** match

- (A) Q, IV, iii                      (B) Q, IV, i                      (C) Q, I, ii                      (D) R, I, ii

24. Identify **CORRECT** match

- (A) R, II, iv                      (B) R, II, ii                      (C) S, III, ii                      (D) S, IV, i

## EXERCISE # JEE-MAINS

1. Which products are expected from the disproportionation of hypochlorous acid : [AIEEE-2002]  
(1)  $\text{HClO}_3$  and  $\text{Cl}_2\text{O}$  (2)  $\text{HClO}_2$  and  $\text{HClO}$  (3)  $\text{HCl}$  and  $\text{Cl}_2\text{O}$  (4)  $\text{HCl}$  and  $\text{HClO}_3$
2. Identify the **INCORRECT** statement among the following : [AIEEE-2002]  
(1) Ozone reacts with  $\text{SO}_2$  to give  $\text{SO}_3$   
(2) Silicon reacts with  $\text{NaOH}(\text{aq.})$  in the presence of air to give  $\text{Na}_2\text{SiO}_3$  and  $\text{H}_2\text{O}$   
(3)  $\text{Cl}_2$  reacts with excess of  $\text{NH}_3$  to give  $\text{N}_2$  and  $\text{HCl}$   
(4)  $\text{Br}_2$  reacts with hot and strong  $\text{NaOH}$  solution to give  $\text{NaBr}$ ,  $\text{NaBrO}_4$  and  $\text{H}_2\text{O}$
3. Aluminium is industrially prepared by: [AIEEE-2002]  
(1) Fused cryolite (2) Bauxite ore (3) Alunite (4) Borax
4. For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be : [AIEEE-2003]  
(1) Sodium (2) Magnesium (3) Mercury (4) Tin
5. What may be expected when phosphine gas is mixed with chlorine gas: [AIEEE-2003]  
(1)  $\text{PCl}_5$  and  $\text{HCl}$  are formed and mixture cools down  
(2)  $\text{PH}_3 \cdot \text{Cl}_2$  is formed with warming up  
(3) The mixture only cools down  
(4)  $\text{PCl}_3$  and  $\text{HCl}$  are formed and the mixture warms up
6. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite : [AIEEE-2003]  
(1) Has molecules of variable molecular masses like polymers  
(2) Has carbon atoms arranged in large plated of rings of strongly bonded carbon atoms with weak interplate bonds  
(3) Is a non crystalline substance  
(4) Is an allotropic form of diamond
7. Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. This is due to : [AIEEE-2003]  
(1) Strong affinity of  $\text{HCl}$  gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke  
(2) Due to strong affinity for water, conc.  $\text{HCl}$  pulls moisture of air towards self. The moisture forms droplets of water and hence the cloud  
(3) Conc.  $\text{HCl}$  emits strongly smelling  $\text{HCl}$  gas all the time  
(4) Oxygen in air reacts with emitted  $\text{HCl}$  gas to form a cloud of  $\text{Cl}_2$  gas

8. Aluminium chloride exists as dimer,  $\text{Al}_2\text{Cl}_6$  in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives- [AIEEE-2004]
- (1)  $\text{Al}^{3+} + 3\text{Cl}^-$  (2)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} + 3\text{Cl}^-$   
(3)  $[\text{Al}(\text{OH})_6]^{3-} + 3\text{HCl}$  (4)  $\text{Al}_2\text{O}_3 + 6\text{HCl}$
9. The soldiers of Napoleon army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White Metallic tin buttons get converted to grey powder. This transformation is related to:- [AIEEE-2004]
- (1) An interaction with water vapour contained in humid air  
(2) A change in crystalline structure of tin  
(3) A change in the partial pressure of  $\text{O}_2$  in air  
(4) An interaction with  $\text{N}_2$  of air at low temperature
10. Which one of the following statements regarding helium is incorrect [AIEEE-2004]
- (1) It is used to produce and sustain powerful superconducting magnets  
(2) It is used as a cryogenic agent for carrying out experiments at low temperatures  
(3) It is used to fill gas balloons instead of hydrogen because it is lighter than hydrogen and non-inflammable  
(4) It is used in gas-cooled nuclear reactors
11. The number of hydrogen atoms attached to phosphorus atom in hypophosphorous acid is : [AIEEE-2005]
- (1) Zero (2) Two (3) One (4) Three
12. Heating an aqueous solution of aluminium chloride to dryness will give :- [AIEEE-2005]
- (1)  $\text{AlCl}_3$  (2)  $\text{Al}_2\text{Cl}_6$  (3)  $\text{Al}_2\text{O}_3$  (4)  $\text{Al}(\text{OH})\text{Cl}_2$
13. Which one of the following is the correct statement [AIEEE-2005]
- (1) Boric acid is a protonic acid  
(2) Beryllium exhibits coordination number of six  
(3) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase  
(4)  $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$  is known as "inorganic benzene"
14. In silicon dioxide : [AIEEE-2005]
- (1) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms  
(2) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms  
(3) Silicon atom is bonded to two oxygen atoms  
(4) There are double bonds between silicon and oxygen atoms

15. Regular use of which of the following fertilizer increases the acidity of soil : [AIEEE-2007]  
 (1) Potassium nitrate (2) Urea  
 (3) Superphosphate of lime (4) Ammonium sulphate
16. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence: [AIEEE-2007]  
 (1)  $\text{GeX}_2 \ll \text{SiX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$  (2)  $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{PbX}_2 \ll \text{SnX}_2$   
 (3)  $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$  (4)  $\text{PbX}_2 \ll \text{SnX}_2 \ll \text{GeX}_2 \ll \text{SiX}_2$
17. Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is [AIEEE-2008]  
 (1)  $\text{R}_4\text{Si}$  (2)  $\text{RSiCl}_3$  (3)  $\text{R}_2\text{SiCl}_2$  (4)  $\text{R}_3\text{SiCl}$
18. Which one of the following reactions of Xenon compounds is not feasible ? [AIEEE-2009]  
 (1)  $2\text{XeF}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Xe} + 4\text{HF} + \text{O}_2$  (2)  $\text{XeF}_6 + \text{RbF} \rightarrow \text{Rb}[\text{XeF}_7]$   
 (3)  $\text{XeO}_3 + 6\text{HF} \rightarrow \text{XeF}_6 + 3\text{H}_2\text{O}$  (4)  $3\text{XeF}_4 + 6\text{H}_2\text{O} \rightarrow 2\text{Xe} + \text{XeO}_3 + 12\text{HF} + 1.5\text{O}_2$
19. Which of the following statement is wrong ? [AIEEE-2011]  
 (1) Single N–N bond is weaker than the single P–P bond  
 (2)  $\text{N}_2\text{O}_4$  has two resonance structures  
 (3) The stability of hydrides increases from  $\text{NH}_3$  to  $\text{BiH}_3$  in group 15 of the periodic table  
 (4) Nitrogen cannot form  $d\pi\text{-}p\pi$  bond
20. Which of the following statements regarding sulphur is incorrect ? [AIEEE-2011]  
 (1) At  $600^\circ\text{C}$  the gas mainly consists of  $\text{S}_2$  molecules  
 (2) The oxidation state of sulphur is never less than +4 in its compounds  
 (3)  $\text{S}_2$  molecule is paramagnetic  
 (4) The vapour at  $200^\circ\text{C}$  consists mostly of  $\text{S}_8$  rings
21. Boron cannot form which one of the following anions ? [AIEEE-2011]  
 (1)  $\text{B}(\text{OH})_4^-$  (2)  $\text{BO}_2^-$  (3)  $\text{BF}_6^{3-}$  (4)  $\text{BH}_4^-$
22. In view of the signs of  $\Delta_r G^\circ$  for the following reactions  
 $\text{PbO}_2 + \text{Pb} \rightarrow 2 \text{PbO}, \Delta_r G^\circ < 0$   
 $\text{SnO}_2 + \text{Sn} \rightarrow 2 \text{SnO}, \Delta_r G^\circ > 0,$   
 Which oxidation states are more characteristic for lead and tin ? [AIEEE-2011]  
 (1) For lead + 4, for tin + 2 (2) For lead + 2, for tin + 2  
 (3) For lead + 4, for tin + 4 (4) For lead + 2, for tin + 4
23. The number of S–S bonds in  $\text{SO}_3, \text{S}_2\text{O}_3^{2-}, \text{S}_2\text{O}_6^{2-}$  and  $\text{S}_2\text{O}_8^{2-}$  respectively are :- [Jee Main(Online)-2012]  
 (1) 1, 0, 1, 0 (2) 0, 1, 1, 0 (3) 1, 0, 0, 1 (4) 0, 1, 0, 1
24. Which one of the following depletes ozone layer ? [Jee Main(Online)-2012]  
 (1) NO and freons (2)  $\text{SO}_2$  (3) CO (4)  $\text{CO}_2$



25. In which of the following arrangements, the sequence is not strictly according to the property written against it ? [Jee Main(Online)-2012]
- (1)  $\text{CO}_2 < \text{SiO}_2 < \text{SnO}_2 < \text{PbO}_2$  : increasing oxidising power  
 (2)  $\text{B} < \text{C} < \text{O} < \text{N}$  : increasing first ionisation enthalpy  
 (3)  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$  : increasing basic strength  
 (4)  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$  : increasing acid strength
26. The formation of molecular complex  $\text{BF}_3 - \text{NH}_3$  results in a change in hybridisation of boron :-
- (1) from  $\text{sp}^3$  to  $\text{sp}^3\text{d}$  (2) from  $\text{sp}^2$  to  $\text{dsp}^2$  [JEE(Main) Online-2012]  
 (3) from  $\text{sp}^3$  to  $\text{sp}^2$  (4) from  $\text{sp}^2$  to  $\text{sp}^3$
27. The catenation tendency of C, Si and Ge is in the order  $\text{Ge} < \text{Si} < \text{C}$ . The bond energies (in  $\text{kJ mol}^{-1}$ ) of C—C, Si—Si and Ge—Ge bonds are respectively : [JEE(Main) Online-2013]
- (1) 348, 260, 297 (2) 348, 297, 260 (3) 297, 348, 260 (4) 260, 297, 348
28. The gas evolved on heating  $\text{CaF}_2$  and  $\text{SiO}_2$  with concentrated  $\text{H}_2\text{SO}_4$ , on hydrolysis gives a white gelatinous precipitate. The precipitate is: [Jee Main(Online)-2014]
- (1) silica gel (2) silicic acid  
 (3) hydrofluosilicic acid (4) calciumfluorosilicate
29. Which of the following series correctly represents relations between the elements from X to Y? [Jee Main(Online)-2014]
- $\text{X} \rightarrow \text{Y}$
- (1)  ${}_{18}\text{Ar} \rightarrow {}_{54}\text{Xe}$  Noble character increases  
 (2)  ${}_3\text{Li} \rightarrow {}_{19}\text{K}$  Ionization enthalpy increases  
 (3)  ${}_6\text{C} \rightarrow {}_{32}\text{Ge}$  Atomic radii increases  
 (4)  ${}_9\text{F} \rightarrow {}_{35}\text{Br}$  Electron gain enthalpy with negative sign increases
30. Which of the following statements about the depletion of ozone layer is correct? [Jee Main(Online)-2014]
- (1) The problem of ozone depletion is more serious at poles because ice crystals in the clouds over poles act as catalyst for photochemical reactions involving the decomposition of ozone by  $\text{Cl}^\bullet$  and  $\text{ClO}^\bullet$  radicals  
 (2) The problem of ozone depletion is less serious at poles because  $\text{NO}_2$  solidifies and is not available for consuming  $\text{ClO}^\bullet$  radicals  
 (3) Oxides of nitrogen also do not react with ozone in stratosphere  
 (4) Freons, chlorofluorocarbons, are inert chemically, they do not react with ozone in stratosphere
31. Which of the following xenon-OXO compounds may not be obtained by hydrolysis of xenon fluorides ? [Jee Main(Online)-2014]
- (1)  $\text{XeO}_2\text{F}_2$  (2)  $\text{XeO}_3$  (3)  $\text{XeO}_4$  (4)  $\text{XeOF}_4$

32. Hydrogen peroxide acts both as an oxidising and as a reducing agent depending upon the nature of the reacting species. In which of the following cases  $\text{H}_2\text{O}_2$  acts as a reducing agent in acid medium ? [Jee Main(Online)-2014]
- (1)  $\text{MnO}_4^-$                       (2)  $\text{SO}_3^{2-}$                       (3) KI                                      (4)  $\text{Cr}_2\text{O}_7^{2-}$
33. Consider the reaction [Jee Main(Online)-2014]
- $$\text{H}_2\text{SO}_{3(\text{aq})} + \text{Sn}_{(\text{aq})}^{4+} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Sn}_{(\text{aq})}^{2+} + \text{HSO}_{4(\text{aq})}^- + 3\text{H}_{(\text{aq})}^+$$
- Which of the following statements is correct?
- (1)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes oxidation  
 (2)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes reduction  
 (3)  $\text{Sn}^{4+}$  is the reducing agent because it undergoes oxidation  
 (4)  $\text{Sn}^{4+}$  is the oxidizing agent because it undergoes oxidation
34. In the following sets of reactants which two sets best exhibit the amphoteric character of  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  ? [JEE(Main) Online-2014]
- Set-1 :**  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{OH}^- (\text{aq})$   
**Set-2 :**  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{H}_2\text{O} (\ell)$   
**Set-3 :**  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{H}^+ (\text{aq})$   
**Set-4 :**  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{NH}_3 (\text{aq})$
- (1) 1 and 2                      (2) 2 and 4                      (3) 1 and 3                                      (4) 3 and 4
35. Which of the following compounds has a P-P bond :- [Jee Main(Online)-2015]
- (1)  $\text{H}_4\text{P}_2\text{O}_5$                       (2)  $(\text{HPO}_3)_3$                       (3)  $\text{H}_4\text{P}_2\text{O}_7$                                       (4)  $\text{H}_4\text{P}_2\text{O}_6$
36. Chlorine water on standing loses its colour and forms :- [Jee Main(Online)-2015]
- (1) HCl and  $\text{HClO}_2$                                       (2) HCl only  
 (3) HOCl and  $\text{HOCl}_2$                                       (4) HCl and HOCl
37. Which among the following is the most reactive ? [Jee Main-2015]
- (1)  $\text{I}_2$                                       (2) ICl                                      (3)  $\text{Cl}_2$                                       (4)  $\text{Br}_2$
38. Which one has the highest boiling point ? [Jee Main-2015]
- (1) Kr                                      (2) Xe                                      (3) He                                      (4) Ne
39. From the following statements regarding  $\text{H}_2\text{O}_2$ , choose the incorrect statement : [Jee Main-2015]
- (1) It has to be stored in plastic or wax lined glass bottles in dark  
 (2) It has to be kept away from dust  
 (3) It can act only as an oxidizing agent  
 (4) It decomposes on exposure to light

40. The reaction of zinc with dilute and concentrated nitric acid, respectively produces :  
[JEE (Main) 2016]  
(1)  $\text{NO}_2$  and  $\text{N}_2\text{O}$       (2)  $\text{N}_2\text{O}$  and  $\text{NO}_2$       (3)  $\text{NO}_2$  and  $\text{NO}$       (4)  $\text{NO}$  and  $\text{N}_2\text{O}$
41. The non-metal that does not exhibit positive oxidation state is : [JEE (Main) 2016]  
(1) Oxygen      (2) Fluorine      (3) Iodine      (4) Chlorine
42. Which intermolecular force is most responsible in allowing xenon gas to liquefy?  
[JEE (Main) Online 2016]  
(1) Ionic      (2) Instantaneous dipole- induced dipole  
(3) Dipole - dipole      (4) Ion - dipole
43. The following statements concern elements in the periodic table. Which of the following is true ?  
[JEE (Main) Online 2016]  
(1) The group 13 elements are all metals.  
(2) For group 15 elements, the stability of +5 oxidation state increases down the group.  
(3) All the elements in Group 17 are gases.  
(4) Elements of group 16 have lower ionization enthalpy values compared to those of group 15 in the corresponding periods.
44. **Assertion** : Among the carbon allotropes, diamond is an insulator, whereas, graphite is a good conductor of electricity. [JEE (Main) Online 2016]  
**Reason** : Hybridization of carbon in diamond and graphite are  $\text{sp}^3$  and  $\text{sp}^2$ , respectively.  
(1) Assertion is incorrect statement, but the reason is correct.  
(2) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.  
(3) Both assertion and reason are incorrect.  
(4) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion.
45. Identify the incorrect statement : [JEE (Main) Online 2016]  
(1)  $\text{S}_8$  ring has a crown shape.  
(2) The S-S-S bond angles in the  $\text{S}_8$  and  $\text{S}_6$  rings are the same  
(3)  $\text{S}_2$  is paramagnetic like oxygen  
(4) Rhombic and monoclinic sulphur have  $\text{S}_8$  molecules.
46. Which of the following reactions is an example of a redox reaction ? [JEE (Main) 2017]  
(1)  $\text{XeF}_4 + \text{O}_2\text{F}_2 \rightarrow \text{XeF}_6 + \text{O}_2$   
(2)  $\text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+ \text{PF}_6^-$   
(3)  $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}$   
(4)  $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$
47. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are :-  
[JEE (Main) 2017]  
(1)  $\text{ClO}^-$  and  $\text{ClO}_3^-$       (2)  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$   
(3)  $\text{Cl}^-$  and  $\text{ClO}^-$       (4)  $\text{Cl}^-$  and  $\text{ClO}_2^-$

48. In which of the following reaction, hydrogen peroxide acts as an oxidizing agent ?  
 (1)  $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$  [JEE (Main) ONLINE 2017]  
 (2)  $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$   
 (3)  $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$   
 (4)  $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$
49.  $XeF_6$  on partial hydrolysis with water produces a compound 'X'. The same compound 'X' is formed when  $XeF_6$  reacts with silica. The compound 'X' is:- [JEE (Main) ONLINE 2017]  
 (1)  $XeO_3$  (2)  $XeF_4$  (3)  $XeOF_4$  (4)  $XeF_2$
50. The compound that does not produce nitrogen gas by the thermal decomposition is [JEE (Main) OFFLINE 2018]  
 (1)  $(NH_4)_2Cr_2O_7$  (2)  $NH_4NO_2$  (3)  $(NH_4)_2SO_4$  (4)  $Ba(N_3)_2$
51. For per gram of reactant, the maximum quantity of  $N_2$  gas is produced in which of the following thermal decomposition reactions ? [JEE (Main) ONLINE 2018]  
**(Given : Atomic wt. – Cr = 52u, Ba = 137u)**  
 (1)  $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$   
 (2)  $Ba(N_3)_2(s) \rightarrow Ba(s) + 3N_2(g)$   
 (3)  $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + 4H_2O(g)$   
 (4)  $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$
52. Lithium aluminium hydride reacts with silicon tetrachloride to form :- [JEE (Main) ONLINE 2018]  
 (1)  $LiCl, AlCl_3$  and  $SiH_4$  (2)  $LiCl, AlH_3$  and  $SiH_4$   
 (3)  $LiH, AlCl_3$  and  $SiCl_2$  (4)  $LiH, AlH_3$  and  $SiH_4$
53. Xenon hexafluoride on partial hydrolysis produces compounds 'X' and 'Y' Compounds 'X' and 'Y' and the oxidation state of Xe are respectively : [JEE (Main) ONLINE 2018]  
 (1)  $XeO_2F_2(+6)$  and  $XeO_2(+4)$  (2)  $XeOF_4(+6)$  and  $XeO_2F_2(+6)$   
 (3)  $XeOF_4(+6)$  and  $XeO_3(+6)$  (4)  $XeO_2(+4)$  and  $XeO_3(+6)$
54. Which of the following is a lewis acid ? [JEE (Main) ONLINE 2018]  
 (1)  $NaH$  (2)  $NF_3$  (3)  $PH_3$  (4)  $B(CH_3)_3$
55. Iodine reacts with concentrated  $HNO_3$  to yield Y along with other products. The oxidation state of iodine in Y, is :- [JEE (Main) ONLINE 2019]  
 (1) 5 (2) 3 (3) 1 (4) 7
56. Among the following reactions of hydrogen with halogens, the one that requires a catalyst is :  
 (1)  $H_2 + I_2 \rightarrow 2HI$  (2)  $H_2 + F_2 \rightarrow 2HF$  [JEE (Main) ONLINE 2019]  
 (3)  $H_2 + Cl_2 \rightarrow 2HCl$  (4)  $H_2 + Br_2 \rightarrow 2HBr$

57. Correct statements among a to d regarding silicones are : [JEE (Main) ONLINE 2019]  
 (a) They are polymers with hydrophobic character  
 (b) They are biocompatible.  
 (c) In general, they have high thermal stability and low dielectric strength.  
 (d) Usually, they are resistant to oxidation and used as greases.  
 (1) (a), (b) and (c) only  
 (2) (a), and (b) only  
 (3) (a), (b), (c) and (d)  
 (4) (a), (b) and (d) only
58. Diborane ( $B_2H_6$ ) reacts independently with  $O_2$  and  $H_2O$  to produce, respectively [JEE (Main) ONLINE 2019]  
 (1)  $HBO_2$  and  $H_3BO_3$  (2)  $H_3BO_3$  and  $B_2O_3$   
 (3)  $B_2O_3$  and  $H_3BO_3$  (4)  $B_2O_3$  and  $[BH_4]^-$
59. The amorphous form of silica is : [JEE (Main) ONLINE 2019]  
 (1) quartz (2) kieselguhr (3) cristobalite (4) tridymite
60. The correct statements among I to III regarding group 13 element oxides are, [JEE (Main) ONLINE 2019]  
 (I) Boron trioxide is acidic.  
 (II) Oxides of aluminium and gallium are amphoteric.  
 (III) Oxides of indium and thallium are basic.  
 (1) (I), (II) and (III) (2) (II) and (III) only (3) (I) and (III) only (4) (I) and (II) only
61. The redox reaction among the following is : [JEE (Main) ONLINE 2020]  
 (1) Combination of dinitrogen with dioxygen at 2000 K  
 (2) Formation of ozone from atmospheric oxygen in the presence of sunlight  
 (3) Reaction of  $H_2SO_4$  with NaOH  
 (4) Reaction of  $[Co(H_2O)_6]Cl_3$  with  $AgNO_3$
62. In the following reactions products (A) and (B), respectively, are : [JEE (Main) ONLINE 2020]  
 $NaOH + Cl_2 \rightarrow (A) + \text{side products}$   
 (hot and conc.)  
 $Ca(OH)_2 + Cl_2 \rightarrow (B) + \text{side products}$   
 (dry)  
 (1)  $NaClO_3$  and  $Ca(OCl)_2$  (2)  $NaOCl$  and  $Ca(ClO_3)_2$   
 (3)  $NaClO_3$  and  $Ca(ClO_3)_2$  (4)  $NaOCl$  and  $Ca(OCl)_2$
63. Chlorine reacts with hot and concentrated NaOH and produces compounds (X) and (Y). Compound (X) gives white precipitate with silver nitrate solution. The average bond order between Cl and O atoms in (Y) is \_\_\_\_\_. [JEE (Main) ONLINE 2020]
64. White Phosphorus on reaction with concentrated NaOH solution in an inert atmosphere of  $CO_2$  gives phosphine and compound (X). (X) on acidification with HCl gives compound (Y). The basicity of compound (Y) is : [JEE (Main) ONLINE 2020]  
 (1) 4 (2) 1 (3) 2 (4) 3

65. When gypsum is heated to 393 K, it forms : [JEE (Main) ONLINE 2020]
- (1) Dead burnt plaster
  - (2) Anhydrous  $\text{CaSO}_4$
  - (3)  $\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$
  - (4)  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$
66. The reaction of  $\text{H}_3\text{N}_3\text{B}_3\text{Cl}_3$  (A) with  $\text{LiBH}_4$  in tetrahydrofuran gives inorganic benzene (B). Further, the reaction of (A) with (C) leads to  $\text{H}_3\text{N}_3\text{B}_3(\text{Me})_3$ . Compounds (B) and (C) respectively, are: [JEE (Main) ONLINE 2020]
- (1) Boron nitride and  $\text{MeBr}$
  - (2) Borazine and  $\text{MeMgBr}$
  - (3) Borazine and  $\text{MeBr}$
  - (4) Diborane and  $\text{MeMgBr}$
67. 'X' melts at low temperature and is a bad conductor of electricity in both liquid and solid state. X is : [JEE (Main) ONLINE 2020]
- |                          |                   |
|--------------------------|-------------------|
| (1) Carbon tetrachloride | (2) Mercury       |
| (3) Silicon carbide      | (4) Zinc sulphide |
68. The compound that cannot act both as oxidising and reducing agent is : [JEE (Main) ONLINE 2020]
- |                            |                             |
|----------------------------|-----------------------------|
| (1) $\text{H}_2\text{O}_2$ | (2) $\text{H}_2\text{SO}_3$ |
| (3) $\text{HNO}_2$         | (4) $\text{H}_3\text{PO}_4$ |

## EXERCISE # J-ADVANCED

## (IIT JEE ASKED QUESTIONS)

## Fill in the blanks

- Give reason : [IIT- 2000]  
Why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus is a tetra atomic molecule.
- Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction. [IIT- 2000]
- Compounds X on reduction with  $\text{LiAlH}_4$  gives a hydride Y containing 21.72% hydrogen alongwith other products. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y. Give balanced reactions involved in the formation of Y and its reaction with air Draw the structure of Y. [IIT- 2001]
- Starting from  $\text{SiCl}_4$ , prepare the following in steps not exceeding the number given in parenthesis (reactions only) [IIT- 2001]
  - Silicon (1)
  - Linear silicon containing methyl group only (4)
  - $\text{Na}_2\text{SiO}_3$  (3)
- Write the balanced chemical equation for developing photographic films. [IIT- 2001]
- Identify (X) in the following synthetic scheme and write their structures. [IIT- 2001]  
 $\text{BaCO}_3^* + \text{H}_2\text{SO}_4 \longrightarrow \text{X (gas)}$  (C denotes  $\text{C}^{14}$ )
- Write the balanced equations for the reactions of the following compounds with water [2002]
  - $\text{Al}_4\text{Cl}_3$
  - $\text{CaNCN}$
  - $\text{BF}_3$
  - $\text{NCl}_3$
  - $\text{XeF}_3$
- Write the balanced equations for the reactions of the following compounds with water: [IIT- 2002]
  - $\text{Al}_4\text{C}_3$
  - $\text{CaNCN}$
  - $\text{BF}_3$
  - $\text{NCl}_3$
  - $\text{XeF}_4$
- Identify the following:  
$$\text{Na}_2\text{CO}_3 \xrightarrow[\text{(aq)}]{\text{SO}_2} \text{A} \xrightarrow{\text{Na}_2\text{CO}_3} \text{B} \xrightarrow[\Delta]{\text{elemental S}} \text{C} \xrightarrow{\text{I}_2} \text{D}$$
 [IIT- 2003]  
Also mention the oxidation state of S in all the compounds.
- Arrange the following oxides in the increasing order of Bronsted basicity. [IIT- 2004]  
 $\text{Cl}_2\text{O}_7, \text{BaO}, \text{SO}_3, \text{CO}_2, \text{B}_2\text{O}_3$
- The number of P—O—P bonds in cyclic tetrametaphosphoric acid is – [IIT-2000]  
(A) Zero (B) Two (C) Three (D) Four
- The correct order of acidic strength is – [IIT- 2000]
  - $\text{Cl}_2\text{O}_7 > \text{SO}_2 > \text{P}_4\text{O}_{10}$
  - $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$
  - $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$
  - $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$

13. Amongst  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ , the one with the highest boiling point is – [IIT- 2000]  
 (A)  $\text{H}_2\text{O}$  because of hydrogen bonding (B)  $\text{H}_2\text{Te}$  because of higher molecular weight  
 (C)  $\text{H}_2\text{S}$  because of hydrogen bonding (D)  $\text{H}_2\text{Se}$  because of lower molecular weight.
14. Ammonia can be dried by – [IIT- 2000]  
 (A) Conc.  $\text{H}_2\text{SO}_4$  (B)  $\text{P}_4\text{O}_{10}$  (C)  $\text{CaO}$  (D) Anhydrous  $\text{CaCl}_2$
15. Which of the following are hydrolysed – [REE 2000]  
 (A)  $\text{NCl}_3$  (B)  $\text{BCl}_3$  (C)  $\text{CCl}_4$  (D)  $\text{SiCl}_4$
16. The set with correct order of acidity is – [IIT- 2001]  
 (A)  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$  (B)  $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$   
 (C)  $\text{HClO} < \text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2$  (D)  $\text{HClO}_4 < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}$
17. The reaction,  $3\text{ClO}^- (\text{aq}) \longrightarrow \text{ClO}_3^- (\text{aq}) + 2\text{Cl}^- (\text{aq})$  is an example of – [IIT- 2001]  
 (A) Oxidation reaction (B) reduction reaction  
 (C) Disproportionation reaction (D) Decomposition reaction
18. The number of S–S bonds in sulphur trioxide trimer, ( $\text{S}_3\text{O}_9$ ) is – [IIT- 2001]  
 (A) Three (B) Two (C) One (D) Zero
19. **Statement-I** : Between  $\text{SiCl}_4$  and  $\text{CCl}_4$ , only  $\text{SiCl}_4$  reacts with water [IIT- 2001]  
**Because :**  
**Statement-II** :  $\text{SiCl}_4$  is ionic and  $\text{CCl}_4$  is covalent  
 (A) If both assertion and reason are correct and reason is the correct explanation of the assertion  
 (B) If both assertion and reason are correct, but reason is not the correct explanation of the assertion  
 (C) If assertion is correct, but reason is incorrect  
 (D) If assertion is incorrect, but reason is correct.
20. Polyphosphates are used as water softening agents because they – [IIT- 2002]  
 (A) Form soluble complexes with anionic species  
 (B) Precipitate anionic species  
 (C) Form soluble complexes with cationic species  
 (D) Precipitate cationic species
21. Identify the correct order of solubility of  $\text{Na}_2\text{S}$ ,  $\text{CuS}$ , and  $\text{ZnS}$  in aqueous medium – [IIT- 2002]  
 (A)  $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$  (B)  $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$   
 (C)  $\text{Na}_2\text{S} > \text{CuS} > \text{ZnS}$  (D)  $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$
22. Identify, the correct order of acidic strength of  $\text{CO}_2$ ,  $\text{CuO}$ ,  $\text{CaO}$ ,  $\text{H}_2\text{O}$  – [IIT- 2002]  
 (A)  $\text{CaO} < \text{CuO} < \text{H}_2\text{O} < \text{CO}_2$  (B)  $\text{H}_2\text{O} < \text{CuO} < \text{CaO} < \text{CO}_2$   
 (C)  $\text{CaO} < \text{H}_2\text{O} < \text{CuO} < \text{CO}_2$  (D)  $\text{H}_2\text{O} < \text{CO}_2 < \text{CaO} < \text{CuO}$



23.  $\text{H}_3\text{BO}_3$  is – [IIT- 2002, 3]  
 (A) Monobasic acid and weak Lewis acid (B) Monobasic and weak Bronsted acid  
 (C) Monobasic and strong Lewis acid (D) Tribasic and weak Bronsted acid
24. When  $\Gamma^-$  is oxidised by  $\text{MnO}_4^-$  in alkaline medium,  $\Gamma^-$  converts into – [IIT- 2003]  
 (A)  $\text{IO}_3^-$  (B)  $\text{I}_2$  (C)  $\text{IO}_4^-$  (D)  $\text{IO}^-$
25. **Column-I (Change)** **Column-II (Given change is done by)**  
 (A)  $\text{Bi}^{3+} \longrightarrow (\text{BiO})^+$  (p) Heat [IIT- 2003]  
 (B)  $[\text{AlO}_2]^- \longrightarrow \text{Al}(\text{OH})_3$  (q) Hydrolysis  
 (C)  $\text{SiO}_4^{4-} \longrightarrow \text{Si}_2\text{O}_7^{6-}$  (r) Acidification  
 (D)  $(\text{B}_4\text{O}_7^{2-}) \longrightarrow [\text{B}(\text{OH})_3]$  (s) Dilution by water
26.  $(\text{Me})_2\text{SiCl}_2$  on hydrolysis will produce – [IIT- 2003]  
 (A)  $(\text{Me})_2\text{Si}(\text{OH})_2$  (B)  $(\text{Me})_2\text{Si}=\text{O}$   
 (C)  $[-(\text{Me})_2\text{Si}-\text{O}-]_n$  (D)  $\text{Me}_2\text{SiCl}(\text{OH})$
27. Which is the most thermodynamically stable allotropic form of phosphorus? [IIT- 2004]  
 (A) Red (B) White (C) Black (D) Yellow
28. When  $\text{PbO}_2$  reacts with conc.  $\text{HNO}_3$  the gas evolved may be : [2005]  
 (A)  $\text{NO}_2$  (B)  $\text{O}_2$  (C)  $\text{N}_2$  (D)  $\text{N}_2\text{O}$
29. Which of the following is not oxidised by  $\text{O}_3$ ? [IIT- 2005]  
 (A) KI (B)  $\text{FeSO}_4$  (C)  $\text{KMnO}_4$  (D)  $\text{K}_2\text{MnO}_4$
30. Which blue-liquid is obtained on reacting equimolar amounts of two gases at  $-30^\circ\text{C}$ ? [IIT- 2005]  
 (A)  $\text{N}_2\text{O}$  (B)  $\text{N}_2\text{O}_3$  (C)  $\text{N}_2\text{O}_4$  (D)  $\text{N}_2\text{O}_5$
31.  $\text{B}(\text{OH})_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na}[\text{B}(\text{OH})_4] + \text{H}_2\text{O}$  how can this reaction is made to proceed in forward direction? [IIT- 2006]  
 (A) Addition of cis 1, 2 diol (B) Addition of borax  
 (C) Addition of trans 1, 2 diol (D) Addition of  $\text{Na}_2\text{HPO}_4$
32. Among the following, the paramagnetic compound is – [IIT- 2007]  
 (A)  $\text{Na}_2\text{O}_2$  (B)  $\text{O}_3$  (C)  $\text{N}_2\text{O}$  (D)  $\text{KO}_2$
33. **Statement-I** : Boron always forms covalent bond [2007]  
**Because :**  
**Statement-II** : The small size of  $\text{B}^{3+}$  favours formation of covalent bond.  
 (A) Statement-I is True, Statement-II is True, Statement-II is a correct explanation for Statement-I  
 (B) Statement-I is True, Statement-II is True, Statement-II is not a correct explanation for Statement-II  
 (C) Statement-I is True, Statement-II is False  
 (D) Statement-I is False, Statement-II is True

34. **Statement-I** : In water, orthoboric acid behaves as a weak monobasic acid. [2007]  
**Statement-II** : In water, orthoboric acid acts as a proton donor.  
 (A) Statement-I is True, Statement-II is True, Statement-II is a correct explanation for Statement-I  
 (B) Statement-I is True, Statement-II is True, Statement-II is not a correct explanation for Statement-I  
 (C) Statement-I is True, Statement-II is False (D) Statement-I is False, Statement-II is True

### Comprehension # 1 (Q. 35 to 37)

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling point of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions. The direct reaction of xenon with fluorine leads to a series of compounds with oxidation number + 2, + 4 and + 6.  $\text{XeF}_4$  reacts violently with water to give  $\text{XeO}_3$ . The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell. [IIT- 2007]

35. Argon is used in arc welding because of its –  
 (A) Low reactivity with metal (B) Ability to lower the melting point of metal  
 (C) Flammability (D) High calorific value
36. The structure of  $\text{XeO}_3$  is –  
 (A) Linear (B) Planar (C) Pyramidal (D) T-shaped
37.  $\text{XeF}_4$  and  $\text{XeF}_6$  are expected to be –  
 (A) Oxidising agent (B) Reducing agent (C) Unreactive (D) Strongly basic

### Comprehension # 2 (Q.38 to 40)

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of  $\text{NH}_3$  and  $\text{PH}_3$ . Phosphine is a flammable gas and is prepared from white phosphorous. [IIT- 2008]

38. Among the following, the correct statement is :-  
 (A) Phosphates have no biological significance in humans  
 (B) Between nitrates and phosphates, phosphates are less abundant in earth's crust  
 (C) Between nitrates and phosphates, nitrates are less abundant in earth's crust  
 (D) Oxidation of nitrates is possible in soil
39. Among the following, the correct statement is :-  
 (A) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional  
 (B) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
 (C) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
 (D) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.

40. White phosphorus on reaction with NaOH gives  $\text{PH}_3$  as one of the products. This is a :-  
 (A) dimerization reaction (B) disproportionation reaction  
 (C) condensation reaction (D) precipitation reaction
41. The reaction of  $\text{P}_4$  with X leads selectively to  $\text{P}_4\text{O}_6$ . The X is [JEE 2009]  
 (A) Dry  $\text{O}_2$  (B) A mixture of  $\text{O}_2$  and  $\text{N}_2$   
 (C) Moist  $\text{O}_2$  (D)  $\text{O}_2$  in the presence of aqueous NaOH
42. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type ; the oxidation states of phosphorus in phosphine and the other product are respectively [JEE 2012]  
 (A) redox reaction ; -3 and -5 (B) redox reaction ; +3 and +5  
 (C) disproportionation reaction ; -3 and +1 (D) disproportionation reaction ; -3 and +3
43. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is :  
 (A)  $\text{Cl}_2\text{O}$  (B)  $\text{Cl}_2\text{O}_7$  (C)  $\text{ClO}_2$  (D)  $\text{Cl}_2\text{O}_6$  [JEE 2012]
44. With respect to graphite and diamond, which of the statement(s) given below is (are) correct ? [JEE 2012]  
 (A) Graphite is harder than diamond.  
 (B) Graphite has higher electrical conductivity than diamond.  
 (C) Graphite has higher thermal conductivity than diamond.  
 (D) Graphite has higher C-C bond order than diamond.
45. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of -  
 (A) NO (B)  $\text{NO}_2$  (C)  $\text{N}_2\text{O}$  (D)  $\text{N}_2\text{O}_4$  [JEE 2013]
46. The correct statement(s) about  $\text{O}_3$  is(are) [JEE 2013]  
 (A) O-O bond lengths are equal (B) Thermal decomposition of  $\text{O}_3$  is endothermic  
 (C)  $\text{O}_3$  is diamagnetic in nature (D)  $\text{O}_3$  has a bent structure

### Comprehension # 3 (Q. 47 and 48)

The reaction of  $\text{Cl}_2$  gas with cold dilute and hot concentrated NaOH in water give sodium salt of two (different) oxoacids of chlorine P and Q respectively. The  $\text{Cl}_2$  gas reacts with  $\text{SO}_2$  gas, in presence of charcoal to give a product R. R reacts with white phosphorous to give a compound S. On hydrolysis, S gives as oxoacid of phosphorous T.

47. R, S and T, respectively are - [JEE 2013]  
 (A)  $\text{SO}_2\text{Cl}_2$ ,  $\text{PCl}_5$  and  $\text{H}_3\text{PO}_4$  (B)  $\text{SO}_2\text{Cl}_2$ ,  $\text{PCl}_3$  and  $\text{H}_3\text{PO}_3$   
 (C)  $\text{SOCl}_2$ ,  $\text{PCl}_3$  and  $\text{H}_3\text{PO}_2$  (D)  $\text{SOCl}_2$ ,  $\text{PCl}_3$  and  $\text{H}_3\text{PO}_3$
48. P and Q, respectively, are the sodium salts of -  
 (A) Hypochlorous and chloric acid (B) Hypochlorous and chlorus acid  
 (C) Chloric and perchloric acids (D) Chloric and hypochlorous acids

49. The unbalanced chemical reactions given in List-I show missing reagent or condition (?) which are provided in List-II. Match List-I with List-II and select the correct answer using the code given below the lists

A

[JEE 2013]

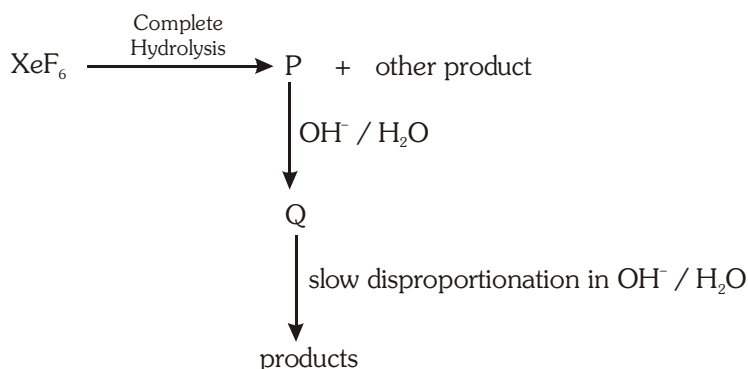
List-I	List-II
(P) $\text{PbO}_2 + \text{H}_2\text{SO}_4 \xrightarrow{?} \text{PbSO}_4 + \text{O}_2 + \text{other product}$	(1) NO
(Q) $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \xrightarrow{?} \text{NaHSO}_4 + \text{other product}$	(2) $\text{I}_2$
(R) $\text{N}_2\text{H}_4 \xrightarrow{?} \overset{\circ}{\text{N}}_2 + \text{other product}$	(3) Warm
(S) $\text{XeF}_2 \xrightarrow{?} \text{Xe} + \text{other product}$	(4) $\text{Cl}_2$

Codes :

	P	Q	R	S		P	Q	R	S
(A)	4	2	3	1	(B)	3	2	1	4
(C)	1	4	2	3	(D)	3	4	2	1

50. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is

[JEE Adv. 2014]



- (A) 0                      (B) 1                      (C) 2                      (D) 3

51. The product formed in the reaction of  $\text{SOCl}_2$  with white phosphorous is

[JEE Adv. 2014]

- (A)  $\text{PCl}_3$                       (B)  $\text{SO}_2\text{Cl}_2$                       (C)  $\text{SCl}_2$                       (D)  $\text{POCl}_3$

52. The **CORRECT** statement(s) for orthoboric acid is / are -

[JEE Adv. 2014]

- (A) It behaves as a weak acid in water due to self ionization  
 (B) Acidity of its aqueous solution increases upon addition of ethylene glycol  
 (C) It has a three dimensional structure due to hydrogen bonding.  
 (D) It is a weak electrolyte in water

53. The correct statement(s) regarding, (i)  $\text{HClO}$ , (ii)  $\text{HClO}_2$ , (iii)  $\text{HClO}_3$  and (iv)  $\text{HClO}_4$ , is(are)

[JEE Adv. 2015]

- (A) The number of  $\text{Cl}=\text{O}$  bonds in (ii) and (iii) together is two  
 (B) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three  
 (C) The hybridization of Cl in (iv) is  $\text{sp}^3$   
 (D) Amongst (i) to (iv), the strongest acid is (i)

54. When  $O_2$  is adsorbed on a metallic surface, electron transfer occurs from the metal to  $O_2$ . The TRUE, statement (s) regarding this adsorption is (are) [JEE Adv. 2015]  
 (A)  $O_2$  is physisorbed (B) heat is released  
 (C) occupancy of  $\pi_{2p}^*$  of  $O_2$  is increased (D) bond length of  $O_2$  is increased
55. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are [JEE (Adv.) 2015]  
 (A)  $CH_3SiCl_3$  and  $Si(CH_3)_4$  (B)  $(CH_3)_2SiCl_2$  and  $(CH_3)_3SiCl$   
 (C)  $(CH_3)_2SiCl_2$  and  $CH_3SiCl_3$  (D)  $SiCl_4$  and  $(CH_3)_3SiCl$
56. Three moles of  $B_2H_6$  are completely reacted with methanol. The number of moles of boron containing product formed is - [JEE (Adv.) 2015]
57. The increasing order of atomic radii of the following group 13 elements is : [JEE Adv. 2016]  
 (A)  $Al < Ga < In < Tl$  (B)  $Ga < Al < In < Tl$   
 (C)  $Al < In < Ga < Tl$  (D)  $Al < Ga < Tl < In$
58. The crystalline form of borax has [JEE Adv. 2016]  
 (A) Tetranuclear  $[B_4O_5(OH)_4]^{2-}$  unit  
 (B) All boron atoms in the same plane  
 (C) Equal number of  $sp^2$  and  $sp^3$  hybridized boron atoms  
 (D) One terminal hydroxide per boron atom
59. The nitrogen containing compound produced in the reaction of  $HNO_3$  with  $P_4O_{10}$  [JEE Adv. 2016]  
 (A) can also be prepared by reaction of  $P_4$  and  $HNO_3$   
 (B) is diamagnetic  
 (C) contains one N-N bond  
 (D) reacts with Na metal producing a brown gas
60. The correct statements(s) about the oxoacids,  $HClO_4$  and  $HClO$ , is (are) - [JEE Adv. 2017]  
 (A)  $HClO_4$  is more acidic than  $HClO$  because of the resonance stabilization of its anion  
 (B)  $HClO_4$  is formed in the reaction between  $Cl_2$  and  $H_2O$   
 (C) The central atom in Both  $HClO_4$  and  $HClO$  is  $sp^3$  hybridized  
 (D) The conjugate base of  $HClO_4$  is weaker base than  $H_2O$
61. The colour of the  $X_2$  molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to - [JEE Adv. 2017]  
 (A) the physical state of  $X_2$  at room temperature changes from gas to solid down the group  
 (B) decrease in HOMO-LUMO gap down the group  
 (C) decrease in  $\pi^*-\sigma^*$  gap down the group  
 (D) decrease in ionization energy down the group

62. The order of the oxidation state of the phosphorus atom in  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_3$  and  $\text{H}_4\text{P}_2\text{O}_6$  is [JEE Adv. 2017]
- (A)  $\text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2$   
 (B)  $\text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6$   
 (C)  $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_4$   
 (D)  $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6$
63. The option(s) with only amphoteric oxides is (are): [JEE Adv. 2017]
- (A)  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}$ ,  $\text{SnO}$ ,  $\text{PbO}$   
 (B)  $\text{NO}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{SnO}_2$   
 (C)  $\text{Cr}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{SnO}$ ,  $\text{SnO}_2$   
 (D)  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{PbO}_2$
64. Among the following, the correct statement(s) is are [JEE Adv. 2017]
- (A)  $\text{Al}(\text{CH}_3)_3$  has the three-centre two-electron bonds in its dimeric structure  
 (B)  $\text{AlCl}_3$  has the three-centre two-electron bonds in its dimeric structure  
 (C)  $\text{BH}_3$  has the three-centre two-electron bonds in its dimeric structure  
 (D) The Lewis acidity of  $\text{BCl}_3$  is greater than that of  $\text{AlCl}_3$

### Paragraph for Q.65 & 66

Upon heating  $\text{KClO}_3$  in the presence of catalytic amount of  $\text{MnO}_2$ , a gas **W** is formed. Excess amount of **W** reacts with white phosphorus to give **X**. The reaction of **X** with pure  $\text{HNO}_3$  gives **Y** and **Z**. [JEE Adv. 2017]

65. **W** and **X** are, respectively
- (A)  $\text{O}_3$  and  $\text{P}_4\text{O}_6$       (B)  $\text{O}_2$  and  $\text{P}_4\text{O}_{10}$       (C)  $\text{O}_3$  and  $\text{P}_4\text{O}_{10}$       (D)  $\text{O}_2$  and  $\text{P}_4\text{O}_6$
66. **Y** and **Z** are, respectively
- (A)  $\text{N}_2\text{O}_4$  and  $\text{H}_3\text{PO}_3$       (B)  $\text{N}_2\text{O}_4$  and  $\text{HPO}_3$   
 (C)  $\text{N}_2\text{O}_5$  and  $\text{HPO}_3$       (D)  $\text{N}_2\text{O}_3$  and  $\text{H}_3\text{PO}_4$
67. The compound(s) which generate(s)  $\text{N}_2$  gas upon thermal decomposition below  $300^\circ\text{C}$  is (are) [IIT JEE 2018]
- (A)  $\text{NH}_4\text{NO}_3$       (B)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$       (C)  $\text{Ba}(\text{N}_3)_2$       (D)  $\text{Mg}_3\text{N}_2$

### INTEGER

68. The total number of compounds having at least one bridging oxo group among the molecules given below is \_\_\_\_\_. [JEE Adv. 2018]
- $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{P}_4\text{O}_6$ ,  $\text{P}_4\text{O}_7$ ,  $\text{H}_4\text{P}_2\text{O}_5$ ,  $\text{H}_5\text{P}_3\text{O}_{10}$ ,  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{S}_2\text{O}_5$

69. A tin chloride **Q** undergoes the following reactions (not balanced) [JEE Adv. 2019]  
 $Q + Cl^- \rightarrow X$   
 $Q + Me_3N \rightarrow Y$   
 $Q + CuCl_2 \rightarrow Z + CuCl$   
X is a monoanion having pyramidal geometry. Both **Y** and **Z** are neutral compounds. Choose the correct option(s).  
(1) The central atoms in **X** is  $sp^3$  hybridized  
(2) The oxidation state of the central atom in **Z** is +2  
(3) The central atom in **Z** has one lone pair of electrons  
(4) There is a coordinate bond in **Y**
70. At 143 K. the reaction of  $XeF_4$  with  $O_2F_2$  produces a xenon compound **Y**. The total number of lone pair(s) of electrons present on the whole molecule of **Y** is \_\_\_\_\_ [JEE Adv. 2019]
71. The amount of water produced (in g) in the oxidation of 1 mole of rhombic sulphur by conc.  $HNO_3$  to a compound with the highest oxidation state of sulphur is \_\_\_\_ [JEE Adv. 2019]  
(Given data : Molar mass of water =  $18 \text{ g mol}^{-1}$ )
72. Each of the following options contains a set of four molecules. Identify the option(s) where all four molecules possess permanent dipole moment at room temperature. [JEE Adv. 2019]  
(1)  $BeCl_2$ ,  $CO_2$ ,  $BCl_3$ ,  $CHCl_3$  (2)  $SO_2$ ,  $C_6H_5Cl$ ,  $H_2Se$ ,  $BrF_5$   
(3)  $BF_3$ ,  $O_3$ ,  $SF_6$ ,  $XeF_6$  (4)  $NO_2$ ,  $NH_3$ ,  $POCl_3$ ,  $CH_3Cl$
73. Among  $B_2H_6$ ,  $B_3N_3H_6$ ,  $N_2O$ ,  $N_2O_4$ ,  $H_2S_2O_3$  and  $H_2S_2O_8$ , the total number of molecules containing covalent bond between two atoms of the same kind is \_\_\_\_\_ [JEE Adv. 2019]

**ANSWER KEY****EXERCISE # I**

(ONLY ONE OPTION IS CORRECT)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	C	C	B	A	B	B	D	C	B	B
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	A	A	A	B	B	A	B	A	A	A
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	B	C	B	D	A	A	B	B	C	B
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	A	D	A	B	C	C	B	C	B	D
Que.	41	42	43	44	45	46	47			
Ans.	A	A	B	C	A	C	A			

**EXERCISE # II**

(ONE OR MORE THAN ONE OPTION MAY BE CORRECT)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A, B	A, B, C	A, C, D	A, B, C	A, B, D	A, B	A, B, C	A, B, C	A, B, C, D	A, C, D
Que.	11	12	13	14	15	16	17			
Ans.	A, B, C, D	C, D	C, D	A, B, C, D	D	B, C, D	A, B, C, D			

**EXERCISE # III**

PARAGRAPH &amp; MATRIX MATCH

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	B	A	D	A	C	D	A	B	A	A
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	D	C	B	C	B	B	C	A	D	C
Que.	21	22	23	24						
Ans.	BCD	B	A	B						

**EXERCISE # J-MAINS**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	4	4	2	3	4	2	2	2	2	3
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	2	3	3	1	4	3	2	3	3	2
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	3	4	2	1	3	4	2	2	3	1
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	3	1	1	3	4	4	2	2	3	2
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	2	2	4	4	2	1	3	3	3	3
Que.	51	52	53	54						
Ans.	4	1	2	4						



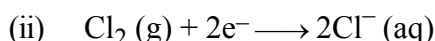
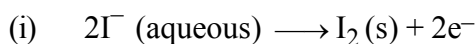
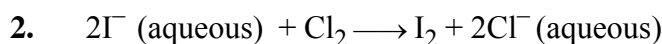
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|------------------------|--------------|-------------|--------------|
| 55. Ans.(1)            | 56. Ans.(1)  | 57. Ans.(3) | 58. Ans.(3)  |
| 59. Ans.(2)            | 60. Ans.(1)  | 61. Ans.(1) | 62. Ans. (1) |
| 63. Ans.(1.66 to 1.67) |              |             |              |
| 64. Ans.(2)            | 65. Ans. (4) | 66. Ans.(2) | 67. Ans.(1)  |
| 68. Ans.(4)            |              |             |              |

### EXERCISE # J- ADVANCED

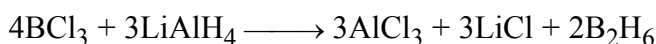
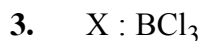
#### Fill in the blanks

1.  $P \equiv P$

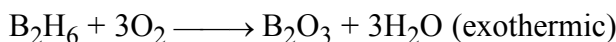
$3p_{\pi}-3p_{\pi}$  bond is not effective due to large size of P.



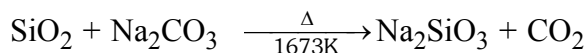
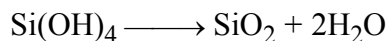
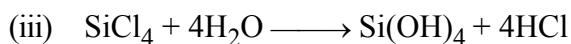
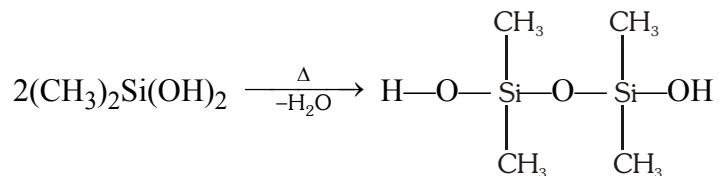
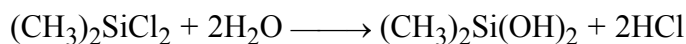
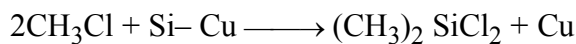
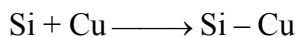
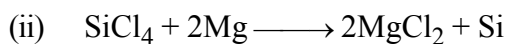
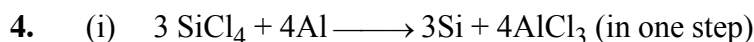
Thus,  $I^{-}$  is oxidised into  $I_2$  by  $Cl_2$  due to higher oxidised potential of  $Cl_2$  than  $I_2$

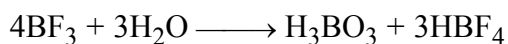
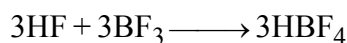
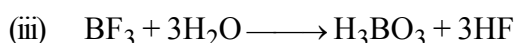
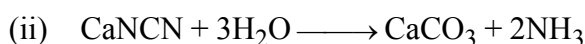
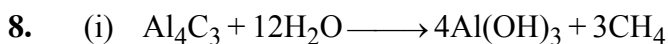
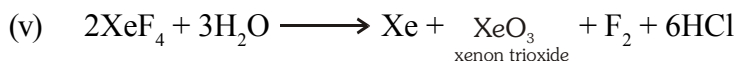
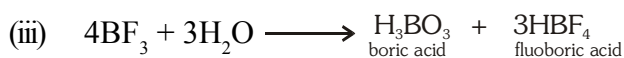
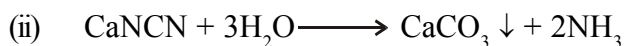
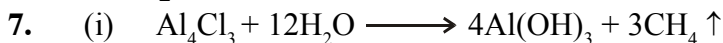
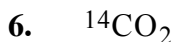
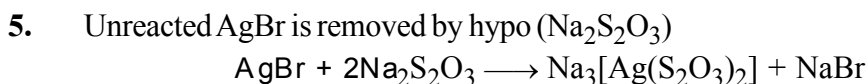


X

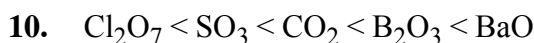
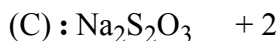


Y

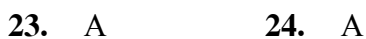




9. Oxidation state

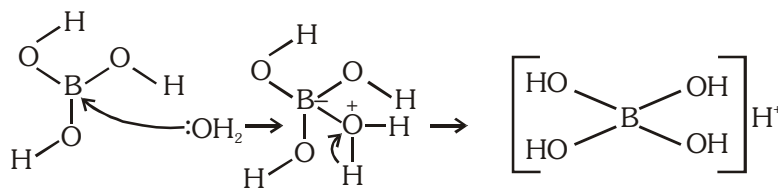


Objective



Boron always forms covalent bond because boron requires very high energy of form  $\text{B}^{3+}$  and again  $\text{B}^{3+}$  due to its very small size having high polarising power thus cause greater polarisation and eventually significant covalent characteristics-Fajans rule.

34. C



Comprehension # 1 (Q. 35 to 37)

35. A                      36. C                      37. A or B

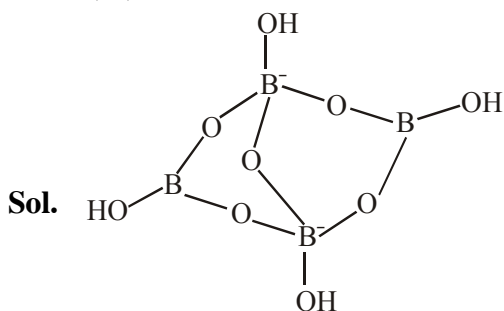
Comprehension # 2 (Q.38 to 40)

38. C                      39. C                      40. B                      41. B                      42. C                      43. A  
 44. B,D                      45. B                      46. A,C,D                      47. A                      48. A                      49. D  
 50. C                      51. A                      52. B,D                      53. B,C                      54. B,C,D                      55. B  
 56. 6  
 57. (B)

Sol. The order of radius of 13<sup>th</sup> group elements is Ga < Al < In < Tl.

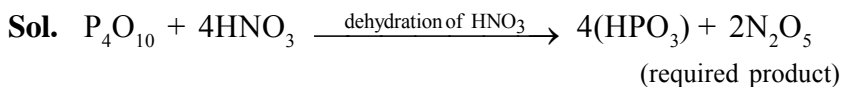
Reason ⇒ Due to poor shielding effect of d-orbital, radius of Ga is smaller than Al.

58. (A,C,D)

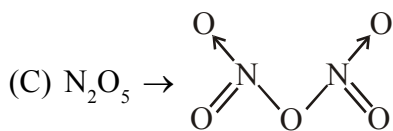


- (A) Having  $[B_4O_5(OH)_4]^{2-}$  tetranuclear (boron) unit  
 (B) All boron atoms not in same plane  
 (C) Two boron are  $sp^2$  hybridised and two boron are  $sp^3$  hybridised  
 (D) One terminal hydroxide per boron atom is present.

59. (B,D)



- (A)  $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 \uparrow + 4H_2O$   
 (B)  $N_2O_5$  is diamagnetic in nature



$N_2O_5$  contains one N-O-N bond not N-N bond.

- (D)  $Na + N_2O_5 \rightarrow NaNO_3 + NO_2 \uparrow$   
 (Brown gas)

60. A,C,D                      61. B,C                      62. A                      63. C,D  
 64. A,C,D                      65. B                      66. C                      67. B,C  
 68. 5 or 6                      69. (1,4)                      70. (19.00)                      71. (288.00)  
 72. (2,4)                      73. (4.00)

## METALLURGY

### □ INTRODUCTION :

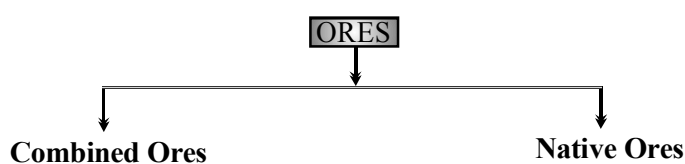
The compound of a metal found in nature is called a **mineral**.

The minerals from which metal can be economically and conveniently extracted are called **ores**.

An ore is usually contaminated with earthy or undesired materials known as **gangue**.

**Note :** All minerals are not ores but all ores are minerals.

Ores may be classified mainly into following two classes.



(a) **Native ores :** Silver, gold, platinum etc, occur as native ores.

(b) **Combined ores :** They contain the metal in combined form.

(i) **Oxidised ores :** Oxide ores , Carbonate ores, Sulphate ores, Phosphate ores, Silicate ores.

(ii) **Sulphurised ores :** These ores consist of sulphides of metals like iron, lead, zinc, mercury etc.

(iii) **Halide ores :** These ores consist of halides of metals

### □ METALLURGY :

The scientific and technological process used for the extraction/isolation of the metal from its ore is called as metallurgy.

The isolation and extraction of metals from their ores involve the following major steps:

(A) Crushing of the ore.

(B) Dressing or concentration of the ore.

(C) Isolation of the crude metal from its ore

(D) Purification or refining of the metal.

(A) **Crushing and Grinding :** The ore is first crushed by crushers and ground to a powder.

(B) **Concentration of the ore :** The removal of unwanted, useless impurities from the ore is called **dressing, concentration or benefaction of ore**.

There are several steps for the concentration of Ores.

**(I) By physical separation**

(a) Gravity separation (Levigation)

(b) Froth Floatation method

(c) Magnetic separation

**(i) Gravity separation or Levigation method :**

It is based on the difference in the densities of the gangue and ore particles. This method is generally used for the concentration of oxide and native ores.

**(ii) Electromagnetic separation :**

It is based on differences in magnetic properties of the ore components.

It is used when either the ore or the impurities associated with it are magnetic in nature.

**Examples :**

Chromite ore( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) is separated from non-magnetic silicious impurities and cassiterite ore( $\text{SnO}_2$ ) is separated from magnetic Wolframite ( $\text{FeWO}_4 + \text{MnWO}_4$ ).

**(iii) Froth floatation process :** This process is based on differential wetting of the ore by oil and gangue by water.

**Examples :** Galena,  $\text{PbS}$  (ore of Pb) ; copper pyrites  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$  or  $\text{CuFeS}_2$  (ore of copper) ; zinc blende,  $\text{ZnS}$  (ore of zinc) etc.

(a) **Frothers :** Oil like pine oil, camphor oil etc., are used as frothers.

(b) **Frothers stablizer :** Aneline & Cressol

(c) **Collectors :** Potassium or sodium ethyl xanthate is used as a collector.

(d) **Activating and depressing agents :** For example galena ( $\text{PbS}$ ) usually contains the minerals namely zinc blende ( $\text{ZnS}$ ) and pyrites ( $\text{FeS}_2$ ) as impurities. Floatation is carried out by using potassium ethyl xanthate (used as a collector) along with  $\text{NaCN}$  and  $\text{Na}_2\text{CO}_3$  (used as depressing agent).

**(II) By Chemical separation**

Some of the ores are concentrated by means of chemical treatment.

**Leaching :** It involves the treatment of the ore with a suitable reagent. as to make it soluble while impurity remain insoluble. The ore is recovered from the solution by suitable chemical method.

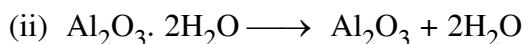
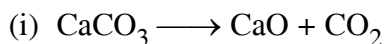
(i) **Bayer's process**

(ii) **Cyanide process**

□ **CALCINATION**

Calcination is a process in which ore is heated, generally in the **absence of air**, to expel water from a hydrated oxide or carbon dioxide from a carbonate at temperature below their melting points.

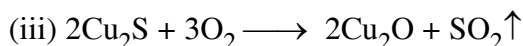
**For Example**



## ROASTING

The removal of the excess sulphur contained in sulphide ores by heating **in an excess of air** is called roasting.

(Metal sulphides  $\xrightarrow{+O_2}$  Metal oxide +  $SO_2$ )



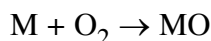
## THERMODYNAMICS OF REDUCTION PROCESSES (ELLINGHAM DIAGRAM)

The extraction of metals from their oxides using carbon or other metals, and by thermal decomposition, involves a number of points which merit detailed discussion.

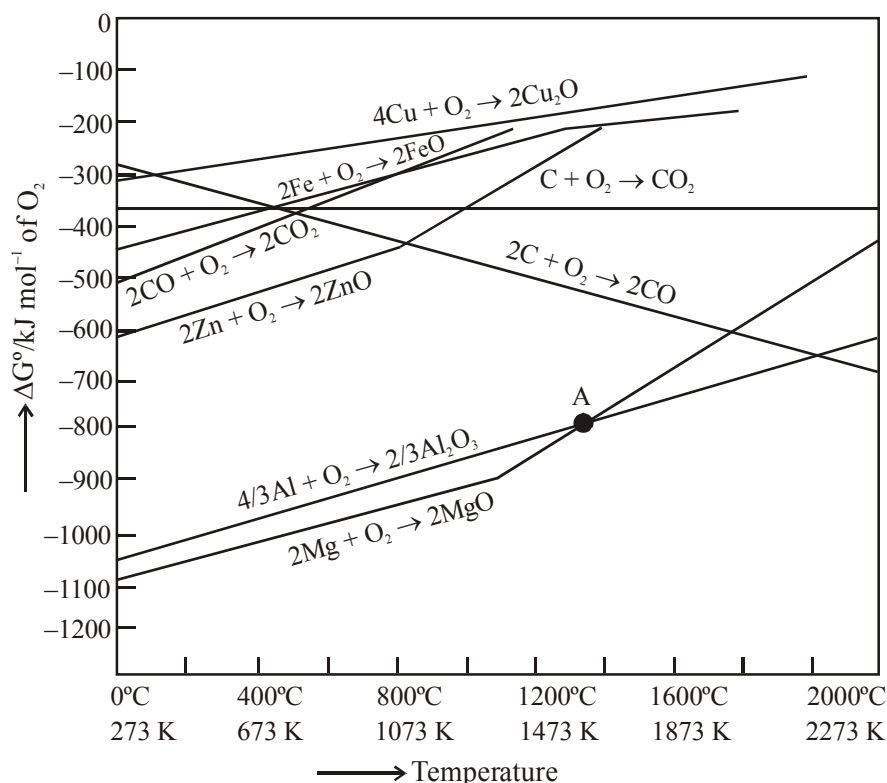
For a spontaneous reaction, the free energy change  $\Delta G$  must be negative.

$$\Delta G = \Delta H - T\Delta S$$

$\Delta H$  is the enthalpy change during the reaction,  $T$  is the absolute temperature, and  $\Delta S$  is the change in entropy during the reaction. Consider a reaction such as the formation of an oxide:



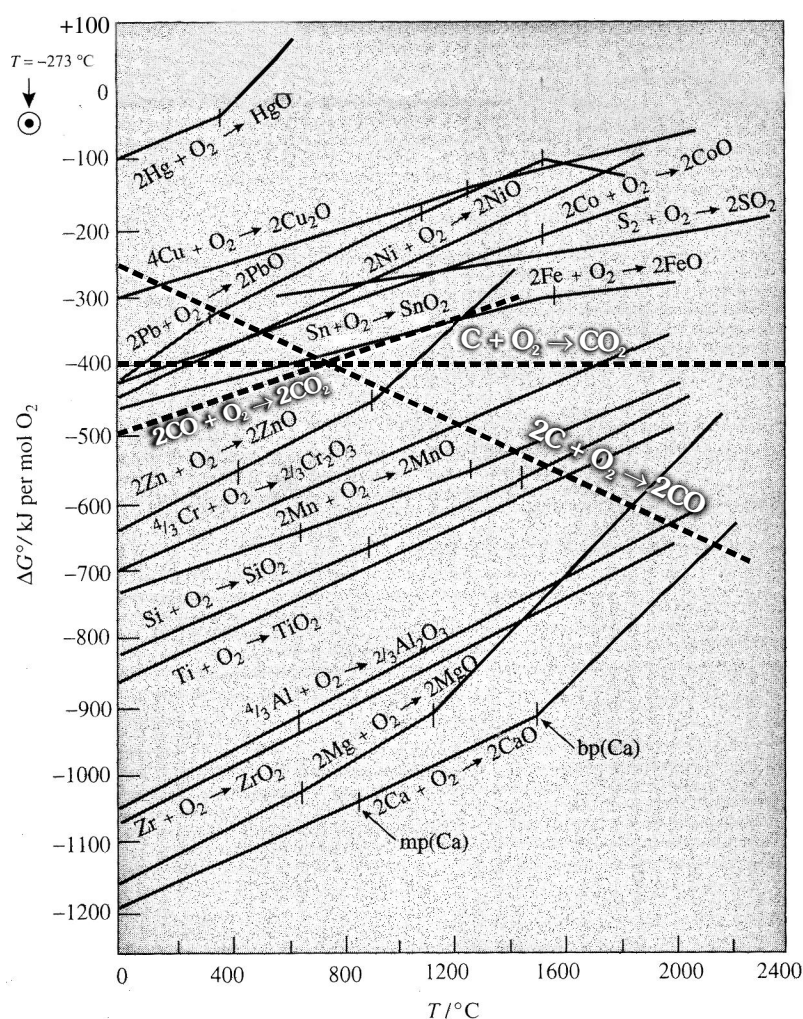
Dioxygen is used up in the course of this reaction. Gases have a more random structure (less ordered) than liquids or solids. Consequently gases have a higher entropy than liquids or solids. In this reaction  $S$  the entropy or randomness decreases, the hence  $\Delta S$  is negative. Thus if the temperature is raised then  $T\Delta S$  becomes more negative. Since  $T\Delta S$  is subtracted in the equation, then  $\Delta G$  becomes less negative. Thus the free energy changed increases with an increase of temperature.



The free energy changes that occur when one gram molecule of a common reactant (in this case dioxygen) is used may be plotted graphically against temperature for a number of reactions of metals of their oxides. This graph is shown in figure and is called an Ellingham diagram (for oxides). Similar diagrams can be produced for one gram molecule of sulphur, giving an Ellingham diagram for sulphides, and similarly for halides.

The Ellingham diagram for oxides shows several important features:

- (i) The graph for metal oxide all slope upwards, because the free energy change increases with an increase of temperature as discussed above.
- (ii) The free energy changes all follows a straight line unless the materials metal or vaporize.
- (iii) When the temperature is raised, a point will be reached where the graph crosses the  $\Delta G = 0$  line. Below this temperature the free energy of formation of the oxide is negative, so the oxide is stable. Above this temperature the free of formation of the oxide is positive, and the oxide becomes unstable, and should decompose into the metal and dioxygen.
- (iv) Any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram because the free energy will become more negative by an amount equal to the different between the two graphs at that particular temperature.



### Limitations of Ellingham Diagram

- (i) The graph simply indicates whether a reaction is possible or not i.e., the tendency of reduction with a reducing agent is indicated. This is so because it is based only on the thermodynamic concepts. It does not say about the kinetics of the reduction process (Cannot answer questions like how fast it could be?).
- (ii) The interpretation of  $\Delta G^\ominus$  is based on  $K(\Delta G^\ominus = -RT \ln K)$ . Thus it is presumed that the reactants of products are in equilibrium.

## REDUCTION OF ORE TO THE METAL

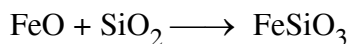
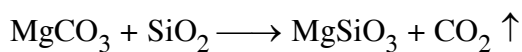
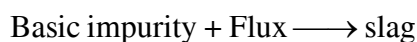
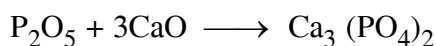
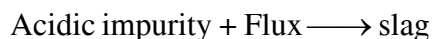
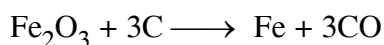
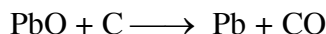
The calcined or roasted ore is then reduced to the metallic state in either of the following ways.

### (i) Reduction by Carbon (Smelting)

- Concentrate ore (ore + gangue) + R.A. (carbon) + Flux  $[\because \text{R.A.} \Rightarrow \text{Reducing agent}]$

↓

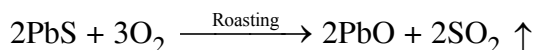
Metal + Slag + gases



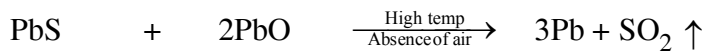
### (ii) Self Reduction

Sulphides of certain metals are reduced to metal without using any additional reducing agent. ores of Cu, Pb, Hg etc.

#### Self Reduction for Pb

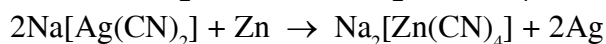
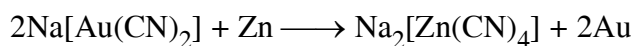


(Galena) (air)



(unroasted ore) (roasted ore) (Self reduction)

### (iii) Metal Displacement Method



Sodium tetra cyanozincate

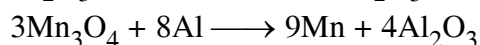
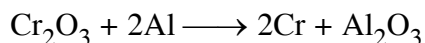
### (iv) Electrolytic Reduction

This process is mainly used for the extraction of **highly electropositive metals**.

**Ex.** Na, K, Mg, Ca, Al, etc.

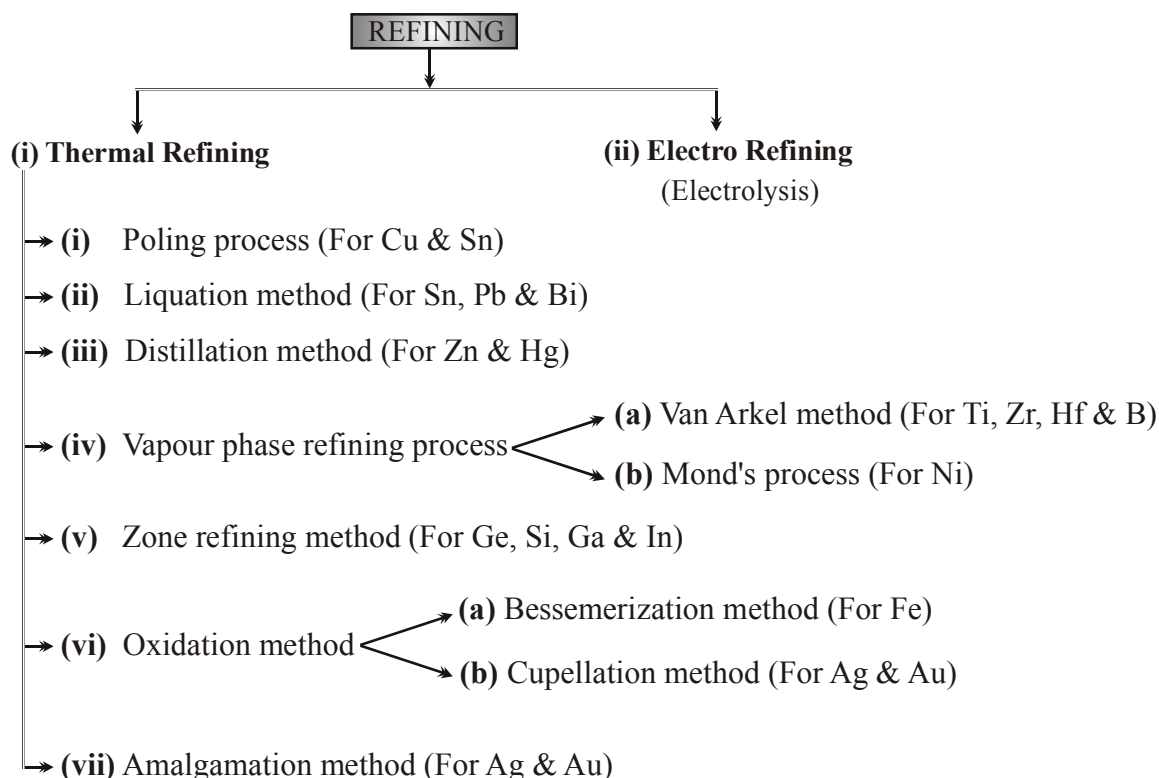
### (v) Thermite Reduction or Thermite Process

Al is used as reducing agent in this process. This process is employed in the case of those metals which have very high melting points and are to be extracted from their oxides





## REFINING OF METALS



## OTHER METHOD : BY CHROMATOGRAPHIC METHOD

This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent.

Different components are adsorbed at different levels on the column. Later the adsorbed components are removed (eluted) by using suitable solvent (eluant). Depending upon the physical state of the moving medium and the adsorbent material and also on the process of passage of the moving medium, the chromatographic method is given the name. In one such method the column of  $\text{Al}_2\text{O}_3$  is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form.

This is an example of column chromatography. This is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified. There are several chromatographic techniques such as paper chromatography, column chromatography, gas chromatography, etc. Procedures followed in column chromatography have been depicted in the following figures.

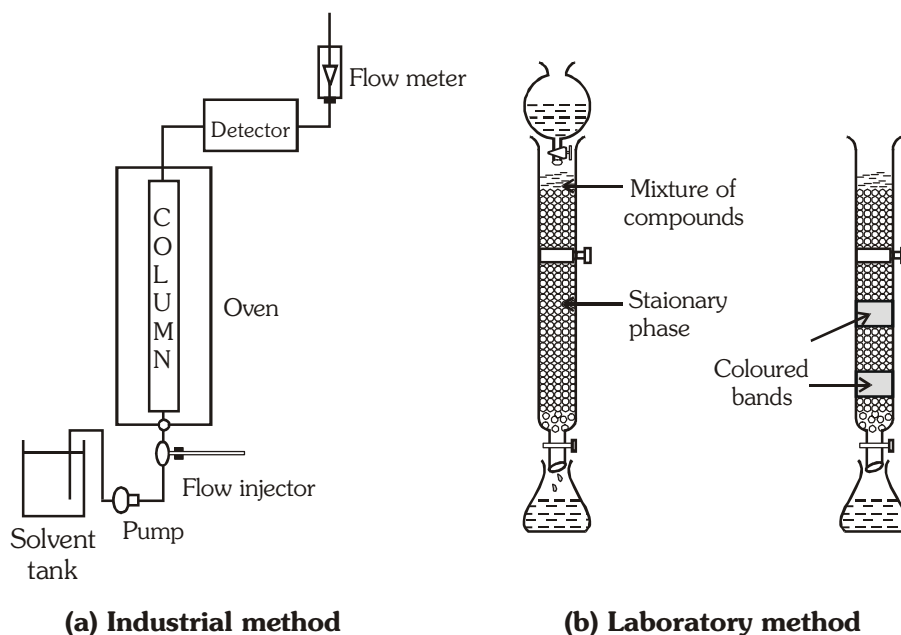


Fig. Schematic diagrams showing column chromatography

## EXTRACTION OF SOME INDIVIDUAL METALS

### EXTRACTION OF COPPER

#### (1) Extraction of copper :

**Occurrence :** Copper occurs in free as well as in combined state. The main ores are as follows.

- |                            |   |
|----------------------------|---|
| (i) Copper pyrites         | $\text{CuFeS}_2$ or $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ |
| (ii) Cuprite (Ruby copper) | $\text{Cu}_2\text{O}$   |
| (iii) Copper glance        | $\text{Cu}_2\text{S}$   |
| (iv) Malachite             | $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$                          |
| (v) Azurite                | $2\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$                         |

#### Extraction :

Copper is extracted from the ores (sulphide) by two process.

#### (A) Pyrometallurgical Process :

This is a dry process and applied to high grade ores (containing 4% or more copper).

#### (B) Hydrometallurgical Process :

This is a wet process and applied to low grade ores.

**(A) Extraction from pyrites by pyrometallurgical process (Smelting Process)****(i) Concentration :**

The finely powdered ore is concentrated by froth floatation process.

**(ii) Roasting :**

The concentrated ore is heated strongly in presence of air.

Sulphur, arsenic, and antimony are removed in form of their volatile oxides while the ore is converted into a mixture of cuprous and ferrous sulphides.

These sulphides are partially oxidised to oxides.

- (a)  $S + O_2 \rightarrow SO_2 \uparrow$   
 (b)  $2As_2S_3 + 9O_2 \rightarrow 2As_2O_3 \uparrow + 6SO_2 \uparrow$   
 (c)  $2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 \uparrow + 6SO_2 \uparrow$   
 (d)  $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$   
 $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$

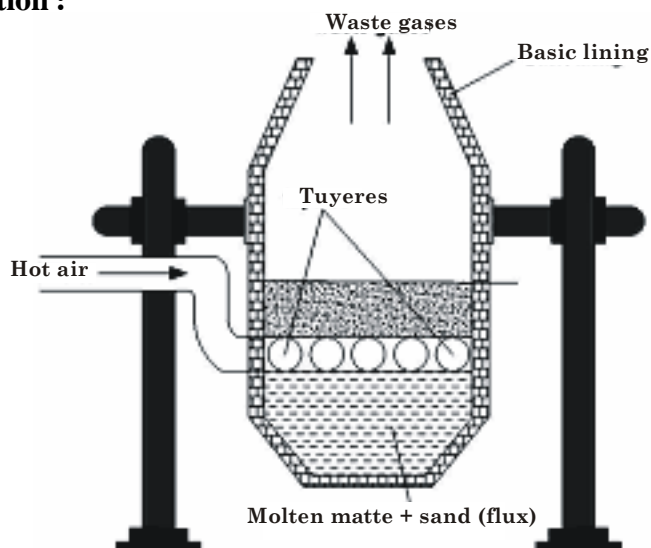
**(iii) Smelting**

The roasted ore is mixed with sand (flux) and coke (fuel) and then heated in a reverberatory furnace water jacketed blast furnace called smelter. The oxidation of ferrous sulphide which started during roasting now goes a step further. Ferrous oxide formed, reacts with sand to form ferrous silicate (slag).

Here some FeS reacts with  $Cu_2O$  to form  $Cu_2S$  again.

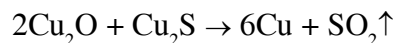
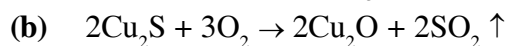
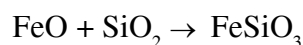
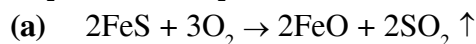
- (a)  $FeO + SiO_2 \rightarrow FeSiO_3$  (Slag)  
 (b)  $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$   
 (c)  $Cu_2O + FeS \rightarrow Cu_2S + FeO$

Slag (forming upper layer) and molten mass consisting of  $Cu_2S$  and a little FeS (**forming lower layer and commonly called matte**) are removed from separate holes.

**(iv) Bessemerisation :**

Molten matte is heated in a Bessemer converter and a blast of air mixed with sand is blown through the molten mass.

Here iron (FeS) is completely removed as slag, a part of  $\text{Cu}_2\text{S}$  is oxidised to  $\text{Cu}_2\text{O}$  and a part of  $\text{Cu}_2\text{S}$  reduces  $\text{Cu}_2\text{O}$  to metallic copper.



The molten copper is poured off into moulds. As it cools it gives up the dissolved sulphur dioxide which forms blister on the surface of the metal. Hence the metal thus obtained is called blister copper and contains 98 percent copper.

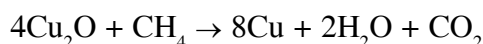
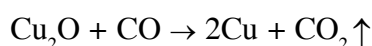
(v) **Refining of copper :**

(a) **Poling :**

The molten blister copper is heated in pressure of air and stirred with green wood **poles**. S and As are oxidised to their volatile oxides.

Iron is oxidised and forms a scum or slag which is **skimmed** off.

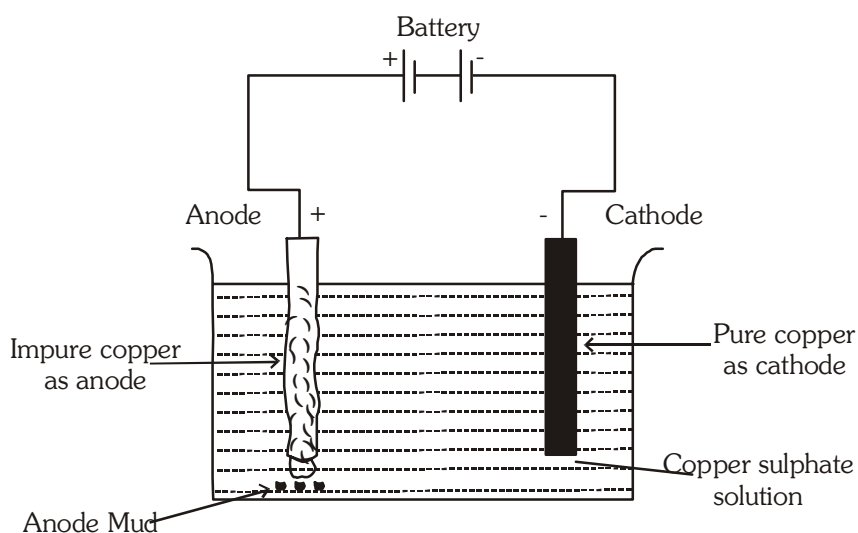
The cuprous oxide is reduced to Cu by CO and  $\text{CH}_4$  from green wood.



(b) **Electrolytic refining :**

The electrolytic bath contains an acidified solution of copper sulphate. Impure copper acts as anode while cathode is of the pure copper strip. When electric current is passed, there is transfer of pure copper from anode to cathode which gradually grows in size.

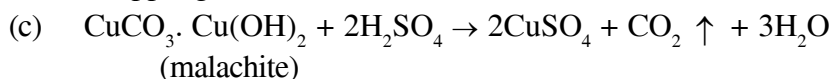
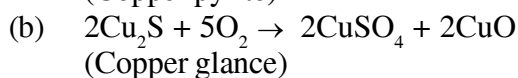
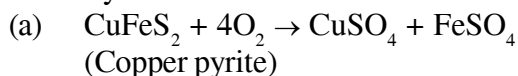
**The impurities** like Fe, Zn, Ni, Co etc. dissolve in the solution as sulphates and others like Au and Ag settle down below the anode as **anode mud**. The cathode is removed and copper of about 99.99% purity is obtained.



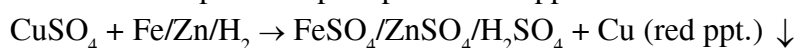
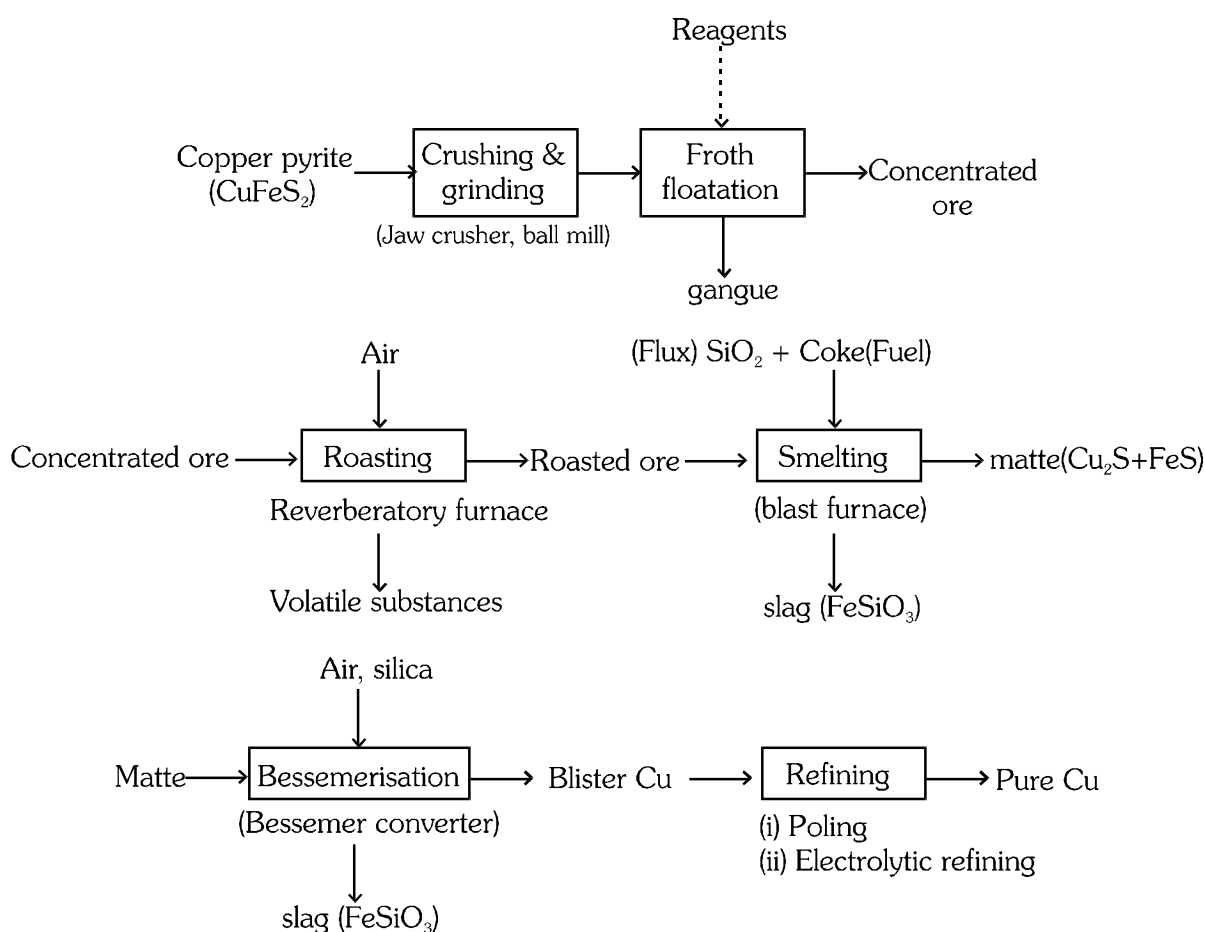
**Electrolytic refining of copper**

**(B) Hydrometallurgical Process :**

Crushed and powdered low grade ore is exposed to air and water then copper sulphide is oxidised to copper sulphate. Some iron sulphate and sulphuric acid is also produced. The process is completed in about a year.



The pale green liquor draining from the bottom of the heaps is  $\text{CuSO}_4$  which is collected in pans and treated with iron scraps which precipitate out copper.

**Process in brief :****Uses :**

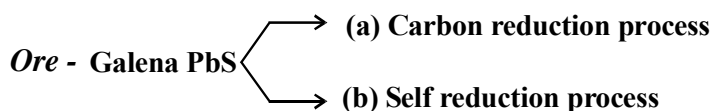
Copper is the second most useful metal (the first being Iron) because of its stability in air and water and excellent conductivity.

It is used :-

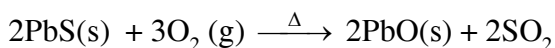
1. In the manufacture of electrical wires, cables etc.
2. For electroplating.
3. As a coinage metal and in ornaments and jewellery.
4. For the manufacture of alloys like brass ( $\text{Cu} + \text{Zn}$ ), bronze ( $\text{Cu} + \text{Sn}$ ) German silver ( $\text{Cu} + \text{Zn} + \text{Ni}$ ) bell metal ( $\text{Cu} + \text{Sn}$ ) gun metal ( $\text{Cu} + \text{Sn} + \text{Zn}$ ), copper coins ( $\text{Cu} + \text{Zn} + \text{Sn}$ ) etc.

**EXTRACTION OF LEAD****(2) Extraction of lead :**

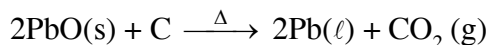
**Main Ore : Galena (PbS) :** There are mainly two types of process used in the extraction of Lead.

**(a) Carbon reduction process (When impurity content is high) :**

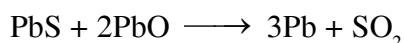
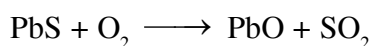
- (i) Crushing & Grinding
- (ii) Concentration by Forth floatation method
- (iii) Roasting process with Lime stone ( $\text{CaCO}_3$ ). Roasting in air to give PbO and  $\text{SO}_2$ .



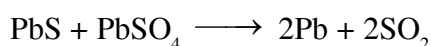
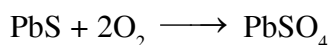
- (iv) Smelting (Carbon reduction method with coke +  $\text{Fe}_2\text{O}_3$ ). Then reduction with coke or CO in a blast furnace take place.

**(b) Self reduction process :** (When the impurity content is less)

- (i) Crushing & Grinding
- (ii) Concentration by Forth floatation method
- (iii) Self reduction process : PbS is partially oxidized by heating and blowing air through it. After some time the air is turned off and heating is continued. The mixture undergoes self reduction as given below.



Parallel reaction

**(c) Refining process :****(a) Liquefaction****(b) Bett's electrorefining**

Anode  $\rightarrow$  Impure Pb

Cathode  $\rightarrow$  Pure Pb

Electrolyte  $\rightarrow$   $\text{Pb}[\text{SiF}_6] + \text{H}_2\text{SiF}_6 + \text{Gelatin}$  (to adjust viscosity)

on the electrolysis Pb is deposited at cathode which give 99.95% pure metal.

## EXTRACTION OF ZINC

### (2) Extraction of zinc :

**Occurrence :** Its important minerals are :-

- (i) Zinc blende or black jack  $\text{ZnS}$
- (ii) Zincite  $\text{ZnO}$
- (iii) Calamine  $\text{ZnCO}_3$

**Extraction :**

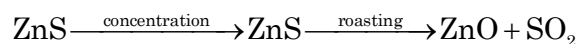
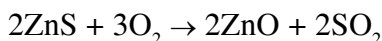
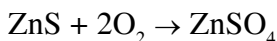
**Electrolytic Process :**

#### (i) Concentration :

The powdered ore  $\text{ZnS}$  is concentrated by froth floatation method.

#### (ii) (a) Roasting :

Concentrated  $\text{ZnS}$  is roasted at  $700^\circ\text{C}$ . A mixture of  $\text{ZnO}$  and  $\text{ZnSO}_4$  is obtained

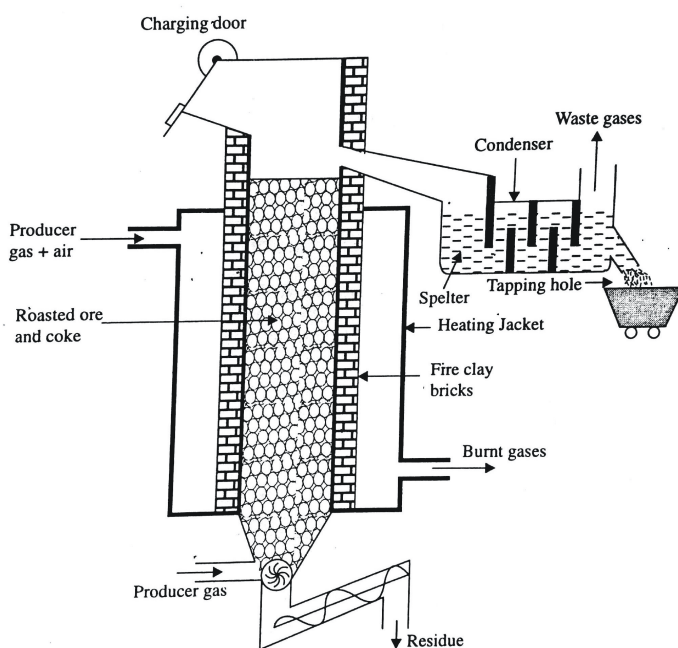
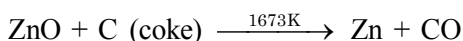


#### (b) Calcination Process



#### (iii) Carbon Reduction (Extraction of zinc from zinc oxide) :-

The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper. For the purpose of heating, the oxide is made into brickettes with coke and clay.



Vertical retort process for the reduction of  $\text{ZnO}$  to  $\text{Zn}$ -metal.

The metal is distilled off and collected by rapid chilling is called **zinc spelter**.

**(iv) Electrolysis** (Electrolytic refining) :

Anode → Impure Zn

Cathode → Thin Al-rod

Electrolyte → Solution of  $\text{ZnSO}_4 + \text{H}_2\text{SO}_4$  (dil.)

on the electrolysis zinc is deposited at cathode. The metal is scrapped off and melted to give 99.95% pure metal.

**Uses :**

- (i) In making alloys e.g. brass, german silver, elektron (Alloy of Mg with smaller amount of Al, Y, Ag, Gd, Zn) etc.
- (ii) In the extraction of silver and gold by cyanide process.
- (iii) It is also used in large quantities in batteries and dry cells for making cathode container.
- (iv) Zn–Cu couple, Zn–Hg, zinc dust etc. are used as reducing agent in organic reactions.
- (v) large amount of zinc is used for galvanizing iron. Zinc is deposited on the surface of iron articles. This process is called galvanization.
- (vi) It is also used in large quantities in batteries, as a constituent of many alloys, e.g., brass, (Cu 60%, Zn 40%) and german silver (Cu 25-30%, Zn 25-30%, Ni 40–50%).
- (vii) Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc.

**EXTRACTION OF TIN****Extraction of tin from cassiterite :****Main Ore :** Cassiterite or Tinstone ( $\text{SnO}_2$ ) + Major impurities[(i)  $\text{SiO}_2$ , (ii) Sulphides of Fe & Cu, (iii)  $\text{FeWO}_4 + \text{MnWO}_4$ ]

Some following steps are involved :

**(i) Crushing and concentration :**

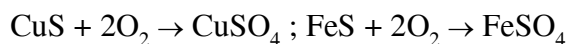
The ore is crushed and washed with a stream of running water to remove the lighter earthy and silicious impurities.

**(ii) Electromagnetic separation :**

The concentrated ore is subjected to the electromagnetic separation to remove magnetic impurity of Wolframite.

**(iii) Roasting :**

The ore is then heated in presence of air, when volatile impurities (S as  $\text{SO}_2$ , As as  $\text{As}_2\text{O}_3$  and Sb as  $\text{Sb}_2\text{O}_3$ ) are removed. The impurities of pyrites of copper and iron are converted into their respective oxides and sulphates

**(iv) Leaching :**

Sulphates of copper and iron are dissolved in water.

**(v) Washing :**

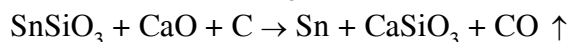
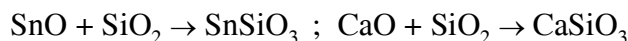
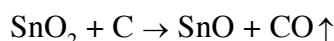
The ore is washed with running water to remove the fine iron oxide produced in roasting. Thus obtained ore contains 60 – 70%  $\text{SnO}_2$  and is called as black tin.

**(vi) Carbon reduction method :** Coke & Lime stone (flux) is used.



**Smelting :**

The black tin is mixed with anthracite coal and heated to about 1500K in a reverberatory furnace. If  $\text{SiO}_2$  is present as impurity then  $\text{CaO}$  is added as flux.



or use scrap iron  $\text{SnSiO}_3 + \text{Fe} \rightarrow \text{Sn} + \text{FeSiO}_3$

**Refining method :**

(a) Poling (b) Electrorefining

Anode  $\rightarrow$  Impure Sn

Cathode  $\rightarrow$  Pure Sn

Electrolyte  $\rightarrow$  ( $\text{SnSO}_4$  solution + dil.  $\text{H}_2\text{SO}_4$ )

**EXTRACTION OF IRON****(1) Extraction of Iron :**

**Main Ore :** Haematite ( $\text{Fe}_2\text{O}_3$ )

Some following steps are involved :

(i) **Crushing & Grinding :**

(ii) **Concentration :** By gravity separation method.

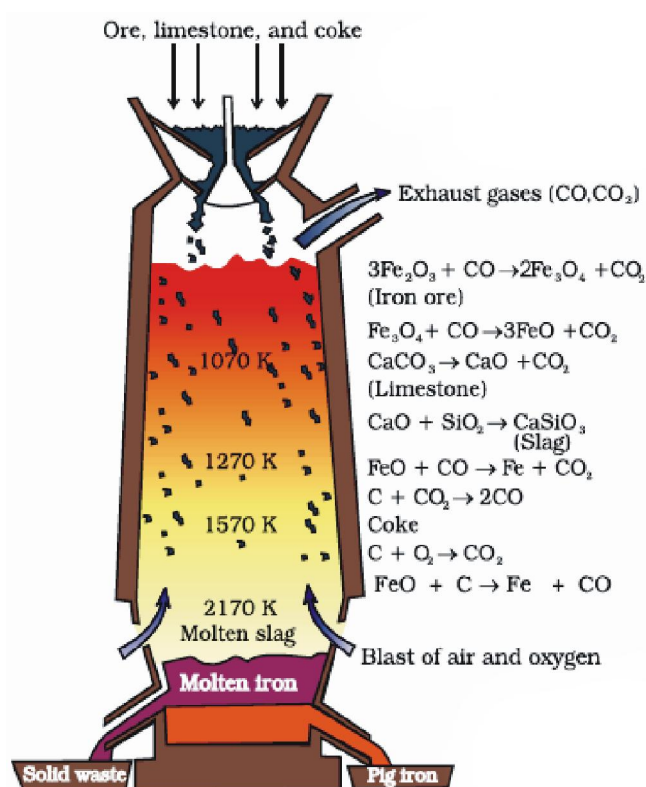
(iii) **Roasting :**

(iv) **Carbon reduction (Blast furnace) :** Pig iron is obtained from this process

**Smelting or reduction :**

The calcined ore (8 parts) mixed with coke, a reducing agent (4 parts) and lime stone a flux (1 part) is reduced in a blast furnace.

Since the blast furnace has different temperatures at different zones, different reactions take place at different zones.



**(a) Zone of combustion (1500 -1600°C)**

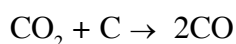
This zone is near at the bottom of the furnace and little above the tuyers. It increases temp. of the furnace because of exothermic reactions.

**(b) Zone of fusion (1200- 1300°C)**

It is just above the zone of combustion. Here the iron melts and trickles down in the hearth while the slag being lighter floats over the molten metal and thus prevents oxidation of Fe by blast of air.

**(c) Zone of heat absorption or slag formation (800- 1000°C)**

This is the middle part of the furnace. Here rising  $CO_2$  is reduced to carbon monoxide.

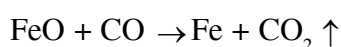
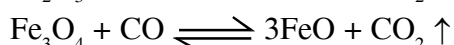
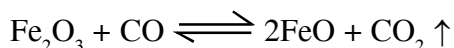


The reaction being endothermic, lowers the temperature of the zone.

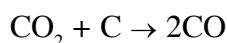
Limestone decomposes forming CaO which reacts with  $SiO_2$  forming slag.

**(d) Zone of reduction (400-700°C)**

It is near the top of the furnace. Here the calcined ore is reduced to Fe by rising CO.



To retard the backward reaction, supply of excess of CO is maintained by the following reaction.



Since the temperature of this zone is too low to melt iron, the metal produced is known as spongy iron.

**Refining :**

Purification of Fe can be done by different method which are as follows :

- Puddling Process
- Bessemerisation Process
- Open hearth Process
- L. D. Process

Thus we got pure iron.

**Types of Iron****Cast iron or pig iron**

It is most impure form of Iron and contains the highest proportion of carbon (2.5 - 4 %) along with traces of S, P, Mn and Si. Cast iron contain 2.5 to 4.3 & pig iron contain 2.5 to 5%.

**Wrought iron (Fibrous iron) or malleable iron**

It is the purest form of iron and contains minimum amount of carbon (0.12 - 0.25%) and less than 0.5% of other impurities.

**Steel**

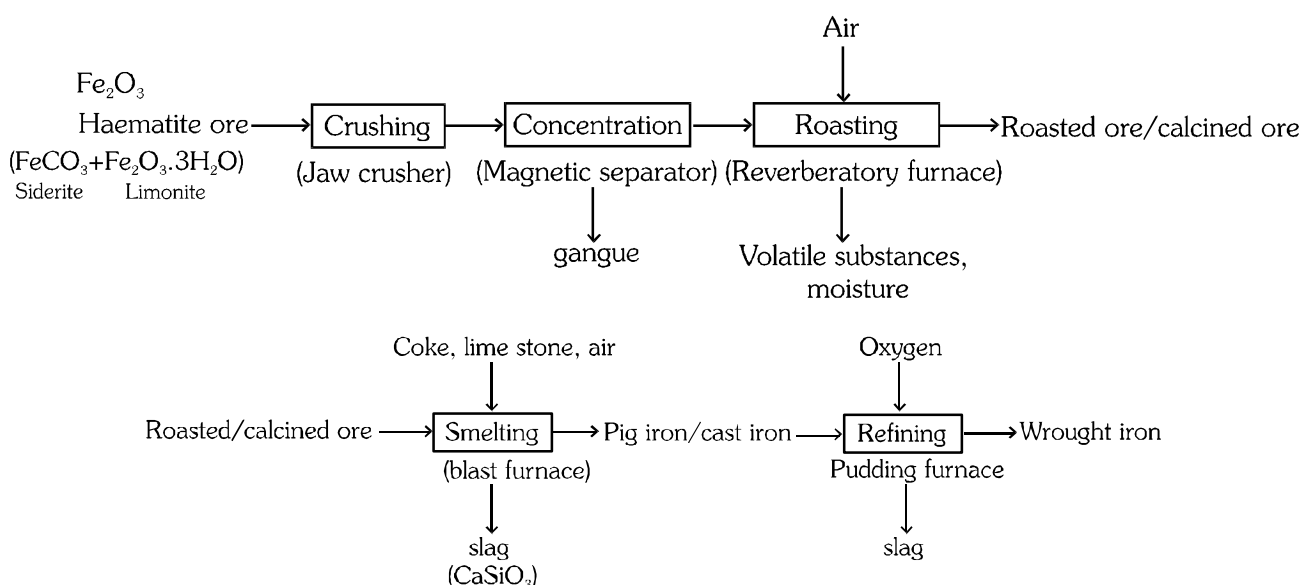
It is the most important form of iron and finds extensive applications. As far as carbon content (impurity) is concerned it is mid-way between cast iron and wrought iron, it contains 0.25- 2% carbon.

Thus all the three forms of iron differ in their carbon contents, both iron and steel are obtained from cast iron.

Order of M.P. Wrought Iron > Steel > Cast Iron or Pig Iron

**% of Carbon in different type of Iron**

NAME	% of C
(1) Wrought iron	0.1 to 0.25
(2) Steel	0.25 to 2.0
(3) Cast Iron	2.6 to 4.3
(4) Pig Iron	2.3 to 4.6

**Process in brief :**

**Manufacture of Steel :** The addition of different desired impurities into molten pure iron is known as steel making

**Bessemer process :**

This process involves the use of a large pear-shaped furnace (vessels) called Bessemer converter. This is made of steel plates lined with silica ( $\text{SiO}_2$ ) or magnesia ( $\text{MgO}$ ) depending upon the nature of impurities. If the impurities are acidic e.g.  $\text{P}_4\text{O}_{10}$  or  $\text{SiO}_2$ , basic lining of lime ( $\text{CaO}$ ) or magnesia is used (Basic process). If the impurities are basic e.g.  $\text{MnO}$ , lining of silica bricks is used (acid process). Silicon and manganese (in acidic process) or phosphorus (in basic process) are oxidised to their oxides and thus removed as slag.

**Acid process :**  $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$  ;  $2\text{Mn} + \text{O}_2 \rightarrow 2\text{MnO}$  ;  $\text{MnO} + \text{SiO}_2 \rightarrow \text{MnSiO}_3$  (Slag)

**Basic process :**  $\text{P}_4 + 5\text{O}_2 \rightarrow \text{P}_4\text{O}_{10}$        $\text{P}_4\text{O}_{10} + 6\text{CaO} \rightarrow 2\text{Ca}_3(\text{PO}_4)_2$  (Thomas slag)

**Properties of Steel :**

Steel combines the useful properties of cast iron and wrought iron. It is hard and elastic. The properties of steel depend upon its carbon content. With the increase in carbon content, the hardness of steel increases while its ductility decreases.

- Low carbon or soft steel contain C upto 0.25%.
- Medium carbon steel or mild steel contain 0.25–0.5% C.
- High carbon or hard steel contain 0.5–1.5% C.

**Heat Treatment of Steel**

- (i) **Quenching or hardening** : Steel is heated to red hot temperature (700 to 800°C) and is then cooled suddenly by plunging into either cold water or oil. It makes steel hard and brittle.
- (ii) **Annealing** : The steel is heated to red hot temperature (700 to 800°C) and then cooled slowly. It makes steel soft.
- (iii) **Tempering** : If quenched steel is heated to temperature between 500 to 575 K and then cooled slowly, it becomes quite hard but brittleness disappears. The process is called tempering.

**Surface treatment of steel**

- (i) **Nitriding** : Process of heating steel at 1000 K in an atmosphere of  $\text{NH}_3$ . This gives hard coating of iron nitride on the surface.
- (ii) **Case hardening** : Process of giving a thin coating of hardened steel, by heating steel in contact with charcoal followed quenching in oil.  
– It is used for axles of railway wagons.

**Uses**

- (i) **Cast iron** : It is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes, toys, etc.
- (ii) It is used in the manufacture of wrought iron and steel.
- (iii) **Wrought iron** : It is used in making anchors, wires, bolts, chains and agricultural implements.
- (iv) **Steel finds a number of uses** : Alloy steel is obtained when other metals are added to it. Nickel steel is used for making cables, automobiles and aeroplane parts, pendulum, measuring tapes, chrome steel for cutting tools and crushing machines, and stainless steel for cycles, automobiles, utensils, pens, etc.

**EXTRACTION OF SILVER & GOLD****(1) Extraction of silver :****Occurrence :**

Ag found in free and combined state in nature.

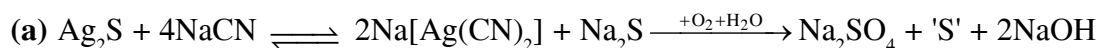
Its main ore is Argentite  $\text{Ag}_2\text{S}$ .

Other ores are

- Copper silver glance –  $\text{Cu}_2\text{S} \cdot \text{Ag}_2\text{S}$   
 Horn silver –  $\text{AgCl}$   
 Argentiferous lead –  $\text{PbS}(0.01 - 0.1\% \text{ Ag})$

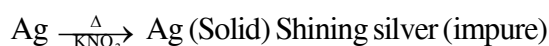
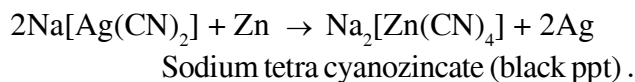
**Steps of Metallurgy :****(A) From Argentite ( $\text{Ag}_2\text{S}$ )**

- (i) **Concentration** : As it is a sulphide ore, so froth floatation process is used.

**(B) Leaching and reduction (Mac Arther cyanide process)****(a) Formation of cyanide complex :**

[∴  $\text{O}_2$  is used to make reaction irreversible which remove  $\text{Na}_2\text{S}$  as  $\text{Na}_2\text{SO}_4 + \text{S}$ ]

$\text{Na}_2\text{SO}_4$  does not reacts with sod. Argento cyanide.

**(b) Displacement of Ag metal :-**

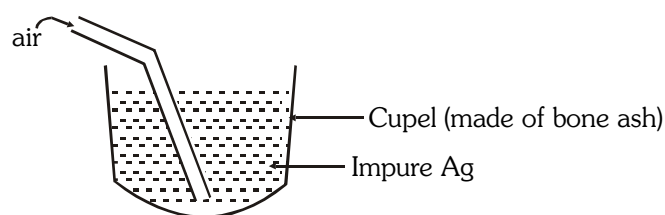
**(C) Purification by electrolytic method :**

Pure Ag — Cathode

Impure Ag — Anode

Electrolyte —  $\text{AgNO}_3$ + 1%  $\text{HNO}_3$  — To increase ionisation and to avoid hydrolysis of  $\text{AgNO}_3$  by common ion effect**(D) Ag from Argentiferous lead (PbS – Galena) :**

Galena has a little amount of silver

**(1) Concentration :** (PbS) by froth floatation process**(E) Reduction of metal :****(a) Parke's process :** Based on distribution law.**(i)** Molten Ag is more soluble in molten zinc. $\text{Pb (molten)} \rightarrow \text{Zn (molten)}$  $(\text{Ag}) \text{ —————}$ **(ii)** Melting point of Zn/Ag alloy is greater than lead, so Zn/Ag freezes first.**(iii)** Density of Zn/Ag is less than Pb so Zn/Ag forms the upper layer and Pb form lower layer.**(iv)** Upper layer taken out.**(v)** Ag is separated by using distillation method. (Vapourisation of Zn)**(b) Pattinson method :-****(i)** It is based upon fractional crystallisation.**(ii)** Ag/Pb is melted then cooled, the process is repeated again & again, concentration of Ag increases. Pb separate out in crystalline form.**(F) Purification :****(a) Cupellation :**

Pb impurities separate (oxidised) out in the form of litharge.

**(b) Electrolytic process :-** As discussed earlier.**Uses****(i)** It is used in silver plating.**(ii)** Silver foils are used in medicine.**(iii)** Silver amalgam is used for dental filling.**(iv)** Compounds of silver are used in silvering of mirrors ( $\text{AgNO}_3 + \text{HCHO} + \text{Red Pb}$ ), in photography, as laboratory reagents etc.**(v)** Silver is easily alloyed with copper, so it is used in making coins, ornaments, silver ware etc.

(vi) It gives black spot on skin due to decomposition so it is also used as hair dye and ink.

**Extraction of Gold :**

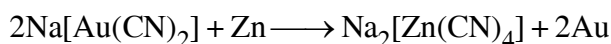
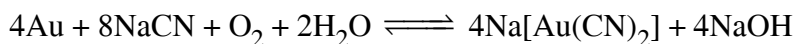
**Occurrence :** Au found in free (native) state in nature.

**Same steps as are involved in the extraction of Silver metal.**

(i) **Crushing & Grinding :**

(ii) **Leaching process :** Gold are extracted by the cyanide process (Mc Arthur - Forest process).

**Reaction involved :**



(iii) **Refining Process :**

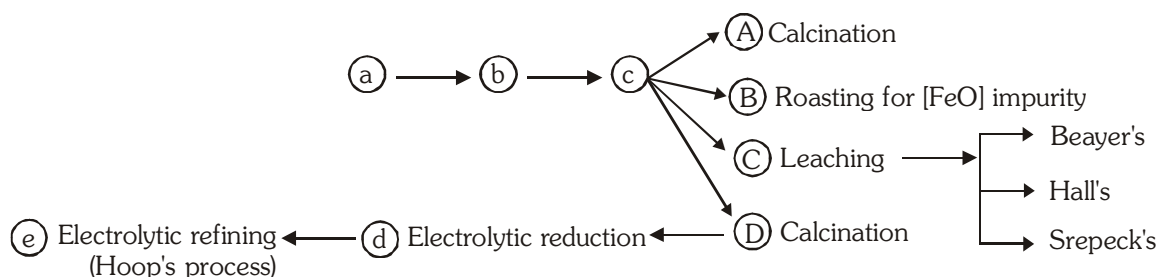
- Anode → Impure Au
- Cathode → Pure Au
- Electrolyte → (AuCl<sub>3</sub> solution + dil. HCl)

**EXTRACTION OF ALUMINIUM :**

**Ore - Bauxite**  $\text{AlO}_x(\text{OH})_{3-2x}$  (where  $0 < x < 1$ )

**Extraction of Aluminium :**

**Short chart of Al from Al<sub>2</sub>O<sub>3</sub>.2H<sub>2</sub>O (Bauxite)**



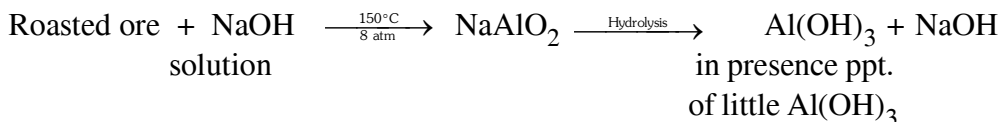
**BAUXITE**



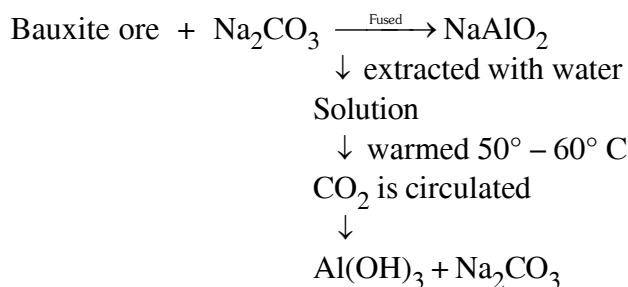
**Step-1: Concentration of Bauxite ore**

(a) **Baeyer's process :** (Used for red bauxite in which main impurity is iron oxide)

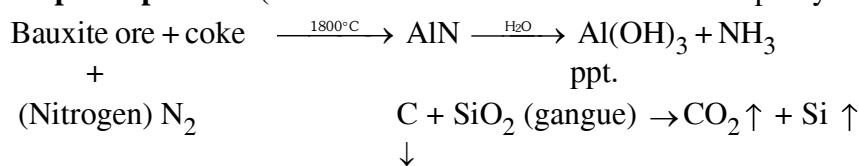
Bauxite ore  $\xrightarrow{\text{Roasted}}$  as to convert FeO into Fe<sub>2</sub>O<sub>3</sub>



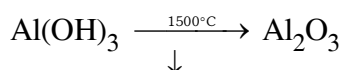
(b) **Hall's Process :** (Red bauxite)



(c) **Serpeck's process :** (Used for white bauxite in which main impurity is silica)



↓  
**Step-2: CALCINATION**



↓  
**Step-3 : Electrolytic Reduction**

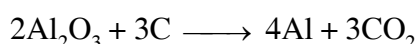
Electrolyte  $\text{Al}_2\text{O}_3$  dissolved in  $\text{Na}_3\text{AlF}_6$  and  $\text{CaF}_2$

**Cathode**–Carbon lining

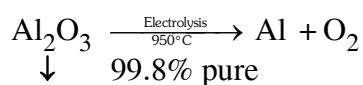
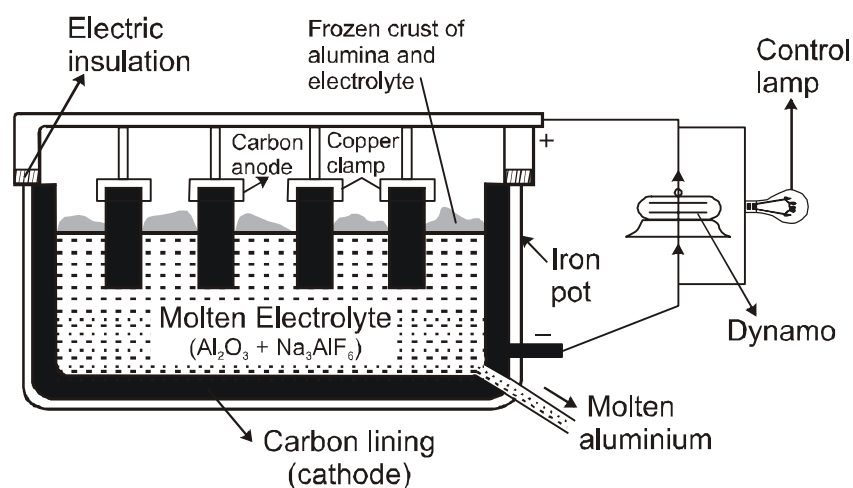
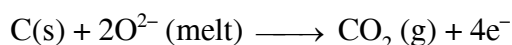
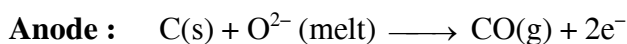
**Anode** – Graphite rods

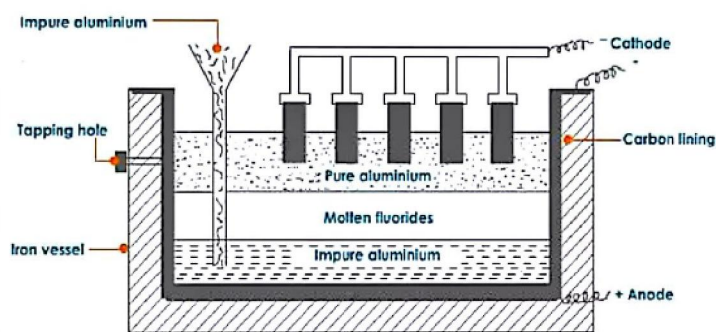
**Electrolytic reduction (Hall-Heroult process) :**

The purified  $\text{Al}_2\text{O}_3$  is mixed with  $\text{Na}_3\text{AlF}_6$  (cryolite) or  $\text{CaF}_2$  (fluorspar) which lowers the melting point of the mixture and brings conductivity. The fused matrix is electrolysed. Steel cathode and graphite anode are used. The graphite anode is useful here for reduction to the metal. The overall reaction may be taken as :



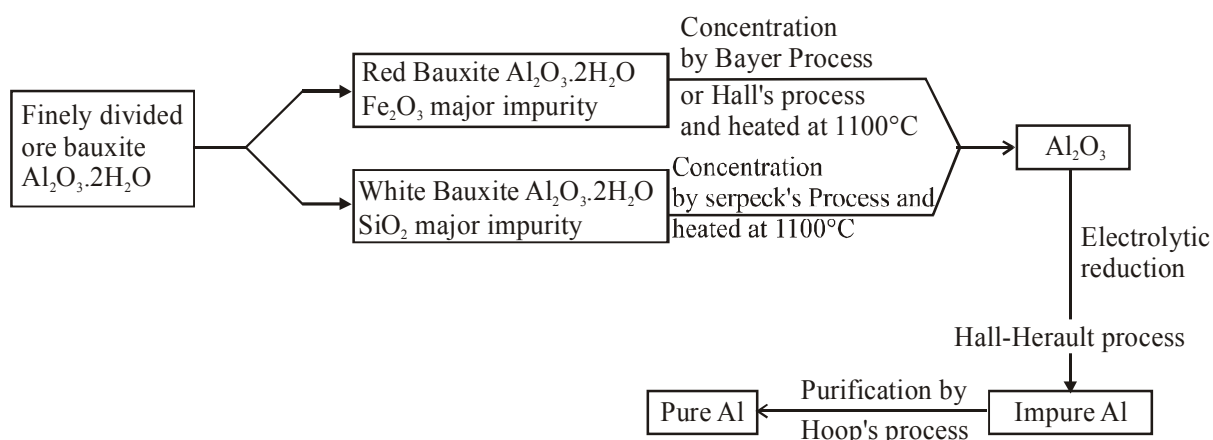
The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and  $\text{CO}_2$ . This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are :



**Step-4 : Electrolytic Refining**

(Hoop's process)

Pure Al (99.98 % pure)

**Flow chart of Al from  $Al_2O_3 \cdot 2H_2O$  (Bauxite)****Important points :**

- Useful gas  $NH_3$  is evolved in the leaching of bauxite by serpeck's process.
- In the electrolytic reduction of  $Al_2O_3$  cryolite ( $Na_3AlF_6$ ) is added along with  $CaF_2$  (fluorspar) to—
  - decrease m.p. of  $Al_2O_3$
  - decrease viscosity of electrolyte ( $CaF_2$  is used)
  - increase conductivity
- In the electrolytic reduction graphite anode get corrode or finishe due to reaction with  $O_2$  liberates at anode, hence it had to be changed periodically.
- In the electrolytic refining (4th step) no electrodes are used. In the Hoop's process molten pure Al is used as cathode and molten impure Al is used as anode.
- In the Hoop's process carbon dust is sprayed over molten Al to
  - avoid heat lose
  - minimise metallic lusture (glaze) which is harmful for the eyes.

**Uses**

- Aluminium foils are used as wrappers for chocolates.
- The fine dust of the metal is used in paints and lacquers.
- Aluminium, being highly reactive, is also used in the extraction of chromium and manganese from their oxides.
- Wires of aluminium are used as electricity conductors.
- Alloys containing aluminium, being light, are very useful.



## EXTRACTION OF MAGNESIUM :

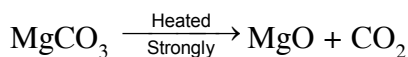
### (1) Extraction of Magnesium :

(i) **From Carnallite :** Carnallite  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

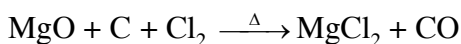
The ore is dehydrated in a current of hydrogen chloride and the mixture of fused chlorides is electrolysed.

(ii) **From Magnesite :**

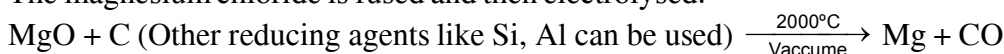
The concentrated ore is calcined at higher temperature



The calcined ore is heated with coke in a current of dry chlorine gas.



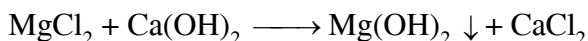
The magnesium chloride is fused and then electrolysed.



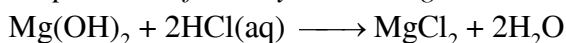
(iii) **From Sea water (Dow's process) :**

Sea water contains 0.13% magnesium as chloride and sulphate. It involves following steps.

(a) **Precipitation of magnesium as magnesium hydroxide by slaked lime :**

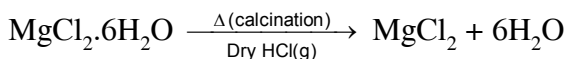


(b) **Preparation of hexahydrated magnesium chloride**

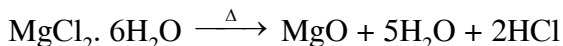


The solution on concentration and crystallisation gives the crystals of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

(c) **Preparation of anhydrous magnesium chloride**



It is not made anhydrous by simple heating because it gets hydrolysed

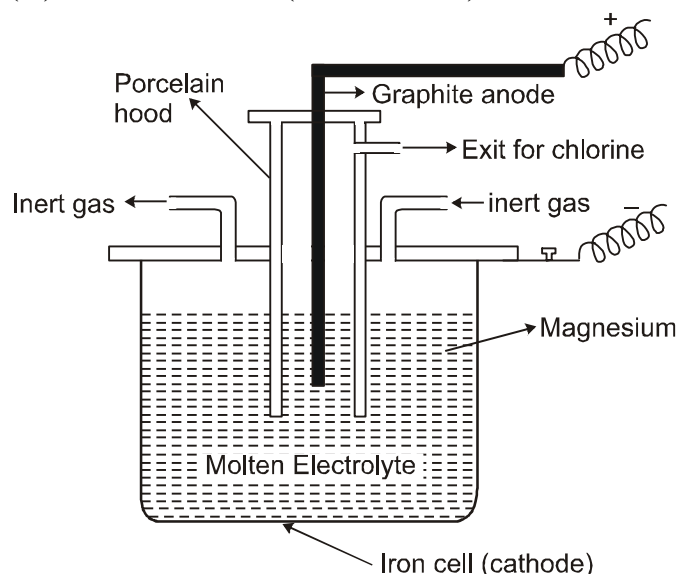


(d) **Electrolysis of fused anhydrous  $\text{MgCl}_2$**

(i) Electrolyte : Molten  $\text{MgCl}_2 + \text{NaCl} + \text{CaCl}_2$

(ii) Anode : Graphite electrode

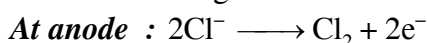
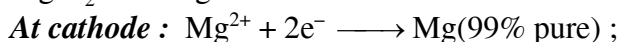
(iii) Cathode : Iron cell (steel container)



Magnesium chloride obtained by any of the above methods is fused and mixed with sodium chloride and calcium chloride in the temperature range of 973 – 1023 K. The molten mixture is electrolysed. Magnesium is liberated at the cathode (iron pot) and chlorine is evolved at graphite anode.

Reaction occurs :

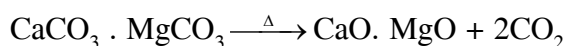
The molten mixture is electrolysed. Magnesium is liberated at the cathode (iron pot) and chlorine is evolved at graphite anode.



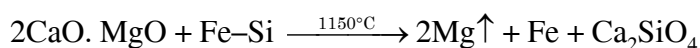
A stream of coal gas is passed through the pot to prevent oxidation of magnesium metal. The magnesium obtained in liquid state is purified by distillation under reduced pressure. (1 mm of Hg at 873 K).

**(iv) From Dolomite : In the Pidgeon Process Mg is Produced.**

The concentrated ore is calcined at higher temperature



It is then reduced by ferrosilicon at 1273 K under reduced pressure.



**Extraction of Na :**

The fused mixture of NaCl and CaCl<sub>2</sub> is taken in Down's cell which consists of circular iron cathode and carbon anode. On passing the electric current the following reactions take place :



Aluminium	1. Bauxite, Al <sub>2</sub> O <sub>3</sub> · x H <sub>2</sub> O 2. Cryolite, Na <sub>3</sub> AlF <sub>6</sub>	Electrolysis of Al <sub>2</sub> O <sub>3</sub> dissolved in molten Na <sub>3</sub> AlF <sub>6</sub>	For the extraction, a good source of electricity is required.
Iron	1. Haematite, Fe <sub>2</sub> O <sub>3</sub> 2. Magnetite, Fe <sub>3</sub> O <sub>4</sub>	Reduction of the oxide with CO and coke in Blast furnace	Temperature approaching 2170 K is required.
Copper	1. Copper pyrites, CuFeS <sub>2</sub> 2. Copper glance, Cu <sub>2</sub> S 3. Malachite, CuCO <sub>3</sub> ·Cu(OH) <sub>2</sub> 4. Cuprite, Cu <sub>2</sub> O	Roasting of sulphide partially and reduction	It is self reduction in a specially designed converter. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc	1. Zinc blende or Sphalerite, ZnS 2. Calamine, ZnCO <sub>3</sub> 3. Zincite, ZnO	Roasting followed by reduction with coke	The metal may be purified by fractional distillation.



## GENERAL PRINCIPLES & PROCESSES OF ISOLATION OF ELEMENTS

### EXERCISE # O-1

*ONLY ONE OPTION IS CORRECT.*

#### ORES

1. Which of the following does not contain Mg:  
 (A) magnetite            (B) magnesite            (C) asbestos            (D) carnallite  
**ML0001**
  
2. Which of the following is not an ore:  
 (A) malachite            (B) calamine            (C) stellite            (D) cerussite  
**ML0002**
  
3. Carnallite does not contain  
 (A) K                      (B) Ca                      (C) Mg                      (D) Cl  
**ML0003**
  
4. Among the following statements, the incorrect one is  
 (A) calamine and siderite are carbonate ores    (B) argentite and cuprite are oxide ores  
 (C) zinc blende and pyrites are sulphide ores    (D) malachite and azurite are ores of copper  
**ML0004**
  
5. Select the correct statement :  
 (A) Magnetite is an ore of manganese            (B) Pyrolusite is an ore of lead  
 (C) Siderite is carbonate ore of iron            (D) FeS<sub>2</sub> is rolled gold  
**ML0005**
  
6. "Fool's gold" is  
 (A) iron pyrites            (B) horn silver            (C) copper pyrites            (D) bronze  
**ML0006**
  
7. **Assertion :** Platinum and gold occur in native state in nature.  
**Reason :** Platinum and gold are noble metals.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.  
**ML0007**

#### CONCENTRATION METHODS

8.  $\text{Ag}_2\text{S} + \text{NaCN} + \text{Zn} \longrightarrow \text{Ag}$   
 This method of extraction of Ag by complex formation and then its displacement is called:  
 (A) Parke's method                                      (B) McArthur-Forest method  
 (C) Serpeck method                                      (D) Hall's method  
**ML0008**

9. Which one of the following is not a method of concentration of ore?  
(A) gravity separation (B) froth floating process  
(C) electromagnetic separation (D) smelting  
**ML0009**
10. Chemical leaching is useful in the concentration of:  
(A) copper pyrites (B) bauxite (C) galena (D) cassiterite  
**ML0010**
11. In froth-floatation process, pine oil functions as  
(A) activator (B) frother (C) collector (D) agitator  
**ML0011**
12. Collectors are the substances which help in attachment of an ore particle to air bubble in froth. A popular collector used industrially is  
(A) sodium ethyl xanthate (B) sodium xenate  
(C) sodium pyrophosphate (D) sodium nitroprusside  
**ML0012**
13. In the cyanide process involving extraction of silver, zinc is used industrially as a(an)  
(A) oxidising agent (B) reducing agent  
(C) solvent (D) solvating agent  
**ML0013**
14. During initial treatment, preferential wetting of ore by oil and gangue by water takes place in  
(A) Levigation (gravity separation) (B) Froth floatation  
(C) Leaching (D) Bessemerisation  
**ML0014**
15. An non-magnetic ore containing the impurity of  $\text{FeCr}_2\text{O}_4$  is concentrated by  
(A) magnetic-separation (B) gravity separation  
(C) froth-floatation method (D) electrostatic method  
**ML0015**
16. The beneficiation of the sulphide ores is usually done by  
(A) Electrolysis (B) Smelting process  
(C) Metal displacement method (D) Froth flotation method  
**ML0016**
17. The process of the isolation of a metal by dissolving the ore in aqueous solution of suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called:  
(A) hydrometallurgy (B) electrometallurgy  
(C) zone refining (D) electrorefining  
**ML0017**

18. Froth floatation process for concentration of ores is an illustration of the practical application of:
- (A) Adsorption (B) Absorption  
(C) Coagulation (D) Sedimentation
- ML0018**
19. **Assertion :** Sulphide ores are concentrated by froth floatation process.  
**Reason :** Pine oil acts as a frothing agent in froth floatation process.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
- ML0019**
20. **Assertion :** Wolframite impurities are separated from cassiterite by electromagnetic separation.  
**Reason :** Cassiterite being magnetic is attracted by the magnet and forms a separate heap.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
- ML0020**

### *CALCINATION/ROASTING*

21. Calcination is the process of heating the ore:
- (A) in inert gas (B) in the presence of air  
(C) in the absence of air (D) in the presence of CaO and MgO
- ML0021**
22. When roasting is carried out :
- (i) Sulphide ore is converted into oxide and sulphate  
(ii) remove water of hydration  
(iii) the ore melts  
(iv) arsenic and sulphur impurities are removed
- Of these statements:
- (A) (i), (ii) and (iii) are correct (B) (i) and (iv) are correct  
(C) (i), (ii) and (iv) are correct (D) (ii), (iii) and (iv) are correct
- ML0022**

## REDUCTION PROCESS

23. In the aluminothermite process, Al acts as  
 (A) An oxidising agent (B) A flux  
 (C) A reducing agent (D) A solder
- ML0023
24. **Assertion :** Al is used as a reducing agent in aluminothermy.  
**Reason :** Al has a lower melting point than Fe, Cr and Mn.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- ML0024
25. Formation of metallic copper from the sulphide ore in the commercial thermo-metallurgical process essentially involves which one of the following reaction:  
 (A)  $\text{Cu}_2\text{S} + \frac{3}{2}\text{O}_2 \longrightarrow \text{Cu}_2\text{O} + \text{SO}_2$  ;  $\text{CuO} + \text{C} \longrightarrow \text{Cu} + \text{CO}$   
 (B)  $\text{Cu}_2\text{S} + \frac{3}{2}\text{O}_2 \longrightarrow \text{Cu}_2\text{O} + \text{SO}_2$  ;  $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$   
 (C)  $\text{Cu}_2\text{S} + 2\text{O}_2 \longrightarrow \text{CuSO}_4$  ;  $\text{CuSO}_4 + \text{Cu}_2\text{S} \longrightarrow 3\text{Cu} + 2\text{SO}_2$   
 (D)  $\text{Cu}_2\text{S} + \frac{3}{2}\text{O}_2 \longrightarrow \text{Cu}_2\text{O} + \text{SO}_2$  ;  $\text{Cu}_2\text{O} + \text{CO} \longrightarrow 2\text{Cu} + \text{CO}_2$
- ML0025
26. The element which could be extracted by electrolytic reduction of its oxide dissolved in a high temperature melt is:  
 (A) sodium (B) magnesium (C) fluorine (D) aluminium
- ML0026
27. In which of the following isolations no reducing agent is required:  
 (A) iron from haematite (B) Tin from cassiterite  
 (C) mercury from cinnabar (D) zinc from zinc blende
- ML0027

## PURIFICATION METHODS

28. A metal has a high concentration into the earth crust and whose oxides cannot be reduced by carbon. The most suitable method for the extraction of such metal is  
 (A) Aluminothermite process (B) Electrolysis process  
 (C) Van-Arkel's process (D) Cupellation
- ML0028

29. **Assertion :** Alkali metals can not be prepared by the electrolysis of their chlorides in aqueous solution

**Reason :** Reduction potentials of alkali metals cations is much lower than that of  $H_2O$ .

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

ML0029

30. **Assertion :** Magnesium can be prepared by the electrolysis of aq.  $MgCl_2$ .

**Reason :** The reduction potential of  $Mg^{2+}$  is much lower than that of  $H_2O$ .

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

ML0030

31. Bessemerisation is carried out for

- |           |             |             |             |
|-----------|-------------|-------------|-------------|
| I : Fe,   | II : Cu,    | III : Al,   | IV : silver |
| (A) I, II | (B) II, III | (C) III, IV | (D) I, III  |

ML0031

32. In the extraction of nickel by Mond process, the metal is obtained by:

- (A) electrochemical reduction  
 (B) thermal decomposition  
 (C) chemical reduction by aluminium  
 (D) reduction by carbon

ML0032

33. Formation of  $Ni(CO)_4$  and subsequent its decomposition into Ni and CO (recycled) makes basis of Mond's process



$T_1$  and  $T_2$  are:

- (A)  $100^\circ C, 50^\circ C$       (B)  $50^\circ C, 100^\circ C$       (C)  $50^\circ C, 230^\circ C$       (D)  $230^\circ C, 50^\circ C$

ML0033

34. Zone refining is based on the principle of

- (A) fractional distillation  
 (B) fractional crystallisation  
 (C) partition coefficient  
 (D) chromatographic separation

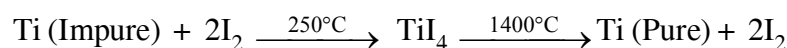
ML0034

35. Si and Ge used for semiconductors are required to be of high purity and hence purified by

- (A) zone-refining  
 (B) electrorefining  
 (C) Van-Arkel's process  
 (D) cupellation process

ML0035

36. Which process of purification is represented by the following equation :



- (A) Cupellation      (B) Poling      (C) Van-Arkel Process      (D) Zone refining

ML0036



37. Which of the following employ(s) thermal decomposition of volatile iodide compounds?  
(A) Thermite process (B) Hall's process (C) Van-Arkel's process (D) Mond's process  
ML0037
38. The method of zone refining of metals is based on the principle of:  
(A) Greater mobility of the pure metal than that of impurity.  
(B) Higher melting point of the impurity than that of the pure metal.  
(C) Greater noble character of the solid metal than that of the impurity  
(D) Greater solubility of the impurity in the molten state than in the solid  
ML0038
39. **Assertion :** Titanium is purified by Van-Arkel method.  
**Reason :** Ti reacts with  $I_2$  to form volatile  $TiI_4$  which decomposes at 1673 K to give pure Ti.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.  
ML0039
40. **Assertion :** Nickel is purified by the thermal decomposition of nickel tetracarbonyl.  
**Reason :** Nickel is a transition element.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.  
ML0040
41. Refining of silver is done by:  
(A) liquation (B) poling (C) cupellation (D) van Arkel method  
ML0041
42. Mercury is purified by:  
(A) Passing through dilute  $HNO_3$  (B) Distillation  
(C) Distribution (D) Vapour phase refining  
ML0042
43. **Assertion :** Lead, tin and bismuth are purified by liquation method.  
**Reason :** Lead, tin and bismuth have low m.p. as compared to impurities.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.  
ML0043

44. When an impurity in a metal has greater affinity for oxygen and is more easily oxidised than the metal itself. Then, the metal is refined by  
 (A) cupellation (B) zone-refining (C) distillation (D) electrolytic process

ML0044

**EXTRACTION OF METALS**

45. Which of the following process is not associated with recovery of the silver -  
 (A) As a side product in electrolytic refining of copper  
 (B) Parke's process in which Zn is used to extract silver by solvent extraction from molten lead  
 (C) By reaction of silver sulphide with KCN and then reaction of soluble complex with Zn  
 (D) By boiling  $\text{Na}[\text{Ag}(\text{CN})_2]$  aq.

ML0045

46. Blister Cu is about:  
 (A) 60% Cu (B) 90% Cu (C) 98% Cu (D) 100% Cu

ML0046

47. Iron obtained from blast furnace is:  
 (A) wrought iron (B) cast iron (C) pig iron (D) steel

ML0047

48. Which of the following term is not related to Al-extraction  
 (A) Serpek's process (B) Hall-Heroult process  
 (C) Thermite process (D) Hoop's process

ML0048

49. Dow's process  
 (A) involves purification of copper (B) involves extraction of magnesium  
 (C) gives metal chloride as product (D) gives pure Na as product

ML0049

50. Silica is added to roasted copper ores during extraction in order to remove  
 (A) cuprous sulphide (B) ferrous oxide (C) ferrous sulphide (D) cuprous oxide

ML0050

51. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese  
 (A) gives hardness to steel (B) helps the formation of oxides of iron  
 (C) can remove oxygen and sulphur (D) can show highest oxidation state of +7

ML0051

52. In the commercial electrochemical process for aluminium extraction the electrolyte used is  
 (A)  $\text{Al}(\text{OH})_3$  in NaOH solution (B) an aqueous solution of  $\text{Al}_2(\text{SO}_4)_3$   
 (C) a molten mixture of  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_3\text{AlF}_6$  &  $\text{CaF}_2$  (D) a molten mixture of  $\text{Al}_2\text{O}_3$  and  $\text{Al}(\text{OH})_3$

ML0052

53. Blister copper is refined by stirring molten impure metal with green logs of wood because such a wood liberates hydrocarbon gases (like  $\text{CH}_4$ ). This process X is called \_\_\_\_\_ and the metal contains impurities of Y is \_\_\_\_\_.
- (A) X = cupellation, Y =  $\text{CuO}_2$  (B) X = poling, Y =  $\text{Cu}_2\text{O}$   
 (C) X = poling, Y =  $\text{CuO}$  (D) X = cupellation, Y =  $\text{CuO}$
- ML0053**
54. A piece of steel is heated until redness and then plunged into cold water or oil. This treatment of steel makes it
- (A) soft and malleable (B) hard but not brittle  
 (C) more brittle (D) hard and brittle
- ML0054**
55. Modern method of steel manufacturing is
- (A) open hearth process (B) L.D. Process  
 (C) Bessemerisation (D) Cupellation
- ML0055**
56. During electrolytic reduction of alumina, two auxiliary electrolytes X and Y are added to increase the electrical conductance and lower the temperature of melt in order to making fused mixture very conducting. X and Y are
- (A) cryolite and flourspar (B) cryolite and alum  
 (C) alum and flourspar (D) flourspar and bauxite
- ML0056**
57. For extraction of sodium from  $\text{NaCl}$ , the electrolytic mixture  $\text{NaCl} + \text{KCl} + \text{CaCl}_2$  is used. During extraction process, only sodium is deposited on cathode but K and Ca do not because
- (A) Na is more reactive than K and Ca  
 (B) Na is less reactive than K and Ca  
 (C)  $\text{NaCl}$  is less stable than  $\text{Na}_3\text{AlF}_6$  and  $\text{CaCl}_2$   
 (D) the discharge potential of  $\text{Na}^+$  is less than that of  $\text{K}^+$  and  $\text{Ca}^{2+}$  ions.
- ML0057**
58. Railway wagon axles are made by heating iron rods embedded in charcoal powder. This process is known as:
- (A) Sherardising (B) Annealing (C) Tempering (D) Case hardening
- ML0058**
59. In the extraction of copper from its sulphide ore the metal is formed by the reduction of  $\text{Cu}_2\text{O}$  with:
- (A)  $\text{FeS}$  (B)  $\text{CO}$  (C)  $\text{Cu}_2\text{S}$  (D)  $\text{SO}_2$
- ML0059**
60. Carnallite on electrolysis gives:
- (A)  $\text{Ca}$  and  $\text{Cl}_2$  (B)  $\text{Na}$  and  $\text{CO}_2$  (C)  $\text{Al}$  and  $\text{Cl}_2$  (D)  $\text{Mg}$  and  $\text{Cl}_2$
- ML0060**

## MISCELLANEOUS

61. Which of the following statement is correct regarding Cu-extraction  
(A) In the smelting step carbon reduction takes places  
(B) During partial roasting  $\text{Cu}_2\text{S}$  remains almost unaffected  
(C) In Bessemer converter, only self reduction occur, not slag formation  
(D) Blister forms in the blister Cu is due to dissolved  $\text{CO}_2$
- ML0061
62. Refractory materials are generally used in furnaces because  
(A) they are chemically inert (B) they can withstand high temperature  
(C) they do not contain impurities (D) they decrease melting point of ore
- ML0062
63. Which of the following statements is correct regarding the slag formation during the extraction of a metal like copper or iron.  
(A) The slag is lighter and has lower melting temperature than the metal  
(B) The slag is heavier and has lower melting temperature than the metal  
(C) The slag is lighter and has higher melting temperature than the metal  
(D) The slag is heavier and has higher melting temperature than the metal
- ML0063
64. **Assertion :** Generally in smelting, roasted/cacinated ore is heated with powdered coke in presence of a flux.  
**Reason :** Oxides are reduced to metals by C or CO. Impurities are removed as slag.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
- ML0064
65. **Assertion :** Magnesia and quick lime are used as basic flux.  
**Reason :** MgO and CaO can withstand very high temperatures.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
- ML0065
66. **Assertion :** Wolframite impurity is separated from  $\text{SnO}_2$  by magnetic separation  
**Reason :** Tin stone is ferromagnetic, therefore attracted by magnet.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
- ML0066

## EXERCISE # O-2

ONE OR MORE THAN ONE OPTION MAY BE CORRECT

1. Which of the following is(are) sulphide ores?  
 (A) Argentite (B) Galena (C) Anglesite (D) Copper glance **ML0067**
2. Which of the following is (are) regarded as iron ores?  
 (A) Haematite (B) Magnetite (C) Limonite (D) Copper pyrites **ML0068**

## CONCENTRATION

3. Which of the following ores is(are) concentrated by froth floatation?  
 (A) haematite (B) galena (C) copper pyrite (D) azurite **ML0069**
4. Which of the following ores is (are) concentrated industrially by froth floatation?  
 (A) Copper pyrites (B) Galena (C) Dolomite (D) Carnallite **ML0070**
5. Leaching is used for the concentration of:  
 (A) Red bauxite (B) Haematite (C) Gold ore (D) Silver ore **ML0071**

## CALCINATION/ROASTING

6. Calcination and roasting processes of ores to form their oxides are beneficial  
 (A) to convert ores into porous form so that their reduction becomes easier  
 (B) as impurities like S, As, Sb, are removed  
 (C) as organic impurities are removed.  
 (D) as the ores are converted into oxide form which makes the reduction easier **ML0072**
7. Which of the following reaction(s) occur during calcination?  
 (A)  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$  (B)  $4\text{FeS}_2 + 11\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$   
 (C)  $2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$  (D)  $\text{CuS} + \text{CuSO}_4 \rightarrow 2\text{Cu} + 2\text{SO}_2$  **ML0073**
8. Which of the following is true for calcination of a metal ore?  
 (A) It makes the ore more porous  
 (B) The ore is heated to a temperature when fusion just begins  
 (C) Hydrated salts lose their water of crystallisation  
 (D) Impurities of S, As and Sb are removed in the form of their volatile oxides. **ML0074**
9. Roasting can be performed in  
 (A) blast furnace (B) reverberatory furnace  
 (C) electric furnace (D) None of these **ML0075**

**REDUCTION**

10. Carbon reduction method is employed for commercial extraction of metal from amongst these :  
 (A) haematite (B) cassiterite (C) iron pyrite (D) corundum **ML0076**
11. Auto reduction process is used in extraction of  
 (A) Cu (B) Hg (C) Al (D) Fe **ML0077**
12. Which of the following reduction reactions are actually employed in commercial extraction of metals?  
 (A)  $\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$   
 (B)  $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$   
 (C)  $2\text{Na}[\text{Au}(\text{CN})_2] + \text{Zn} \rightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Au}$   
 (D)  $\text{Cu}_2\text{S} + \text{Pb} \rightarrow \text{Cu} + \text{PbS} \downarrow$  **MA0078**

**PURIFICATION**

13. In the manufacturing of metallic sodium by fused salt-electrolysis method (Down's process), small amount of  $\text{CaCl}_2$  that added is known as auxiliary electrolyte and is used to  
 (A) improve the electrical conductance (B) decrease the melting point of electrolyte  
 (C) stabilise the metallic sodium (D) increase the temperature of electrolysis **ML0079**
14. Poling is employed in refining of  
 (A) iron (B) copper (C) tin (D) lead **ML0080**
15. Zone refining is used for purification of  
 (A) Ge (B) Si (C) Ga (D) In **ML0081**
16. Metal(s) which does/do not form amalgam is/are  
 (A) Fe (B) Pt (C) Zn (D) Au **ML0082**
17. Metals which can be commercially extracted by smelting process  
 (A) Pb (B) Fe (C) Zn (D) Mg **ML0083**

**EXTRACTION OF METALS**

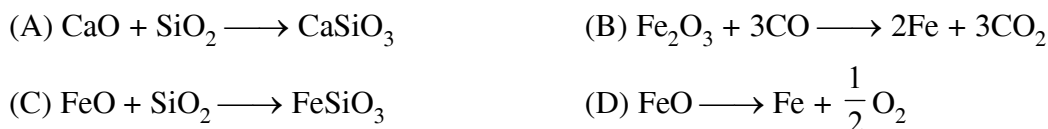
18. Hoop's process of purification of aluminium involves formation of layers during electrolysis. It involves  
 (A) the three layers have same densities but different materials.  
 (B) the three layers have different densities  
 (C) the upper layer is of pure aluminium which acts as a cathode  
 (D) the bottom layer is of impure aluminium which acts as an anode and middle layer consists of cryolite and  $\text{BaF}_2$ . **ML0084**

19. Metallurgical process of zinc involves roasting of zinc sulphide followed by reduction. Metallic zinc distills over as it is volatile and impurities like Cu, Pb and Fe gets condensed. The crude metal obtained is called spelter, which may be purified by  
 (A) electrolysis process (B) fractional distillation  
 (C) polling (D) heating with iodine  
**ML0085**
20. Which of the following process (es) are used for purification of Bauxite ore?  
 (A) Hall's process (B) Serpeck's process (C) Baeyer's process (D) Mond's process  
**ML0086**
21. Common impurities present in Bauxite are  
 (A) CuO (B) ZnO (C) Fe<sub>2</sub>O<sub>3</sub> (D) SiO<sub>2</sub>  
**ML0087**
22. Calcium silicate slag formed in extraction of iron  
 (A) prevents the reoxidation of molten iron.  
 (B) catalyses the combustion of carbon.  
 (C) reduces CO<sub>2</sub> to CO at the bottom of the furnace.  
 (D) is used in cement industry.  
**ML0088**
23. Amphoteric nature of aluminium is employed in which of the following process for extraction of aluminium?  
 (A) Baeyer's process (B) Hall's process  
 (C) Serpeck's process (D) Dow's process  
**ML0089**
24. The chief reaction(s) occurring in blast furnace during extraction of iron from haematite is(are)  
 (A)  $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$  (B)  $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$   
 (C)  $\text{Fe}_2\text{O}_3 + \text{C} \rightarrow 2\text{Fe} + 3\text{CO}$  (D)  $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$   
**ML0090**
25. Which of the following are true for electrolytic extraction of aluminium  
 (A) cathode material contains graphite  
 (B) anode material contains graphite  
 (C) cathode reacts away forming CO<sub>2</sub>  
 (D) anode reacts away forming CO<sub>2</sub>  
**ML0091**
26. During extraction of copper, it is obtained in the form of molten *matte*. Which of the following is **not true**?  
 (A) *matte* is further treated in Bessemer's converter  
 (B) molten *matte* is electrolysed  
 (C) It is treated with a blast of air and sand  
 (D) It is dissolved in CuSiF<sub>6</sub> and crystallised.  
**ML0092**

27. The major role of fluorspar ( $\text{CaF}_2$ ) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite ( $\text{Na}_3\text{AlF}_6$ ) is
- (A) as a catalyst
  - (B) to make the fused mixture very conducting
  - (C) to lower the melting temperature of the mixture
  - (D) to decrease the rate of oxidation of carbon at the anode.

ML0093

28. Which of the following reaction does not occur in blast furnace during extraction of iron :



ML0094

### MISCELLANEOUS

29. Which of the following employ downward movement of ore due to gravity?

- (A) Gravity separation
- (B) Froth floatation
- (C) Blast furnace
- (D) Bessemer's coverter

ML0095

30. The **CORRECT** statements are :

- (A) generally the calcination and roasting is done in blast furnace
- (B) the sandy and rocky materials associated with ore are called matrix
- (C) froth floatation process is suitable for sulphide ores
- (D) substance that reacts with gangue to form fusible mass is called slag

ML0096



## EXERCISE # S-1

1. Find the number of ore which are concentrated by magnetic separation method.  
Haemetite, Cassiterite, Copper Glance, Chromite, Cinnabar

ML0097

2. Find the number of metals which are commercially extracted by carbon reduction method  
Pb, Fe, Zn, Mg, Al, Na, Au, Ag

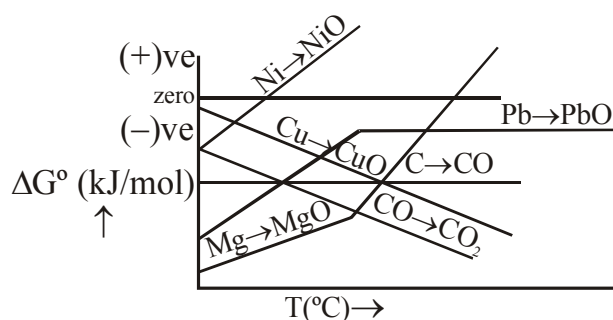
ML0098

3. The number of following pairs is correctly matched

- (i) Van Arkel method – Zirconium  
(ii) Mond Process – Titanium  
(iii) Froth Floatation Method – Cerussite  
(iv) Distillation method – Zinc  
(v) Poling Process – Copper  
(vi) amalgamation – Gold

ML0099

4. Find the number of curves which are wrongly presented in the Ellingham diagram.



ML0100

5. How many of the following minerals containing Mg.  
Magnetite, Carnallite, Epsom salt, Siderite

ML0101

6. Find out the number of minerals given below contain iron as Fe(II).  
Haematite, Magnetite, Limonite, Siderite, Chromite, Wolframite

ML0102

7. Amongst the following ores, the total number of oxide ores are  
Siderite, Magnetite, Haematite, Malachite, Zincite, Cuprite

ML0103

8. Amongst the following, total number of sulphide ores are  
Calamine, Sphalertie, Copper pyrites, Copper glance, Iron pyrites, Bauxite

ML0104

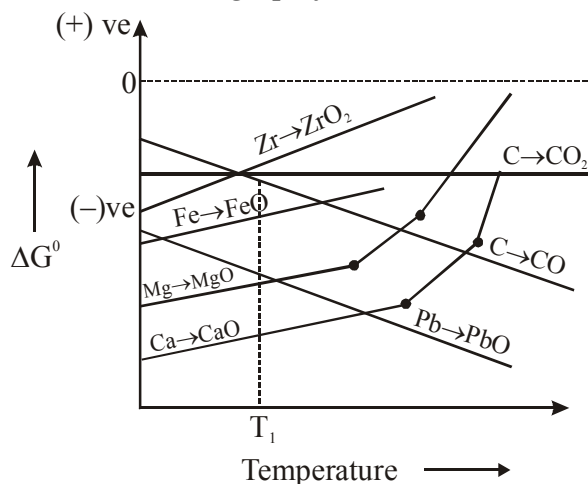
9. How many of the following ores of silver ?  
Hornsilver, Cerrusite, Chalcopyrite, Galena, Anglesite, Argentite

ML0105

**EXERCISE # S-2**

**COMPREHENSION AND MATCH THE COLUMN  
ELLINGHAM DIAGRAM**

*Paragraph for 1 to 3*

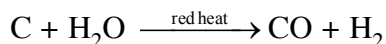


- Which of the above curve is wrongly presented -  
 (A)  $C \rightarrow CO_2$       (B)  $Pb \rightarrow PbO$       (C)  $Zr \rightarrow ZrO_2$       (D)  $Mg \rightarrow MgO$   
**ML0106**
- Which of the above metal oxide is having minimum thermal decomposition temperature.  
 (A) CaO      (B) FeO      (C)  $ZrO_2$       (D) MgO  
**ML0106**
- Which of the following metal's oxide can be reduced by Fe as reducing agent at temperature ( $T_1$ )  
 (A) Zr      (B) Ca      (C) Mg      (D) None of these  
**ML0106**

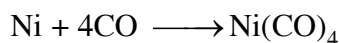
**PURIFICATION METHOD**

*Paragraph for 4 to 5*

At high temperature carbon reacts with water to produce a mixture of carbon monoxide, CO and hydrogen,  $H_2$ .



CO is separated from  $H_2$  and then used to separate nickel from cobalt by forming a volatile compound, nickel tetracarbonyl,  $Ni(CO)_4$ .



- How many moles of  $Ni(CO)_4$  could be obtained from the CO produced by the reaction of 75.0g of carbon ? Assume 100% reaction and 100% recovery in both steps.  
 (A) 6.25      (B) 1.563      (C) 3.125      (D) 25.0  
**ML0107**
- Formation of volatile  $Ni(CO)_4$  and its subsequent heating gives pure Ni. Process is called -  
 (A) Hall      (B) Dow      (C) Serpeck      (D) Mond  
**ML0107**

## MISCELLANEOUS

Match Column

6. Match Column-I with Column-II

Column-I (Metals)	Column-II (Method used for refining)
(A) Iron & copper	(P) Poling
(B) Zirconium & Titanium	(Q) Bessemerisation
(C) Lead & Tin	(R) Van-Arkel
(D) Copper & Tin	(S) Liquefaction

ML0108

7. Match the following choosing one item from column X and the appropriate item from column Y.

Column -X	Column-Y
(A) Zinc from $ZnCO_3$	(P) Calcination
(B) Lead from PbS	(Q) Removal of iron
(C) Cu from $CuFeS_2$	(R) Froth floatation process
(D) Tin from cassiterite	(S) Poling

ML0109

8. Match column (I) (process) with column (II) (electrolyte)

Column (I) (process)	Column (II) (electrolyte)
(A) Downs cell	(P) fused $MgCl_2$
(B) Dow's sea water process	(Q) fused $(Al_2O_3 + Na_3AlF_6 + CaF_2)$
(C) Hall-Heroult	(R) fused $(40\% NaCl + 60\% CaCl_2)$
	(S) $(AlN + C + N_2)$

ML0110

9. Match column - I with column - II

Column - I (Property)	Column - II (Element/compound)
(A) Explosive	(P) Cu
(B) Self-reduction	(Q) $Fe_3O_4$
(C) Ferrimagnetic material	(R) $Cu(CH_3COO)_2 \cdot Cu(OH)_2$
(D) Verdigris	(S) $Pb(NO_3)_2$

ML0111

10. Match column - I and column - II and select the correct answer using the codes given below the lists:

Column - I	Column - II
(A) Cyanide process	(P) Ultrapure Ge
(B) Floatation process	(Q) Dressing of HgS
(C) Electrolytic reduction	(R) Extraction of Al
(D) Zone refining	(S) Extraction of Au

ML0112

11. Match the items of Column I with items of Column II and assign the correct code :

Column I	Column II
(P) Blistered Cu	(1) Aluminium
(Q) Blast furnace	(2) $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$
(R) Reverberatory furnace	(3) Iron
(S) Hall-Heroult process	(4) $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$
	(5) $2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$

Code :

- (A) P → (2) ; Q → (3) ; R → (4) ; S → (1)    (B) P → (1) ; Q → (2) ; R → (3) ; S → (5)  
 (C) P → (5) ; Q → (4) ; R → (3) ; S → (2)    (D) P → (4) ; Q → (5) ; R → (3) ; S → (2)

ML0113

Answer Q.12, Q.13 and Q.14 by appropriately matching the information given in the three columns of the following table.

Column - I Extraction of metal	Column - II Methods for Reduction	Column - III Refining Method
(1) $\text{SnO}_2 \rightarrow \text{Sn}$	(i) Carbon Reduction	(P) Poling
(2) $\text{Al}_2\text{O}_3 \rightarrow \text{Al}$	(ii) Hydrometallurgic Reduction	(Q) Electrolytic Refining
(3) $\text{Cu}_2\text{S} \rightarrow \text{Cu}$	(iii) Electrolytic Reduction	(R) Distillation
(4) $\text{ZnS} \rightarrow \text{Zn}$	(iv) Self-Reduction	(S) Puddling Process

12. Which of the following is **NOT** correctly matched?

- (A) (1), (iv), (S)      (B) (3), (iv), (P)      (C) (4), (i), (R)      (D) (2), (iii), (Q)

ML0114

13. Which of the following match is the **CORRECT** reduction and purification methods for Zn

- (A) (i), (R)      (B) (iv), (S)      (C) (iv), (P)      (D) None of these

ML0114

14. Which of the following set of code shows the **CORRECT** similarity with the extraction processes for Pb?

- (A) (1), (ii), (S)      (B) (4), (iii), (P)      (C) (2), (iii), (Q)      (D) (3), (iv), (Q)

ML0114

## EXERCISE # JEE-MAINS

1. Aluminium is extracted by the electrolysis of :- [AIEEE-2002]  
 (1) Bauxite (2) Alumina  
 (3) Alumina mixed with molten cryolite (4) Molten cryolite  
 ML0115
2. Pyrolusite is a/an :- [AIEEE-2002]  
 (1) Oxide ore (2) Sulphide ore (3) Carbide ore (4) Not an ore  
 ML0116
3. Which one of the following ores is best concentrated by froth-flotation method : [AIEEE-2004]  
 (1) Galena (2) Cassiterite (3) Magnetite (4) Malachite  
 ML0117
4. Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly ? [AIEEE-2008]  
 (1) Metal sulphides are thermodynamically more stable than  $CS_2$   
 (2)  $CO_2$  is thermodynamically more stable than  $CS_2$   
 (3) Metal sulphides are less stable than the corresponding oxides  
 (4)  $CO_2$  is more volatile than  $CS_2$   
 ML0118
5. Which method of purification is represented by the following equation : [AIEEE-2012]  

$$Ti(s) + 2I_2(g) \xrightarrow{523K} TiI_4(g) \xrightarrow{1700K} Ti(s) + 2I_2(g)$$
  
 (1) Van Arkel (2) Zone refining (3) Cupellation (4) Poling  
 ML0119
6. The substance used as froth stabilisers in froth-floatation process is : [J-Mains-2012 (On line)]  
 (1) Copper sulphate (2) Aniline  
 (3) Sodium cyanide (4) Potassium ethyl xanthate  
 ML0120
7. Which of the oxide groups among the following cannot be reduced by carbon :- [J-Mains-2012 (On line)]  
 (1)  $Fe_3O_4$ , ZnO (2) PbO,  $Fe_3O_4$  (3)  $Cu_2O$ ,  $SnO_2$  (4) CaO,  $K_2O$   
 ML0121
8. In Goldschmidt aluminothermic process which of the following reducing agents is used : [J-Mains-2013 (On line)]  
 (1) Calcium (2) Coke (3) Sodium (4) Al-powder  
 ML0122

9. Calcination is the process in which :
- (1) Ore is heated strongly below its melting point in the presence of excess of air and is used for the conversion of carbonates and hydrated oxide ores to their respective oxides.
  - (2) Ore is heated strongly below its melting point in the absence or limited supply of air and is used for conversion of sulphide ores to their respective oxides
  - (3) Ore is heated strongly below its melting point either in the limited supply or absence of air and is used to convert carbonates and hydrated oxide ores to their respective oxides
  - (4) Ore is heated strongly above its melting point in the limited supply of air to convert sulphide ores to their respective oxides.
- ML0123**
10. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is : **[JEE-MAINS-2014]**
- (1) Cu                      (2) Cr                      (3) Ag                      (4) Ca
- ML0124**
11. The form of iron obtained from blast furnace is : **[J-Mains-2014 (On line)]**
- (1) Steel                      (2) Wrought Iron                      (3) Cast Iron                      (4) Pig iron
- ML0125**
12. In the context of the Hall-Heroult process for the extraction of Al, which of the following statements is false ? **[JEE-MAINS-2015]**
- (1)  $\text{Al}^{3+}$  is reduced at the cathode to form Al
  - (2)  $\text{Na}_3\text{AlF}_6$  serves as the electrolyte
  - (3) CO and  $\text{CO}_2$  are produced in this process
  - (4)  $\text{Al}_2\text{O}_3$  is mixed with  $\text{CaF}_2$  which lowers the melting point of the mixture and brings conductivity
- ML0126**
13. Galvanization is applying a coating of :- **[JEE-MAINS-2016]**
- (1) Zn                      (2) Pb                      (3) Cr                      (4) Cu
- ML0127**
14. Which one of the following ores is best concentrated by froth floatation method ? **[JEE-MAINS-2016]**
- (1) Malachite                      (2) Magnetite                      (3) Siderite                      (4) Galena
- ML0128**
15. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1M  $\text{ZnSO}_4$  ? **[JEE-MAINS (Online) - 2016]**
- (1) The copper metal will dissolve and zinc metal will be deposited
  - (2) No reaction will occur
  - (3) The copper metal will dissolve with evolution of oxygen gas
  - (4) The copper metal will dissolve with evolution of hydrogen gas

**ML0129**

16. In the leaching method, bauxite ore is digested with a concentrated solution of NaOH that produces 'X'. When CO<sub>2</sub> gas is passed through the aqueous solution of 'X', a hydrated compound 'Y' is precipitated. 'X' and 'Y' respectively are :- [JEE MAIN ONLINE. 2018]

- (1) Na[Al(OH)<sub>4</sub>] and Al<sub>2</sub>O<sub>3</sub>·x H<sub>2</sub>O
- (2) Al(OH)<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>·x H<sub>2</sub>O
- (3) Na[Al(OH)<sub>4</sub>] and Al<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·x H<sub>2</sub>O
- (4) Na AlO<sub>2</sub> and Al<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·x H<sub>2</sub>O

ML0130

17. When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is [JEE MAIN OFFLINE. 2018]

- (1) Ca
- (2) Al
- (3) Fe
- (4) Zn

ML0131

**EXERCISE # JEE-ADVANCED**

1. Carnallite does not contain  
(A) K (B) Ca (C) Mg (D) Cl **ML0132**
2. During initial treatment, preferential wetting of ore by oil and gangue by water takes place in  
(A) Levigation (gravity separation) (B) Froth floatation  
(C) Leaching (D) Bessemerisation **ML0133**
3. Which of the following is true for calcination of a metal ore?  
(A) It makes the ore more porous  
(B) The ore is heated to a temperature when fusion just begins  
(C) Hydrated salts lose their water of crystallisation  
(D) Sulphur in sulphides is oxidised to  $\text{SO}_2$   
(E) Heating with carbon leads to better calcination **ML0134**
4. In the commercial electrochemical process for aluminium extraction, the electrolyte used as :  
[JEE-1999]  
(A)  $\text{Al(OH)}_3$  in NaOH solution  
(B) an aqueous solution of  $\text{Al}_2(\text{SO}_4)_3$   
(C) a molten mixture of  $\text{Al}_2\text{O}_3$  and  $\text{Na}_3\text{AlF}_6$   
(D) a molten mixture of  $\text{AlO(OH)}$  and  $\text{Al(OH)}_3$  **ML0135**
5. The chemical process in the production of steel from haematite ore involve: [2000 Qualifying]  
(A) reduction (B) oxidation  
(C) reduction followed by oxidation (D) oxidation followed by reduction **ML0136**
6. Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out:  
(A) in the presence of NaCl [2000 Qualifying]  
(B) in the presence of fluorite  
(C) in the presence of cryolite which forms a melt with lower melting temperature  
(D) in the presence of cryolite which forms a melt with higher melting temperature **ML0137**
7. The chemical composition of "slag" formed during the smelting process in the extraction of copper is : [2001 Qualifying]  
(A)  $\text{Cu}_2\text{O} + \text{FeS}$  (B)  $\text{FeSiO}_3$  (C)  $\text{CuFeS}_2$  (D)  $\text{Cu}_2\text{S} + \text{FeO}$  **ML0138**
8. Which of the following processes is used in extractive metallurgy of magnesium? [2002 Qualifying]  
(A) Fused salt electrolysis (B) Self reduction  
(C) Aqueous solution electrolysis (D) Thermite reduction **ML0139**



9. In the process of extraction of gold, [2003 Qualifying]  
 Roasted gold ore +  $\text{CN}^- + \text{H}_2\text{O} \xrightarrow{\text{O}_2} [\text{X}] + \text{OH}^-$   
 $[\text{X}] + \text{Zn} \longrightarrow [\text{Y}] + \text{Au}$   
 Identify the complexes [X] and [Y] :  
 (A)  $\text{X} = [\text{Au}(\text{CN})_2]^-$ ,  $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$       (B)  $\text{X} = [\text{Au}(\text{CN})_4]^{3-}$ ,  $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$   
 (C)  $\text{X} = [\text{Au}(\text{CN})_2]^-$ ,  $\text{Y} = [\text{Zn}(\text{CN})_6]^{4-}$       (D)  $\text{X} = [\text{Au}(\text{CN})_4]^-$ ,  $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$   
ML0140
10. The methods chiefly used for the extraction of lead and tin from their ores are respectively : [JEE-2004]  
 (A) self reduction and carbon reduction      (B) self reduction and electrolytic reduction  
 (C) carbon reduction and self reduction      (D) cyanide process and carbon reduction  
ML0141
11. Which ore contains both iron and copper ? JEE-2004]  
 (A) Cuprite      (B) Chalcocite      (C) Chalcopyrite      (D) Malachite  
ML0142
12. Extraction for zinc from zinc blende is achieved by : [JEE-2007]  
 (A) electrolytic reduction  
 (B) roasting followed by reduction with carbon  
 (C) roasting followed by reduction with another metal  
 (D) roasting followed by self-reduction  
ML0143
13. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of :-  
 (A) nitrogen      (B) oxygen      (C) carbon dioxide      (D) argon [JEE-2008]  
ML0144

#### Paragraph for questions 14 to 16

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcocite ( $\text{Cu}_2\text{O}$ ), atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ), cuprite ( $\text{Cu}_2\text{O}$ ), copper glance ( $\text{Cu}_2\text{S}$ ) and malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ). However, 80% of the world copper production comes from the ore chalcopyrite ( $\text{CuFeS}_2$ ). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction. [JEE-2010]

14. Partial roasting of chalcopyrite produces :-  
 (A)  $\text{Cu}_2\text{S}$  and  $\text{FeO}$       (B)  $\text{Cu}_2\text{O}$  and  $\text{FeO}$       (C)  $\text{CuS}$  and  $\text{Fe}_2\text{O}_3$       (D)  $\text{Cu}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$   
ML0145
15. Iron is removed from chalcopyrite as :-  
 (A)  $\text{FeO}$       (B)  $\text{FeS}$       (C)  $\text{Fe}_2\text{O}_3$       (D)  $\text{FeSiO}_3$   
ML0145

16. In self-reduction, the reducing species is :-  
 (A) S (B)  $O^{2-}$  (C)  $S^{2-}$  (D)  $SO_2$  ML0145
17. Match the extraction processes listed in column I with metals listed in column II. [JEE-2006]
- | Column I  | Column II  |
|---|------------|
| (A) Self reduction                              | (P) Lead   |
| (B) Carbon reduction                            | (Q) Silver |
| (C) Complex formation and displacement by metal | (R) Copper |
| (D) Decomposition of iodide                     | (S) Boron  |
- ML0146
18. Match the conversions in **Column I** with the type(s) of reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS. [JEE-2008]
- | Column I                     | Column II            |
|------------------------------|----------------------|
| (A) $PbS \rightarrow PbO$    | (P) Roasting         |
| (B) $CaCO_3 \rightarrow CaO$ | (Q) Calcination      |
| (C) $ZnS \rightarrow Zn$     | (R) Carbon reduction |
| (D) $Cu_2S \rightarrow Cu$   | (S) Self reduction   |
- ML0147
19. In extractive metallurgy of zinc partial fusion of  $ZnO$  with coke is called \_\_\_\_\_ and reduction of the ore to the molten metal is called \_\_\_\_\_ (smelting, calcining, roasting, sintering). [JEE-1988]
- ML0148
20. Extraction of metal from the ore cassiterite involves [JEE-2011]
- |                                      |                                      |
|--------------------------------------|--------------------------------------|
| (A) carbon reduction of an oxide ore | (B) self-reduction of a sulphide ore |
| (C) removal of copper impurity       | (D) removal of iron impurity         |
- ML0149
21. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are [JEE-2011]
- |   |   |
|---|---|
| (A) II, III in haematite and III in magnetite | (B) II, III in haematite and II in magnetite  |
| (C) II in haematite and II, III in magnetite  | (D) III in haematite and II, III in magnetite |
- ML0150
22. In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are : [JEE-2012]
- |                                       |                                     |
|---------------------------------------|-------------------------------------|
| (A) $O_2$ and CO respectively.        | (B) $O_2$ and Zn dust respectively. |
| (C) $HNO_3$ and Zn dust respectively. | (D) $HNO_3$ and CO respectively.    |
- ML0151
23. Sulfide ores are common for the metals - [JEE-2013]
- |                   |                   |                   |                   |
|-------------------|-------------------|-------------------|-------------------|
| (A) Ag, Cu and Pb | (B) Ag, Cu and Sn | (C) Ag, Mg and Pb | (D) Al, Cu and Pb |
|-------------------|-------------------|-------------------|-------------------|
- ML0152
24. The carbon-based reduction method is **NOT** used for the extraction of [JEE-2013]
- |                              |  |
|------------------------------|--|
| (A) tin from $SnO_2$         | (B) Iron from $Fe_2O_3$                  |
| (C) aluminium from $Al_2O_3$ | (D) magnesium from $MgCO_3 \cdot CaCO_3$ |
- ML0153
25. Upon heating with  $Cu_2S$ , the reagent(s) that give copper metal is/are [JEE Adv. 2014]
- |               |           |             |              |
|---------------|-----------|-------------|--------------|
| (A) $CuFeS_2$ | (B) $CuO$ | (C) $Cu_2O$ | (D) $CuSO_4$ |
|---------------|-----------|-------------|--------------|
- ML0154

26. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is (are) [JEE Adv. 2015]

- (A) Impure Cu strip is used as cathode  
 (B) Acidified aqueous  $\text{CuSO}_4$  is used as electrolyte  
 (C) Pure Cu deposits at cathode  
 (D) Impurities settle as anode-mud

ML0155

27. Match the anionic species given in Column-I that are present in the ore(s) given in Column-II [JEE Adv. 2015]

**Column - I****Column - II**

- |               |               |
|---------------|---------------|
| (A) Carbonate | (P) Siderite  |
| (B) Sulphide  | (Q) Malachite |
| (C) Hydroxide | (R) Bauxite   |
| (D) Oxide     | (S) Calamine  |
|               | (T) Argentite |

ML0156

28. Extraction of copper from copper pyrite ( $\text{CuFeS}_2$ ) involves [JEE Adv. 2016]

- (A) crushing followed by concentration of the ore by froth-flotation  
 (B) removal of iron as slag  
 (C) self-reduction step to produce 'blister copper' following evolution of  $\text{SO}_2$   
 (D) refining of 'blister copper' by carbon reduction

ML0157

29. Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the contents undergo self-reduction. The weight (in kg) of Pb produced per kg of  $\text{O}_2$  consumed is \_\_\_\_\_. (Atomic weights in  $\text{g mol}^{-1}$  : O = 16, S = 32, Pb = 207) [JEE ADV. 2018]

ML0158

30. Calamine, malachite, magnetite and cryolite, respectively are [JEE ADV. 2019]

- |  |  |
|--|--|
| (1) $\text{ZnSO}_4$ , $\text{CuCO}_3$ , $\text{Fe}_2\text{O}_3$ , $\text{AlF}_3$                     | (2) $\text{ZnCO}_3$ , $\text{CuCO}_3$ , $\text{Cu}(\text{OH})_2$ , $\text{Fe}_3\text{O}_4$ , $\text{Na}_3\text{AlF}_6$ |
| (3) $\text{ZnSO}_4$ , $\text{Cu}(\text{OH})_2$ , $\text{Fe}_3\text{O}_4$ , $\text{Na}_3\text{AlF}_6$ | (4) $\text{ZnCO}_3$ , $\text{CuCO}_3$ , $\text{Fe}_2\text{O}_3$ , $\text{Na}_3\text{AlF}_6$                            |

ML0159

31. The cyanide process of gold extraction involves leaching out gold from its ore with  $\text{CN}^-$  in the presence of **Q** in water to form **R**. Subsequently, **R** is treated with **T** to obtain Au and **Z**. Choose the correct option(s). [JEE ADV. 2019]

- (1) **T** is Zn                      (2) **R** is  $[\text{Au}(\text{CN})_4]^-$       (3) **Z** is  $[\text{Zn}(\text{CN})_4]^{2-}$       (4) **Q** is  $\text{O}_2$

ML0160

**ANSWER-KEY****EXERCISE # O-I**

1. (A)	2. (C)	3. (B)	4. (B)	5. (C)	6. (A)
7. (A)	8. (B)	9. (D)	10. (B)	11. (B)	12. (A)
13. (B)	14. (B)	15. (A)	16. (D)	17. (A)	18. (A)
19. (B)	20. (C)	21. (C)	22. (C)	23. (C)	24. (B)
25. (B)	26. (D)	27. (C)	28. (B)	29. (A)	30. (D)
31. (A)	32. (B)	33. (C)	34. (B)	35. (A)	36. (C)
37. (C)	38. (D)	39. (A)	40. (B)	41. (C)	42. (B)
43. (A)	44. (A)	45. (D)	46. (C)	47. (C)	48. (C)
49. (B)	50. (B)	51. (A)	52. (C)	53. (B)	54. (D)
55. (B)	56. (A)	57. (D)	58. (D)	59. (C)	60. (D)
61. (B)	62. (B)	63. (A)	64. (A)	65. (B)	66. (C)

**EXERCISE # O-II**

1. (A,B,D)	2. (A,B,C)	3. (B,C)	4. (A,B)	5. (A,C,D)	6. (A,B,C,D)
7. (A, C)	8. (A, C)	9. (A, B)	10. (A, B)	11. (A,B)	12. (B, C)
13. (A,B)	14. (B,C)	15. (A,B,C, D)	16. (A,B)	17. (A,B, C)	18. (B,C,D)
19. (A,B)	20. (A,B,C)	21. (C,D)	22. (A, D)	23. (A,B)	24. (A, D)
25. (A,B,D)	26. (B,D)	27. (B,C)	28. (C,D)	29. (A,C)	30. (B, C)

**EXERCISE # S-1**

1. (3)	2. (3)	3. (4)	4. (4)	5. (2)	6. (4)
7. (4)	8. (4)	9. (2)			

**EXERCISE # S-2**

1. (B)	2. (C)	3. (A)	4. (B)	5. (D)	
6. (A) Q; (B) R; (C) S; (D)P	7. (A) → P, (B) → R ; (C) → Q, R, S (D) → Q, S				
8. (A) R ; (B) P; (C) Q	9. (A) S ; (B) P; (C) Q; (D) R				
10. (A) S ; (B) Q ; (C) R ; (D) P	11. (A)	12. (A)	13. (A)	14. (D)	

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**EXERCISE # JEE-MAINS**


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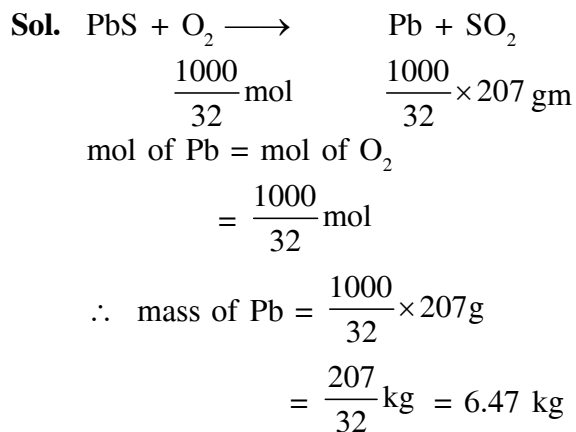
- |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|
| 1. (3)  | 2. (1)  | 3. (1)  | 4. (3)  | 5. (1)  | 6. (2)  |
| 7. (4)  | 8. (4)  | 9. (3)  | 10. (4) | 11. (4) | 12. (2) |
| 13. (1) | 14. (4) | 15. (2) | 16. (1) | 17. (2) |         |

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**EXERCISE # JEE-ADVANCED**


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- |   |         |   |               |               |                 |
|---|---------|---|---------------|---------------|-----------------|
| 1. (B)  | 2. (B)  | 3. (A,C)  | 4. (C)        | 5. (C)        | 6. (C)          |
| 7. (B)  | 8. (A)  | 9. (A)  | 10. (A)       | 11. (C)       | 12. (B)         |
| 13. (B)   | 14. (A) | 15. (D)   | 16. (C)       |               |                 |
| 17. (A) – P, R ; (B) – P ; (C) – Q ; (D) – S          |         | 18. (A) – P ; (B) – Q ; (C) – P, R ; (D) – P, S |               |               |                 |
| 19. Sintering , Smelting                              |         | 20. (A, D) or (A, C, D)                         |               | 21. (D)       |                 |
| 22. (B)   | 23. (A) | 24. (C, D)                                      | 25. (B, C, D) | 26. (B, C, D) |                 |
| 27. (A) – P , Q , S ; (B) – T ; (C) – Q , R ; (D) – R |         |   |               | 28. (A, B, C) |                 |
| 29. Ans. (6.47)                                       |         |   | 30. Ans.(2)   |               | 31. Ans.(1,3,4) |



## HYDROGEN & ITS COMPOUND

### POSITION OF HYDROGEN IN THE PERIODIC TABLE

Hydrogen is the first element in the periodic table. However, its placement in the periodic table has been a subject of discussion in the past. As you know by now that the elements in the periodic table are arranged according to their electronic configurations. Hydrogen has electronic configuration  $1s^1$ . On one hand, its electronic configuration is similar to the outer electronic configuration ( $ns^1$ ) of alkali metals, which belong to the first group of the periodic table. On the other hand, like halogens (with  $ns^2np^5$  configuration belonging to the seventeenth group of the periodic table), it is short by one electron to the corresponding noble gas configuration, helium ( $1s^2$ ). Hydrogen, therefore, has resemblance to alkali metals, which lose one electron to form unipositive ions, as well as with halogens, which gain one electron to form uninegative ion. Like alkali metals, hydrogen forms oxides, halides and sulphides. However, unlike alkali metals, it has a very high ionization enthalpy and does not possess metallic characteristics under normal conditions. In fact, in terms of ionization enthalpy, hydrogen resembles more with halogens,  $\Delta_i H$  of Li is  $520 \text{ kJ mol}^{-1}$ , F is  $1680 \text{ kJ mol}^{-1}$  and that of H is  $1312 \text{ kJ mol}^{-1}$ . Like halogens, it forms a diatomic molecule, combines with elements to form hydrides and a large number of covalent compounds. However, in terms of reactivity, it is very low as compared to halogens.

In spite of the fact that hydrogen, to a certain extent resembles both with alkali metals and halogens, it differs from them as well. Now the pertinent question arises as where should it be placed in the periodic table? Loss of the electron from hydrogen atom results in nucleus ( $H^+$ ) of  $\sim 1.510^{-3} \text{ pm}$  size. This is extremely small as compared to normal atomic and ionic sizes of 50 to 200 pm. As a consequence,  $H^+$  does not exist freely and is always associated with other atoms or molecules. Thus, it is unique in behaviour and is, therefore, best placed separately in the periodic table.

### DIHYDROGEN, $H_2$

#### Occurrence

Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist mostly of hydrogen. However, due to its light nature, it is much less abundant (0.15% by mass) in the earth's atmosphere. Of course, in the combined form it constitutes 15.4% of the earth's crust and the oceans. In the combined form besides in water, it occurs in plant and animal tissues, carbohydrates, proteins, hydrides including hydrocarbons and many other compounds.

#### Isotopes of Hydrogen

Hydrogen has three isotopes: **protium**,  $^1_1H$ , **deuterium**,  $^2_1H$  or D and **tritium**,  $^3_1H$  or T. These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen, protium, has no neutrons, deuterium (also known as heavy hydrogen) has one and tritium has two neutrons in the nucleus. In the year 1934, an American scientist, Harold C. Urey, got Nobel Prize for separating hydrogen isotope of mass number 2 by physical methods.

The predominant form is protium. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD. The tritium concentration is about one atom per 1018 atoms of protium. Of these isotopes, only tritium is radioactive and emits low energy  $\beta^-$  particles.

### Atomic and Physical Properties of Hydrogen

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	$10^{-15}$
Relative atomic mass ( $\text{g mol}^{-1}$ )	1.008	2.014	3.016
Melting point / K	13.96	18.73	20.62
Boiling point / K	20.39	23.67	25.0
Density / $\text{g L}^{-1}$	0.09	0.18	0.27
Enthalpy of fusion/ $\text{kJ mol}^{-1}$	0.117	0.197	–
Enthalpy of vaporization/ $\text{kJ mol}^{-1}$	0.904	1.226	–
Enthalpy of bond dissociation/ $\text{kJ mol}^{-1}$ at 298.2K	435.88	443.35	–
Internuclear distance/pm	74.14	74.14	–
Ionization enthalpy/ $\text{kJ mol}^{-1}$	1312	–	–
Electron gain enthalpy/ $\text{kJ mol}^{-1}$	–73	–	–
Covalent radius/pm	37	–	–
Ionic radius( $\text{H}^-$ )/pm	208		

Since the isotopes have the same electronic configuration, they have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation. However, in physical properties these isotopes differ considerably due to their large mass differences.

#### ◆ Different forms of Hydrogen :

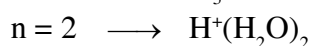
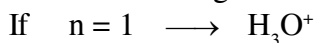
##### (a) Based on oxidation Number.

There are three types of hydrogen

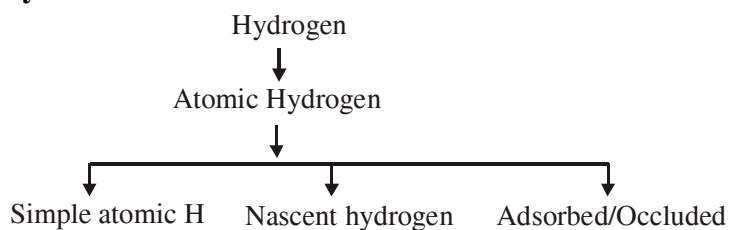
	$\text{H}^+$	$\text{H}^-$	H
	Proton	Hydride	Atomic hydrogen
Number of electron	0	2	1
Oxidation number	+1	–1	0
Formation	$\text{H} \rightarrow \text{H}^+ + \text{e}^-$	$\text{H} + \text{e}^- \rightarrow \text{H}^-$	$\text{H}_2 \xrightarrow{\Delta} 2\text{H}$

**Note :** In the aqueous state proton ( $\text{H}^+$ ) exist as  $\text{H}^+(\text{H}_2\text{O})_n$

Where n is a large number.

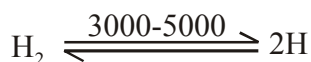


(b) Based on reactivity :



♦ **Atomic hydrogen :**

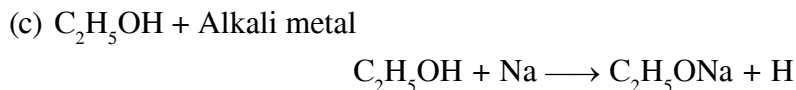
(i) **Simple atomic hydrogen** – It is formed by simple dissociation of hydrogen.



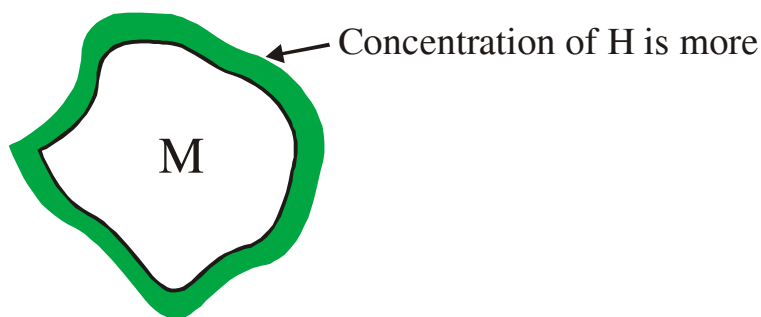
Favourable condition – Favourable condition are high temp & low pressure.

(ii) **Nascent hydrogen** – Hydrogen at the moment of its birth it called nascent hydrogen means which forms at the instant is known as Nascent hydrogen.

It is formed only by some specific chemical reaction.



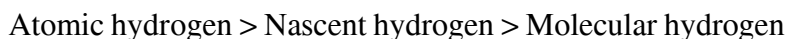
(iii) **Adsorbed/Occluded hydrogens**



Adsorbed H is hydrogen present at the outer surface of metal.

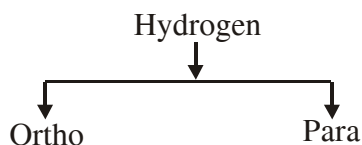
♦ **Occlusion :** The property of metal to adsorb any gas is called occlusion.

**Reactivity order**





## (iii) Based on Nuclear spin (Nuclear isomers)



(a) **Ortho hydrogen** : The molecular form of hydrogen having same spin of nucleus is called ortho hydrogen.

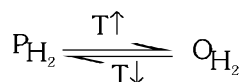
(b) **Para hydrogen** : The molecular form of hydrogen having opposite spin of nucleus is called para hydrogen.

In ortho hydrogen spin of nucleus is same, so they will repel each other & because of this repulsion, internal energy of ortho hydrogen increases. So ortho hydrogen has more internal energy.

◆ **Stability of ortho & Para hydrogen**

Stability of ortho & para hydrogen depends upon temperature condition.

At low temp : para hydrogen is more stable than ortho hydrogen while at high temp ortho hydrogen is more stable than para hydrogen.



	Ortho	Para
At high temperature	75%	25%
At absolute zero temp.	0	100%

◆ **Imp. Note :**

- (i) We can obtain 100% pure para hydrogen at low temp but can't ortho because at high temp parahydrogen will dissociate into atomic hydrogen.
- (ii) Ortho & Para hydrogen differs only in physical properties but have same chemical properties.

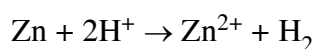
□ **PREPARATION OF DIHYDROGEN, H<sub>2</sub>**

There are a number of methods for preparing dihydrogen from metals and metal hydrides.

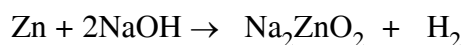
◆ **Laboratory Preparation of**

**Dihydrogen**

- (i) It is usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.



- (ii) It can also be prepared by the reaction of zinc with aqueous alkali.

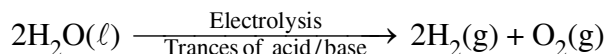


Sodium zincate

### Commercial Production of Dihydrogen

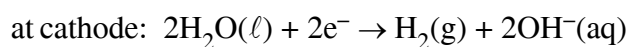
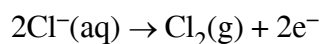
The commonly used processes are outlined below :

- (i) Electrolysis of acidified water using platinum electrodes gives hydrogen.

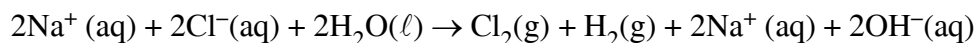


- (ii) High purity (>99.95%) dihydrogen is obtained by electrolysis of warm aqueous barium hydroxide solution between nickel electrodes.

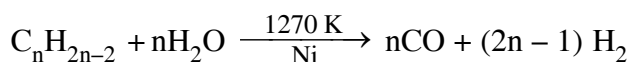
- (iii) It is obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. During electrolysis, the reactions that take place are: at anode:



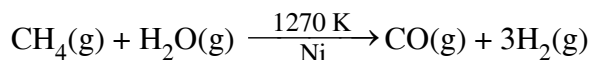
The overall reaction is



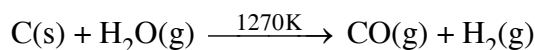
- (iv) Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen.



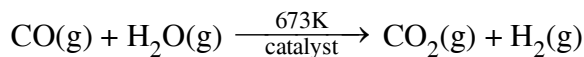
e.g.,



The mixture of CO and H<sub>2</sub> is called *water gas*. As this mixture of CO and H<sub>2</sub> is used for the synthesis of methanol and a number of hydrocarbons, it is also called *synthesis gas* or '**syngas**'. Nowadays 'syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called '*coal gasification*'.



The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst (Fe<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>).



This is called water-gas shift reaction /**Bosch process**. Carbon dioxide is removed by scrubbing with sodium arsenite solution. Presently ~77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

## PROPERTIES OF DIHYDROGEN

### Physical Properties

Dihydrogen is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water. Its other physical properties alongwith those of deuterium are given in Table.

### ◆ Chemical Properties

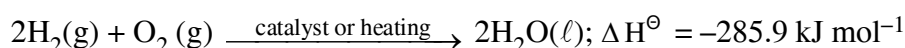
The chemical behaviour of dihydrogen (and for that matter any molecule) is determined, to a large extent, by bond dissociation enthalpy. The H–H bond dissociation enthalpy is the highest for a single bond between two atoms of any element. What inferences would you draw from this fact? It is because of this factor that the dissociation of dihydrogen into its atoms is only ~0.081% around 2000K which increases to 95.5% at 5000K. Also, it is relatively inert at room temperature due to the high H–H bond enthalpy. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations. Since its orbital is incomplete with  $1s^1$  electronic configuration, it does combine with almost all the elements. It accomplishes reactions by (i) loss of the only electron to give  $H^+$ , (ii) gain of an electron to form  $H^-$ , and (iii) sharing electrons to form a single covalent bond. The chemistry of dihydrogen can be illustrated by the following reactions:

- ◆ **Reaction with halogens** : It reacts with halogens,  $X_2$  to give hydrogen halides HX,

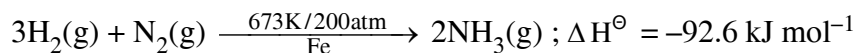


While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

- ◆ **Reaction with dioxygen**: It reacts with dioxygen to form water. The reaction is highly exothermic.

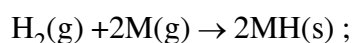


- ◆ **Reaction with dinitrogen**: With dinitrogen it forms ammonia.



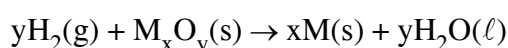
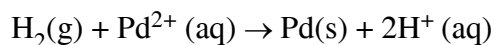
This is the method for the manufacture of ammonia by the Haber process.

- ◆ **Reactions with metals** : With many metals it combines at a high temperature to yield the corresponding hydrides.



where M is an alkali metal

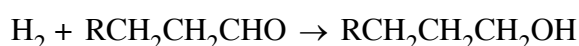
- ◆ **Reactions with metal ions and metal oxides**: It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.



- ◆ **Reactions with organic compounds**: It reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance. For example :

(i) Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee)

(ii) Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.



**Problem-1**

Comment on the reactions of dihydrogen with (i) chlorine, (ii) sodium, and (iii) copper(II) oxide.

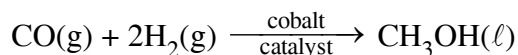
**Solution**

- (i) Dihydrogen reduces chlorine into chloride ( $\text{Cl}^-$ ) ion and itself gets oxidised to  $\text{H}^+$  ion by chlorine to form hydrogen chloride. An electron pair is shared between H and Cl leading to the formation of a covalent molecule.
- (ii) Dihydrogen is reduced by sodium to form NaH. An electron is transferred from Na to H leading to the formation of an ionic compound,  $\text{Na}^+\text{H}^-$ .
- (iii) Dihydrogen reduces copper(II) oxide to copper in zero oxidation state and itself gets oxidised to  $\text{H}_2\text{O}$ , which is a covalent molecule.

**Uses of Dihydrogen**

The largest single use of dihydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.

- ◆ Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc. . It is used in the manufacture of bulk organic chemicals, particularly methanol.



- ◆ It is widely used for the manufacture of metal hydrides.
- ◆ It is used for the preparation of hydrogen chloride, a highly useful chemical.
- ◆ In metallurgical processes, it is used to reduce heavy metal oxides to metals.
- ◆ Atomic hydrogen and oxy-hydrogen torches find use for cutting and welding purposes. Atomic hydrogen atoms (produced by dissociation of dihydrogen with the help of an electric arc) are allowed to recombine on the surface to be welded to generate the temperature of 4000 K.
- ◆ It is used as a rocket fuel in space research.
- ◆ Dihydrogen is used in fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels and electric power. It does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

**HYDRIDES**

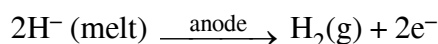
Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called **hydrides**. If 'E' is the symbol of an element then hydride can be expressed as  $\text{EH}_x$  (e.g.,  $\text{MgH}_2$ ) or  $\text{E}_m\text{H}_n$  (e.g.,  $\text{B}_2\text{H}_6$ ).

The hydrides are classified into three categories :

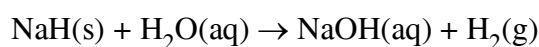
- (i) Ionic or saline or saltlike hydrides
- (ii) Covalent or molecular hydrides
- (iii) Metallic or non-stoichiometric hydrides

### ♦ Ionic or Saline Hydrides

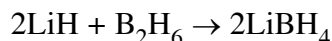
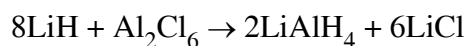
These are stoichiometric compounds of dihydrogen formed with most of the *s*-block elements which are highly electropositive in character. However, significant covalent character is found in the lighter metal hydrides such as LiH, BeH<sub>2</sub> and MgH<sub>2</sub>. In fact BeH<sub>2</sub> and MgH<sub>2</sub> are polymeric in structure. The ionic hydrides are crystalline, non-volatile and nonconducting in solid state. However, their melts conduct electricity and on electrolysis liberate dihydrogen gas at anode, which confirms the existence of H<sup>-</sup> ion.



Saline hydrides react violently with water producing dihydrogen gas.



Lithium hydride is rather unreactive at moderate temperatures with O<sub>2</sub> or Cl<sub>2</sub>. It is, therefore, used in the synthesis of other useful hydrides, e.g.,



### ♦ Covalent or Molecular Hydride

Dihydrogen forms molecular compounds with most of the *p*-block elements. Most familiar examples are CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and HF. For convenience hydrogen compounds of nonmetals have also been considered as hydrides. Being covalent, they are volatile compounds. Molecular hydrides are further classified according to the relative numbers of electrons and bonds in their Lewis structure into :

**(i) electron-deficient, (ii) electron-precise, and (iii) electron-rich hydrides.**

An electron-deficient hydride, as the name suggests, has too few electrons for writing its conventional Lewis structure. Diborane (B<sub>2</sub>H<sub>6</sub>) is an example. In fact all elements of group 13 will form electron-deficient compounds. They act as Lewis acids i.e., electron acceptors.

Electron-precise compounds have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds (e.g., CH<sub>4</sub>) which are tetrahedral in geometry.

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. (NH<sub>3</sub> has 1- lone pair, H<sub>2</sub>O – 2 and HF –3 lone pairs). They will behave as Lewis bases i.e., electron donors. The presence of lone pairs on highly electronegative atoms like N, O and F in hydrides results in hydrogen bond formation between the molecules. This leads to the association of molecules.

**Problem -2**

Would you expect the hydrides of N, O and F to have lower boiling points than the hydrides of their subsequent group members? Give reasons.

**Solution**

On the basis of molecular masses of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$ , their boiling points are expected to be lower than those of the subsequent group member hydrides. However, due to higher electronegativity of N, O and F, the magnitude of hydrogen bonding in their hydrides will be quite appreciable. Hence, the boiling points  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$  will be higher than the hydrides of their subsequent group members.

**♦ Metallic or Non-stoichiometric (or Interstitial) Hydrides**

These are formed by many *d*-block and *f*-block elements. However, the metals of group 7, 8 and 9 do not form hydride. Even from group 6, only chromium forms  $\text{CrH}$ . These hydrides conduct heat and electricity though not as efficiently as their parent metals do. Unlike saline hydrides, they are almost always nonstoichiometric, being deficient in hydrogen. For example,  $\text{LaH}_{2.87}$ ,  $\text{YbH}_{2.55}$ ,  $\text{TiH}_{1.5-1.8}$ ,  $\text{ZrH}_{1.3-1.75}$ ,  $\text{VH}_{0.56}$ ,  $\text{NiH}_{0.6-0.7}$ ,  $\text{PdH}_{0.6-0.8}$  etc. In such hydrides, the law of constant composition does not hold good.

Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. Consequently, they were termed as interstitial hydrides. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metal. The property of absorption of hydrogen on transition metals is widely used in catalytic reduction / hydrogenation reactions for the preparation of large number of compounds. Some of the metals (e.g., Pd, Pt) can accommodate a very large volume of hydrogen and, therefore, can be used as its storage media. This property has high potential for **hydrogen storage** and as a **source of energy**.

**□ WATER**

A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water. It is a crucial compound for the survival of all life forms. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform. The estimated world water supply is given in Table.

### Estimated World Water Supply

Source	% of total
Oceans	97.33
Saline lakes and inland seas	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes	0.009
Soil moisture	0.005
Atomspheric water vapour	0.001
Rivers	0.001

### Physical Properties of Water

It is a colourless and tasteless liquid. Its physical properties are given in Table along with the physical properties of heavy water. The unusual properties of water in the condensed phase (liquid and solid states) are due to the presence of extensive hydrogen bonding between water molecules. This leads to high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparison to  $H_2S$  and  $H_2Se$ . In comparison to other liquids, water has a higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc. These properties allow water to play a key role in the biosphere.

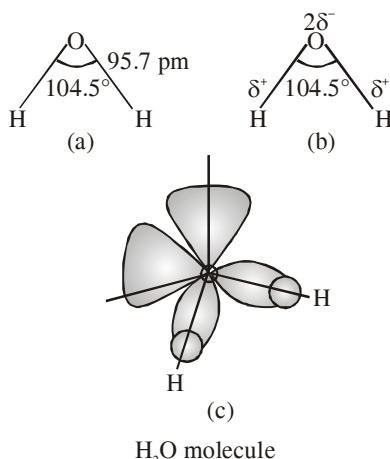
### Physical Properties of $H_2O$ and $D_2O$

Property	$H_2O$	$D_2O$
Molecular mass ( $g\ mol^{-1}$ )	18.0151	20.0276
Melting point/K	273.0	276.8
Boiling point/K	373.0	374.4
Enthalpy of formation/ $kJ\ mol^{-1}$	-285.9	-294.6
Enthalpy of vaporisation (373K)/ $kJ\ mol^{-1}$	40.66	41.61
Enthalpy of fusion/ $kJ\ mol^{-1}$	6.01	-
Temp of max. density/K	276.98	284.2
Density(298K)/ $g\ cm^{-3}$	1.0000	1.1059
Viscosity/centipoise	0.8903	1.107
Dielectric constant/ $C^2/N.m^2$	78.39	78.06
Electrical conductivity (293K)/ $ohm^{-1}\ cm^{-1}$	$5.7 \times 10^{-8}$	-

The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of ions and molecules required for plant and animal metabolism. Due to hydrogen bonding with polar molecules, even covalent compounds like alcohol and carbohydrates dissolve in water.

### ◆ Structure of Water

In the gas phase water is a bent molecule with a bond angle of  $104.5^\circ$  and O–H bond length of 95.7 pm as shown in Fig (a).



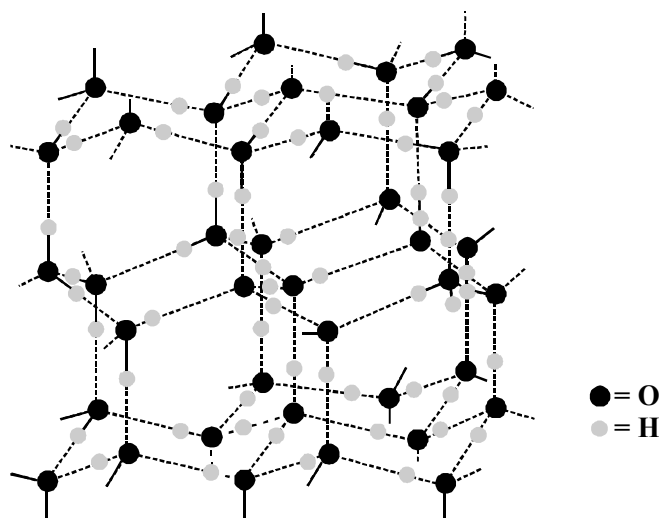
(a) The bent structure of water; (b) the water molecule as a dipole and (c) the orbital overlap picture in water molecule.

It is a highly polar molecule, (Fig (b)). Its orbital overlap picture is shown in Fig. (c). In the liquid phase water molecules are associated together by hydrogen bonds.

The crystalline form of water is ice. At atmospheric pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to cubic form. Density of ice is less than that of water. Therefore, an ice cube floats on water. In winter season ice formed on the surface of a lake provides thermal insulation which ensures the survival of the aquatic life. This fact is of great ecological significance.

### ◆ Structure of Ice

Ice has a highly ordered three dimensional hydrogen bonded structure as shown in Fig. Examination of ice crystals with X-rays shows that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm. Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially.



The Structure of Ice

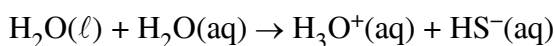
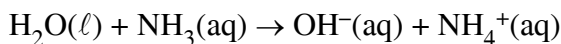


◆ **Chemical Properties of Water**

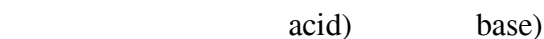
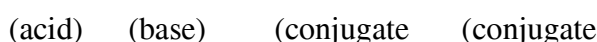
Water reacts with a large number of substances. Some of the important reactions are given below.

(1) **Amphoteric Nature :**

It has the ability to act as an acid as well as a base i.e., it behaves as an amphoteric substance. In the Brönsted sense it acts as an acid with  $\text{NH}_3$  and a base with  $\text{H}_2\text{S}$ .

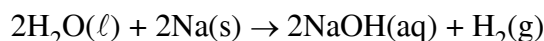


The auto-protolysis (self-ionization) of water takes place as follows :



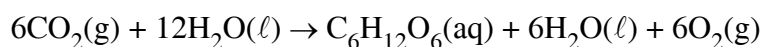
(2) **Redox Reactions Involving Water:**

Water can be easily reduced to dihydrogen by highly electropositive metals.

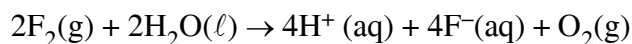


Thus, it is a great source of dihydrogen.

Water is oxidised to  $\text{O}_2$  during photosynthesis.

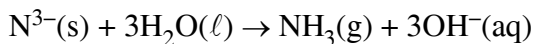
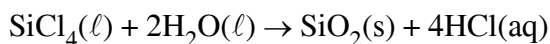
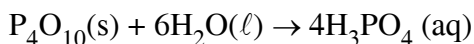


With fluorine also it is oxidised to  $\text{O}_2$ .



(3) **Hydrolysis Reaction:**

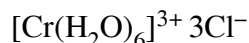
Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds. However, certain covalent and some ionic compounds are hydrolysed in water.



(4) **Hydrates Formation:**

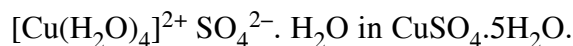
From aqueous solutions many salts can be crystallised as hydrated salts. Such an association of water is of different types viz.,

(i) coordinated water e.g.,



(ii) interstitial water e.g.,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

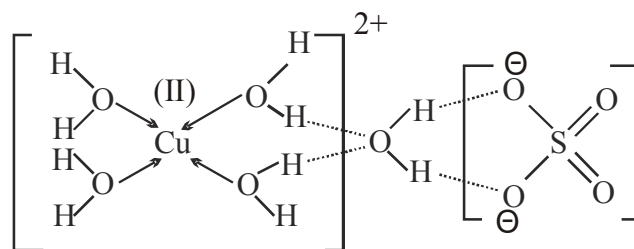
(iii) hydrogen-bonded water e.g.,



## Problem -3

The number of water molecule(s) directly bonded to the metal centre in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is - [JEE 2009]

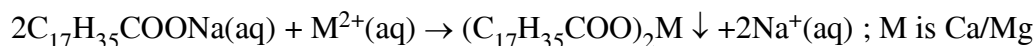
Solution. 3 ,



◆ **Hard and Soft Water**

Rain water is almost pure (may contain some dissolved gases from the atmosphere). Being a good solvent, when it flows on the surface of the earth, it dissolves many salts. Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes water '**hard**'. **Hard water** does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ( $\text{C}_{17}\text{H}_{35}\text{COONa}$ ) reacts with hard water to precipitate out Ca/Mg stearate.

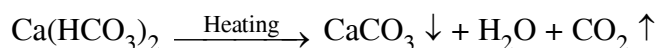
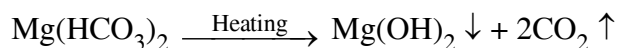


It is, therefore, unsuitable for laundry. It is harmful for boilers as well, because of deposition of salts in the form of scale. This reduces the efficiency of the boiler. The hardness of water is of two types: (i) temporary hardness, and (ii) permanent hardness.

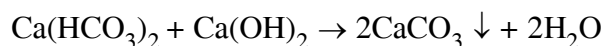
◆ **Temporary Hardness :**

Temporary hardness is due to the presence of magnesium and calcium hydrogencarbonates. It can be removed by :

(i) **Boiling :** During boiling, the soluble  $\text{Mg}(\text{HCO}_3)_2$  is converted into insoluble  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{HCO}_3)_2$  is changed to insoluble  $\text{CaCO}_3$ . It is because of high solubility product of  $\text{Mg}(\text{OH})_2$  as compared to that of  $\text{MgCO}_3$ , that  $\text{Mg}(\text{OH})_2$  is precipitated. These precipitates can be removed by filtration. Filtrate thus obtained will be soft water.



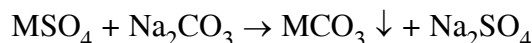
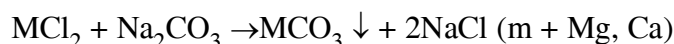
(ii) **Clark's method :** In this method calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.



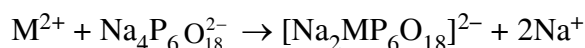
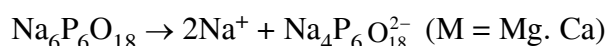
◆ **Permanent Hardness**

It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. Permanent hardness is not removed by boiling. It can be removed by the following methods:

(i) **Treatment with washing soda (sodium carbonate)** : Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

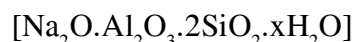


(ii) **Calgon's method** : Sodium hexametaphosphate ( $Na_6P_6O_{18}$ ), commercially called 'calgon', when added to hard water, the following reactions take place.

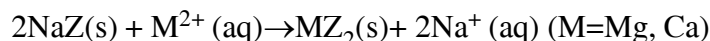


The complex anion keeps the  $Mg^{2+}$  and  $Ca^{2+}$  ions in solution.

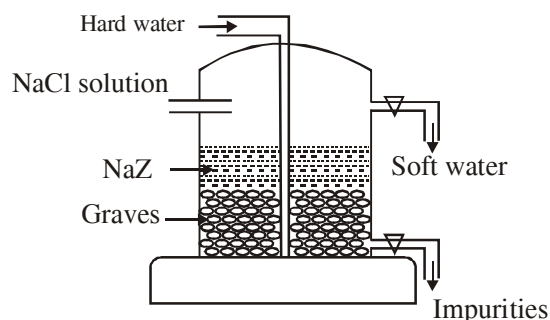
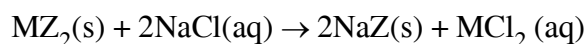
(iii) **Ion-exchange method (By Zeolite)** : This method is also called zeolite / permutit process.



Hydrated sodium aluminium silicate is zeolite/ permutit. For the sake of simplicity, sodium aluminium silicate ( $NaAlSiO_4$ ) can be written as  $NaZ$ . When this is added in hard water, exchange reactions take place.

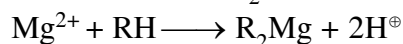
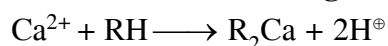


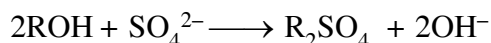
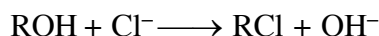
Permutit/zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.



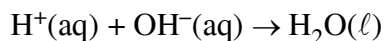
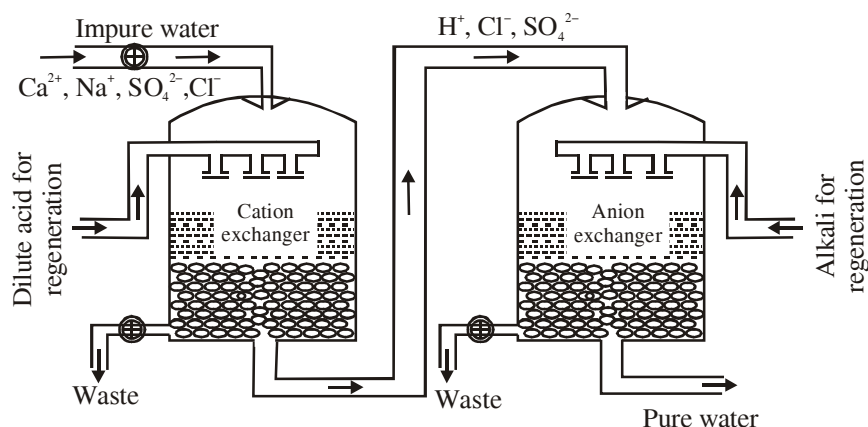
(iv) **Ion exchange method (By synthetic resins)** : Ion exchange resins are the most popular water softener these days. These resins are synthetic substances. The **cation exchanger** consists of granular insoluble organic acid resins having giant molecules with  $-SO_3H$  or  $-COOH$  groups (represented as  $RH$ ) while the **anion exchanger** contains giant organic molecules with basic groups derived from amine (represented as  $ROH$ ). Ion exchange resins remove all soluble minerals from water.

**Reaction at Cation exchanger**



**Reaction at Anion exchanger**

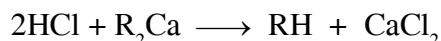
The water coming from cation exchanger is acidic due to  $\text{H}^+$ . This water is then passed through another bed containing anion exchanger. This exchanger removes anion like  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  by exchanging with  $\text{OH}^-$  ions.



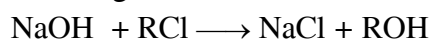
This water is free from impurities & can be used for drinking purpose. After some times when both resin gets exhausted process is stopped.

**Regeneration of resin :**

(i) Cation exchange resin : We use dil acid.



(ii) Anion exchange resin : We use dil NaOH solution



❑ **HYDROGEN PEROXIDE ( $\text{H}_2\text{O}_2$ )**

This article has been taken in p-block chapter.

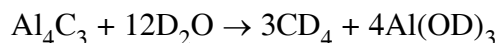
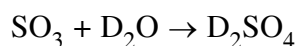
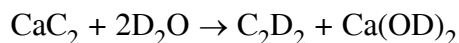
❑ **HEAVY WATER,  $\text{D}_2\text{O}$  :**

It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries.

◆ **Physical properties :**

(a) Heavy water is a colourless, odourless and tasteless mobile liquid, (b) Nearly all the physical constants are higher than the corresponding values of ordinary water.

It is used for the preparation of other deuterium compounds, for example:



- ◆ **Uses :** It is extensively used as a moderator & coolant in nuclear reactors and in exchange reactions for the study of reaction mechanisms. **As a neutron moderator :** Fission in uranium-235 is brought by slow speed neutrons. The substances which are used for slowing down the speed of neutrons are called moderators. Heavy water is used for this purpose in nuclear reactors.

### □ DIHYDROGEN AS A FUEL

Dihydrogen releases large quantities of heat on combustion. The data on energy released by combustion of fuels like dihydrogen, methane, LPG etc. are compared in terms of the same amounts in mole, mass and volume, are shown in Table.

From this table it is clear that on a mass for mass basis dihydrogen can release more energy than petrol (about three times). Moreover, pollutants in combustion of dihydrogen will be less than petrol. The only pollutants will be the oxides of dinitrogen (due to the presence of dinitrogen as impurity with dihydrogen).

This, of course, can be minimised by injecting a small amount of water into the cylinder to lower the temperature so that the reaction between dinitrogen and dioxygen may not take place. However, the mass of the containers in which dihydrogen will be kept must be taken into consideration. A cylinder of compressed dihydrogen weighs about 30 times as much as a tank of petrol containing the same amount of energy. Also, dihydrogen gas is converted into liquid state by cooling to 20K. This would require expensive insulated tanks. Tanks of metal alloy like  $\text{NaNi}_5$ ,  $\text{Ti-TiH}_2$ ,  $\text{Mg-MgH}_2$  etc. are in use for storage of dihydrogen in small quantities. These limitations have prompted researchers to search for alternative techniques to use dihydrogen in an efficient way.

In this view Hydrogen Economy is an alternative. The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen. Advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power. It is for the first time in the history of India that a pilot project using dihydrogen as fuel was launched in October 2005 for running automobiles. Initially 5% dihydrogen has been mixed in CNG for use in four-wheeler vehicles. The percentage of dihydrogen would be gradually increased to reach the optimum level.

Nowadays, it is also used in fuel cells for generation of electric power. It is expected that economically viable and safe sources of dihydrogen will be identified in the years to come, for its usage as a common source of energy.

#### The Energy Released by Combustion of Various Fuels in Moles, Mass and Volume

Energy released on Combustion in kJ state)	Dihydrogen in gaseous state)	Dihydrogen (in liquid)	LPG	CH <sub>4</sub> gas	Octance (in liquid state)
per mole	286	285	2220	880	5511
per gram	143	142	50	53	47
per litre	12	9968	25590	35	34005

## EXERCISE # O-1

## DIHYDROGEN

1. The sum number of neutrons and protons in one of the isotopes of hydrogen is :-  
(A) 3 (B) 4 (C) 5 (D) 6  
HY0001
2. The catalyst used in Bosch process of manufacture of  $H_2$  is :-  
(A) Finely divided Ni (B)  $V_2O_5$  (C) Pb (D)  $Fe_2O_3 + Cr_2O_3$   
HY0002
3. The most abundant isotope of hydrogen is :-  
(A) Tritium (B) Deuterium (C) Protium (D) Para hydrogen  
HY0003
4. The n/p ratio for  ${}_1H^1$  is :-  
(A) 1 (B) 2 (C) 3 (D) Zero  
HY0004
5. Ordinary hydrogen at high temperature is a mixture of :-  
(A) 75% o-Hydrogen + 25% p-Hydrogen (B) 25% o-Hydrogen + 75% p-Hydrogen  
(C) 50% o-Hydrogen + 50% p-Hydrogen (D) 1% o-Hydrogen + 99% p-Hydrogen  
HY0005
6. Hydrogen is behave as :-  
(A) Electropositive  
(B) Electronegative  
(C) Both electropositive as well as electro-negative  
(D) Neither electropositive nor electronegative  
HY0006
7. At high temperature Para hydrogen is :-  
(A) Less stable than ortho hydrogen  
(B) More stable than ortho hydrogen  
(C) As stable as ortho hydrogen  
(D) None of these  
HY0007
8. When the same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volumes of hydrogen evolved is :-  
(A) 1 : 1 (B) 1 : 2 (C) 2 : 1 (D) 9 : 4  
HY0008

9. The lightest gas is :-  
(A) Nitrogen (B) Helium (C) Oxygen (D) Hydrogen  
HY0009
10. The ratio of electron, proton and neutron in tritium is :-  
(A) 1 : 1 : 1 (B) 1 : 1 : 2 (C) 2 : 1 : 1 (D) 1 : 2 : 1  
HY0010
11. The nuclei of tritium ( $H^3$ ) atom would contain neutrons :-  
(A) 1 (B) 2 (C) 3 (D) 4  
HY0011
12. The adsorption of hydrogen by metals is called :-  
(A) Dehydrogenation (B) Hydrogenation (C) Occlusion (D) Adsorption  
HY0012
13. At absolute zero :-  
(A) Only para hydrogen exists (B) Only ortho hydrogen exists  
(C) Both para and ortho hydrogen exist (D) None  
HY0013

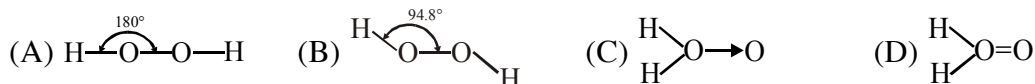
**WATER ( $H_2O$ )**

14. Only temporary hardness in water is removed by :-  
(A) Boiling (B) Filtration (C) Calgon's process (D) None of these  
HY0014
15. Both temporary and permanent hardness is removed on boiling water with :-  
(A)  $Ca(OH)_2$  (B)  $Na_2CO_3$  (C)  $CaCO_3$  (D)  $CaO$   
HY0015
16. Temporary hardness is caused due to the presence of :-  
(A)  $CaSO_4$  (B)  $CaCl_2$  (C)  $CaCO_3$  (D)  $Ca(HCO_3)_2$   
HY0016
17. High boiling point of water is due to :-  
(A) Its high specific heat (B) Hydrogen bonding  
(C) High dielectric constant (D) Low dissociation constant  
HY0017
18. Calgon is an industrial name given to :-  
(A) Normal sodium phosphate (B) Sodium meta-aluminate  
(C) Sodium hexametaphosphate (D) Hydrated sodium aluminium silicate  
HY0018

19. Permutit is :-  
 (A) Hydrated sodium aluminium silicate (B) Sodium hexametaphosphate  
 (C) Sodium silicate (D) Sodium meta-aluminate  
**HY0019**
20. Heavy water has found application in atomic reactor as :-  
 (A) Coolant (B) Moderator  
 (C) Both coolant and moderator (D) Neither coolant nor moderator  
**HY0020**
21. Calgon (a water softener) is :-  
 (A)  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$  (B)  $\text{Na}_4[\text{Na}_2(\text{PO}_3)]_6$  (C)  $\text{Na}_2[\text{Na}_4(\text{PO}_4)]_6$  (D)  $\text{Na}_4[\text{Na}_2(\text{PO}_4)]_6$   
**HY0021**
22. The hardness of water is due to.....metal ions  
 (A)  $\text{Ca}^{2+}$  and  $\text{Na}^+$  (B)  $\text{Mg}^{2+}$  and  $\text{K}^+$  (C)  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (D)  $\text{Zn}^{2+}$  and  $\text{Ba}^{2+}$   
**HY0022**
23. The formula of heavy water is :-  
 (A)  $\text{H}_2\text{O}^{18}$  (B)  $\text{D}_2\text{O}$  (C)  $\text{T}_2\text{O}$  (D)  $\text{H}_2\text{O}^{17}$   
**HY0023**
24. Pure de-mineralised water can be obtained by -  
 (A)  $\text{Na}^+$  cation exchanger and  $\text{Cl}^-$  anion exchanger  
 (B)  $\text{H}^+$  cation exchanger only  
 (C)  $\text{H}^+$  cation exchanger and  $\text{OH}^-$  anion exchanger  
 (D)  $\text{Na}^+$  cation exchanger only  
**HY0024**
- HYDROGEN PEROXIDE ( $\text{H}_2\text{O}_2$ )**
25. The bleaching properties of  $\text{H}_2\text{O}_2$  are due to its :-  
 (A) Reducing properties (B) Oxidising properties  
 (C) Unstable nature (D) Acidic nature  
**HY0025**
26. Hydrogen peroxide has a :-  
 (A) Linear structure (B) Pyramidal structure  
 (C) Closed book type structure (D) Half open book type structure  
**HY0026**
27. Hydrogen peroxide is a :-  
 (A) Liquid (B) Gas (C) Solid (D) Semi-solid  
**HY0027**

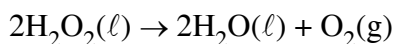


28. Which of the following is a true structure of  $\text{H}_2\text{O}_2$



HY0028

29. Decomposition of  $\text{H}_2\text{O}_2$  is retarded by :-



- (A) Acetanilide      (B)  $\text{MnO}_2$   
(C) Zinc      (D) Finely divided metals

HY0029

30.  $\text{H}_2\text{O}_2$  is :-

- (A) An oxidising agent      (B) Both oxidising and reducing agent  
(C) Reducing agent      (D) None of the above

HY0030

31.  $\text{H}_2\text{O}_2$  is always stored in black bottles because :-

- (A) It is highly unstable  
(B) Its enthalpy of decomposition is high  
(C) It undergoes auto-oxidation on prolonged standing  
(D) None of these

HY0031

32. Acidified solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  on treatment with  $\text{H}_2\text{O}_2$  yields :-

- (A)  $\text{CrO}_3 + \text{H}_2\text{O} + \text{O}_2$       (B)  $\text{Cr}_2\text{O}_2 + \text{H}_2\text{O} + \text{O}_2$   
(C)  $\text{CrO}_5 + \text{H}_2\text{O} + \text{K}_2\text{SO}_4$       (D)  $\text{H}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} + \text{O}_2$

HY0032

33.  $\text{H}_2\text{O}_2$  restores the colour of old lead paintings, blackened by the action of  $\text{H}_2\text{S}$  gas by :-

- (A) Converting  $\text{PbO}_2$  to Pb      (B) By oxidising PbS to  $\text{PbSO}_4$   
(C) Converting  $\text{PbCO}_3$  to Pb      (D) Oxidising  $\text{PbSO}_3$  to  $\text{PbSO}_4$

HY0033

34. The reaction,  $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \longrightarrow \text{S} + 2\text{H}_2\text{O}$  manifests:

- (A) Acidic nature of  $\text{H}_2\text{O}_2$       (B) Alkaline nature of  $\text{H}_2\text{O}_2$   
(C) Oxidising nature of  $\text{H}_2\text{O}_2$       (D) Reducing nature of  $\text{H}_2\text{O}_2$

HY0034

35. Hydrogen peroxide is now generally prepared on industrial scale by the :-

- (A) Action of  $\text{H}_2\text{SO}_4$  on barium peroxide      (B) Action of  $\text{H}_2\text{SO}_4$  on sodium peroxide  
(C) auto-oxidation of 2-alkylanthraquinols      (D) Burning hydrogen in excess of oxygen

HY0035

## EXERCISE # O-2

1. Which of the following is / are same for Ortho and Para hydrogen :-  
(A) In the number of protons  
(B) In the molecular mass  
(C) In the nature of spins of nucleus  
(D) In the nature of spins of electrons  
**HY0036**
2. In Bosch's process which gas is **NOT** utilised for the production of hydrogen :-  
(A) Producer gas      (B) Water gas      (C) Coal gas      (D) Natural gas  
**HY0037**
3. The gas(es) used in the hydrogenation of oils in presence of nickel as a catalyst is / are :-  
(A) Methane      (B) Ethane      (C) Ozone      (D) Hydrogen  
**HY0038**
4. Water softening by Clarke's process does **NOT** uses :-  
(A) Calcium bicarbonate      (B) Sodium bicarbonate  
(C) Potash alum      (D) Calcium hydroxide  
**HY0039**
5. Which of the following produces hydrolith with dihydrogen :-  
(A) Mg      (B) Al      (C) Cu      (D) Ca  
**HY0040**
6. Which process is/are used to remove permanent hardness :-  
(A) Boiling      (B) Clark's method  
(C) On reaction with NaOH      (D) Permutit process  
**HY0041**
7. Ionic hydrides is/are usually :-  
(A) Good electrically conductors when solid      (B) Easily reduced  
(C) Good reducing agents      (D) Liquid at room temperature  
**HY0042**
8. Which of the following will produce hydrogen gas :-  
(A) Reaction between Fe and dil. HCl  
(B) Reaction between Zn and conc.  $H_2SO_4$   
(C) Reaction between Zn and NaOH  
(D) Electrolysis of NaCl (aq.) in Nelson's cell  
**HY0043**

9. Ortho-hydrogen and para-hydrogen resembles in which of the following property :-

- (A) Thermal conductivity (B) Magnetic properties  
(C) Chemical properties (D) Heat capacity

HY0044

10. Which of the following statements concerning protium, deuterium and tritium is / are true :-

- (A) They are isotopes of each other  
(B) They have similar electronic configurations  
(C) They exist in the nature in the ratio of 1 : 2 : 3  
(D) Their mass numbers are in the ratio of 1 : 2 : 3

HY0045

11. Ionic hydrides are formed by :-

- (A) Transition metals  
(B) Elements of very high electropositivity  
(C) Elements of very low electropositivity  
(D) Metalloids

HY0046

12. Which of the following statements is/are correct :

- (A) Atomic hydrogen is obtained by passing hydrogen gas through an electric arc  
(B) 30% (w/v) or 100V  $H_2O_2$  solution is not called perhydrol.  
(C) Finely divided palladium absorbs large volume of hydrogen gas.  
(D) Ortho and para hydrogen have same physical properties.

HY0047

13. Which hydride is/are an ionic hydride :-

- (A)  $NH_3$  (B)  $H_2S$  (C)  $TiH_{1.73}$  (D) NaH

HY0048

14. Which of the following hydride is/are 'electron-precise' type ?

- (A) HF (B)  $H_2O$  (C)  $SiH_4$  (D)  $PH_3$

HY0049

15. Hydrogen peroxide can act as a :-

- (A) A reducing agent (B) An oxidising agent  
(C) A dehydrating agent (D) A bleaching agent

HY0050

**EXERCISE # S-1****Integer Type**

1. Find out the sum of protons, electrons and neutrons in the heaviest isotope of hydrogen. **HY0051**
2. Find out the number of following orders which are correct against the mentioned properties :
- (i)  $H_2 < D_2 < T_2$  (Number of protons)
  - (ii)  $H_2 < D_2$  (Bond energy)
  - (iii)  $H_2 < D_2 < T_2$  (Boiling point)
  - (iv)  $H_2 < D_2 < T_2$  (No. of neutrons)
- HY0052**
3. Find out the number of following orders which are **NOT** correct against the mentioned properties :
- (i)  $CaH_2 < BeH_2$  (Electrical conductance in molten condition)
  - (ii)  $LiH < NaH < CsH$  (Ionic character)
  - (iii)  $H_2 < D_2 < F_2$  (Bond dissociation enthalpy)
  - (iv)  $NaH < MgH_2 < H_2O$  (Reducing property)
- HY0053**
4. What is the oxidation state of oxygen of  $H_2O_2$  in the final product when it reacts with  $ClO_3^-$ . **HY0054**
5. Find out the value of 'x' in ion  $[H_xO_4]^+$  : **HY0055**

## EXERCISE # S-2

## Matrix Match Type

1. Match List I with List II and select the correct answer using the codes given below the lists :-

## List – I

- P. Heavy water  
Q. Temporary hard  
R. Soft water  
S. Permanent hard

## List II

1. Bicarbonates of Mg and Ca in water  
2. No foreign ions in water  
3. D<sub>2</sub>O  
4. Sulphates and chlorides of Mg and Ca in water

## Code :

P	Q	R	S
(A) 3	1	2	4
(B) 3	4	2	3
(C) 3	2	1	4
(D) 2	3	1	4

HY0056

2. Match List I with List II and select the correct answer using the codes given below the lists :-

## List – I

- P. Calgon  
Q. Non-stoichiometric compound  
R. Covalent hydride  
S. Salt-like hydride

## List II

1. Metallic hydride  
2. Polymetaphosphate of sodium  
3. Hydrolith  
4. Hydrogen compounds of non-metals

## Code :

P	Q	R	S
(A) 2	1	3	4
(B) 3	4	2	3
(C) 2	1	4	3
(D) 2	3	1	4

HY0057

## Comprehension Type :

## Passage for Q.3 to Q.5

Hydrogen accounts for approximately 75% of the mass of the universe. Hydrogen serves as the nuclear fuel of our Sun and other stars, and these are mainly composed of hydrogen.

Hydrogen has three isotopes : hydrogen or protium ( ${}^1_1\text{H}$ ), deuterium or heavy hydrogen (D or  ${}^2_1\text{H}$ ), tritium (T or  ${}^3_1\text{H}$ ).

3. Which of the following is radioactive in nature ?
- (A) hydrogen only (B) deuterium only  
(C) tritium only (D) deuterium and tritium

HY0058

4. Hydrogen,  $\text{H}_2$ , is very less abundant in the atmosphere due to -
- (A) inflammable nature of  $\text{H}_2$   
(B) weak earth's gravity which is not able to hold light  $\text{H}_2$  molecules  
(C) diatomic nature of hydrogen  
(D) very rapid reaction between hydrogen and atmospheric oxygen

HY0058

5. Liquid  $\text{H}_2$  has been used as rocket fuel as
- (A) its reaction with oxygen is highly exothermic  
(B) it occupies small space  
(C) it has high thrust  
(D) all of the above

HY0058

## MATCHING LIST TYPE 1 × 3 Q. (THREE LIST TYPE Q.)

Column - I Name	Column - II] Formula	Column - III Specification
(1) Calogen	(P) $\text{Na}_6\text{P}_6\text{O}_{18}$	(i) Used to Remove temporary Hardness
(2) Permutit	(Q) $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$	(ii) Used to remove permanent hardness
(3) Perhydrol	(R) '100 V' $\text{H}_2\text{O}_2$	(iii) Used in Rocket propellant
(4) Washing Soda	(S) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	(iv) Also named as zeolite

6. Which combination is **NOT** related to removal of  $\text{Ca}^{+2}/\text{Mg}^{+2}$  form the sample of water
- (A) (1)-(P)-(i)(ii) (B) (2)-(Q)-(i)(ii)(iv) (C) (3)-(R)-(i)(ii) (D) (4)-(S)-(i)(ii)

HY0059

7. Which of the following is **INCORRECT** between column I & II

- (A) 1-P                      (B) 2-Q                      (C) 3-R                      (D) 2-S

**HY0059**

8. Which of the following is **INCORRECT** matching between column III & column II

- (A) (iii) – R                      (B) (iv) – Q                      (C) (iv) – P                      (D) none of these

**HY0059**

## EXERCISE # JEE-MAIN

1. Which one of the following processes will produce hard water :- [AIEEE 2003]  
 (1) Saturation of water with  $\text{CaSO}_4$  (2) Addition of  $\text{Na}_2\text{SO}_4$  to water  
 (3) Saturation of water with  $\text{CaCO}_3$  (4) Saturation of water with  $\text{MgCO}_3$
- HY0060
2. Very pure hydrogen (99.9%) can be made by which of the following processes? [AIEEE 2012]  
 (1) Reaction of salt like hydrides with water  
 (2) Reaction of methane with steam  
 (3) Mixing natural hydrocarbons of high molecular weight  
 (4) Electrolysis of water
- HY0061
3. In which of the following reaction  $\text{H}_2\text{O}_2$  acts as a reducing agent ? [JEE(Main) 2014]  
 (a)  $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$  (b)  $\text{H}_2\text{O}_2 - 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}^+$   
 (c)  $\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$  (d)  $\text{H}_2\text{O}_2 + 2\text{OH}^- - 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$   
 (1) (a), (c) (2) (b), (d) (3) (a), (b) (4) (c), (d)
- HY0062
4. Which of the following statements about  $\text{Na}_2\text{O}_2$  is **not** correct ? [JEE(Main) 2014]  
 (1)  $\text{Na}_2\text{O}_2$  oxidises  $\text{Cr}^{3+}$  to  $\text{CrO}_4^{2-}$  in acid medium  
 (2) It is diamagnetic in nature  
 (3) It is the super oxide of sodium  
 (4) It is a derivative of  $\text{H}_2\text{O}_2$
- HY0063
5. Hydrogen peroxide acts both as an oxidising and as a reducing agent depending upon the nature of the reacting species. In which of the following cases  $\text{H}_2\text{O}_2$  acts as a reducing agent in acid medium ? :- [JEE(Main)Online-2014]  
 (1)  $\text{MnO}_4^-$  (2)  $\text{SO}_3^{2-}$  (3) KI (4)  $\text{Cr}_2\text{O}_7^{2-}$
- HY0064
6. Permanent hardness in water cannot be cured by: [JEE(Main)Online-2015]  
 (1) Treatment with washing soda (2) Calgon's method  
 (3) Boiling (4) Ion exchange method
- HY0065
7. From the following statements regarding  $\text{H}_2\text{O}_2$ , choose the incorrect statement : [JEE(Main)Online-2015]  
 (1) It has to be stored in plastic or wax lined glass bottles in dark  
 (2) It has to be kept away from dust  
 (3) It can act only as an oxidizing agent  
 (4) It decomposes on exposure to light
- HY0066



8. In which of the following reaction, hydrogen peroxide acts as an oxidizing agent ?  
 (1)  $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$  **JEE(Main)-2017]**  
 (2)  $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$   
 (3)  $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$   
 (4)  $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$   
**HY0067**
9. Hydrogen peroxide oxidises  $[Fe(CN)_6]^{4-}$  to  $[Fe(CN)_6]^{3-}$  in acidic medium but reduces  $[Fe(CN)_6]^{3-}$  to  $[Fe(CN)_6]^{4-}$  in alkaline medium. The other products formed are, respectively :  
 (1)  $(H_2O + O_2)$  and  $(H_2O + OH^-)$  **JEE(Main) -2018]**  
 (2)  $H_2O$  and  $(H_2O + O_2)$   
 (3)  $H_2O$  and  $(H_2O + OH^-)$   
 (4)  $(H_2O + O_2)$  and  $H_2O$   
**HY0068**
10. The chemical nature of hydrogen peroxide is :- **JEE(Main) -2019]**  
 (1) Oxidising and reducing agent in acidic medium, but not in basic medium.  
 (2) Oxidising and reducing agent in both acidic and basic medium  
 (3) Reducing agent in basic medium, but not in acidic medium  
 (4) Oxidising agent in acidic medium, but not in basic medium.  
**HY0069**
11. The total number of isotopes of hydrogen and number of radioactive isotopes among them, respectively, are : **JEE(Main) -2019]**  
 (1) 2 and 0                      (2) 3 and 2                      (3) 3 and 1                      (4) 2 and 1  
**HY0070**
12. The correct statements among (a) to (d) regarding  $H_2$  as a fuel are : **JEE(Main) -2019]**  
 (a) It produces less pollutant than petrol  
 (b) A cylinder of compressed dihydrogen weighs ~ 30 times more than a petrol tank producing the same amount of energy  
 (c) Dihydrogen is stored in tanks of metal alloys like  $NaNi_5$   
 (d) On combustion, values of energy released per gram of liquid dihydrogen and LPG are 50 and 142 kJ, respectively  
 (1) b and d only                      (2) a, b and c only                      (3) b, c and d only                      (4) a and c only  
**HY0071**
13. The correct statements among (a) to (d) are: **JEE(Main) -2019]**  
 (a) saline hydrides produce  $H_2$  gas when reacted with  $H_2O$ .  
 (b) reaction of  $LiAlH_4$  with  $BF_3$  leads to  $B_2H_6$ .  
 (c)  $PH_3$  and  $CH_4$  are electron - rich and electron-precise hydrides, respectively.  
 (d)  $HF$  and  $CH_4$  are called as molecular hydrides.  
 (1) (c) and (d) only                      (2) (a), (b) and (c) only  
 (3) (a), (b), (c) and (d)                      (4) (a), (c) and (d) only  
**HY0072**

14. In comparison to the zeolite process for the removal of permanent hardness, the synthetic resins method is : **JEE(Main) -2020]**
- (1) less efficient as it exchanges only anions
  - (2) more efficient as it can exchange only cations
  - (3) less efficient as the resins cannot be regenerated
  - (4) more efficient as it can exchange both cations as well as anions
- HY0073**
15. Hydrogen has three isotopes (A), (B) and (C). If the number of neutron(s) in (A), (B) and (C) respectively, are (x), (y) and (z), the sum of (x), (y) and (z) is : **JEE(Main) -2020]**
- (1) 4                      (2) 3                      (3) 2                      (4) 1
- HY0074**
16. Among the statements (a) - (d), the correct ones are - **JEE(Main) -2020]**
- (a) Decomposition of hydrogen peroxide gives dioxygen
  - (b) Like hydrogen peroxide, compounds, such as  $\text{KClO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{NaNO}_3$  when heated liberate dioxygen
  - (c) 2-Ethylanthraquinone is useful for the industrial preparation of hydrogen peroxide.
  - (d) Hydrogen peroxide is used for the manufacture of sodium perborate
- (1) (a), (b) and (c) only                      (2) (a) and (c) only  
(3) (a), (b), (c) and (d)                      (4) (a), (c) and (d) only

**HY0075**

**EXERCISE # JEE ADVANCED**

1. When zeolite (hydrated sodium aluminium silicate) is treated with hard water, the sodium ions are exchanged with :- [IIT 1990]  
(A)  $H^+$  ions                      (B)  $Ca^{2+}$  ions                      (C)  $SO_4^{2-}$  ions                      (D)  $OH^-$  ions  
**HY0076**
2. Which of the following statement is correct :-  
(A) Hydrogen has same ionisation potential as sodium  
(B) H has same electronegativity as halogens  
(C) It will not be liberated at anode  
(D) H has oxidation state + 1, zero and - 1  
**HY0077**
3. Polyphosphates are used as water softening agent because they :- [IIT 2002]  
(A) Form soluble complexes with anionic species  
(B) Precipitate anionic species  
(C) Form soluble complexes with cationic species  
(D) Precipitate cationic species.  
**HY0078**
4. Hydrogen peroxide in its reaction with  $KIO_4$  and  $NH_2OH$  respectively, is acting as a [JEE Adv. 2014]  
(A) reducing agent, oxidising agent                      (B) reducing agent, reducing agent  
(C) oxidising agent, oxidising agent                      (D) oxidising agent, reducing agent  
**HY0079**
5. Which of the following combination will produce  $H_2$  gas? [JEE Adv. 2017]  
(A) Zn metal and  $NaOH(aq.)$                       (B) Au metal and  $NaCN(aq.)$  in the presence of air  
(C) Cu metal and conc.  $HNO_3$                       (D) Fe metal and conc.  $HNO_3$   
**HY0080**

**ANSWERS KEY**

**EXERCISE : O-1**

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	A	D	C	D	A	C	A	A	D	B	B	C	A	A	B
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	D	B	C	A	C	A	C	B	C	B	D	A	B	A	B
Que.	31	32	33	34	35										
Ans.	C	C	B	C	C										

**EXERCISE : O-2**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A,B,D	A,C,D	D	A,B,C	D	D	C	A,C,D	C	A,B,D
Que.	11	12	13	14	15					
Ans.	B	A,C	D	C	A,B,D					

**EXERCISE : S-1**

Que.	1	2	3	4	5
Ans.	4	3	3	0	9

**EXERCISE : S-2**

Que.	1	2	3	4	5	6	7	8
Ans.	A	C	C	B	D	C	D	C

**EXERCISE : JEE-MAINS**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	1	4	2	3	1	3	3	3	2	2
Que.	11	12	13	14	15	16				
Ans.	3	2	3	4	2	3				

**EXERCISE : JEE-ADVANCED**

Que.	1	2	3	4	5
Ans.	B	D	C	A	A



## Oxidation states :

Lanthanides	Oxidation	Actinides	Oxidation state
Ce <sub>58</sub>	+3, +4	Th <sub>90</sub>	+4
Pr <sub>59</sub>	+3, (+4)	Pa <sub>91</sub>	(+4), +5
Nd <sub>60</sub>	+3	U <sub>92</sub>	(+3), (+4), (+5), +6
Pm <sub>61</sub>	+3	Np <sub>93</sub>	(+3), (+4), +5, (+6), (+7)
Sm <sub>62</sub>	(+2), +3	Pu <sub>94</sub>	(+3), +4, (+5), (+6), (+7)
Eu <sub>63</sub>	+2, +3	Am <sub>95</sub>	+2, (+3), (+4), (+5), (+6)
Gd <sub>64</sub>	+3	Cm <sub>96</sub>	+3, (+4)
Tb <sub>65</sub>	+3, +4	Bk <sub>97</sub>	+3, (+4)
Dy <sub>66</sub>	+3, (+4)	Cf <sub>98</sub>	+3
Ho <sub>67</sub>	+3	Es <sub>99</sub>	+3
Er <sub>68</sub>	(+2), +3	Fm <sub>100</sub>	+3
Tm <sub>69</sub>	(+2), +3	Md <sub>101</sub>	+3
Yb <sub>70</sub>	+2, +3	No <sub>102</sub>	+3
Lu <sub>71</sub>	+3	Lr <sub>103</sub>	+3

**(Oxidation states in brackets are unstable states)**

- (i) The lanthanides contains two s electrons in the outermost shell, they are therefore expected to exhibit a characteristic oxidation state of +2. But for the lanthanides, the +3 oxidation is common.
- (ii) This corresponds to the use of two outermost electrons ( $6s^2$ ) alongwith one inner electron. The inner electron used is a 5d electron (in La, Gd and Lu), or one of the 4f electron if no 5d electrons present.
- (iii) All the lanthanides attains +3 oxidation state and only **Cerium, Praseodymium, and Terbium** exhibit **higher oxidation state (+4)**. **Eu and Yb** exhibit +2 oxidation state.
- (iv) Oxidation states +2 and +4 occur particularly when they lead to -
  - (a) A noble gas configuration **Ex.** Ce<sup>4+</sup> ( $f^0$ ). The formation of Ce<sup>IV</sup> is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The  $E^\circ$  value for Ce<sup>4+</sup>/Ce<sup>3+</sup> is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent.
  - (b) A half filled 'f' orbital **Ex.** Eu<sup>2+</sup>, ( $f^7$ ), Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO<sub>2</sub>. Eu<sup>2+</sup> is formed by losing the two s electrons and its  $f^7$  configuration accounts for the formation of this ion. However, Eu<sup>2+</sup> is a strong reducing agent changing to the common +3 state. Similarly Yb<sup>2+</sup> which has  $f^{14}$  configuration is a reductant.
  - (c) A completely filled 'f' orbital **Ex.** Yb<sup>2+</sup> ( $f^{14}$ )
- (v) Therefore, in higher oxidation state, they act as oxidising while in lower state as reducing agents.

**Magnetic properties :**

- (i) In tripositive lanthanide ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases upto lutecium (7 to 0).
- (ii) lanthanum and lutecium ions are diamagnetic, while all other tripositive lanthanide ions are paramagnetic. (Exception – Neodymium is the most paramagnetic lanthanide).
- (iii) Ce<sup>+4</sup> and Yb<sup>+2</sup> are also diamagnetic ions.

**Colour :**

- (i) The lanthanide ions have unpaired electrons in their 4f orbitals. Thus these ions absorb visible region of light and undergo f–f transition and hence exhibit colour.
- (ii) The colour exhibited depends on the number of unpaired electrons in the 4f orbitals.
- (iii) The ions often with  $4f^n$  configuration have similar colour to those ions having  $4f^{14-n}$  configuration.
- (iv) Lanthanide ions having  $4f^0$ ,  $4f^{14}$  are colourless.

**Other Properties :**

- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.
- The hardness increases with increasing atomic number, samarium being steel hard. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K.
- They have typical metallic structure and are good conductors of heat and electricity.
- Highly dense metals with high m.p.s. do not show any regular trend.
- **Ionisation Energies :** Lanthanides have fairly low ionisation energies comparable to alkaline earth metals.
- **Electro positive character :** High due to low I.P.
- **Complex formation :** Do not have much tendency to form complexes due to low charge density because of their large size.  $\text{Lu}^{+3}$  is smallest in size can only form complex.
- **Reducing Agent :** They readily lose electrons so are good reducing agent.
- **Alloy :** Alloys of lanthanides with Fe are called Misch **metals**, which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al.
- **Basic Nature :**  $\text{La}(\text{OH})_3$  is most basic in nature while  $\text{Lu}(\text{OH})_3$  least basic.
- **Carbide :** Lanthanides form  $\text{MC}_2$  type carbide with carbon, which on hydrolysis gives  $\text{C}_2\text{H}_2$ .
- The lanthanide elements Eu and Yb dissolve directly in very high concentration in liquid ammonia.

**Lanthanide contraction :**

- (i) In the lanthanide series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutetium or from  $\text{La}^{+3}$  to  $\text{Lu}^{+3}$ . This contraction in size is known as lanthanide contraction.
- (ii) The general electronic configuration of these elements is  $4f^{1-14}5s^2p^6d^{0-1}6s^2$ . In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.
- (iii) Due to very poor shielding effect of (n-2)f electrons, they exert very little screening effect on the outermost  $6s^2$  electrons.

Hence, with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.

- (iv) The atomic volumes of Europium and Ytterbium are unexceptionally large. The large atomic size of Eu and Yb suggest weaker bonding in the solid elements. Both these elements have only two electrons extra than the stable configurations (half filled,  $f^7$ , and completely filled,  $f^{14}$ ), hence they utilise two electrons in metallic bonding as in the case with barium.

**Effects of Lanthanide Contraction :**

**Close resemblance of Lanthanides :** The general decrease in the sizes of the lanthanides with an increase in their nuclear charges result in a small increase in their ionisation energies. Hence their basic and ionic nature gradually decreases from La to Lu. This also explains the variations in properties such as increased tendency for hydrolysis and formation of complex salts and decreased thermal stability, solubility of their salts.

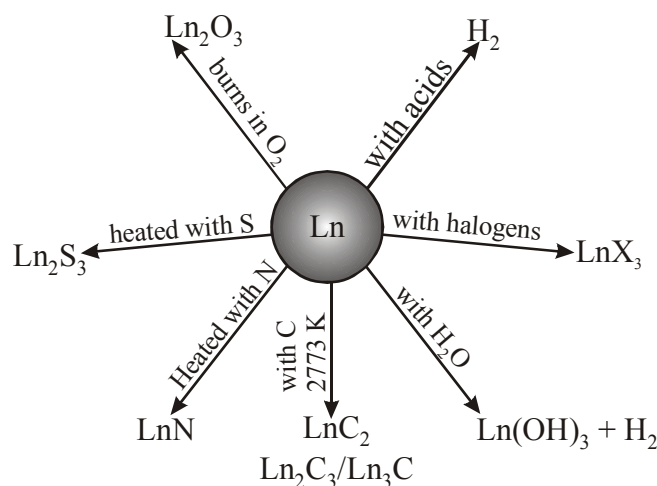
**Similarity of Yttrium with lanthanides :** The properties of Yttrium are so similar to the lanthanides that it is considered more a member of the lanthanide series than a congener of scandium.

**Anomalous behaviour of post-lanthanides :** The following anomalies may be observed in the behaviour of post-lanthanide elements.

- (a) **Atomic size :** The ionic radii of  $Zr^{+4}$  is about 9% more than  $Ti^{+4}$ . Similar trend is not maintained on passing from the second to third transition series. The ionic radius of  $Hf^{+4}$ , instead of increasing (because of inclusion of one more electronic shell), decreases (or is virtually equal to  $Zr^{+4}$ ) as a consequence of the lanthanide contraction. This explains the close similarities between the members of the second and third transition series than between the elements of the first and second series.
- (b) **Ionisation potential and electronegativity :** The effect of lanthanide contraction is also seen in the increase in the ionisation potential values and electronegativities of the elements of the third transition series, contrary to the general trend. Because of the lanthanide contraction, the post-lanthanide elements have stronger positive field and thus the electrons are held more tightly.

The greater effective nuclear charge of the former make them more electronegative than the latter.

- (c) **High density :** Because of lanthanide contraction, the atomic sizes of the post lanthanide elements become very small. Consequently, the packing of atoms in their metallic crystals become so much compact that their densities are very high. The densities of the third transition series elements are almost double to those of the second series elements.
- (d) **Chemical reactions of the lanthanoids.**





**Application of lanthanides :**

Cerium is most useful element in the lanthanides –

- Ceramic application –  $\text{CeO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{Pr}_2\text{O}_3$  are used as decolourizing agents for glasses.
- $\text{CeS}$  (m.p. –  $2000^\circ\text{C}$ ) is used in the manufacture of a special type of crucibles and refractories.
- Lanthanide compounds like cerium molybdate, cerium tungstate are used as paints and dyes.
- In textile and leather industries (Ce salts).
- Mish metal is pyrophoric and is used in cigarette & gas lighter.

**ACTINIDES (5f - BLOCK ELEMENTS)**

- The elements in which the extra electron enters 5f-orbitals of  $(n-2)$ th main shell are known as actinides.
- The man-made eleven elements  $\text{Np}_{93}$  –  $\text{Lr}_{103}$  are placed beyond uranium in the periodic table and are collectively called trans-uranium elements.
- Th, Pa and U first three actinides are natural elements.

**Electronic configuration :**

The general configuration of actinides may be given as  $5f^{1-14} 6d^{0-1} 7s^2$ .

Atomic No.	Elements	Symbol	Electronic Configuration
90	<b>Thorium</b>	<b>Th</b>	<b><math>5f^0 6d^2 7s^2</math></b>
91	Protactinium	Pa	$5f^2 6d^1 7s^2$
92	<b>Uranium</b>	<b>U</b>	<b><math>5f^3 6d^1 7s^2</math></b>
93	<b>Neptunium</b>	<b>Np</b>	<b><math>5f^4 6d^1 7s^2</math></b>
94	<b>Plutonium</b>	<b>Pu</b>	<b><math>5f^6 6d^0 7s^2</math></b>
95	Americium	Am	$5f^7 6d^0 7s^2$
96	<b>Curium</b>	<b>Cm</b>	<b><math>5f^7 6d^1 7s^2</math></b>
97	Berkelium	Bk	$5f^9 6d^0 7s^2$
98	Californium	Cf	$5f^{10} 6d^0 7s^2$
99	Einsteinium	Es	$5f^{11} 6d^0 7s^2$
100	Fermium	Fm	$5f^{12} 6d^0 7s^2$
101	Mendelevium	Md	$5f^{13} 6d^0 7s^2$
102	<b>Nobelium</b>	<b>No</b>	<b><math>5f^{14} 6d^0 7s^2</math></b>
103	<b>Lawrencium</b>	<b>Lr</b>	<b><math>5f^{14} 6d^1 7s^2</math></b>

**Oxidation states :**

- In lanthanides and actinides +3 oxidation is the most common for both of the series of elements.
- This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series.
- Highest oxidation states in the actinides is +7 exhibited by  $\text{Np}_{93}$  &  $\text{Pu}_{94}$ , it is unstable.
- Highest stable oxidation state is +6 shown by  $\text{U}_{92}$ .

**Other Properties :**

- **Physical appearance :** Actinides are silvery white metals. They get tarnished when exposed to the attack of alkalis.
- **Density :** All the actinides except **thorium** and **americium** have high densities.
- **Colour :** Actinide ions are generally coloured. The colour of actinide ions depends upon the number of 5f-electrons. The ions containing no unpaired 5f-electrons (exactly full filled f-subshell) are colourless, as expected.
- **Ionisation energies :** Ionisation energies values of actinides are low.
- **Electropositive character :** All the known actinide metals are **highly electropositive**. They resemble lanthanide series in this respect.
- **Melting Boiling properties :** They have **high melting and boiling points**. They do not follow regular gradation of melting or boiling points with increase in atomic number.
- **Magnetic properties :** The actinide elements are paramagnetic due to the presence of unpaired electrons.
- **Radioactive nature :** All the actinides are radioactive in nature.
- **Actinide contraction :** The size of atom/cation decrease regularly along the actinides series. The steady decrease in ionic radii with increase in atomic number is referred to as **actinide contraction**. This is due to poor shielding of 5f-electrons.

**Comparison of lanthanides and Actinides****Points of Resemblance :**

- Both lanthanides and actinides show a dominant oxidation state of +3.
- Both are electropositive and act as strong reducing agents.
- Cations with unpaired electrons in both of them are paramagnetic.
- Most of the cations of lanthanides and actinides are coloured.
- Both of them show a steady decrease in their ionic radii along the series. Thus, lanthanides show **lanthanide contraction** and actinides show **actinide contraction**.

**Difference between lanthanides & Actinides :**

Lathanides		Actinides	
1.	Besides the most common oxidation state of +3 lanthanides show +2 and +4 oxidation states in case of certain elements.	1.	Besides the most common oxidation state of +3, actinides show +4, +5 and +6 oxidation states in case of certain elements.
2.	Lanthanides have less tendency towards complex formation.	2.	Actinides have a stronger tendency towards complex formation.
3.	Except promethium, they are non radioactive.	3.	All the actinides are radioactive.
4.	Oxides and hydroxide of lanthanides are less basic.	4.	Oxides and hydroxides of actinides are more basic

**Some important uses of actinides are as follows –**

**Thorium :** Thorium is used in atomic reactors as fuel rods and in the treatment of cancer.

**Uranium :** Uranium is used as nuclear fuel. Its salts are used in glass industry (for imparting green colour), textile industry and also in medicines.

**Plutonium :** Plutonium is used as fuel for atomic reactors as well as in atomic bombs.

## EXERCISE # O-1

1. 5f-subshell is filled by electron(s) -  
 (A) In actinides (B) After filling of 7s-subshell  
 (C) Before filling of electron in 6d series (D) All are correct  
**FB0001**
2.  $\text{Ln (Lanthanide)} \xrightarrow[\text{Halogen}]{\text{With}}$  (X)  
 $\text{Ln (Lanthanide)} \xrightarrow[\text{O}_2]{\text{Burn With}}$  (Y)  
 $\text{Ln (Lanthanide)} \xrightarrow[\text{N}_2]{\text{Heated with}}$  (Z)  
 X, Y & Z are respectively -  
 (A)  $\text{LnX}_3$ ,  $\text{Ln}_2\text{O}_3$ ,  $\text{Ln}_3\text{N}$  (B)  $\text{LnX}_3$ ,  $\text{Ln}_2\text{O}_3$ ,  $\text{LnN}$   
 (C)  $\text{LnX}_2$ ,  $\text{LnO}$ ,  $\text{LnN}$  (D)  $\text{LnX}_2$ ,  $\text{Ln}_2\text{O}_3$ ,  $\text{Ln}_3\text{N}$   
**FB0002**
3. Last element of lanthanide series is -  
 (A) Lawrencium (B) Lutetium (C) Thulium (D) Hafnium  
**FB0003**
4. Which is consequence of lanthanide contraction -  
 (A) Size of Zr  $\gg$  Hf (B) Size of Zr  $\ll$  Hf (C) Size of Zr  $\approx$  Hf (D) Size of Zr  $>$   $\text{Zr}^{4+}$   
**FB0004**
5. Select the ion which is larger than  $\text{Ce}^{3+}$   
 (A)  $\text{Lu}^{3+}$  (B)  $\text{Eu}^{3+}$  (C)  $\text{Ce}^{4+}$  (D)  $\text{La}^{3+}$   
**FB0005**
6. Select the reducing agent out of given options-  
 (A)  $\text{Ce}^{4+}$  (B)  $\text{Eu}^{2+}$  (C)  $\text{La}^{3+}$  (D)  $\text{Na}^+$   
**FB0006**
7. The correct order of ionic radii of  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Lu}^{3+}$  is :-  
 (A)  $\text{Y}^{3+} < \text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+}$  (B)  $\text{Y}^{3+} < \text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$   
 (C)  $\text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+} < \text{Y}^{3+}$  (D)  $\text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+} < \text{Y}^{3+}$   
**FB0007**
8. Which of the following statement is **NOT CORRECT** ?  
 (A)  $\text{La(OH)}_3$ , is less basic than  $\text{Lu(OH)}_3$   
 (B) In lanthanide series, ionic radius of  $\text{Ln}^{3+}$  ions decreases  
 (C) La is actually an element of transition series rather than lanthanide series  
 (D) Atomic radii of Zr and Hf are same because of lanthanide contraction.  
**FB0008**
9. In the lanthanide series, the basicity of the lanthanide hydroxides  
 (A) Increases (B) Decreases  
 (C) First increase and then decrease (D) First decrease and then increases  
**FB0009**

10. The reason for the stability of  $Gd^{3+}$  ion is  
 (A)  $4f$  subshell — half filled  
 (B)  $4f$  subshell — completely filled  
 (C) Possesses the general electronic configuration of noble gases  
 (D)  $4f$  subshell empty

FB0010

11. Which of the following pairs has the same size ?  
 (A)  $Zn^{2+}$ ,  $Hf^{4+}$       (B)  $Fe^{2+}$ ,  $Ni^{2+}$       (C)  $Zr^{4+}$ ,  $Ti^{4+}$       (D)  $Zr^{4+}$ ,  $Hf^{4+}$

FB0011

12. Which of the following ions will exhibit colour in aqueous solutions ?  
 (A)  $Sc^{3+}$  ( $Z = 21$ )      (B)  $La^{3+}$  ( $Z = 57$ )      (C)  $Ti^{3+}$  ( $Z = 22$ )      (D)  $Lu^{3+}$  ( $Z = 71$ )

FB0012

13. Which of the following exhibits only +3 oxidation state ?  
 (A) Ac      (B) Pa      (C) U      (D) Th

FB0013

## EXERCISE # JEE-MAIN

1. Arrange  $\text{Ce}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Pm}^{3+}$  and  $\text{Yb}^{3+}$  in increasing order of their ionic radius - [AIEEE-2002]  
 (1)  $\text{Yb}^{3+} < \text{Pm}^{3+} < \text{Ce}^{3+} < \text{La}^{3+}$  (2)  $\text{Ce}^{3+} > \text{Yb}^{3+} < \text{Pm}^{3+} < \text{La}^{3+}$   
 (3)  $\text{Yb}^{3+} > \text{Pm}^{3+} < \text{La}^{3+} < \text{Ce}^{3+}$  (4)  $\text{Pm}^{3+} < \text{La}^{3+} < \text{Ce}^{3+} > \text{Yb}^{3+}$
- FB0014
2. Most common oxidation states shown by cerium are : [AIEEE-2002]  
 (1) +2, +4 (2) +3, +4 (3) +3, +5 (4) +2, +3
- FB0015
3. A reduction in atomic size with increase in atomic number is a characteristic of elements of :  
 (1) f-Block (2) Radioactive series [AIEEE-2003]  
 (3) High atomic masses (4) d-Block
- FB0016
4. The radius of  $\text{La}^{3+}$  is  $1.06 \text{ \AA}$ , which of the following given values will be closest to the radius of  $\text{Lu}^{3+}$  (At no. of Lu = 71, La = 57)- [AIEEE-2003]  
 (1)  $1.6 \text{ \AA}$  (2)  $1.4 \text{ \AA}$  (3)  $1.06 \text{ \AA}$  (4)  $0.85 \text{ \AA}$
- FB0017
5. Cerium ( $Z = 58$ ) is an important member of the lanthanoids. Which of the following statements about cerium is **INCORRECT** - [AIEEE-2004]  
 (1) Cerium (IV) acts as an oxidising agent  
 (2) The +3 oxidation state of cerium is more stable than the +4 oxidation state  
 (3) The +4 oxidation state of cerium is not known in solutions  
 (4) The common oxidation states of cerium are +3 and +4
- FB0018
6. The lanthanoid contraction is responsible for the fact that - [AIEEE-2005]  
 (1) Zr and Y have about the same radius (2) Zr and Nb have similar oxidation state  
 (3) Zr and Hf have about the same radius (4) Zr and Zn have similar oxidation state
- FB0019
7. Lanthanoid contraction is caused due to [AIEEE-2006]  
 (1) the same effective nuclear charge from Ce to Lu  
 (2) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge  
 (3) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge  
 (4) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge
- FB0020
8. Identify the **INCORRECT** statement among the following- [AIEEE-2007]  
 (1) d-block elements show irregular and erratic chemical properties among themselves  
 (2) La and Lu have partially filled d-orbitals and no other partially filled orbitals  
 (3) The chemistry of various lanthanoids is very similar  
 (4) 4f and 5f-orbitals are equally shielded

FB0021

9. The actinoids exhibits more number of oxidation states in general than the lanthanoids. This is because - [AIEEE-2007]  
 (1) The  $5f$ -orbitals are more buried than the  $4f$ -orbitals  
 (2) There is a similarity between  $4f$ -and- $5f$  in their angular part of the wave function  
 (3) The actinoids are more reactive than the lanthanoids  
 (4) The  $5f$ -orbitals extend further from the nucleus than the  $4f$ -orbitals  
**FB0022**
10. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being [AIEEE-2008]  
 (1)  $4f$  orbitals more diffused than the  $5f$  orbitals  
 (2) lesser energy difference between  $5f$  and  $6d$  than between  $4f$  and  $5d$  orbitals  
 (3) more energy difference between  $5f$  and  $6d$  than between  $4f$  and  $5d$  orbitals  
 (4) more reactive nature of the actinides than the lanthanides  
**FB0023**
11. Knowing that the chemistry of lanthanoids ( $Ln$ ) is dominated by its +3 oxidation state, which of the following statements is **INCORRECT** ? [AIEEE-2009]  
 (1)  $Ln(III)$  compounds are generally colourless  
 (2)  $Ln(III)$  hydroxides are mainly basic in character  
 (3) Because of the large size of the  $Ln(III)$  ions the bonding in its compounds is predominantly ionic in character  
 (4) The ionic sizes of  $Ln(III)$  decrease in general with increasing atomic number  
**FB0024**
12. In context of the lanthanoids, which of the following statements is **NOT CORRECT** ? [AIEEE-2011]  
 (1) Because of similar properties the separation of lanthanoids is not easy  
 (2) Availability of  $4f$  electrons results in the formation of compounds in +4 state for all the members of the series  
 (3) There is a gradual decrease in the radii of the members with increasing atomic number in the series  
 (4) All the members exhibit +3 oxidation state  
**FB0025**
13. Which of the following forms stable +4 oxidation state ? [Jee-Main 2012, Online]  
 (1)  $La(Z = 57)$       (2)  $Eu(Z = 63)$       (3)  $Gd(Z = 64)$       (4)  $Ce(Z = 58)$   
**FB0026**
14. The number of unpaired electrons in Gadolinium [ $Z = 64$ ] is :- [Jee-Main 2012, Online]  
 (1) 2      (2) 6      (3) 8      (4) 3  
**FB0027**

- 15.** The lanthanide ion that would show colour is- [Jee-Main 2019, Online]  
 (1)  $\text{Sm}^{3+}$  (2)  $\text{La}^{3+}$  (3)  $\text{Lu}^{3+}$  (4)  $\text{Gd}^{3+}$   
**FB0028**
- 16.** The highest possible oxidation states of uranium and plutonium, respectively, are :- [Jee-Main 2019, Online]  
 (1) 6 and 4 (2) 7 and 6  
 (3) 4 and 6 (4) 6 and 7  
**FB0029**
- 17.** The correct order of atomic radii is : [Jee-Main 2019, Online]  
 (1)  $\text{Ce} > \text{Eu} > \text{Ho} > \text{N}$  (2)  $\text{N} > \text{Ce} > \text{Eu} > \text{Ho}$   
 (3)  $\text{Eu} > \text{Ce} > \text{Ho} > \text{N}$  (4)  $\text{Ho} > \text{N} > \text{Eu} > \text{Ce}$   
**FB0030**
- 18.** The maximum number of possible oxidation states of actinoides are shown by [Jee-Main 2020, Online]  
 (1) berkelium (Bk) and californium (Cf) (2) nobelium (No) and lawrencium (Lr)  
 (3) actinium (Ac) and thorium (Th) (4) neptunium (Np) and plutonium (Pu)  
**FB0031**
- 19.** The electronic configurations of bivalent europium and trivalent cerium are [Jee-Main 2020, Online]  
 (atomic number : Xe = 54, Ce = 58, Eu = 63)  
 (1)  $[\text{Xe}] 4f^4$  and  $[\text{Xe}] 4f^9$  (2)  $[\text{Xe}] 4f^7$  and  $[\text{Xe}] 4f^1$   
 (3)  $[\text{Xe}] 4f^7 6s^2$  and  $[\text{Xe}] 4f^2 6s^2$  (4)  $[\text{Xe}] 4f^2$  and  $[\text{Xe}] 4f^7$   
**FB0032**

## ANSWERS KEY

### EXERCISE # O-1

<b>Que.</b>	1	2	3	4	5	6	7	8	9	10	11	12	13	
<b>Ans</b>	D	B	B	C	D	B	B	A	B	A	D	C	A	

### EXERCISE # JEE-MAIN

<b>Que.</b>	1	2	3	4	5	6	7	8	9	10
<b>Ans.</b>	1	2	1	4	3	3	2	4	4	2
<b>Que.</b>	11	12	13	14	15	16	17	18	19	
<b>Ans.</b>	1	2	4	3	1	4	3	4	2	

## ENVIRONMENTAL CHEMISTRY

### 1. ENVIRONMENTAL POLLUTION

A substance, which causes pollution, is known as pollutant. Pollutants can be solid, liquid or gaseous substances present in greater concentration than in natural abundance and are produced due to human activities or due to natural happenings.

### 2. ATMOSPHERIC POLLUTION

The lowest region of atmosphere in which the human beings along with other organisms live is called **troposphere**. It extends up to the height of ~ 10 km from sea level.

Above the troposphere, between 10 and 50 km above sea level lies **stratosphere**. The stratosphere contains dinitrogen, dioxygen, ozone and little water vapour.

The presence of ozone in the stratosphere prevents about 99.5 per cent of the sun's harmful ultraviolet (UV) radiations from reaching the earth's surface

#### 2.1 Tropospheric Pollution

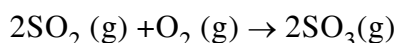
Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air.

- Gaseous air pollutants:** These are oxides of sulphur, nitrogen and carbon, hydrogen sulphide, hydrocarbons, ozone and other oxidants.
- Particulate pollutants:** These are dust, mist, fumes, smoke, smog etc.

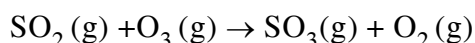
#### 1. Gaseous air pollutants

- Oxides of Sulphur :** Oxides of sulphur are produced when sulphur containing fossil fuel is burnt.

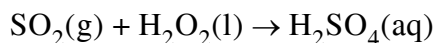
- Sulphur dioxide is a gas that is poisonous to both animals and plants. It causes respiratory diseases e.g., asthma, bronchitis, emphysema in human beings. Sulphur dioxide causes irritation to the eyes, resulting in tears and redness.
- High concentration of  $\text{SO}_2$  leads to stiffness of flower buds which eventually fall off from plants.
- Uncatalysed oxidation of sulphur dioxide is slow. However, the presence of particulate matter in polluted air catalyses the oxidation of sulphur dioxide to sulphur trioxide.



The reaction can also be promoted by ozone and hydrogen peroxide.

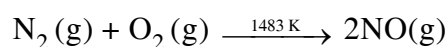




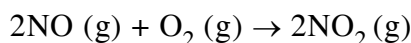


(b) **Oxides of Nitrogen :** Dinitrogen and dioxygen do not react with each other at a normal temperature. At high altitudes when lightning strikes, they combine to form oxides of nitrogen.

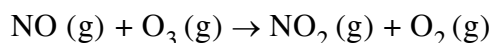
- $\text{NO}_2$  is oxidised to nitrate ion,  $\text{NO}_3^-$  which is washed into soil, where it serves as a fertilizer.
- In an automobile engine (at high temperature), when fossil fuel is burnt, dinitrogen and dioxygen combine to yield significant quantities of nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ) as given below:



NO reacts instantly with oxygen to give  $\text{NO}_2$



Rate of production of  $\text{NO}_2$  is faster when nitric oxide reacts with ozone in the stratosphere.



The irritant red haze in the traffic and congested places is due to oxides of nitrogen. Higher concentrations of  $\text{NO}_2$  damage the leaves of plants and retard the rate of photosynthesis. It is also a lung irritant.

(c) **Hydrocarbons :** Hydrocarbons are formed by incomplete combustion of fuel used in automobiles and are carcinogenic.

(d) **Oxides of Carbon :**

- (i) **Carbon monoxide :** It blocks the delivery of oxygen to the organs and tissues. It is produced as a result of incomplete combustion of carbon.
- It binds to haemoglobin to form carboxyhaemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. In blood, when the concentration of carboxyhaemoglobin reaches about 3 – 4 per cent, the oxygen carrying capacity of blood is greatly reduced.
- (ii) **Carbon dioxide :** Carbon dioxide ( $\text{CO}_2$ ) is released into the atmosphere by respiration, burning of fossil fuels for energy, and by decomposition of limestone during the manufacture of cement.
- It forms about 0.03 per cent by volume of the atmosphere.

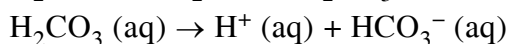
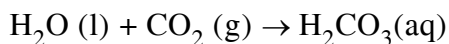
- The increased amount of  $\text{CO}_2$  in the air is mainly responsible for global warming.

### Global Warming and Greenhouse Effect

- About 75 % of the solar energy reaching the earth is absorbed by the earth's surface, which increases its temperature. The rest of the heat radiates back to the atmosphere. Some of the heat is trapped by gases such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFCs) and water vapour in the atmosphere. Thus, they add to the heating of the atmosphere. This causes global warming.
- The atmosphere has kept the temperature on earth constant. As the glass in a greenhouse holds the sun's warmth inside, atmosphere traps the sun's heat near the earth's surface and keeps it warm. This is called natural greenhouse effect.

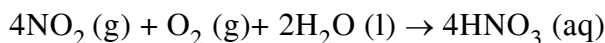
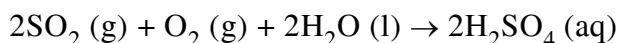
### Acid rain :

- Normally rain water has a pH of 5.6 due to the presence of  $\text{H}^+$  ions formed by the reaction of rain water with carbon dioxide present in the atmosphere.



When the pH of the rain water drops below 5.6, it is called acid rain.

- Burning of fossil fuels (which contain sulphur and nitrogenous matter) such as coal and oil in power stations and furnaces or petrol and diesel in motor engines produce sulphur dioxide and nitrogen oxides.  $\text{SO}_2$  and  $\text{NO}_2$  after oxidation and reaction with water are major contributors to acid rain.



- Acid rain is harmful for agriculture, trees and plants as it dissolves and washes away nutrients needed for their growth.
- The Taj Mahal in India has been affected by acid rain.

### 2. Particulate Pollutants :

- Particulates pollutants are the minute solid particles present in vehicle emissions, smoke particles from fires, dust particles and ash from industries.
- Non-viable particulates may be classified as follows :
  - (a) Smoke
  - (b) Dust
  - (c) Mists
  - (d) Fumes
- Lead used to be a major air pollutant emitted by vehicles.

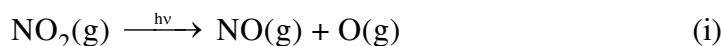
### Smog :

- The word smog is derived from smoke and fog. There are two types of smog :
  - (a) Classical smog is a mixture of smoke, fog and sulphur dioxide. Chemically it is a reducing mixture and so it is also called as reducing smog.
  - (b) Photochemical smog : The main components of the photochemical smog result from the action of sunlight on unsaturated hydrocarbons and nitrogen oxides produced by

automobiles and factories. Photochemical smog has high concentration of oxidising agents and is, therefore, called as oxidising smog.

### Formation of photochemical smog :

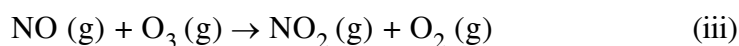
Two pollutants, hydrocarbons (unburnt fuels) and nitric oxide (NO) when build up to sufficiently high levels, a chain reaction occurs from their interaction with sunlight in which NO is converted into nitrogen dioxide (NO<sub>2</sub>). This NO<sub>2</sub> in turn absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atom.



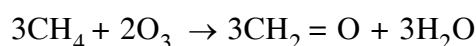
Oxygen atoms are very reactive and combine with the O<sub>2</sub> in air to produce ozone.



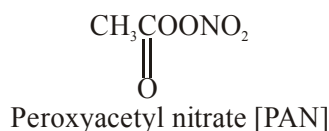
The ozone formed in the above reaction (ii) reacts rapidly with the NO(g) formed in the reaction (i) to regenerate NO<sub>2</sub>. NO<sub>2</sub> is a brown gas and at sufficiently high levels can contribute to haze.



Ozone is a toxic gas and both NO<sub>2</sub> and O<sub>3</sub> are strong oxidising agents and can react with the unburnt hydrocarbons in the polluted air to produce chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN).



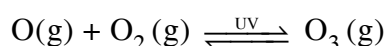
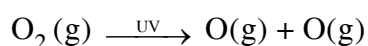
Formaldehyde



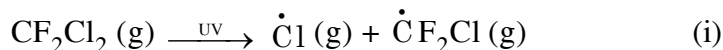
Both ozone and PAN act as powerful eye irritants. Ozone and nitric oxide irritate the nose and throat and their high concentration causes headache, chest pain, dryness of the throat, cough and difficulty in breathing.

### 2.2 Stratospheric Pollution Formation and Breakdown of Ozone :

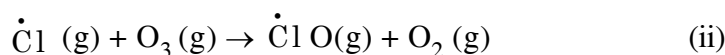
- ❑ The upper stratosphere consists of considerable amount of ozone (O<sub>3</sub>), which protects us from the harmful ultraviolet (UV) radiations (λ 255 nm) coming from the sun. These radiations cause skin cancer (melanoma) in humans.
- ❑ Ozone in the stratosphere is a product of UV radiations acting on dioxygen (O<sub>2</sub>) molecules. The UV radiations split apart molecular oxygen into free oxygen (O) atoms. These oxygen atoms combine with the molecular oxygen to form ozone.



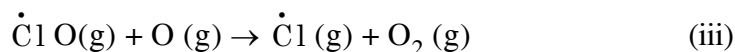
- Ozone is thermodynamically unstable and decomposes to molecular oxygen. Thus, a dynamic equilibrium exists between the production and decomposition of ozone molecules. The main reason of ozone layer depletion is the release of chlorofluorocarbon.
- Compounds (CFCs), also known as freons. These compounds are nonreactive, non flammable, non toxic organic molecules. Once CFCs are released in the atmosphere, they get broken down by powerful UV radiations, releasing chlorine free radical.



The chlorine radical then reacts with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen.



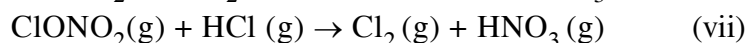
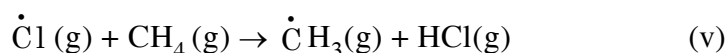
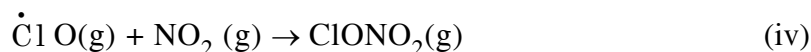
Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.



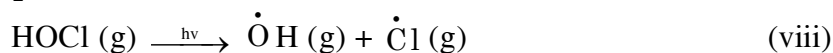
The chlorine radicals are continuously regenerated and cause the breakdown of ozone.

### The Ozone Hole

- In summer season, nitrogen dioxide and methane react with chlorine monoxide (reaction iv) and chlorine atoms (reaction v) forming chlorine sinks, preventing much ozone depletion, whereas in winter, special type of clouds called polar stratospheric clouds provide surface on which chlorine nitrate formed (reaction iv) gets hydrolysed to form hypochlorous acid (reaction (vi)).
- It also reacts with hydrogen chloride produced as per reaction (v) to give molecular chlorine.



When sunlight returns to the Antarctica in the spring, the sun's warmth breaks up the clouds and HOCl and Cl<sub>2</sub> are photolysed by sunlight, as given in reactions (viii) and (ix).



The chlorine radicals thus formed, initiate the chain reaction for ozone depletion.

## 3. WATER POLLUTION

Pollution of water originates from human activities.

### 3.1 Causes of Water Pollution

- Pathogens :** The most serious water pollutants are the disease causing agents called pathogens.
- Organic wastes :** Organic matter such as leaves, grass, trash etc. pollute water as a consequence of run off.

The large population of bacteria decomposes organic matter present in water. They

consume oxygen dissolved in water. In cold water, dissolved oxygen (DO) can reach a concentration up to 10 ppm (parts per million).

- The concentration of dissolved oxygen in water is very important for aquatic life. If the concentration of dissolved oxygen of water is below 6 ppm, the growth of fish gets inhibited.
- The amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called **Biochemical Oxygen Demand (BOD)**. Clean water would have BOD value of less than 5 ppm where as highly polluted water could have a BOD value of 17 ppm or more.

(iii) **Chemical Pollutants** : Water soluble inorganic chemicals that include heavy metals such as cadmium, mercury, nickel etc constitute an important class of pollutants. The process in which nutrient enriched water bodies support a dense plant population, which kills animal life by depriving it of oxygen and results in subsequent loss of biodiversity is known as **Eutrophication**.

### 3.2. International Standards for Drinking Water

**Fluoride** : Fluoride ion concentration deficiency in drinking water causes diseases such as tooth decay etc. Soluble fluoride is often added to drinking water to bring its concentration upto 1 ppm or  $1 \text{ mg dm}^{-3}$ .

- However,  $\text{F}^-$  ion concentration above 2 ppm causes brown mottling of teeth. At the same time, excess fluoride (over 10 ppm) causes harmful effect to bones and teeth. The  $\text{F}^-$  ions make the enamel on teeth much harder by converting hydroxyapatite,  $[\text{3}(\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2)]$ , the enamel on the surface of the teeth, into much harder fluorapatite,  $[\text{3}(\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2)]$ .

**Lead** : The prescribed upper limit concentration of lead in drinking water is about 50 ppb. Lead can damage kidney, liver, reproductive system etc.

**Sulphate**: Excessive sulphate (>500 ppm) in drinking water causes laxative effect, otherwise at moderate levels it is harmless.

**Nitrate**: The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome).

**Table : Maximum Prescribed Concentration of Some Metals in Drinking Water.**

Metal	Maximum concentration (ppm or $\text{mg dm}^{-3}$ )
Fe	0.2
Mn	0.05
Al	0.2
Cu	3.0
Zn	5.0
Cd	0.005

## 4. SOIL POLLUTION

### 4.1 Pesticides :

Pesticides are basically synthetic toxic chemicals with ecological repercussions.

## 5. INDUSTRIAL WASTE

- Industrial solid wastes are also sorted out as biodegradable and non-degradable wastes. Biodegradable wastes are generated by cotton mills, food processing units, paper mills, and textile factories.
- Non-biodegradable wastes are generated by thermal power plants which produce fly ash; integrated iron and steel plants which produce blast furnace slag and steel melting slag. Nowadays, fly ash and slag from the steel industry are utilised by the cement industry.

## 6. STRATEGIES TO CONTROL ENVIRONMENTAL POLLUTION

### 6.1 Waste Management :

The improper disposal of wastes is one of the major causes of environmental degradation. Therefore, the management of wastes is of utmost importance.

#### *Collection and Disposal :*

Domestic wastes are collected in small bins, which are then transferred to community bins by private or municipal workers.

## 7. GREEN CHEMISTRY :

### 7.1 Introduction :

- Green chemistry is a production process that would bring about minimum pollution or deterioration to the environment.
- The byproducts generated during a process, if not used gainfully, add to the environmental pollution.
- Such processes are not only environmental unfriendly but also cost-ineffective. The waste generation and its disposal both are economically unsound.
- Utilisation of existing knowledge base for reducing the chemical hazards along with the developmental activities is the foundation of green chemistry.

### 7.2 *Green Chemistry in day-to-day Life*

#### (i) *Dry Cleaning of Clothes*

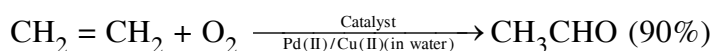
Tetra chloroethene ( $\text{Cl}_2\text{C}=\text{CCl}_2$ ) was earlier used as solvent for dry cleaning. The compound contaminates the ground water and is also a suspected carcinogen. Replacement of halogenated solvent by liquid  $\text{CO}_2$  will result in less harm to ground water.

#### (ii) *Bleaching of Paper*

Chlorine gas was used earlier for bleaching paper. These days, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) with suitable catalyst.

#### (iii) *Synthesis of Chemicals*

Ethanal ( $\text{CH}_3\text{CHO}$ ) is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium with a yield of 90%.



## EXERCISE # I

1. Which one is not the correct statement ?  
Pollutions means :
- (A) The presence of anything in the environment in excess of the required limit  
(B) anything put into the environment which was not there in its natural state.  
(C) direct or indirect changes in one or more components of the ecosystem which are not harmful to living organisms  
(D) international release of any chemical substance in the environment with harmful effects
- EN0001**
2. Which is the main air pollutant ?  
(A) CO<sub>2</sub>                      (B) CO                      (C) N<sub>2</sub>                      (D) S
- EN0002**
3. The acid rain possesses :  
(A) Sulphuric acid      (B) nitric acid      (C) sulphurous acid      (D) all of these
- EN0003**
4. Carbon monoxide (CO) is harmful to man because -  
(A) It competes with O<sub>2</sub> for haemoglobin                      (B) It forms carboic acid  
(C) It generates excess CO<sub>2</sub>                      (D) It is carcinogenic
- EN0004**
5. Lung diseases are four times more in urban areas than rural areas. This is due to the presence of :-  
(A) SO<sub>2</sub>                      (B) CO<sub>2</sub>                      (C) N<sub>2</sub>                      (D) Water-vapour
- EN0005**
6. Which one is not correct ?  
Greenhouse effect :
- (A) is due to high concentration of CO<sub>2</sub> in atmosphere  
(B) is influenced by gases such as CH<sub>4</sub>, O<sub>3</sub> and chlorofluorocarbons  
(C) would result in the warming up of the earth  
(D) would result in lowering the level of oceans due to high evaporation
- EN0006**
7. Which is not a green house gas -  
(A) CFC's                      (B) Methane                      (C) H<sub>2</sub>                      (D) CO<sub>2</sub>
- EN0007**
8. Green house effect is related to -  
(A) Cultivation of green plants                      (C) Global wanning  
(B) Cultivation of vegetables in houses                      (D) Global green algae
- EN0008**
9. Acid rains are produced by-  
(A) Excess production of NH<sub>3</sub> by industry and coal gas  
(B) Excess release of carbon monoxide by incomplete combustion  
(C) Excess formation of CO<sub>2</sub> by combustion and animal respiration  
(D) Excess NO<sub>2</sub> and SO<sub>2</sub>, from burning of fossil fuels
- EN0009**

10. If there was no  $\text{CO}_2$  in the earth's atmosphere, the temperature of earth's surface would be -  
 (A) Less than the present  
 (B) The same  
 (C) Dependent on the amount of oxygen in the atmosphere  
 (D) Higher than the present  
 EN0010
11. The pH of acid rain water is :  
 (A) 1.2 (B) 3.1 (C) 5 (D) 6  
 EN0011
12. Which air pollutant is not released by scooters and cars ?  
 (A)  $\text{SO}_2$  (B) Fly ash (C) Hydrocarbons (D) CO  
 EN0012
13.  $\text{CFCl}_3$  is responsible for the decomposition of ozone to form oxygen. Which of the following reacts with ozone to form oxygen ?  
 (A)  $\text{Cl}_2$  (B)  $\text{Cl}^-$  (C)  $\text{F}^-$  (D)  $\dot{\text{C}}\text{l}$   
 EN0013
14. Pick up the correct statement  
 (A) CO which is major pollutant resulting from the combustion of fuels in automobiles plays a major role in photochemical smog  
 (B) Classical smog has an oxidizing character while the photochemical smog is reducing in character  
 (C) Photochemical smog occurs in day time whereas the classical smog occurs in early morning hours  
 (D) During formation of smog the level of ozone in the atmosphere goes down  
 EN0014
15. Air pollutants that produce photochemical smog -  
 (A) Ozone, chlorine and sulphur dioxide (B) Oxygen, chlorine and nitric acid  
 (C) Nitrous oxide, PAN and acrolein (D)  $\text{CO}_2$ , CO and  $\text{SO}_2$   
 EN0015
16. P.A.N, stands for-  
 (A) Peroxy acetyl nitrite (B) Peroxy acetyl nitrate  
 (C) peroxy acetyl nitrile (D) Pyridine aceto-nitrite  
 EN0016
17. The photochemical smog can be suppressed by :  
 (A) nitrogen oxides (B) hydrocarbons (C) radical traps (D) formaldehyde  
 EN0017
18. The chief pollutants which are responsible for ozone depletion :-  
 (A)  $\text{SO}_2$  (B)  $\text{CO}_2$   
 (C) CO (D) Oxides of nitrogen and chlorofluorocarbons  
 EN0018
19. Taj mahal is threatened due to effect of :-  
 (A) Chlorine (B) Sulphur dioxide (C) Oxygen (D) Hydrogen  
 EN0019



20. Ozone hole refers to :-  
(A) Increased concentration of ozone  
(B) Reduction in the thickness of ozone layer in troposphere  
(C) Reduction in the thickness of ozone layer in stratosphere  
(D) Hole in ozone layer
- EN0020**
21. One of the pollutants that is generally helping in the early degradation of the ozone layer is :-  
(A) SO<sub>2</sub>                      (B) DDT                      (C) CO<sub>2</sub>                      (D) Freons
- EN0021**
22. In coming years, skin related disorders will become more common due to -  
(A) Airpollution                      (B) Excessive use of detergents  
(C) Depletion of ozone layer                      (D) Water pollution
- EN0022**
23. Often in water bodies subjected to sewage pollution, fishes die because of the-  
(A) Foul smell  
(B) Reduction in dissolved oxygen caused by microbial activity  
(C) Clogging of their gills by solid substances  
(D) Pathogens released by the sewage
- EN0023**
24. Which one is not a water pollutant ?  
(A) Automobile exhaust                      (B) Plant nutrients  
(C) Oxygen demanding wastes                      (D) Disease causing agents
- EN0024**
25. If BOD of river is high, it means that the river is :-  
(A) Not polluted  
(B) Very much polluted with inorganic chemicals  
(C) Very much polluted with organic chemicals which are decomposed by micro-organisms  
(D) Polluted with pesticides
- EN0025**
26. When huge amount of sewage is dumped in a river, the BOD will :-  
(A) Increase                      (B) Remain unchanged  
(C) Decrease                      (D) Increase or decrease
- EN0026**
27. By what method the quantity of organic pollutants in water can be determined  
(A) By measuring BOD                      (B) By pH Measurement  
(C) By transparency measurements                      (D) By measuring the change of colour/CFC
- EN0027**
28. A dental disease characterised by mottling of teeth is due to presence of a certain chemical element in drinking water. Which is the element -  
(A) Fluorine                      (B) Mercury                      (C) Boron                      (D) Chlorine
- EN0028**

29. Excess of nitrate in drinking water causes :-  
(A) itai-itai syndrome (B) Rickets syndrome  
(C) Laxative effect (D) Methemoglobinemia ('blue baby' syndrome)  
EN0029
30. Eutrophication is caused by  
(A) Increase nutrient concentration (B) Petrochemical and fertilizer plant effluents  
(C)  $\text{NO}_3^{-1}$  and  $\text{SO}_4^{-2}$  present in acid rains (D) Mine effluents  
EN0030
31. Continuous sewage flow into a stream would lead to-  
(A) Increase in temperature (B) Algal bloom  
(C) Eutrophication (D) Depletion of oxygen  
EN0031
32. Indiscriminate use of DDT is undesirable because -  
(A) It is harmful (B) It is dcgradable  
(C) It causes mutation (D) It is accumulated in food chain  
EN0032
33. Fluorosis, a bone disease, is caused by the presence of :-  
(A) Pesticides in water (B) Fluorides in water  
(C) Carbon monoxide in air (D) Sulphur dioxide in air  
EN0033
34. Major source of methane in India is :  
(A) fruit orchards (B) sugar cane plantatton  
(C) rice fields (D) wheat fields  
EN0034
35. Green chemistry means such reactions which :  
(A) are related to the depletion of ozone layer  
(B) produce colour during reactions  
(C) study the reactions in plants  
(D) reduce the use and production of hazardous chemicals  
EN0035
36. Among the following, the one that is is not a green house gas is :-  
(A) Nitrous oxide (B) Methane (C) Ozone (D) Sulphur dioxide  
EN0036
37. Which oxide of nitrogen is not a common pollutant introduced into the atmosphere both due to natural and human activity?  
(A)  $\text{NO}_2$  (B)  $\text{N}_2\text{O}$  (C)  $\text{N}_2\text{O}_5$  (D) NO  
EN0037
38. Which of the following is a sink for  $\text{CO}$ ?  
(A) Haemoglobin (B) Micro-organisms present in the soil  
(C) Oceans (D) Plants  
EN0038

## EXERCISE # JEE-MAINS

1. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value  
 (1) slightly higher than that when the thunderstorm is not there [AIEEE-2003]  
 (2) uninfluenced by occurrence of thunderstorm  
 (3) which depends on the amount of dust in air  
 (4) slightly lower than that of rain water without thunderstorm  
 EN0039
2. The smog is essentially caused by the presence of : [AIEEE-2004]  
 (1)  $O_2$  and  $O_3$  (2)  $O_3$  and  $N_2$   
 (3) Oxides of sulphur and nitrogen (4)  $O_2$  and  $N_2$   
 EN0040
3. Regular use of which of the following fertilizers increases the acidity of soil ? [AIEEE-2007]  
 (1) potassium nitrate (2) Urea  
 (3) Superphosphate of lime (4) Ammonium sulphate  
 EN0041
4. Identify the wrong statements in the following : [AIEEE-2008]  
 (1) Chlorofluorocarbons are responsible for ozone layer depletion  
 (2) Greenhouse effect is responsible for global warming  
 (3) Ozone layer does not permit infrared radiation from the sun to reach the earth  
 (4) Acid rains is mostly because of oxides of nitrogen and sulphur  
 EN0042
5. What is DDT among the following : [JEE-MAINS-2012]  
 (1) Greenhouse gas (2) A fertilizer  
 (3) Biodegradable pollutant (4) Non-biodegradable pollutant  
 EN0043
6. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was :  
 (1) Methylisocyanate (2) Methylamine [JEE-MAINS-2013]  
 (3) Ammonia (4) Phosgene  
 EN0044
7. **Assertion :** Nitrogen and Oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen. [JEE-MAINS-2015]  
**Reason :** The reaction between nitrogen and oxygen requires high temperature.  
 (1) Both assertion and reason are correct, and the reason is the correct explanation for the assertion  
 (2) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion  
 (3) The assertion is incorrect, but the reason is correct  
 (4) Both the assertion and reason are incorrect  
 EN0045

8. The concentration of fluoride, lead, nitrate and iron in a water sample from an underground lake was found to be 1000 ppb, 40 ppb, 100 ppm and 0.2 ppm, respectively. This water is unsuitable for drinking due to high concentration of :

[JEE-MAINS-2016]

- (1) Fluoride                      (2) Lead                      (3) Nitrate                      (4) Iron

EN0046

9. A water sample has ppm level concentration of following anions  $F^- = 10$ ;  $SO_4^{2-} = 100$ ;  $NO_3^- = 50$  the anion/anions that make / makes the water sample unsuitable for drinking is / are :

- (1) only  $NO_3^-$                       (2) both  $SO_4^{2-}$  and  $NO_3^-$                       [JEE-MAINS-2017]  
(3) only  $F^-$                       (4) only  $SO_4^{2-}$

EN0047

10. Identify the pollutant gases largely responsible for the discoloured and lustreless nature of marble of the Taj Mahal

[JEE-MAINS-2017]

- (1)  $O_3$  and  $CO_2$                       (2)  $CO_2$  and  $NO_2$                       (3)  $SO_2$  and  $O_3$                       (4)  $SO_2$  and  $NO_2$

EN0048

11. Which of the following is a set of green house gases ?

[JEE-MAINS-2017]

- (1)  $O_3$ ,  $N_2$ ,  $CO_2$ ,  $NO_2$                       (2)  $CH_4$ ,  $O_3$ ,  $N_2$ ,  $SO_2$   
(3)  $CO_2$ ,  $CH_4$ ,  $N_2O$ ,  $O_3$                       (4)  $O_3$ ,  $NO_2$ ,  $SO_2$ ,  $Cl_2$

EN0049

12. Biochemical Oxygen Demand (BOD) value can be a measure of water pollution caused by the organic matter. Which of the following statements is correct -

[JEE-MAINS ONLINE-2018]

- (1) Anaerobic bacteria increase the BOD value  
(2) Aerobic bacteria decrease the BOD value  
(3) Polluted water has BOD value higher than 10 ppm  
(4) Clean water has BOD value higher than 10 ppm

EN0050

13. The recommended concentration of fluoride ion in drinking water is up to 1 ppm as fluoride ion is required to make teeth enamel harder by converting  $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2]$  to :

- (1)  $[3(CaF_2) \cdot Ca(OH)_2]$                       [JEE-MAINS-2018]  
(2)  $[3(Ca_3(PO_4)_2 \cdot CaF_2)]$   
(3)  $[3(Ca(OH)_2) \cdot CaF_2]$   
(4)  $[CaF_2]$

EN0051

14. A water sample has ppm level concentration of the following metals: Fe = 0.2; Mn = 5.0; Cu = 3.0; Zn = 5.0. The metal that makes the water sample unsuitable drinking is : [JEE-MAINS-2019]

(1) Zn (2) Fe (3) Mn (4) Cu

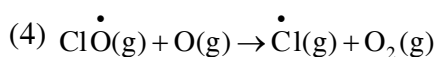
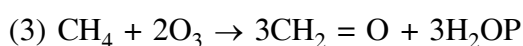
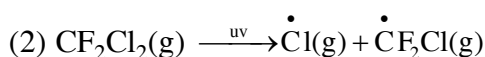
EN0052

15. Which of the following conditions in drinking water causes methemoglobinemia ?

(1) > 50ppm of load (2) > 100 ppm of sulphate [JEE-MAINS-2019]  
 (3) > 50 ppm of chloride (4) > 50 ppm of nitrate

EN0053

16. The reaction that is NOT involved in the ozone layer depletion mechanism in the stratosphere is:



EN0054

17. The compound that is NOT a common component of photochemical smog is : [JEE-MAINS-2019]

(1)  $\text{O}_3$  (2)  $\text{CH}_2=\text{CHCHO}$   
 (3)  $\text{CF}_2\text{Cl}_2$  (4)  $\text{H}_3\text{C}-\underset{\text{O}}{\text{C}}-\text{OONO}_2$

EN0055

18. The upper stratosphere consisting of the ozone layer protects us from the sun's radiation that falls in the wavelength region of : [JEE-MAINS-2019]

(1) 600-750 nm (2) 0.8-1.5 nm (3) 400-550 nm (4) 200-315 nm

EN0056

19. Biochemical Oxygen Demand (BOD) is the amount of oxygen required (in ppm):

(1) by anaerobic bacteria to breakdown inorganic waste present in a water body.  
 (2) for the photochemical breakdown of waste present in 1 m<sup>3</sup> volume of a water body.  
 (3) by bacteria to break-down organic waste in a certain volume of a water sample.  
 (4) for sustaining life in a water body. [JEE-MAINS-2020]

EN0057

20. Among the gases (a) - (e), the gases that cause greenhouse effect are : [JEE-MAINS-2020]

(a)  $\text{CO}_2$  (b)  $\text{H}_2\text{O}$  (c) CFCs (d)  $\text{O}_2$  (e)  $\text{O}_3$   
 (1) (a), (b), (c) and (d) (2) (a), (c), (d) and (e)  
 (3) (a) and (d) (4) (a), (b), (c) and (e)

EN0058

**ANSWER KEY****EXERCISE # I**

1. Ans. (C)	2. Ans. (B)	3. Ans. (D)	4. Ans. (A)	5. Ans. (A)
6. Ans. (D)	7. Ans. (C)	8. Ans. (C)	9. Ans. (D)	10. Ans. (A)
11. Ans. (C)	12. Ans. (B)	13. Ans. (D)	14. Ans. (C)	15. Ans. (C)
16. Ans. (B)	17. Ans. (C)	18. Ans. (D)	19. Ans. (B)	20. Ans. (C)
21. Ans. (D)	22. Ans. (C)	23. Ans. (B)	24. Ans. (A)	25. Ans. (C)
26. Ans. (A)	27. Ans. (A)	28. Ans. (A)	29. Ans. (D)	30. Ans. (A)
31. Ans. (D)	32. Ans. (D)	33. Ans. (B)	34. Ans. (C)	35. Ans. (D)
36. Ans.(D)	37. Ans.(C)	38. Ans.(B)		

**EXERCISE # JEE-MAINS**

1. Ans. (4)	2. Ans. (3)	3. Ans. (4)	4. Ans. (3)	5. Ans. (4)
6. Ans. (1)	7. Ans. (1)	8. Ans. (3)	9. Ans. (3)	10. Ans.(4)
11. Ans.(3)	12. Ans.(2)	13. Ans.(2)	14. Ans.(3)	15. Ans.(4)
16. Ans.(3)	17. Ans.(3)	18. Ans.(4)	19. Ans.(3)	20. Ans.(4)



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ORGANIC

E

**CHEMISTRY**







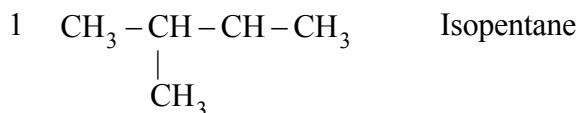
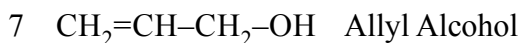
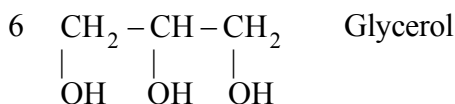
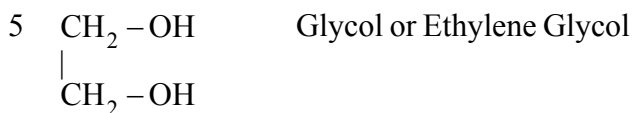
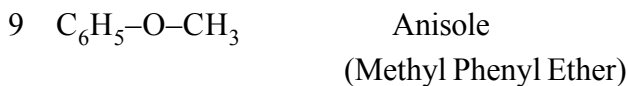
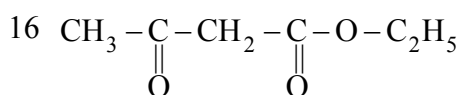
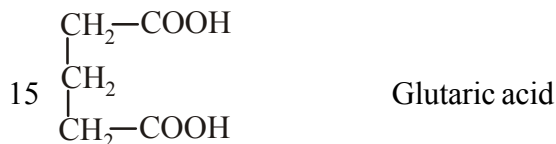
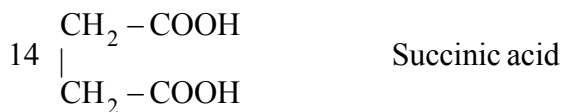
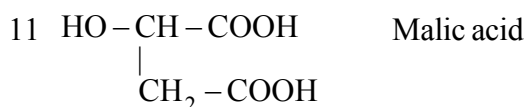
# Chapter Contents

# 01

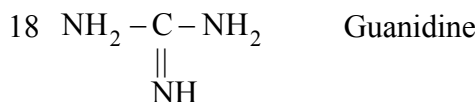
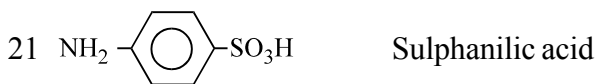
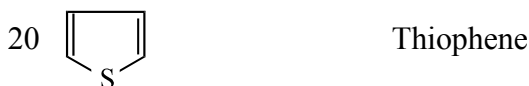
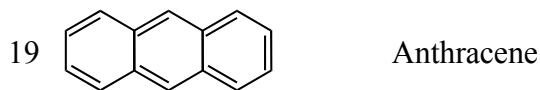
## NOMENCLATURE AND COMMON NAMES

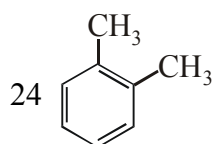
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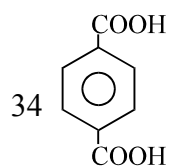
**-ESSENTIAL COMMON NAMES-****ALKANE****ALKENE****ALKYL HALIDE****ALCOHOL****ETHER****KETONE****CARBOXYLIC ACID**

Aceto Acetic Ester (AAE)  
or Ethyl Aceto Acetate

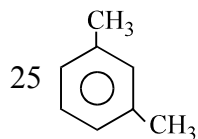
**N-DERIVATIVES****AROMATIC COMPOUNDS**



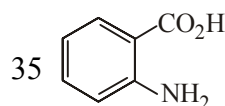
o-xylene



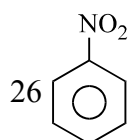
Terephthalic acid



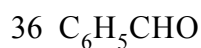
m-xylene



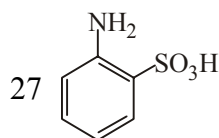
Anthranilic acid (o-aminobenzoic acid)



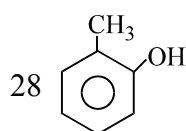
Nitrobenzene (oil of mirbane)



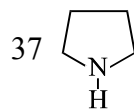
Benzaldehyde



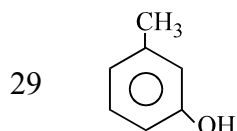
Orthanilic Acid

**HETROCYCLIC COMPOUNDS**

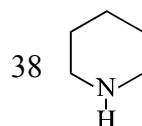
o-Cresol



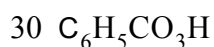
Pyrrolidine



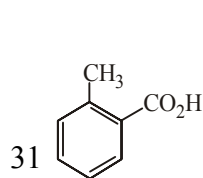
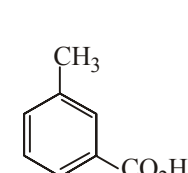
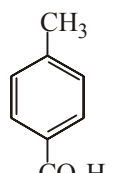
m-Cresol



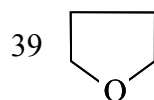
Piperidine



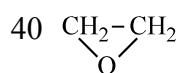
Perbenzoic acid

o-toluic acid,  
m.p. 105°Cm-toluic acid,  
m.p. 111°Cp-toluic acid,  
m.p. 180°C

Toluic acids

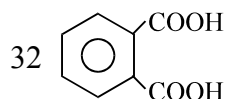


Tetrahydrofuran (THF)

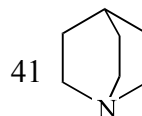


Oxirane or Ethylene Oxide or

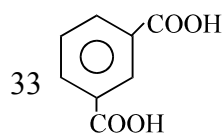
Oxo Cyclo Propane



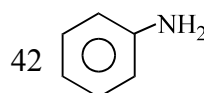
Phthalic acid



Quinuclidine



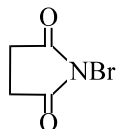
Isophthalic acid



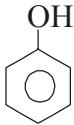
Aniline

## SOME REAGENTS

- 43 Grignard's reagent  $\text{RMgX}$
- 44 NBS N-Bromosuccinimide

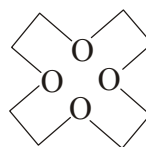


## POLAR PROTIC SOLVENTS

- 45  $\text{H}-\text{O}-\text{H}$  Water
- 46  $\text{R}-\text{O}-\text{H}$  Alcohol
- 47  Phenol
- 48  $\text{CH}_3-\text{C}-\text{OH}$   
 $\parallel$   
 $\text{O}$  Acetic acid
- 49  $\text{HF}$  Hydrogen Fluoride
- 50  $\text{NH}_3$  Ammonia

## POLAR APROTIC SOLVENTS

- 51 DMS Dimethyl sulphide  $\text{CH}_3-\text{S}-\text{CH}_3$
- 52 DMSO Dimethyl sulphoxide  $\text{Me}_2\text{S}=\text{O}$
- 53 HMPT Hexamethylphosphoramide  
or  
HMPTA  $\text{O}=\text{P}-(\text{NMe}_2)_3$
- 54 DMF Dimethyl formamide  
 $\text{H}-\text{C}-\text{NMe}_2$   
 $\parallel$   
 $\text{O}$
- 55 Crown ethers Cyclic polyethers



(12 - C - 4)

**-DESIRABLE COMMON NAMES-****ALKANES**

- 1  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{CH} - \text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$  Triptane
- 2  $\begin{array}{c} -\text{CH}_2 - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$  Isopentyl Group

**ALKENES**

- 3  $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$   $\alpha$ -Butylene
- 4  $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$   $\beta$ -Butylene
- 5  $\begin{array}{c} \text{CH}_3 - \text{C} = \text{CH}_2 \\ | \\ \text{CH}_3 \end{array}$  Iso Butylene

**ALKYNES**

- 6  $\text{HC} \equiv \text{CH}$  Purified Acetylene or Norcelyne
- 7  $\text{CH}_3 - \text{C} \equiv \text{CH}$  Allylene

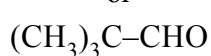
**ETHER**

- 8  $\text{CH}_3\text{CH}(\text{OCH}_3)_2$  Methylal

**ALDEHYDE**

- 9  $\begin{array}{c} \text{CHO} \\ | \\ \text{COOH} \end{array}$  Glyoxalic acid

- 10  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{CHO} \\ | \\ \text{CH}_3 \end{array}$  Pivaldehyde



- 11  $(\text{CH}_3)_2\text{CHCHO}$  Isobutyraldehyde

- 12  $\begin{array}{c} \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \\ || \quad || \\ \text{O} \quad \text{O} \end{array}$  Dimethyl Glyoxal

- 13  $\begin{array}{c} \text{CH}_3 - \text{C} - \text{C} - \text{H} \\ || \quad || \\ \text{O} \quad \text{O} \end{array}$  Methyl Glyoxal or Pyruvialdehyde

**KETONE**

- 14  $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} = \text{CH} - \text{C} - \text{CH} = \text{C} \\ \diagup \quad || \quad \diagdown \\ \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \end{array}$  Phorone

- 15  $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} = \text{CH} - \text{C} - \text{CH}_3 \\ \diagup \quad || \\ \text{CH}_3 \quad \text{O} \end{array}$  Mesityl Oxide

- 16  $\text{H}_2\text{C} = \text{C} = \text{O}$  Ketene

**CARBOXYLIC ACID**

- 17  $\text{CH}_3 - \text{CO} - \text{COOH}$  Pyruvic Acid

- 18  $\begin{array}{c} \text{C}_6\text{H}_5 - \text{CH} - \text{COOH} \\ | \\ \text{OH} \end{array}$  Mandelic Acid

- 19  $\text{NH}_2\text{COOH}$  Carbamic Acid  
(Amino formic Acid)

- 20  $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$  Oxalic acid

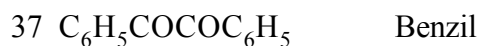
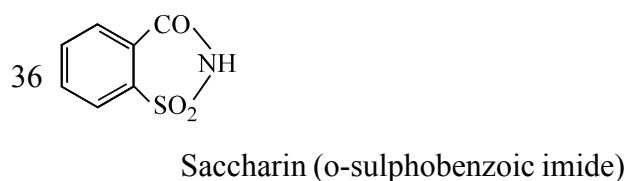
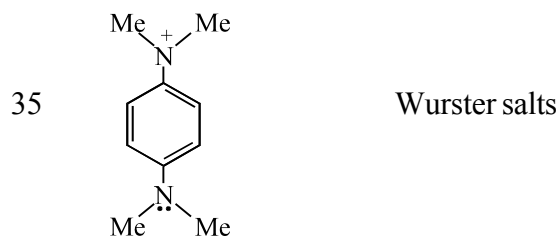
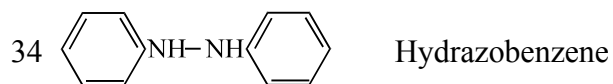
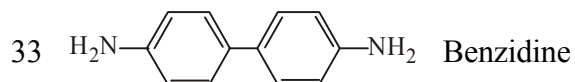
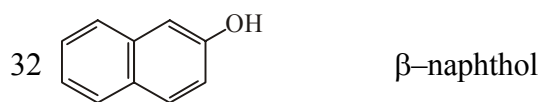
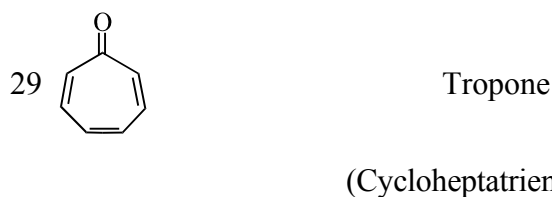
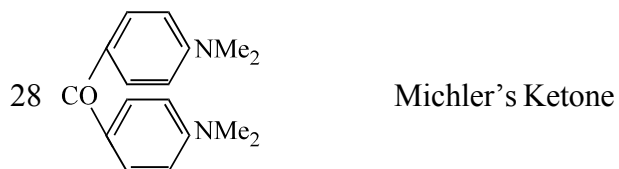
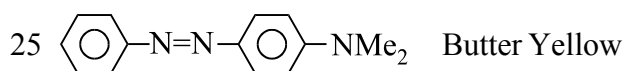
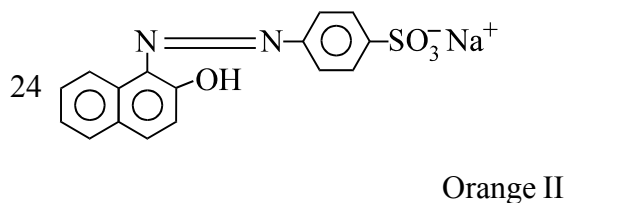
**ACID DERIVATIVES**

- 21  $\begin{array}{c} \text{Cl} - \text{C} - \text{C} - \text{Cl} \\ || \quad || \\ \text{O} \quad \text{O} \end{array}$  Oxalyl Chloride

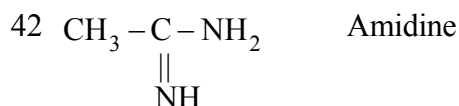
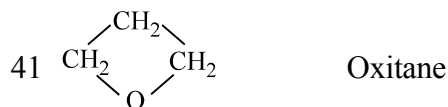
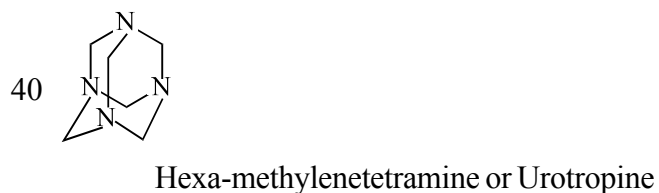
- 22  $\text{NH}_2\text{COONH}_4$  Ammonium Carbamate

- 23  $\begin{array}{c} \text{NH}_2 - \text{C} - \text{C} - \text{NH}_2 \\ || \quad || \\ \text{O} \quad \text{O} \end{array}$  Oxanamide

AROMATIC COMPOUNDS

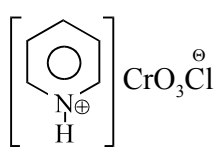
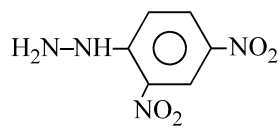


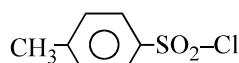
HETEROCYCLIC COMPOUNDS



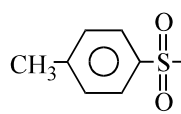
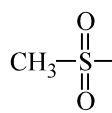
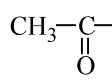
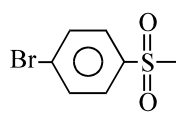
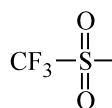


## SOME REAGENTS

43 LAH	Lithium aluminium hydride : $\text{LiAlH}_4$
44 SBH	Sodium borohydride $\text{NaBH}_4$
45 PCC	Pyridinium chlorochromate 
46 Raney Nickel	Ni–Al alloy
47 Wilkinson's catalyst	Tris(Triphenylphosphine) chlororhodium (I) $(\text{PPh}_3)_3\text{RH}^+\text{Cl}^-$
48 Bayer's reagent	1% dil. alkaline aq.sol. of $\text{KMnO}_4$
49 Braddy's reagent 2,4 DNP	
50 Liemieux reagent	$\text{NaIO}_4 + \text{dil.alk.KMnO}_4$

51 TEL	Tetra ethyl lead
52 Gillman's reagent	$\text{R}_2\text{CuLi}/[\text{R}_2\text{Cu}]^- \text{Li}^+$
53 Tollen's reagent	alk. sol. of $\text{AgNO}_3$
54 Fehling's reagent	alk. sol. of $\text{CuSO}_4$
55 Hinsberg's reagent	

## SOME GROUPS

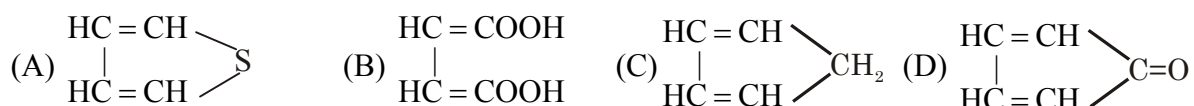
56 Ts	Tosyl	
57 Ms	Mesyl	
58 Ac	Acyl	
59 Bs	Brosyl	
60 Tf	Triflate	



- Q.8 The molecular formula of the first member of the family of alkenynes and its name is given by the set
- (A)  $C_3H_6$ , Alkene (B)  $C_5H_6$ , Pent-1-en-3-yne  
(C)  $C_6H_8$ , Hex-1-en-5-yne (D)  $C_4H_4$ , Butenyne

NC0008

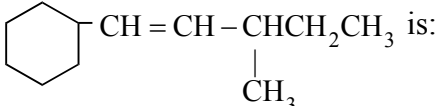
- Q.9 Which of the following is a heterocyclic compound :



NC0009

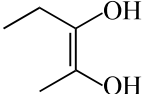
- Q.10 The correct IUPAC name of the compound  $CH_3 - CH_2 - \overset{\overset{CH_3}{|}}{C} = C - \underset{\underset{C_2H_5}{|}}{CH} - \overset{\overset{CH_3}{|}}{C} - CH_2 - CH_2 - CH_3$  :
- (A) 5-Ethyl-3, 6-dimethyl non-3-ene (B) 5-Ethyl-4, 7-dimethyl non-3-ene  
(C) 4-Methyl-5, 7-diethyl oct-2-ene (D) 2,4-Ethyl-5-methyl oct-2-ene

NC0010

- Q.11 The IUPAC name of  is:

- (A) 1-Cyclohexyl-3-methyl pent-1-ene (B) 3-Methyl-5-cyclohexyl pent-1-ene  
(C) 1-Cyclohexyl-3-ethyl but-1-ene (D) 1-Cyclohexyl-3,4-dimethyl but-1-ene

NC0011

- Q.12 IUPAC name of  is:

- (A) But-2-ene-2,3-diol (B) Pent-2-ene-2,3-diol  
(C) 2-Methylbut-2-ene-2,3-diol (D) Pent-3-ene-3,4-diol

NC0012

- Q.13 IUPAC name of  $CH_2=CH - CN$  is:

- (A) Ethenenitrile (B) Vinyl cyanide (C) Cyano ethene (D) Prop-2-enenitrile

NC0013

- Q.14 The IUPAC name of  $CH_3 CH_2 - \underset{\underset{CH_3}{|}}{N} - CH_2 CH_3$  is:

- (A) N-Methyl-N-ethyl ethanamine (B) Diethyl methanamine  
(C) N-Ethyl-N-methyl ethanamine (D) Methyl diethyl ethanamine

NC0014

Q.15 The IUPAC name of acetyl acetone is :

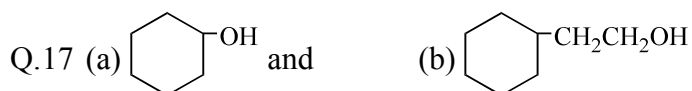
- (A) Pentane-2,5- dione (B) Pentane -2,4-dione  
(C) Hexane-2,4-dione (D) Butane-2,4-dione

NC0015

Q.16 When vinyl & allyl are joined each other, we get

- (A) Conjugated alkadiene (B) cumulative alkadiene  
(C) Isolated alkadiene (D) Allenes

NC0016



True statement for the above compounds is :

- (A) (a) is phenol while (b) is alcohol (B) Both (a) and (b) are primary alcohol  
(C) (a) is primary and (b) is secondary alcohol (D) (a) is secondary and (b) is primary alcohol

NC0017

Q.18 The IUPAC name of the following structure  $(\text{CH}_3)\text{C}.\text{C}.\text{C}.\text{C}.\text{C}.\text{C}(\text{CH}_3)\text{CH}(\text{CH}_3)$  is:

- (A) 3-Methylhex-4-yn-2-ene (B) 3-Methylhex-2-en-4-yne  
(C) 4-Methylhex-4-en-4-yne (D) All are correct

NC0018

Q.19 The IUPAC name of the following structure is  $[\text{CH}_3\text{CH}(\text{CH}_3)]_2 \text{C}(\text{CH}_2\text{CH}_3)\text{C}(\text{CH}_3) \text{C}(\text{CH}_2\text{CH}_3)_2$

- (A) 3,5-Diethyl-4,6-dimethyl-5-[1-methylethyl]hept-3-ene  
(B) 3,5-Diethyl-5-isopropyl-4,6-dimethylhept-2-ene  
(C) 3,5-Diethyl-5-propyl-4,6-dimethylhept-3-ene  
(D) None of these

NC0019

Q.20 The correct IUPAC name of  $\text{CH}_3 - \text{CH}_2 - \text{C} - \text{COOH}$  is:



- (A) 2-Methyl butanoic acid (B) 2-Ethylprop-2-enoic acid  
(C) 2-Carboxybutene (D) None of the above

NC0020

Q.21 The correct IUPAC name of 2-ethylpent-3-yne is:

- (A) 3-Methyl hex-4-yne (B) 4-Ethyl pent-2-yne  
(C) 4-methyl hex-2 yne (D) None of these

NC0021

Q.22 All the following IUPAC names are correct except:

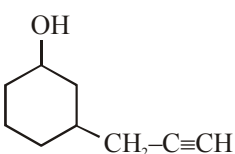
- (A) 1-Chloro-1-ethoxy propane (B) 1-Amino-1-ethoxypropane  
(C) 1-Ethoxy-2-propanol (D) 1-Ethoxy-1-propanamine

NC0022

Q.23 The IUPAC name of the compound  $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHC}\equiv\text{CCH}_3$  is:

- (A) Octa-4,6-diene-2-yne (B) Octa-2,4-diene-6-yne  
(C) Oct-2-yne-4,6-diene (D) Oct-6-yne-2,4-diene

NC0023

Q.24 The correct IUPAC name of 

- (A) 3-Cyclohexanol Propyne (B) 3-[3-Hydroxy Cyclohexyl] Propyne  
(C) 3-Propynyl Cyclohexanol (D) 3-(2-propynyl) Cyclohexanol

NC0024

Q.25 The IUPAC name of  $\beta$ -ethoxy- $\alpha$ -hydroxy propionic acid (trivial name) is:


- (A) 1,2-Dihydroxy-1-oxo-3-ethoxy propane (B) 1-Carboxy-2-ethoxy ethanol  
(C) 3-Ethoxy-2-hydroxy propanoic acid (D) All above

NC0025

Q.26 As per IUPAC rules, which one of the following groups, will be regarded as the principal functional group ?

- (A)  $\text{—C}\equiv\text{C—}$  (B)  $\text{—OH}$  (C)  $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$  (D)  $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—H}$

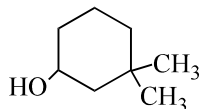
NC0026

Q.27 The IUPAC name of the compound  is :

- (A) 4-Prop-1-enyl hepta-1,6-diene (B) 4-Propylidene hepta-1,6-diene  
(C) 4-Propenyl hepta-1,6-diene (D) 4-[Prop-2-enyl] hepta-1,6-diene

NC0027

Q.28 The IUPAC name of the given compound is:



- (A) 1,1-Dimethyl-3-hydroxy cyclohexane (B) 3,3-Dimethyl-1-hydroxy cyclohexane  
(C) 3,3-Dimethylcyclohexanol (D) 1,1-Dimethylcyclohexan-3-ol

NC0028

Q.29 The IUPAC name of  $(C_2H_5)_2NCH_2CH(COCl)COOH$  is:



- (A) 2-Chloro-4-N-ethylpentanoic acid      (B) 2-Chloro-3-(N,N-diethyl amino)-propanoic acid  
 (C) 2-Chloro-2-oxo diethylamine      (D) 2-Chloro-2-carboxy-N-ethyl ethane

NC0029

Q.30 The IUPAC name of the compound is  $CH_3-CH(CH_3)-CH(Ph)-NH_2$

- (A) 1-Amino-1-phenyl-2-methyl propane      (B) 2-Methyl-1-phenyl propan-1-amine  
 (C) 2-Methyl-1-amino-1-phenyl propane      (D) 1-Isopropyl-1-phenyl methyl amine

NC0030

Q.31 Which of the following compound is wrongly named ?

(A)  $CH_3CH_2CH_2CH(Cl)COOH$  ; 2-Chloro pentanoic acid

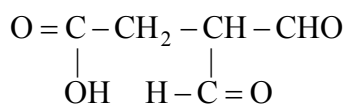
(B)  $CH_3C \equiv CCH(CH_3)COOH$  ; 2-Methyl hex-3-enoic acid

(C)  $CH_3CH_2CH=CHCOCH_3$  ; Hex-3-en-2-one

(D)  $CH_3-CH(CH_3)CH_2CH_2CHO$  ; 4-Methyl pentanal

NC0031

Q.32 The correct IUPAC name of the following compound is:



- (A) 3,3-Diformylpropanoic acid      (B) 3-Formyl-4-oxo-butanoic acid  
 (C) 3,3-Dioxo propanoic acid      (D) 3,3-Dicarbaldehyde propanoic acid

NC0032

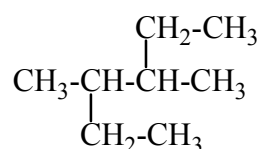
Q.33 The correct IUPAC name of compound  $CH_3-CH_2-C(=O)-CH(CN)-CHO$  is :



- (A) 2-Cyano-3-oxopentanal      (B) 2-Formyl-3-oxopentanenitrile  
 (C) 2-Cyanopentane-1,3-dione      (D) 1,3-Dioxo-2-cyanopentane

NC0033

Q.34 IUPAC name of compound



- (A) 2, 3-diethyl butane (B) 2-ethyl-3-methyl pentane  
(C) 3-methyl-2-ethyl pentane (D) 3,4-dimethyl hexane

NC0034

Q.35 The IUPAC name of compound  $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-CH(CH}_3\text{)-CH(CH}_3\text{)-CHO}$  is:

- (A) 3,5-Dimethyl-4-Formyl pentanone (B) 1-Isopropyl-2-methyl-4-oxo butanal  
(C) 2-Isopropyl-3-methyl-4-oxo pentanal (D) None of the above

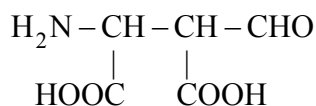
NC0035

Q.36 The IUPAC name of compound  $\text{CH}_3\text{-}\overset{\text{HO-C=O}}{\text{C}}\text{=}\overset{\text{CH}_3}{\text{C}}\text{-}\overset{\text{NH}_2}{\text{C}}\text{-H}$  is :

- (A) 2-Amino-3-chloro-2-methylpent-2-enoic acid (B) 3-Amino-4-chloro-2-methylpent-2-enoic acid  
(C) 4-Amino-3-chloro-2-methylpent-2-enoic acid (D) All of the above

NC0036

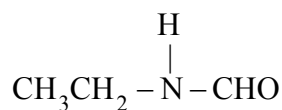
Q.37 The IUPAC name of the structure is:



- (A) 3-Amino-2-formyl butane-1, 4-dioic acid (B) 3-Amino-2, 3-dicarboxy propanal  
(C) 2-Amino-3-formyl butane-1, 4-dioic acid (D) 1-Amino-2-formyl succinic acid

NC0037

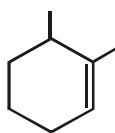
Q.38 One among the following is the correct IUPAC name of the compound



- (A) N-Formyl aminoethane (B) N-Ethyl formyl amine  
(C) N-Ethyl methanamide (D) Ethylamino methanal

NC0038

Q.39 The IUPAC name of the structure is :



- (A) 1,2-Dimethyl-Cyclohexane (B) 1,6-Dimethyl-Cyclohexene  
(C) 1,2-Dimethyl-Cyclohex-2-ene (D) 2,3-Dimethyl-Cyclohexane

NC0039

Q.40 The IUPAC name of  $C_6H_5CH=CH-COOH$  is :

- (A) Cinnamic acid (B) 1-Phenyl-2-carboxy ethane  
(C) 3-Phenyl prop-2-enoic acid (D) Dihydroxy-3-phenyl propionic acid

NC0040

Q.41 The IUPAC name of  $BrCH_2-CH(CO-CH_2-CH_2CH_3)-CONH_2$  is:

- (A) 2-Bromomethyl-3-oxohexanamide (B) 1-Bromo-2-amino-3-oxohexane  
(C) 1-Bromo-2-amino-n-propyl ketone (D) 3-Bromo-2-propyl propanamide

NC0041

Q.42 IUPAC name will be  $CH_2-CH-CH_2$   
                  |      |      |  
                  CN   CN   CN

- (A) 1,2,3-Tricyano propane (B) Propane-1,2,3- trinitrile  
(C) 1,2,3-Cyano propane (D) Propane-1,2,3-tricarbonitrile

NC0042

Q.43 The IUPAC name of compound is:

- (A) 3-Carbonyl methoxy -5- Ethanoyl oxy cyclohexanoic acid  
(B) 3-Ethanoyl oxy -5- Methoxy carbonyl cyclohexane carboxylic acid  
(C) 5-Ethanoyl oxy -5- Methoxy carbonyl cyclohexanoic acid  
(D) 3-Methoxy carbonyl -5- Ethanoyl oxy cyclohexane carboxylic acid

NC0043



Q.44 The IUPAC name of  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$  is:

- (A) 1-Acetoxy acetic acid (B) 2-Acetoxy ethanoic acid  
(C) 2-Ethanoyloxyacetic acid (D) 2-Ethanoyloxyethanoic acid

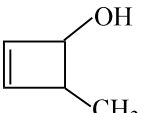
NC0044

Q.45  $\text{CH}_3-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{COOH}$

The correct IUPAC systematic name of the above compound is:

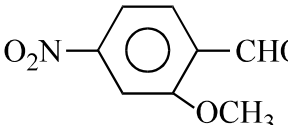
- (A) 2-Acetoxy ethanoic acid (B) 2-Methoxy carbonyl ethanoic acid  
(C) 3-Methoxy formyl ethanoic acid (D) 2-Methoxy formyl acetic acid

NC0045

Q.46 The IUPAC name of  is:

- (A) 3-Methyl cyclobut-1-ene-2-ol (B) 4-Methyl cyclobut-2-ene-1-ol  
(C) 4-Methyl cyclobut-1-ene-3-ol (D) 2-Methyl cyclobut-3-ene-1-ol

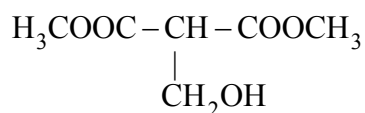
NC0046

Q.47 The IUPAC name of  is:

- (A) 2-Methoxy-4-nitro benzaldehyde (B) 4-Nitro anisaldehyde  
(C) 3-Methoxy-4-formyl nitro benzene (D) 2-Formyl-4-nitro anisole

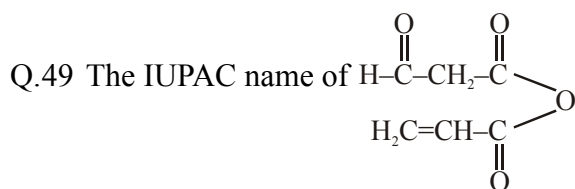
NC0047

Q.48 The IUPAC name of compound



- (A) 2-(Hydroxy methyl) methyl propanedioate (B) Methyl-2-(hydroxy methyl) propanedioate  
(C) 2-(Hydroxy methyl) dimethyl propanedioate (D) None of these

NC0048



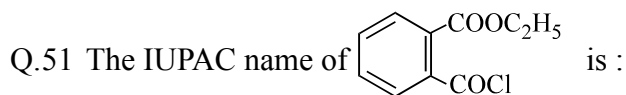
- (A) 2-Formyl ethanoic propanoic Anhydride (B) 2-Oxo-propanoic prop-2-enoic Anhydride  
 (C) Prop-2-enoic-2-formyl propanoic Anhydride (D) 2-Formyl ethanoic prop-2-enoic Anhydride

**NC0049**



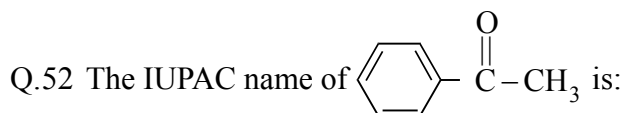
- (A) 4,4-Di(formylmethyl) butanal (B) 2-(Formylmethyl) butane-1, 4-dicarbaldehyde  
 (C) Hexane-3-acetal-1, 6-dial (D) 3-(Formylmethyl) hexane-1, 6-dial

**NC0050**



- (A) 2-Chlorocarbonyl ethylbenzoate (B) 2-Carboxyethyl benzoyl chloride  
 (C) Ethyl-2-(chlorocarbonyl)benzoate (D) Ethyl-1-(chlorocarbonyl)benzoate

**NC0051**



- (A) Phenyl ethanone (B) Methyl phenyl ketone  
 (C) Acetophenone (D) Phenyl methyl ketone

**NC0052**

Q.53 Structural formula of isopropyl methanoate is :

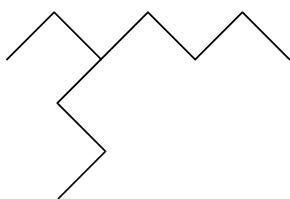
- (A)  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$  (B)  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$   
 (C)  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}_2}$  (D)  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$

**NC0053**

## EXERCISE # O-II

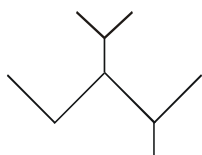
Give the IUPAC names for each of the following :

Q.1



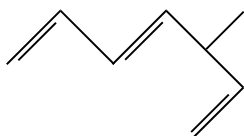
NC0054

Q.2



NC0055

Q.3



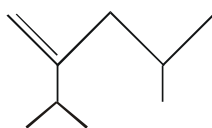
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Q.4



NC0057

Q.5



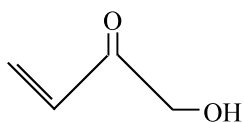
NC0058

Q.6



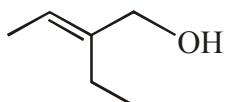
NC0059

Q.7



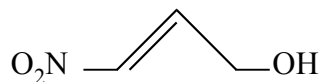
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Q.8



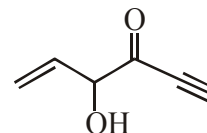
NC0061

Q.9



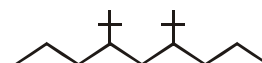
NC0062

Q.10



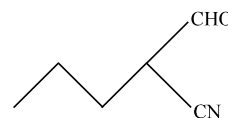
NC0063

Q.11



NC0064

Q.12



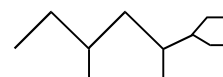
NC0065

Q.13



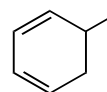
NC0066

Q.14



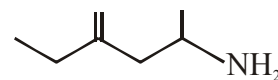
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Q.15



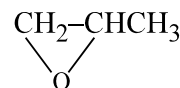
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Q.16



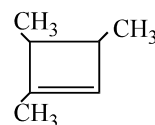
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Q.17

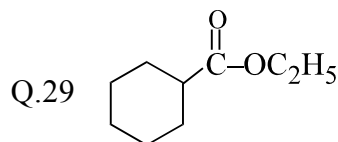
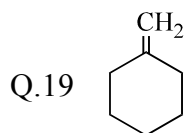


NC0070

Q.18

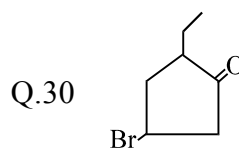
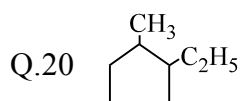


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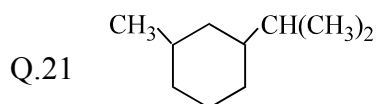
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NC0082

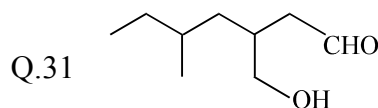


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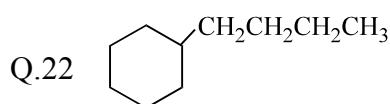
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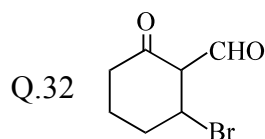
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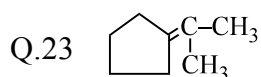
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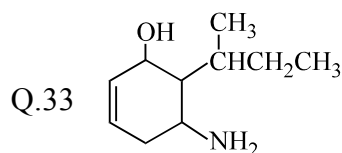
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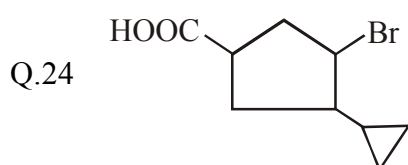
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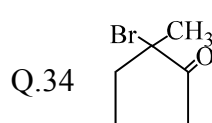
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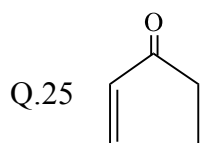
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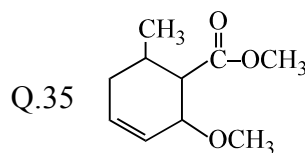
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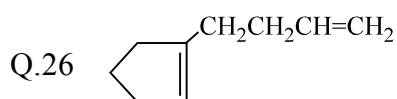
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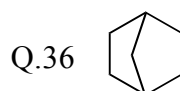
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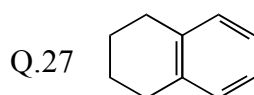
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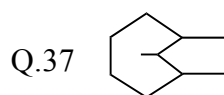
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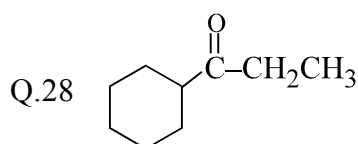
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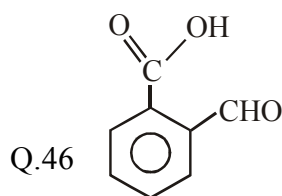
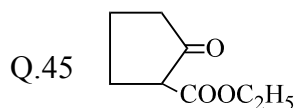
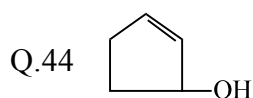
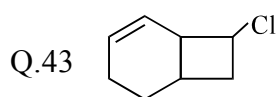
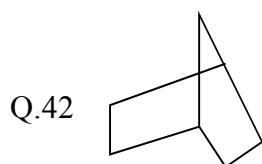
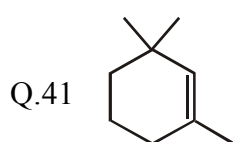
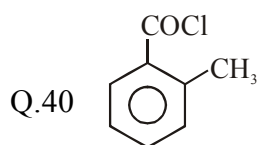
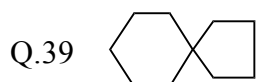
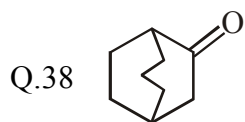
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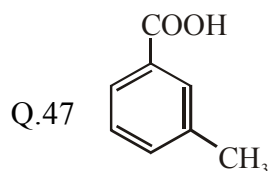
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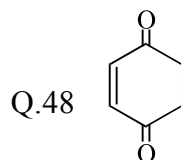
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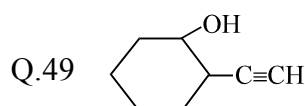
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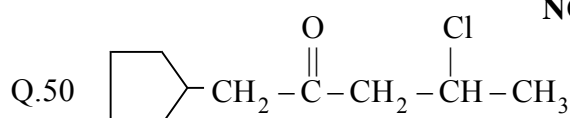
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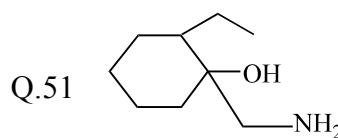
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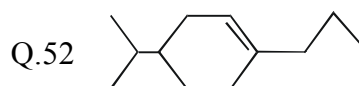
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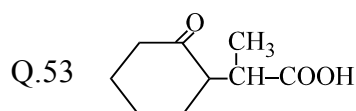
NC0095



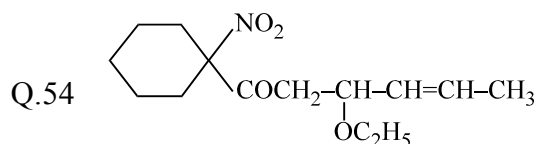
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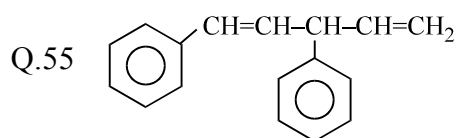
NC0097



NC0098



NC0099



NC0100

NC0101

NC0102

NC0103

NC0104

NC0105

NC0106

NC0107

NC0108

## EXERCISE # S-I

- Q.1 Which of the following pairs have absence of carbocyclic ring in both compounds?  
 (A) Pyridine, Benzene (B) Benzene, Cyclohexane  
 (C) Cyclohexane, Furane (D) Furane, Pyridine  
 NC0109
- Q.2 The commercial name of trichloroethene is:  
 (A) Westron (B) Perclene (C) Westrosol (D) Orlone  
 NC0110
- Q.3 A substance containing an equal number of primary, secondary and tertiary carbon atoms is:  
 (A) Mesityl Oxide (B) Mesitylene (C) Maleic acid (D) Malonic acid  
 NC0111
- Q.4 The IUPAC name of the compound Glycerine  $\text{CH}_2 - \text{CH} - \text{CH}_2$  is:  

$$\begin{array}{c} | \quad | \quad | \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$$
  
 (A) 1,2,3-Tri hydroxy propane (B) 3-Hydroxy pentane-1,5-diol  
 (C) 1,2,3-Hydroxy propane (D) Propane-1,2,3-triol  
 NC0112
- Q.5 Which of the following is crotonic acid:  
 (A)  $\text{CH}_2 = \text{CH} - \text{COOH}$  (B)  $\text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{COOH}$   
 (C)  $\text{CH}_3 - \text{CH} = \text{CH} - \text{COOH}$  (D)  $\begin{array}{c} \text{CH} - \text{COOH} \\ || \\ \text{CH} - \text{COOH} \end{array}$   
 NC0113
- Q.6 The group of heterocyclic compounds is:  
 (A) Phenol, Furane (B) Furane, Thiophene  
 (C) Thiophene, Phenol (D) Furane, Aniline  
 NC0114

## Q.7 Column - I

(Common Name)

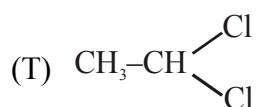
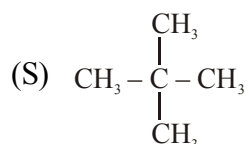
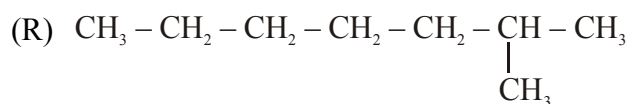
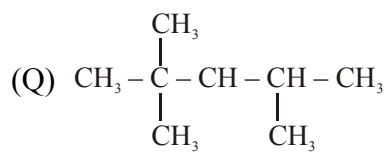
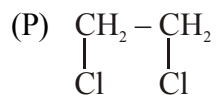
(A) Isooctane

(B) Neopentane

(C) Ethylidene chloride  
(Geminal dihalide)(D) Ethylene Dichloride  
(Vicinal dihalide)

## Column - II

(Structural formula)



## Q.8 Column - I

(Common Name)

(A) Acetone

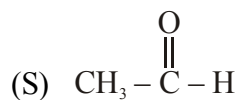
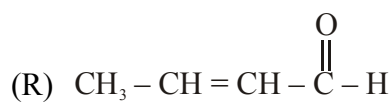
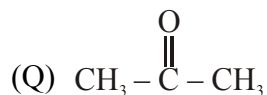
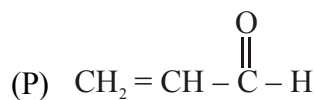
(B) Acetaldehyde

(C) Crotonaldehyde

(D) Acrolein

## Column - II

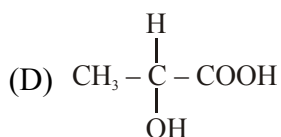
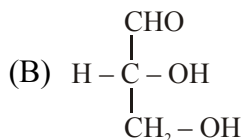
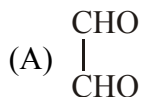
(Structural formula)



NC0115

**NC0116**

**Q.9 Column - I**  
**(Common Name)**



**Column - II**  
**(Structural formula)**

(P) Lactic acid (In milk)

(Q) Glyoxal

(R) Glyceraldehyde

(S) Glycine

(T) Glycerol

**NC0117**

**Q.10 Column - I**  
**(Common Name)**

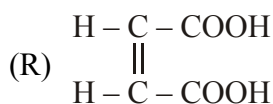
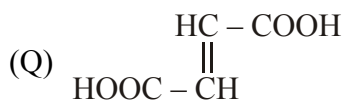
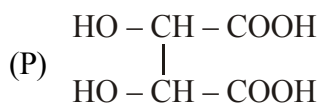
(A) Fumaric acid

(B) Adipic acid

(C) Maleic acid

(D) Tartaric acid

**Column - II**  
**(Structural formula)**

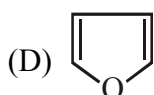
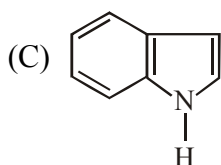
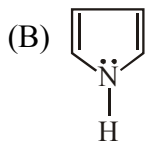
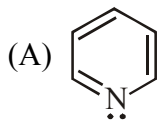


(S)  $\text{COOH}(\text{CH}_2)_4\text{COOH}$

**NC0118**



Q.11 Column - I  
(Common Name)



Column - II  
(Structural formula)

(P) Pyrrole

(Q) Furan

(R) Thiophene

(S) Indol

(T) Pyridine

NC0119

Q.12 Column - I  
(Common Name)

(A) p-Cresol

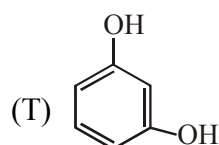
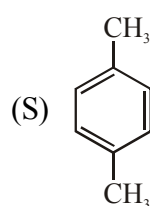
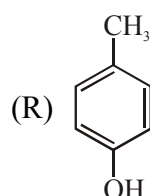
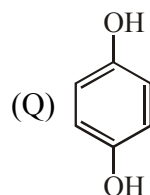
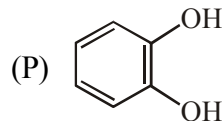
(B) p-Xylene

(C) Resorcinol

(D) Quinol

(E) Catechol

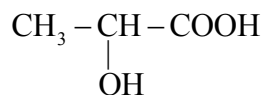
Column - II  
(Structural formula)



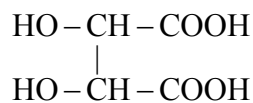
NC0120

Q.13 Which of the following is not correctly matched:

(A) Lactic acid



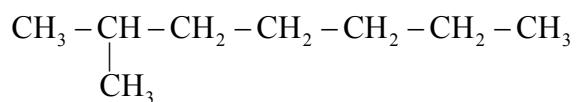
(B) Tartaric acid



(C) Pivaldehyde

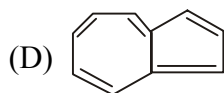
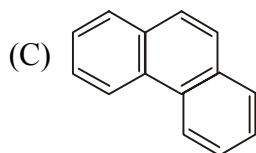
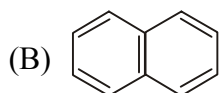
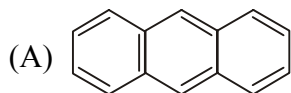


(D) Iso-octane



**NC0121**

Q.14 **Column - I**



**Column - II**

(P) Phenanthrene

(Q) Anthracene

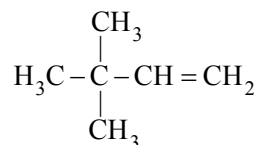
(R) Azulene

(S) Naphthalene

**NC0122**

## EXERCISE # JEE-ADVANCED &amp; MAINS

- Q.1 The IUPAC name of the compound having the formula is : [JEE 1984]



- (A) 3,3,3-trimethyl-1-propene  
 (B) 1,1,1-trimethyl-2-propene  
 (C) 3,3-dimethyl-1-butene  
 (D) 2,2-dimethyl-3-butene

NC0123

- Q.2 Write the IUPAC name of  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}\cdot\text{COOH}$  [JEE 1986]

NC0124

- Q.3 The IUPAC name of the compound  $\text{CH}_2=\text{CH}-\text{CH}(\text{CH}_3)_2$  is :

- (A) 1,1-dimethyl-2-propene (B) 3-methyl-1-butene  
 (C) 2-vinyl propane (D) None of the above

[JEE 1987]

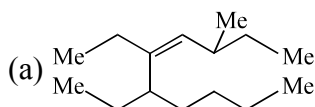
NC0125

- Q.4 The number of sigma and pi-bonds in 1-butene 3-yne are: [JEE 1989]

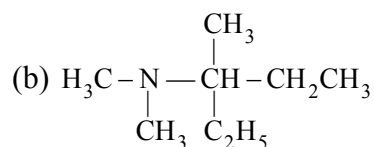
- (A) 5 sigma and 5 pi (B) 7 sigma and 3 pi  
 (C) 8 sigma and 2 pi (D) 6 sigma and 4 pi

NC0126

- Q.5 Write I.U.P.A.C name of following :



Me = methyl group



[JEE 1990]

NC0127

- Q.6 Write IUPAC name of succinic acid. [JEE 1994]

NC0128

- Q.7 The IUPAC name of  $\text{C}_6\text{H}_5\text{COCl}$  is

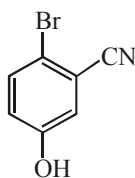
- (A) Benzoyl chloride (B) Benzene chloro ketone  
 (C) Benzene carbonyl chloride (D) Chloro phenyl ketone

[JEE 2006]

NC0129

Q.8 The IUPAC name of the following compound is

[JEE 2009]



(A) 4-Bromo-3-cyanophenol

(B) 2-Bromo-5-hydroxybenzonitrile

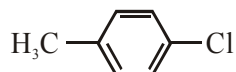
(C) 2-Cyano-4-hydroxybromobenzene

(D) 6-Bromo-3-hydroxybenzonitrile

NC0130

Q.9 The IUPAC name(s) of the following compound is(are) :

[JEE 2017]



(A) 4-methylchlorobenzene

(B) 4-chlorotoluene

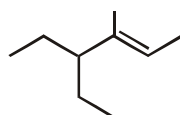
(C) 1-chloro-4-methylbenzene

(D) 1-methyl-4-chlorobenzene

NC0131

10. The IUPAC name of the following compound is :

[JEE Mains On\_line 2018]



(A) 4-methyl-3-ethylhex-4-ene

(B) 4,4-diethyl-3-methylbut-2-ene

(C) 3-ethyl-4-methylhex-4-ene

(D) 4-ethyl-3-methylhex-2-ene

NC0132

**ANSWER-KEY****EXERCISE # O-I**

Q.1	B	Q.2	B	Q.3	D	Q.4	D	Q.5	C	Q.6	B	Q.7	A
Q.8	D	Q.9	A	Q.10	A	Q.11	A	Q.12	B	Q.13	D	Q.14	C
Q.15	B	Q.16	C	Q.17	D	Q.18	B	Q.19	A	Q.20	B	Q.21	C
Q.22	B	Q.23	B	Q.24	D	Q.25	C	Q.26	D	Q.27	D	Q.28	C
Q.29	B	Q.30	B	Q.31	B	Q.32	B	Q.33	B	Q.34	D	Q.35	C
Q.36	B	Q.37	C	Q.38	C	Q.39	B	Q.40	C	Q.41	A	Q.42	D
Q.43	B	Q.44	D	Q.45	B	Q.46	B	Q.47	A	Q.48	B	Q.49	D
Q.50	D	Q.51	C	Q.52	A	Q.53	D						

**EXERCISE # O-II**

Q.1	4-Ethyl octane	Q.17	1,2-epoxy propane
Q.2	3-Ethyl-2,4-dimethyl pentane	Q.18	1,3,4-trimethyl cyclobutene
Q.3	5-Methyl hepta-1,3,6-triene	Q.19	Methylene cyclohexane
Q.4	Hepta-1,5-dien-3-yne	Q.20	1-ethyl-2-methylcyclopentane
Q.5	2-Isopropyl-4-methyl pent-1-ene or 4-Methyl-2-(methyl ethyl) pent-1-ene	Q.21	1-methyl-3-(methyl ethyl) cyclohexane or 1-isopropyl-3-methylcyclohexane
Q.6	3-Methoxypropene	Q.22	Butyl cyclohexane
Q.7	1-Hydroxybut-3-en-2-one	Q.23	Isopropylidenecyclopentane or 1-methyl ethylidene cyclopentane
Q.8	2-Ethylbut-2-en-1-ol	Q.24	3-Bromo-4-cyclopropyl cyclopentane carboxylic acid
Q.9	3-nitroprop-2-en-1-ol	Q.25	Cyclopent-2-en-1-one
Q.10	4-hydroxyhex-5-en-1-yn-3-one	Q.26	1-(3-butenyl) cyclopentene
Q.11	4,6-Bis-[1,1-Dimethyl ethyl] Nonane	Q.27	1,2-diethenyl cyclohexene
Q.12	2-Formyl pentane nitrile	Q.28	1-cyclohexyl-1-propanone
Q.13	2,2,6,7-tetramethylcatane	Q.29	Ethyl cyclohexanecarboxylate
Q.14	3-Ethyl-4,6-dimethyloctane	Q.30	4-Bromo-2-ethyl cyclopentanone
Q.15	5-Methyl cyclohexa-1,3-diene	Q.31	3-(hydroxymethyl)-5-methylheptanal
Q.16	4-Ethyl Pent-4-en-2-amine		

- Q.32** 2-Bromo-6-oxocyclohexanecarbaldehyde
- Q.33** 5-amino-6-(1-methyl propyl)  
cyclo hex-2-enol
- Q.34** 2-bromo-2-methyl cyclopentanone
- Q.35** Methyl-2-methoxy-6-methyl-3- cyclohexene  
carboxylate
- Q.36** Bicyclo(2,2,1)heptane
- Q.37** 9-methyl bicyclo(4,2,1) nonane
- Q.38** Bicyclo [3,2,2] Non-6-one
- Q.39** spiro(4,5) decane
- Q.40** 2-Methyl Benzoyl Chloride
- Q.41** 1,3,3-Trimethyl cyclohexene
- Q.42** Bicyclo(2,2,1) heptane
- Q.43** 8-chloro bicyclo(4,2,0) oct-2-ene
- Q.44** 2-cyclopenten-1-ol
- Q.45** Ethyl-2-oxo cyclo pentane carboxylate
- Q.46** 2-Formyl Benzoic acid
- Q.47** 3-Mthyl Benzoic acid
- Q.48** Cyclohex-2-en-1,4-dione
- Q.49** 2-ethynyl cyclohexanol
- Q.50** 4-chloro-1-cyclopentyl pentane-2-one
- Q.51** 1-Amino methyl-2-ethyl cyclohexanol
- Q.52** 4-isopropyl -1-propyl cyclohexene  
or 4-(methyl ethyl)-1-propyl cyclohexene
- Q.53** 2-(2-oxo-cyclohexyl) propanoic acid
- Q.54** 3-ethoxy-1(1-nitrocyclohexyl)-hex-4-en-1-one
- Q.55** 1,3-diphenyl-1,4-pentadiene

## EXERCISE # S-I

- Q.1 D    Q.2 C    Q.3 B    Q.4 D    Q.5 C    Q.6 B
- Q.7 (A) Q, (B) S, (C) T, (D) P    Q.8 (A) Q, (B) S, (C) R, (D) P
- Q.9 (A) Q, (B) R, (C) S, (D) P    Q.10 (A) Q, (B) S, (C) R, (D) P
- Q.11 (A) T, (B) P, (C) S, (D) Q    Q.12 (A) R, (B) S, (C) T, (D) Q, (E) P
- Q.13 D    Q.14 (A) Q, (B) S, (C) P, (D) R

## EXERCISE # JEE-ADVANCED &amp; MAINS

- Q.1 C
- Q.2  $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{COOH}$   
           5      4      3      2      1  
 2-pentene-1-oic acid and or 2-pentenoic acid
- Q.3 B    Q.4 B
- Q.5 (a) 5,6-diethyl-3-methyl-dec-4-ene  
 (b) N,N, 3-trimethyl-3-pentanamine
- Q.6 Butane-1,4-dioic acid    Q.7 C    Q.8 B    Q.9 B,C
10. D

# Chapter Contents

## 02

### ELECTRONIC DISPLACEMENT EFFECTS

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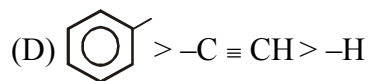
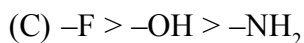
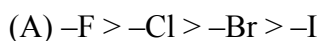




## ELECTRONIC DISPLACEMENT EFFECTS

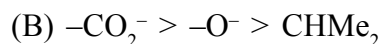
## EXERCISE # O-I

1. Which of the following is false order of -I effect ?



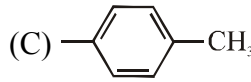
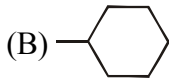
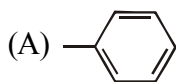
GC0001

2. What is the correct order of inductive effect ?



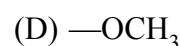
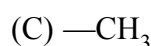
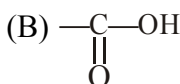
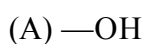
GC0002

3. Which of the following groups have +I effect :



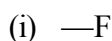
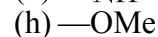
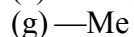
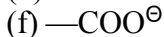
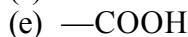
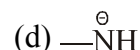
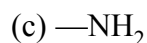
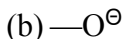
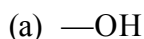
GC0003

4. Which of the following groups have -I effect :



GC0004

5. How many of the following groups have +I effect :



GC0005

6. Which of the following statements is (are) true about resonance.

- Resonance is an intramolecular phenomenon.
- Resonance involves delocalization of both  $\sigma$  and  $\pi$  electrons.
- Resonance involves delocalization of  $\pi$  electrons only.
- Resonance decreases potential energy of an acyclic molecule.
- Resonance has no effect on the potential energy of a molecule.
- Resonance is the only way to increase molecular stability.
- Resonance is not the only way to increase molecular stability.
- Any resonating molecule is always more stable than any non resonating molecule.
- The canonical structure explains all features of a molecule.
- The resonance hybrid explains all features of a molecule.
- Resonating structures are real and resonance hybrid is imaginary.
- Resonance hybrid is real and resonating structures are imaginary.
- Resonance hybrid is always more stable than all canonical structures.

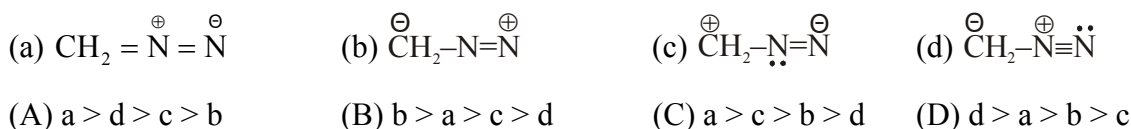
7. Which of the following statement is incorrect ?
- (A) Resonating structure are real & have real existence  
 (B) Equivalent contributing structures make resonance hybrid very stable.  
 (C) Contributing structures are hypothetical having no real existence  
 (D) Contributing structures are less stable than the resonance hybrid.

GC0007

8. Which of the following is most stable.
- (A) Conjugated alkadiene ( $\text{CH}_2 = \text{CH}-\text{CH} = \text{CH}_2$ )  
 (B) Isolated alkadiene ( $\text{CH}_2 = \text{CH}-\text{CH}_2-\text{CH} = \text{CH}_2$ )  
 (C) Cumulated alkadiene ( $\text{CH}_2 = \text{C} = \text{CH}_2$ )  
 (D) All are equally stable

GC0008

9. Arrange the following resonating structure according to their contribution towards resonance hybrid?

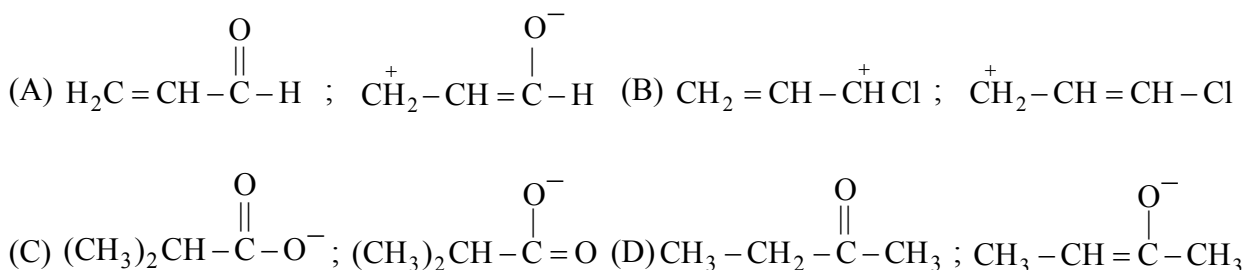


GC0024

10. A canonical structure will be more stable if
- (A) it involves cyclic delocalization of  $(4n + 2) \pi$  - electrons than if it involves acyclic delocalization of  $(4n + 2) \pi$  - electrons.  
 (B) it involves cyclic delocalization  $(4n) \pi$  - electrons than if it involves acyclic delocalization of  $(4n) \pi$  - electrons.  
 (C) +ve charge is on more electronegative atom than if +ve charge is on less electronegative atom provided atoms are in the same period.  
 (D) -ve charge is on more electronegative atom than if -ve charge is on less electronegative atom provided atoms are in the same period.

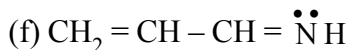
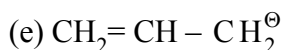
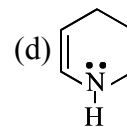
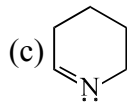
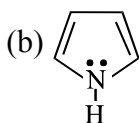
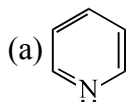
GC0010

11. Which one of the following pair of structures does not represent the phenomenon of resonance?



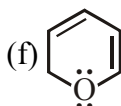
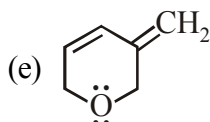
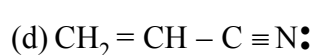
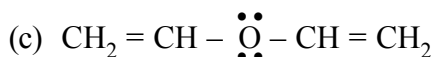
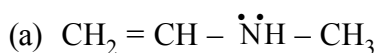
GC0011

12. In which of the following, lone-pair indicated is involved in resonance :



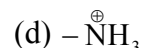
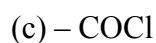
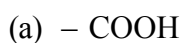
GC0012

13. In which of the following lone-pair indicated is not involved in resonance :



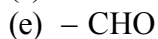
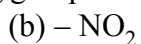
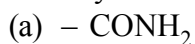
GC0013

14. Which of the following groups cannot participate in resonance with other suitable group :



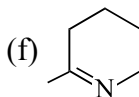
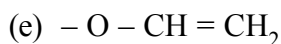
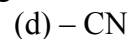
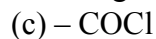
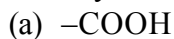
GC0014

15. Identify electron donating groups in resonance among the following :



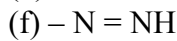
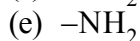
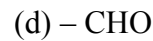
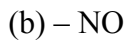
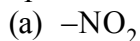
GC0015

16. Identify electron withdrawing groups in resonance among the following :



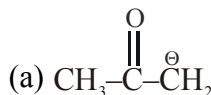
GC0016

17. Which of the following groups can either donate or withdraw a pair of electrons in resonance depending upon situation :

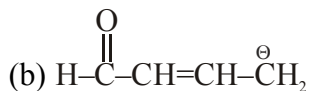


GC0017

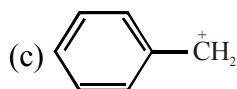
18. Draw the resonance forms to show the delocalization of charges in the following ions



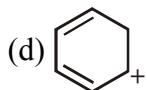
GC0018



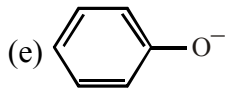
GC0018



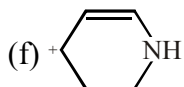
GC0018



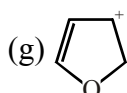
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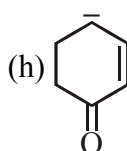
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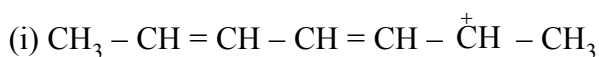
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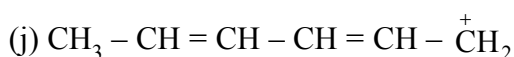
GC0019



GC0019

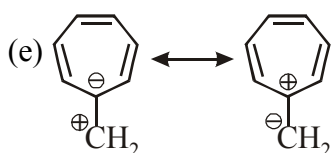
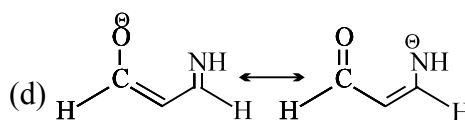
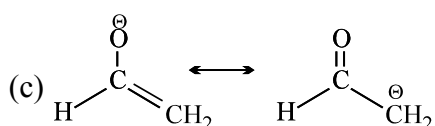
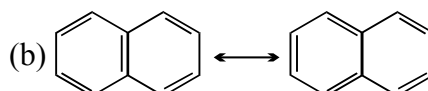
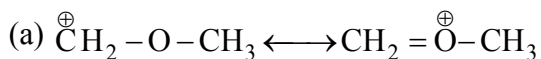


GC0019



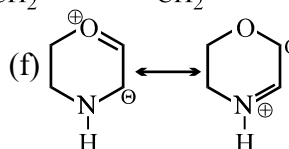
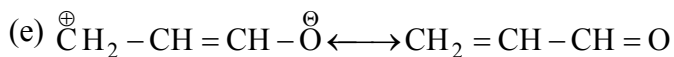
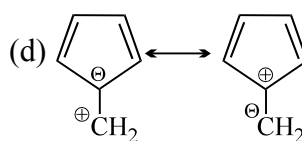
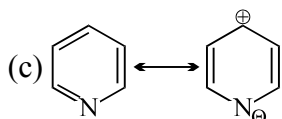
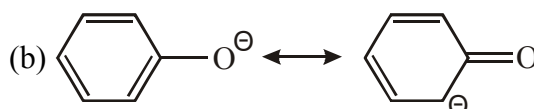
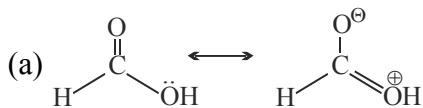
GC0019

19. Identify less stable canonical structure in each of the following pairs :



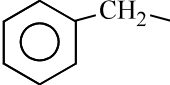
GC0020

20. Identify more stable canonical structure in each of the following pairs :

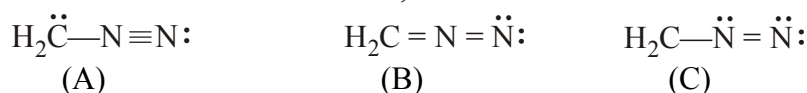


GC0021

21. Which of the following group can participate in resonance with other suitable group :

- (a)  $-\text{OH}$  GC0022  
 (b)  $-\text{CH}_2 - \bar{\text{C}}\text{H}_2$  GC0022  
 (c)  $-\text{CH}_2 - \overset{\oplus}{\text{C}}\text{H}_2$  GC0022  
 (d)  GC0022  
 (e)  GC0023  
 (f)  $-\text{BH}_2$  GC0023  
 (g)  $-\overset{\oplus}{\text{P}}\text{Ph}_3$  GC0023

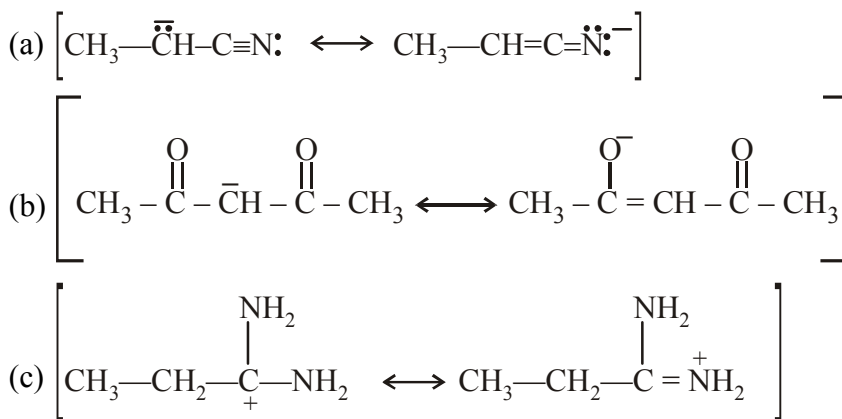
22. Consider structural formulas A, B and C:



- (a) Are A, B and C isomers, or are they resonance forms ?  
 (b) Which structures have a negatively charged carbon?  
 (c) Which structures have a positively charged carbon?  
 (d) Which structures have a positively charged nitrogen?  
 (e) Which structures have a negatively charged nitrogen?  
 (f) What is the net charge on each structure?  
 (g) Which is a more stable structure, A or B? Why?  
 (h) Which is a more stable structure, B or C? Why?

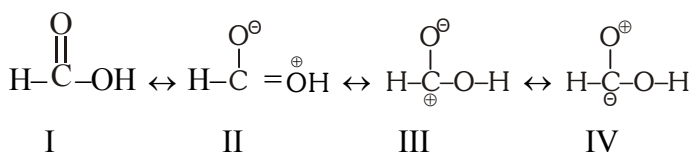
GC0009

23. In each of the following pairs of resonating structure which resonating structure is more stable :



GC0025

24. Formic acid is considered as a hybrid of the four structures

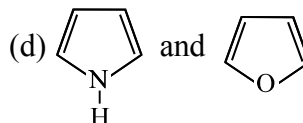
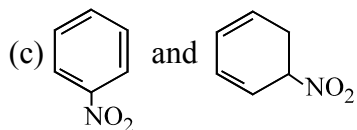
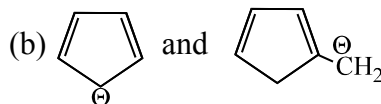
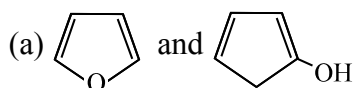


Which of the following order is correct for the stability of four contributing structures.

- (A) I > II > III > IV (B) I > II > IV > III (C) I > III > II > IV (D) I > IV > III > II

GC0026

25. In the given pair of compounds select the one in each pair having lesser resonance energy :



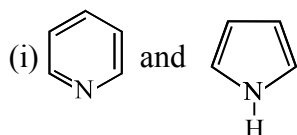
GC0027

26. Resonance energy of resonance hybrid of a molecule will be more if :

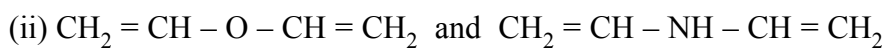
- (a) canonical structures are equivalent than if canonical structures are non-equivalent  
 (b) molecule is aromatic than if molecule is not aromatic.

GC0028

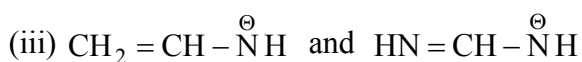
27. In the given pair of compounds select the one in each pair having higher resonance energy :



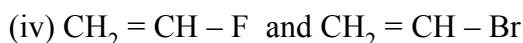
GC0029



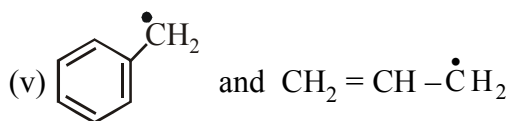
GC0029



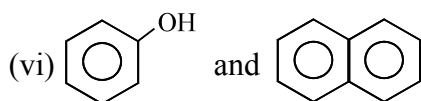
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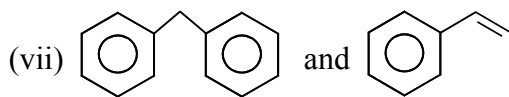
GC0029



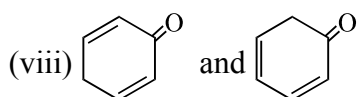
GC0029



GC0029



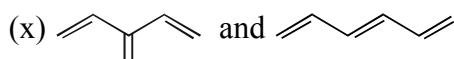
GC0030



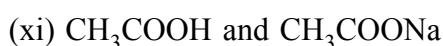
GC0030



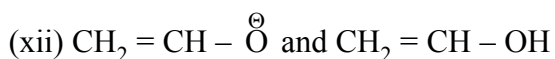
GC0030



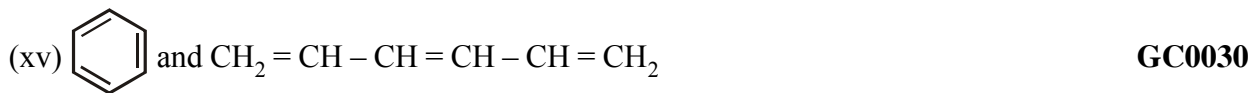
GC0030



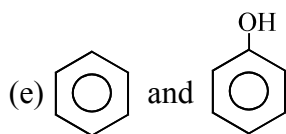
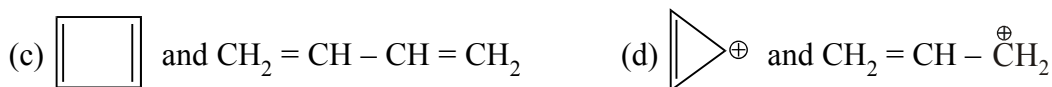
GC0030



GC0030

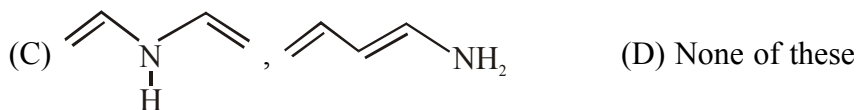


28. In the given pair of compounds select the one in each pair having lesser resonance energy :



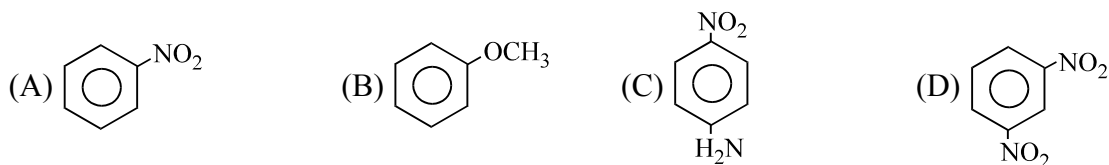
GC0031

29. In which of the following pairs first one is having more resonance energy than the second one -



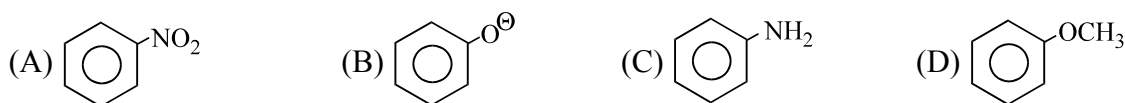
GC0032

30. In which of the following molecules  $\pi$  - electron density in ring is minimum :



GC0033

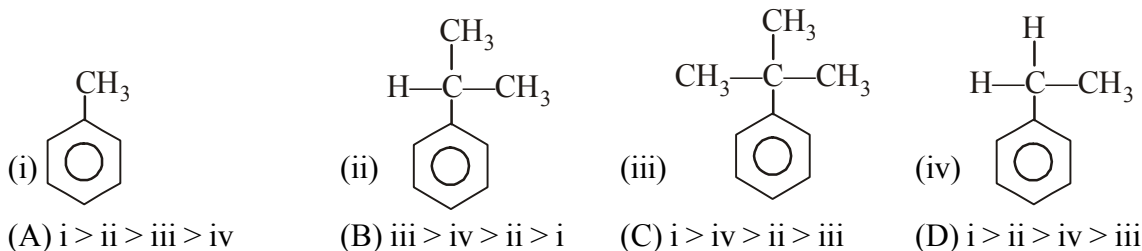
31. In which of the following molecules  $\pi$  - electron density in ring is maximum :



GC0034

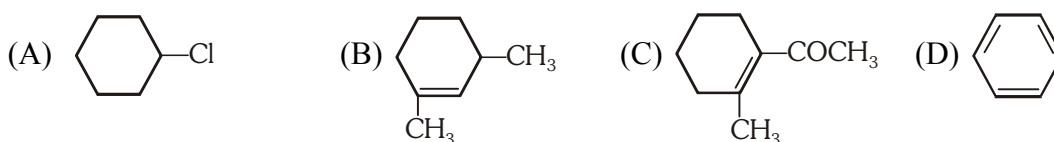


32. Arrange following compounds in decreasing order of reactivity of ring towards attack of electron deficient species -



GC0035

33. In which of the following molecule all the effect namely inductive, mesomeric & hyperconjugation operate:



GC0036

34. Which one of the following molecules has all the effect, namely inductive, mesomeric and hyperconjugative?



GC0037

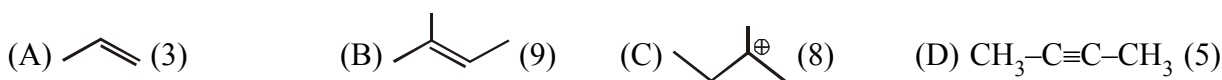
35. Select the correct statement.

- (i) Delocalisation of  $\sigma$ -electron is hyperconjugation.  
 (ii) Delocalisation of  $\pi$ -electron is resonance.  
 (iii) Permanent partial displacement of  $\sigma$ -electron is inductive effect.

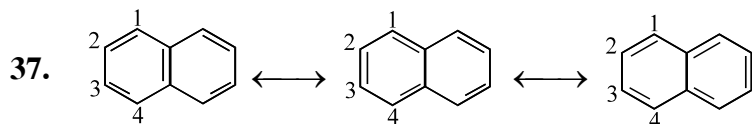
- (A) i & iii      (B) ii & iii      (C) i & ii      (D) i, ii, iii

GC0038

36. Which of the following compound is correctly matched with number of hyperconjugating structures (involving C—H bond):



GC0039

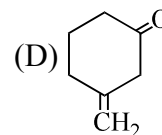
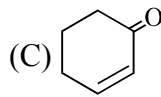
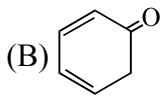
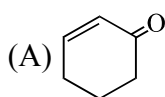


These are three canonical structures of naphthalene. Examine them and find correct statement among the following :

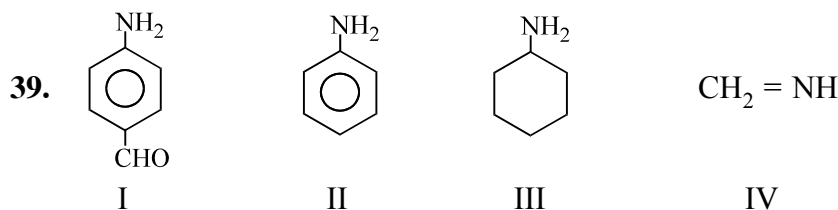
- (A) All C – C bonds are of same length      (B) C1 – C2 bond is shorter than C2 – C3 bond.  
 (C) C1 – C2 bond is longer than C2 – C3 bond      (D) None

GC0040

38. Which of the following has longest C – O bond :



GC0041

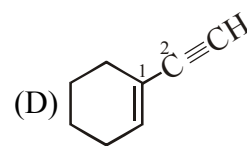
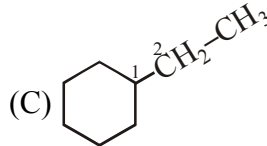
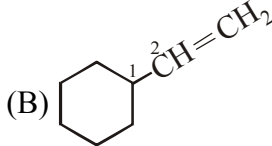
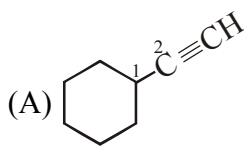


Among these compounds, the correct order of C – N bond lengths is :

- (A) IV > I > II > III      (B) III > I > II > IV      (C) III > II > I > IV      (D) III > I > IV > II

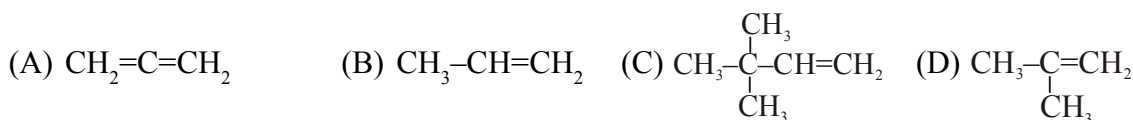
GC0042

40. C1 – C2 bond is shortest in



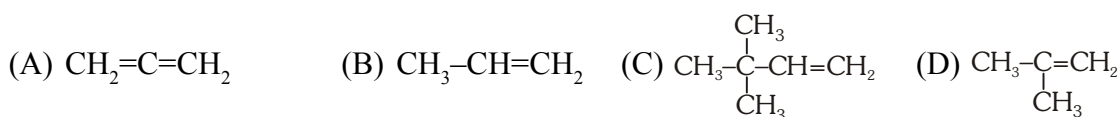
GC0043

41. Which of the following molecule has longest C=C bond length ?



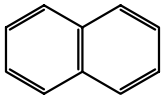
GC0044

42. Which of the following molecule has shortest C=C bond length ?



GC0045

43. C—C and C=C bond lengths are unequal in :

- (A) Benzene (B) 1,3-butadiene (C) 1,3-cyclohexadiene (D) 

GC0046

44. Among the following molecules, the correct order of C—C bond length is ( $C_6H_6$  is benzene)

- (A)  $C_2H_6 > C_2H_4 > C_6H_6 > C_2H_2$  (B)  $C_2H_6 > C_6H_6 > C_2H_4 > C_2H_2$   
 (C)  $C_2H_4 > C_2H_6 > C_2H_2 > C_6H_6$  (D)  $C_2H_6 > C_2H_4 > C_2H_2 > C_6H_6$

GC0047

45.  $CH_3O-CH=CH-NO_2$  I

$CH_2=CH-NO_2$  II

$CH_2=CH-Cl$  III

$CH_2=CH_2$  IV

Which of the following is the correct order of C—C bond lengths among these compounds :

- (A) I > II > III > IV (B) IV > III > II > I (C) I > III > II > IV (D) II > III > I > IV

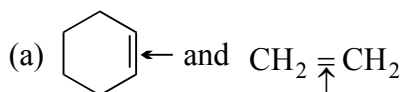
GC0048

46. Which of the following is (are) the correct order of bond lengths :

- (A)  $C-C > C=C > C \equiv C > C \equiv N$  (B)  $C=N > C=O > C=C$   
 (C)  $C=C > C=N > C=O$  (D)  $C-C > C=C > C \equiv C > C-H$

GC0049

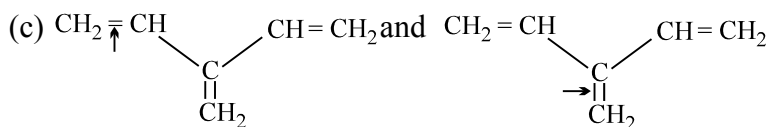
47. In which of the following pairs, indicated bond having less bond dissociation energy :



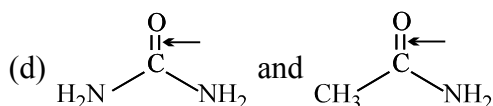
GC0050



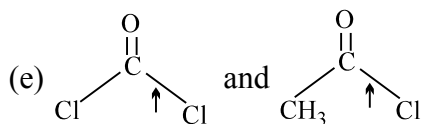
GC0050



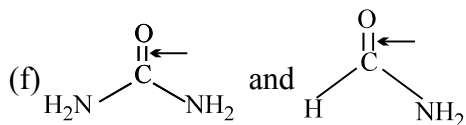
GC0050



GC0051

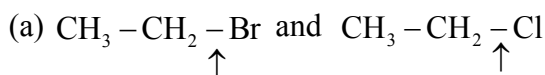


GC0051

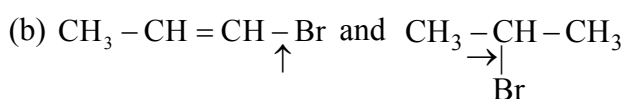


GC0051

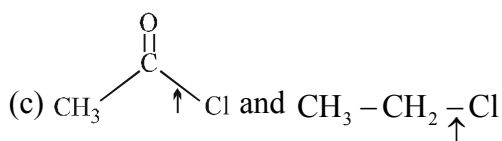
48. In which of the following pairs, indicated bond is of greater strength :



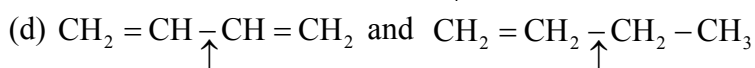
GC0052



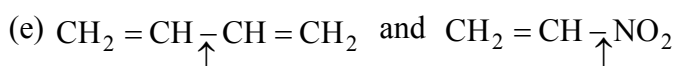
GC0052



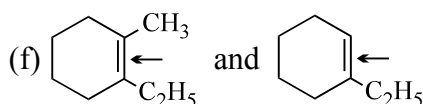
GC0052



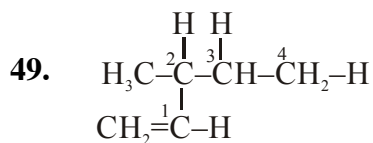
GC0052



GC0053



GC0053

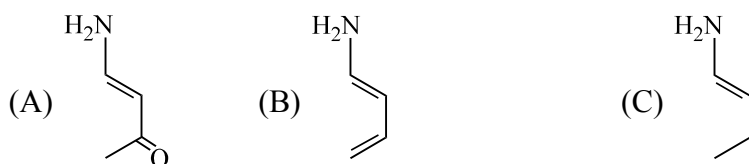


the correct order of bond dissociation energy (provided bond undergoes homolytic cleavage):



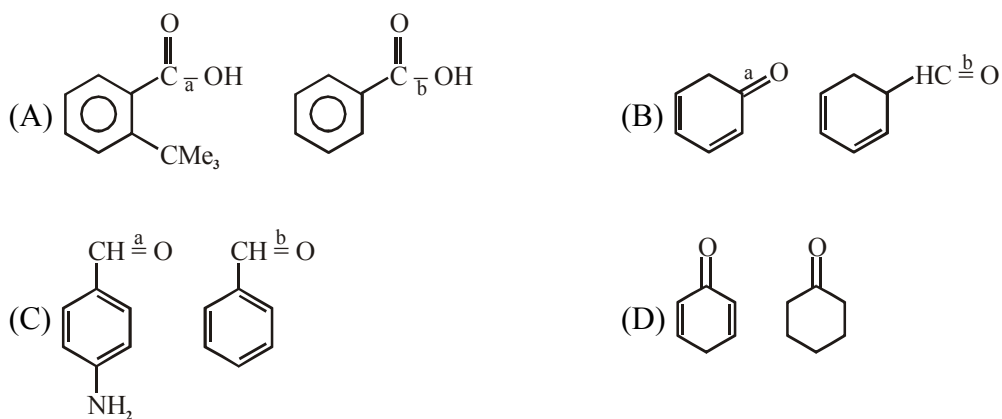
GC0054

50. Compare the C-N bond-length in the following species:



GC0055

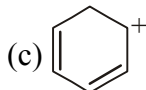
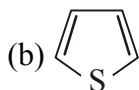
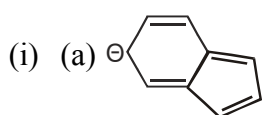
51. In which case, C – O bond length is shorter for I<sup>st</sup> compound :



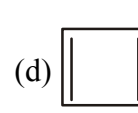
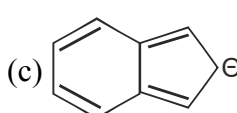
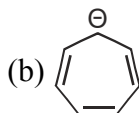
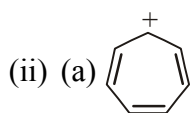
GC0056

EXERCISE # O-II

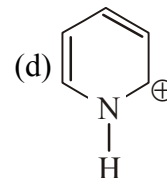
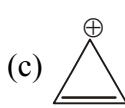
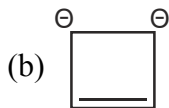
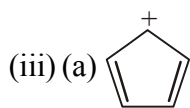
1. In each set of species select the aromatic species.



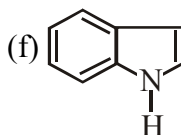
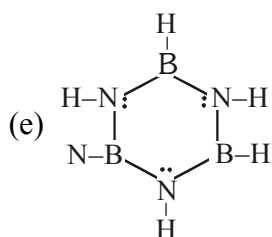
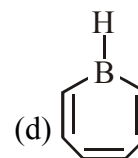
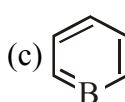
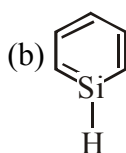
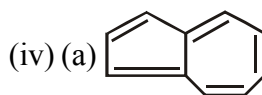
GC0057



GC0058

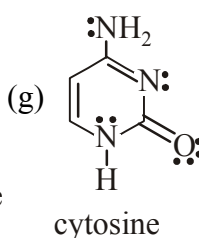
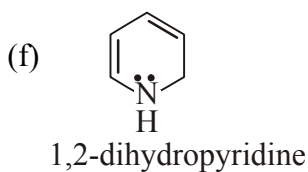
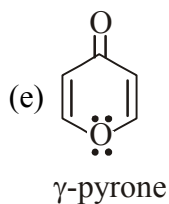
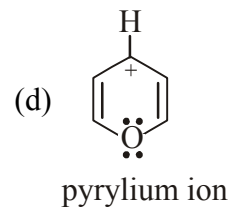
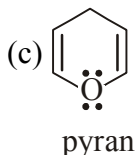
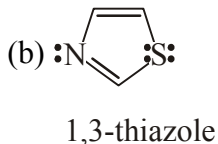
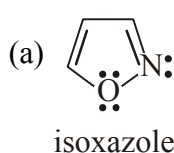


GC0059

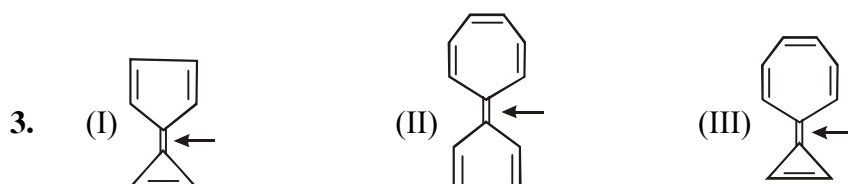


GC0060

2. Which of the given compound is aromatic, antiaromatic or nonaromatic.



GC0061

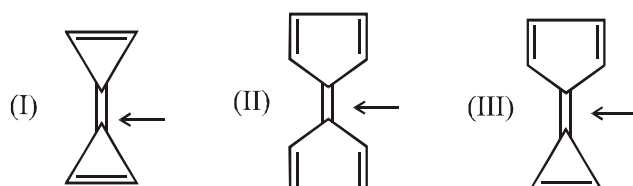


Compare carbon-carbon bond rotation across I, II, III.

- (A)  $I > II > III$       (B)  $I > III > II$       (C)  $II > I > III$       (D)  $II > III > I$

GC0062

4. Which of the given compounds has minimum rotation energy barrier across indicated carbon-carbon bond.



- (A) I      (B) II      (C) III      (D) All are equal

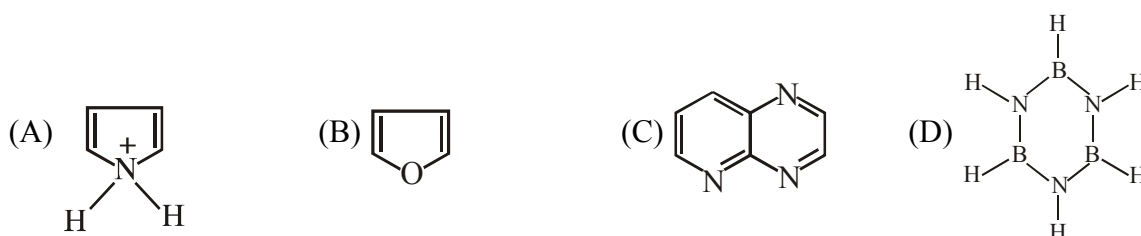
GC0063

5. Which species is not aromatic ?



GC0064

6. Which of the following are non-aromatic



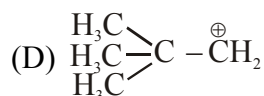
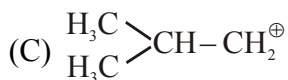
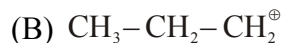
GC0065

7. Write down the structure of the following molecule and comment on aromaticity ?

- (a)  $B_3H_3O_3$       (b)  $C_3N_3(NH_2)_3$       (c) Trimer of isocyanic acid  $(HN=C=O)_3$

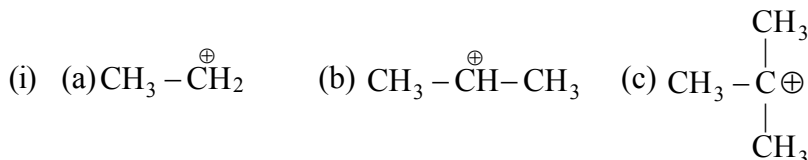
GC0066

8. Select the least stable one :

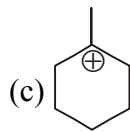
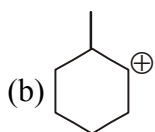
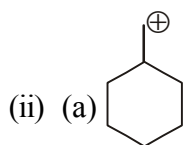


GC0067

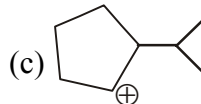
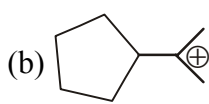
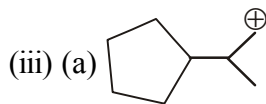
9. Write stability in decreasing order of following intermediates:



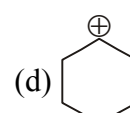
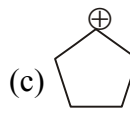
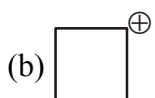
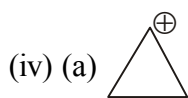
GC0068



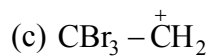
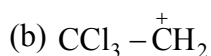
GC0069



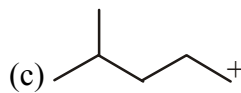
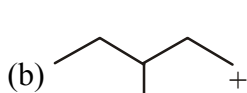
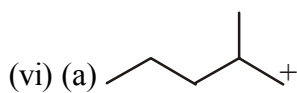
GC0070



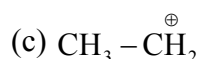
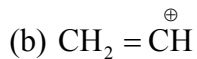
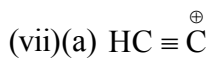
GC0071



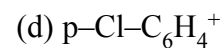
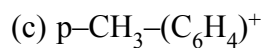
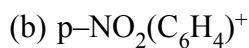
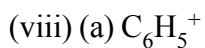
GC0072



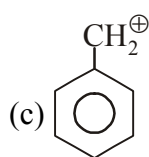
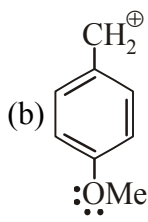
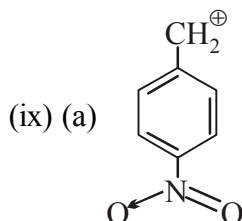
GC0073



GC0074

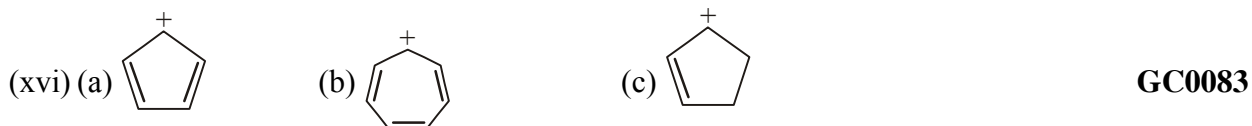
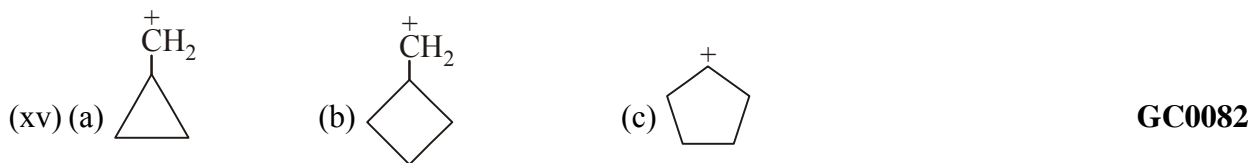
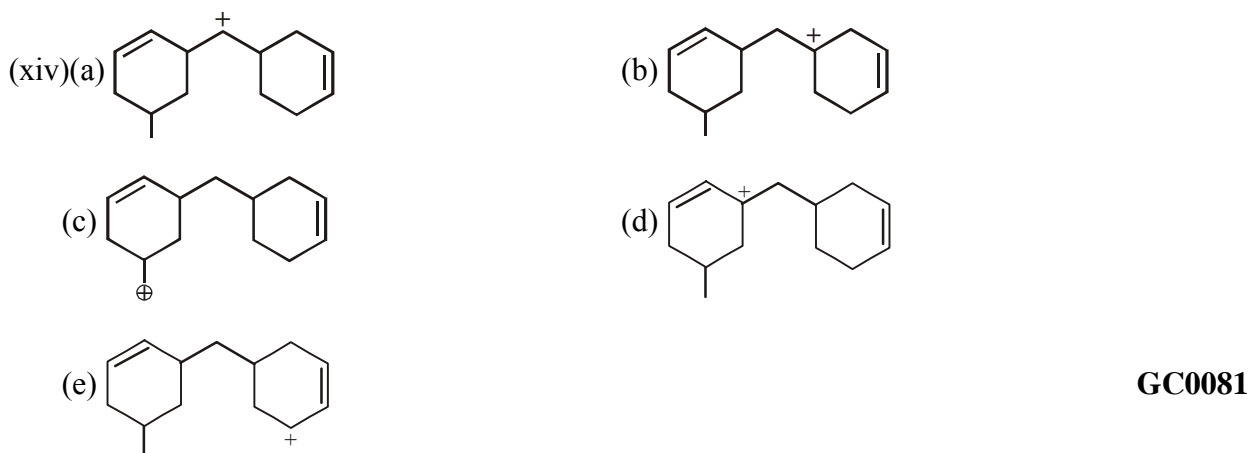
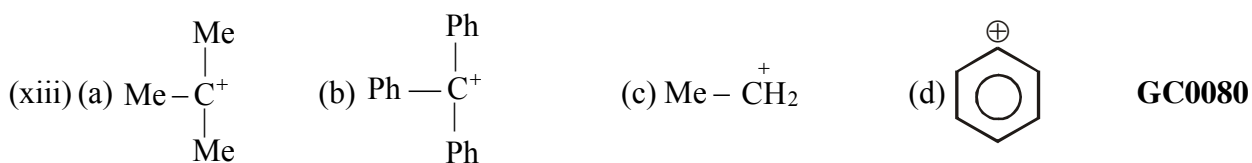
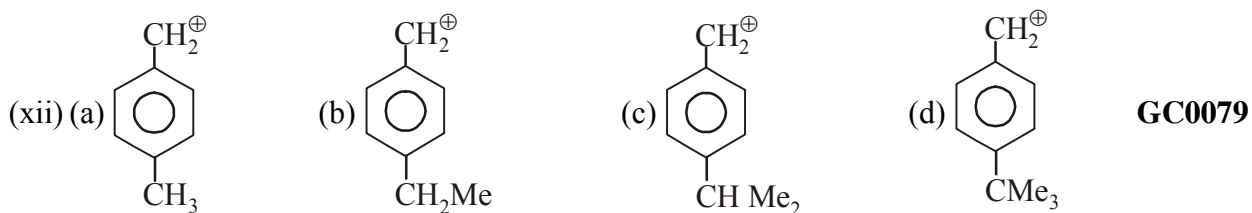
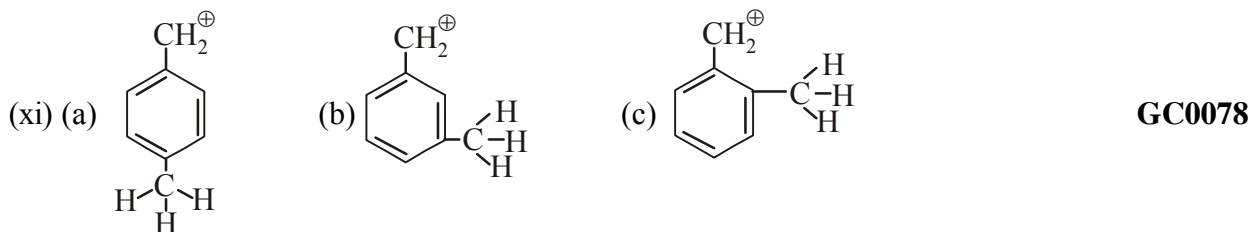
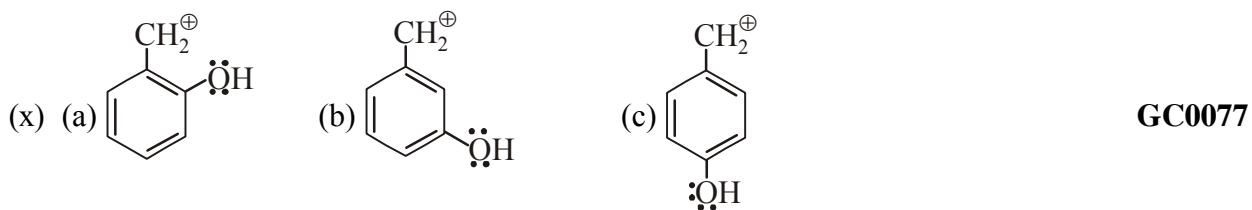


GC0075

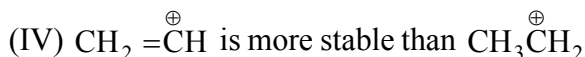
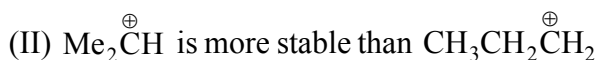
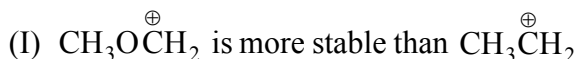


GC0076





10. Consider the following statements:



Of these statements:

(A) I and II are correct

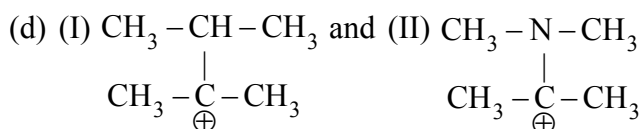
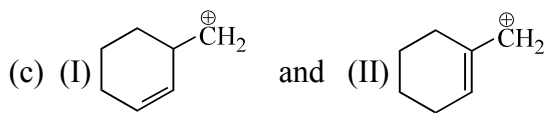
(B) III and IV are correct

(C) I, II and III are correct

(D) II, III and IV are correct

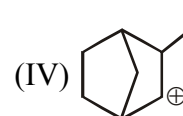
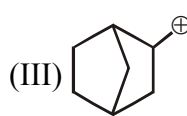
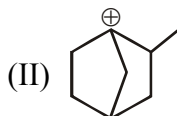
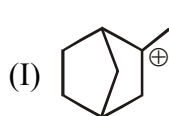
GC0084

11. In each of the following pairs of ions which ion is more stable:



GC0085

12. Find out correct stability order in the following carbocations-



(A) IV > I > III > II

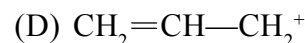
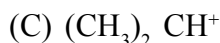
(B) IV > III > I > II

(C) I > IV > III > II

(D) I > III > IV > II

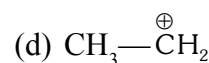
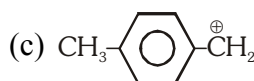
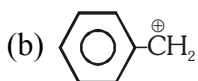
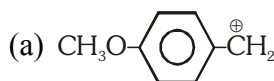
GC0086

13. Which of the following carbonium ion is most stable ?



GC0087

14. Consider the following carbocations



The relative stabilities of these carbocations are such that :-

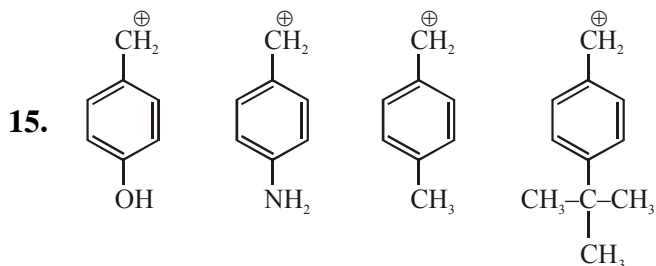
(A)  $d < b < c < a$

(B)  $b < d < c < a$

(C)  $d < b < a < c$

(D)  $b < d < a < c$

GC0088

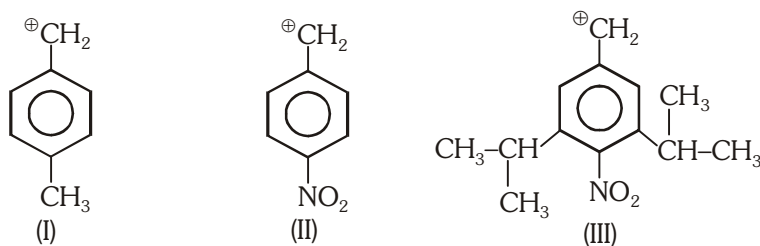


Correct order of carbocation stability is :

- (A)  $2 > 1 > 4 > 3$     (B)  $1 > 2 > 4 > 3$     (C)  $3 > 4 > 2 > 1$     (D)  $2 > 1 > 3 > 4$

GC0089

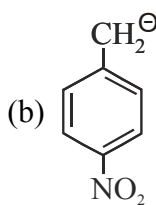
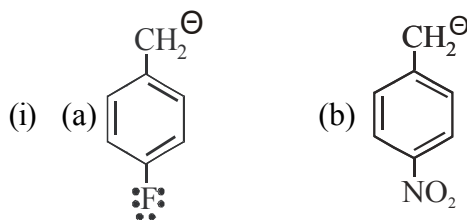
16. Arrange the following carbocation in the increasing order of stability :



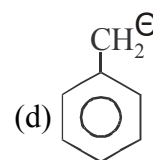
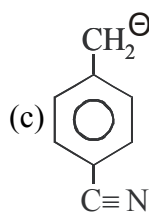
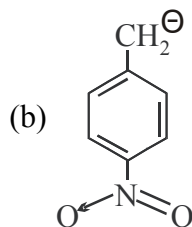
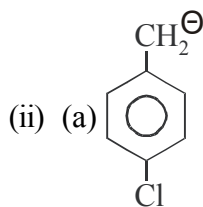
- (A)  $I < II < III$     (B)  $II < III < I$     (C)  $III < II < I$     (D)  $III < I < II$

GC0090

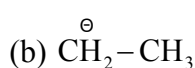
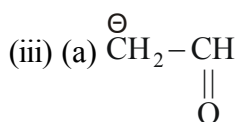
17. Rank the following sets of intermediates in increasing order of their stability.



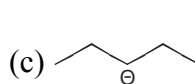
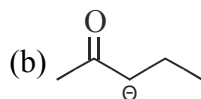
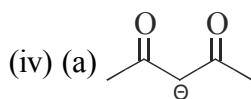
GC0091



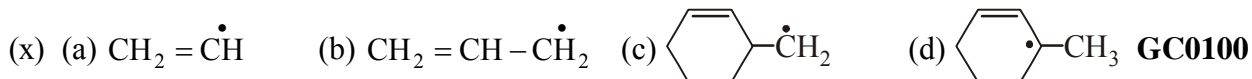
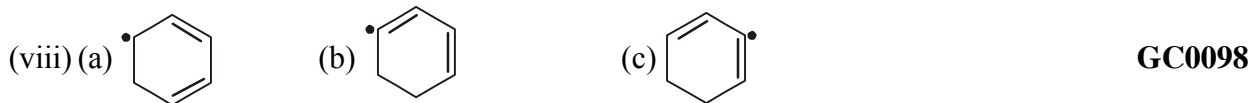
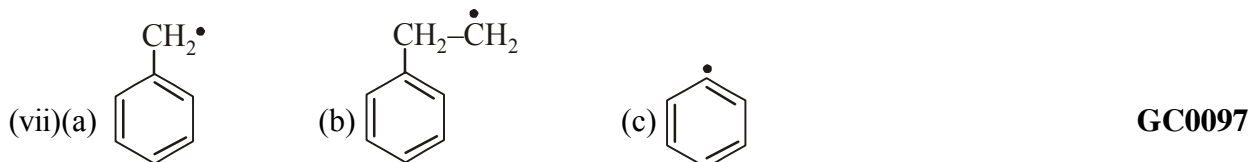
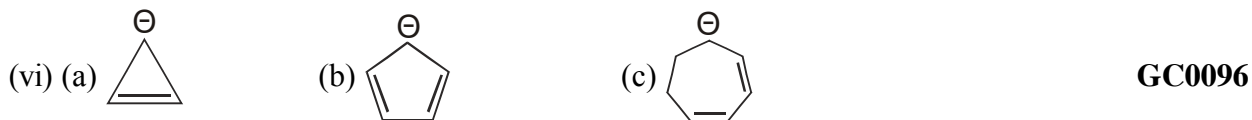
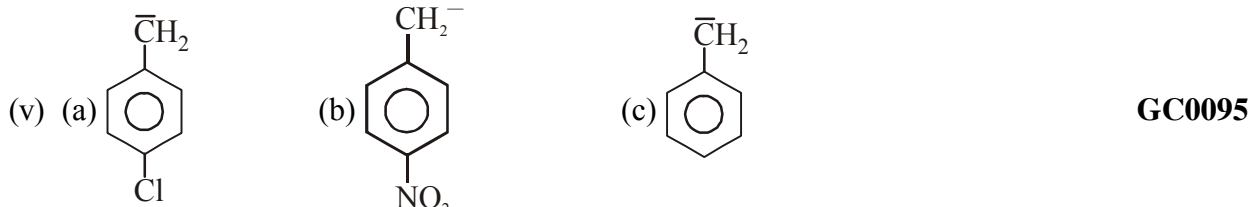
GC0092



GC0093



GC0094

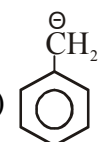
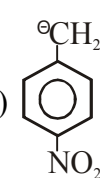


18. Most stable carbanion is :-

- (A)  $\text{HC}\equiv\text{C}^\ominus$  (B)  $\text{C}_6\text{H}_5^\ominus$  (C)  $(\text{CH}_3)_3\text{C}-\text{CH}_2^\ominus$  (D)  $(\text{CH}_3)_2\text{C}=\text{CH}^\ominus$

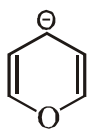
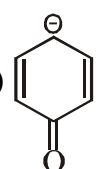
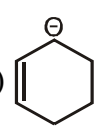
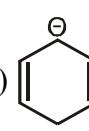
GC0101

19. Most stable carbanion is :

- (A)  $\text{CH}_3^\ominus$  (B)  $\text{CH}_2 = \text{CH} - \dot{\text{C}}\text{H}_2$  (C)  (D) 

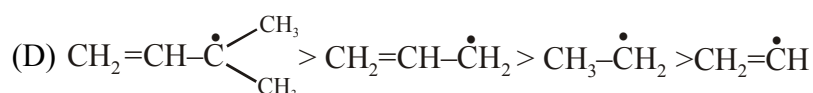
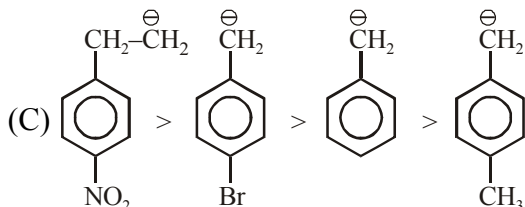
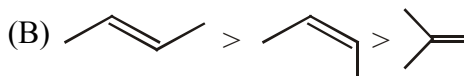
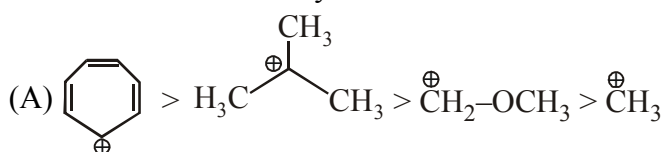
GC0102

20. Identify the most stable anion.

- (A)  (B)  (C)  (D) 

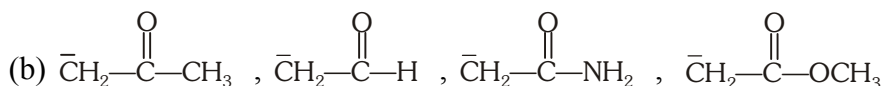
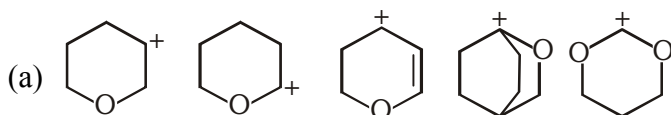
GC0103

21. Correct order of stability :



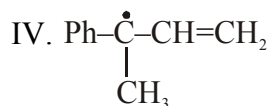
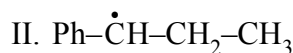
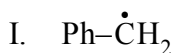
GC0104

22. Rank the following sets of intermediates in increasing order of their stability giving appropriate reasons for your choice.



GC0105

23. Select the correct order of stability of carbon free radicals :



(A) IV > III > I > II    (B) IV > III > II > I    (C) I > II > III > IV    (D) I > III > II > IV

GC0106

24.  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$  is more stable than  $\text{CH}_3 - \text{CH} = \text{C} = \text{CH} - \text{CH}_3$  because

(I)

(II)

(A) there is resonance in I but not in II

(B) there is tautomerism in I but not in II

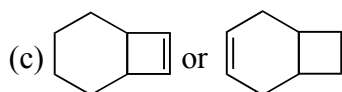
(C) there is hyperconjugation in I but not in II    (D) II has more cononical structures than I.

GC0107

25. Choose the more stable alkene in each of the following pairs. Explain your reasoning.

(a) 1-Methylcyclohexene or 3-methylcyclohexene

(b) Isopropenylcyclopentane or allylcyclopentane



GC0108

26. Match each alkene with the appropriate heat of combustion:

Heats of combustion (kJ/mol) : 5293 ; 4658; 4650; 4638; 4632

(a) 1-Heptene

(b) 2,4-Dimethyl-1-pentene

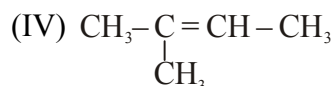
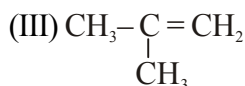
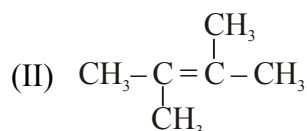
(c) 2,4-Dimethyl-2-pentene

(d) 4,4-Dimethyl-2-pentene

(e) 2,4,4-Trimethyl-2-pentene

GC0109

27. Stability of :



in the increasing order is :

(A) I < III < IV < II

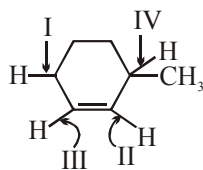
(B) I < II < III < IV

(C) I < IV < III < I

(D) II < III < IV < I

GC0110

28. Which of the following C-H bonds participate in hyperconjugation ?



(A) I and II

(B) I and IV

(C) I and III

(D) III and IV

GC0111

29. Rank the following alkenes in decreasing order of heat of combustion values :



(I)



(II)



(III)



(IV)

(A) II &gt; III &gt; IV &gt; I

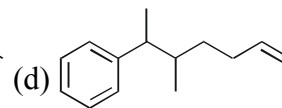
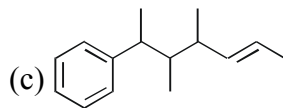
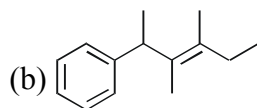
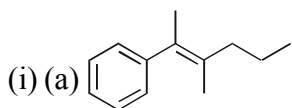
(B) II &gt; IV &gt; III &gt; I

(C) I &gt; III &gt; IV &gt; II

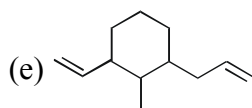
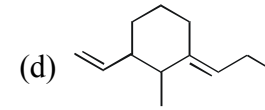
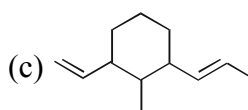
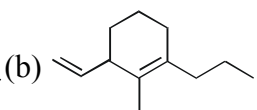
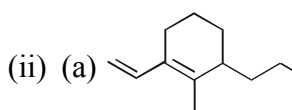
(D) I &gt; IV &gt; III &gt; II

GC0112

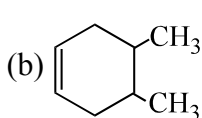
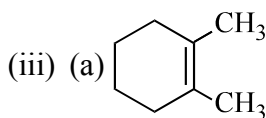
30. Write decreasing order of heat of hydrogenation :



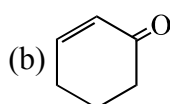
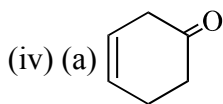
GC0113



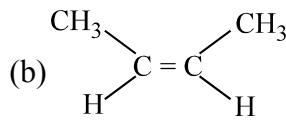
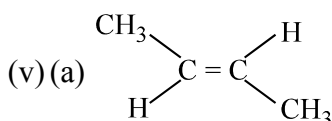
GC0114



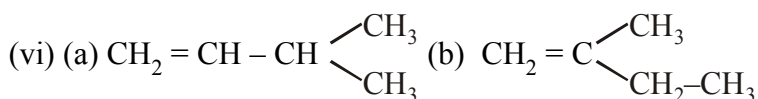
GC0115



GC0116

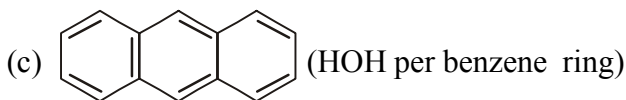
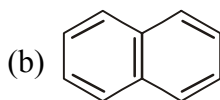
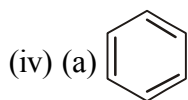
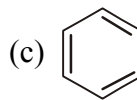
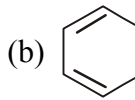
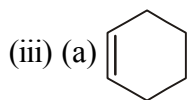
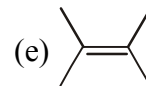
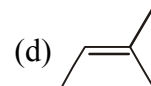
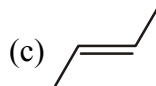
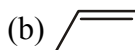
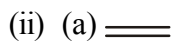
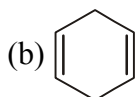
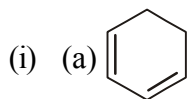


GC0117



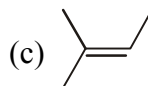
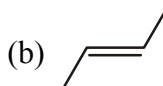
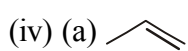
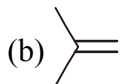
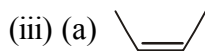
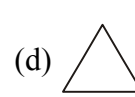
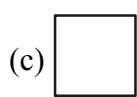
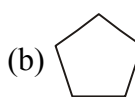
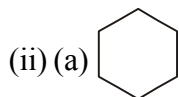
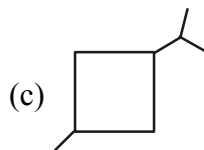
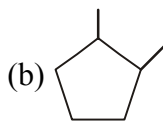
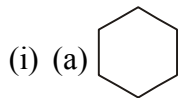
GC0118

31. Write increasing order of heat of hydrogenation :



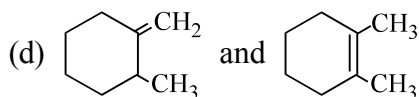
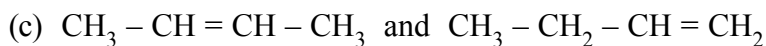
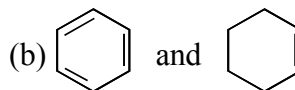
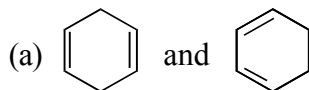
GC0119

32. Give decreasing order of heat of combustion (HOC):



GC0120

33. Among the following pairs identify the one which gives higher heat of hydrogenation :

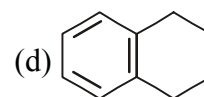
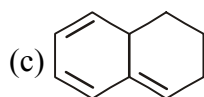
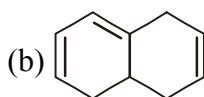
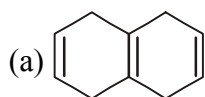


GC0121

34. Arrange the following compounds in order of :

(I) Stability

(II) Heat of hydrogenation



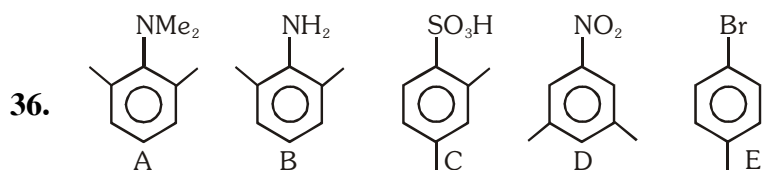
GC0122



35. If Heat of hydrogenation of 1-butene is 30 Kcal/mol then heat of hydrogenation of 1,3-butadiene is ?

- (A) 30                      (B) 60                      (C) 57                      (D) 25

GC0123

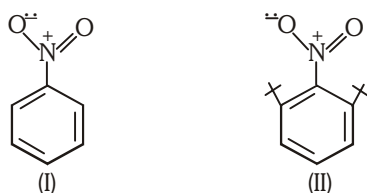


Steric inhibition of resonance takes place :

- (A) In A,B only              (B) In A, B, C, E              (C) C only              (D) In A only

GC0124

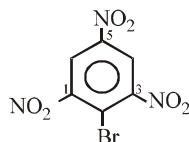
37. Consider the following two structures and choose the correct statements -



- (A) carbon-nitrogen bond length structure I is greater than that in structure II  
 (B) carbon-nitrogen bond length in structure I is less than in structure II  
 (C) carbon-nitrogen bond length in both structure is same  
 (D) It can not be compared

GC0125

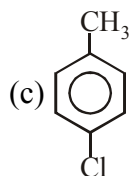
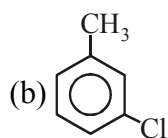
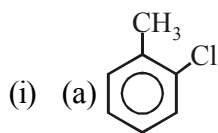
38. Which of the following statements would be true about this compound :



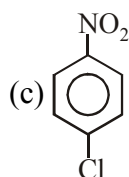
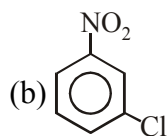
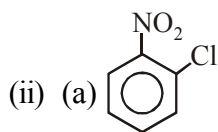
- (A) All three C – N bonds are of same length.  
 (B) C1 – N and C3 – N bonds are of same length but shorter than C5 – N bond.  
 (C) C1 – N and C3 – N bonds are of same length but longer than C5 – N bond.  
 (D) C1 – N and C3 – N bonds are of different length but both are longer than C5 – N bond

GC0126

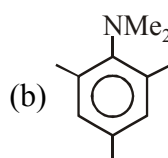
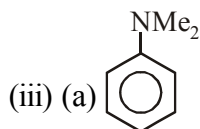
39. Arrange given compounds in decreasing order of dipole moment :



GC0127



GC0128



GC0129

40. Why a cation like is not possible.

GC0130

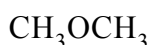
## EXERCISE # S-I

1. Cyclopentadienyl anion is much more stable than allyl anion because :

- (A) Cyclic anion is more stable than acyclic anion  
 (B) Delocalised anion is more stable than localised anion  
 (C) Cyclopentadienyl anion is aromatic in nature  
 (D) None of these

GC0131

2. Select correct statement regarding given compounds :



I



II

- (A) Boiling point of II is higher than I  
 (B) Boiling point of II is lower than I  
 (C) Compound I forms intramolecular H-bonding  
 (D) Compound II forms intermolecular H-bonding

GC0132

3. In the compound,  $\text{CH}_3\text{—CH=CH—C}\equiv\text{N}$ , the most electronegative carbon is :

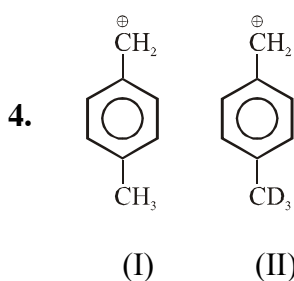
(A) I

(B) II

(C) III

(D) IV

GC0133



Carbocation (I) is more stable than carbocation (II), because :

- (A)  $\text{—CD}_3$  has more + I effect than  $\text{—CH}_3$                   (B)  $\text{—CH}_3$  has more + I effect than  $\text{—CD}_3$   
 (C)  $\text{—CH}_3$  has more + H effect than  $\text{—CD}_3$                   (D)  $\text{—CD}_3$  has more + H effect than  $\text{—CH}_3$

GC0134

5. Select correct statement :

- (A) Carbon-oxygen bonds are of equal length in acetate ion
- (B) Resonating structures of acetate ion are equivalent
- (C) Carbon-oxygen bonds are of unequal length in formate ion
- (D) Resonating structures of formate ion are equivalent

GC0135

6. Match the column I with column II.

**Column-I**

(Group attached with benzene ring)

- (A) —NO<sub>2</sub>
- (B) —O<sup>-</sup>
- (C) —O—CH<sub>3</sub>
- (D) —C ≡ N

**Column-II**

(Effect shown by the group)

- (P) - R effect
- (Q) + R effect
- (R) + I effect
- (S) - I effect

GC0136

7. **Column- I**

(Groups attached to phenyl ring)

- (A) — $\ddot{N} = O$
- (B) —CH<sub>3</sub>
- (C) — $\ddot{N}H - C \begin{matrix} \diagup O \\ \diagdown CH_3 \end{matrix}$
- (D) — $\begin{matrix} O \\ || \\ C - OCH_3 \end{matrix}$

**Column- II**

(Effect shown)

- (P) +M
- (Q) -M
- (R) +H
- (S) -I

GC0137

8. Match the column :

**Column-I**

- (A) Group donate e<sup>-</sup> inductively but does not donate / withdraw by resonance
- (B) Group withdraw e<sup>-</sup> inductively but does not donate / withdraw by resonance
- (C) Group withdraw e<sup>-</sup> inductively & donate e<sup>-</sup> by resonance
- (D) Group withdraw e<sup>-</sup> inductively & withdraw e<sup>-</sup> by resonance

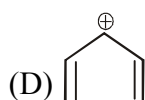
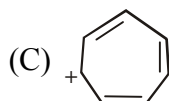
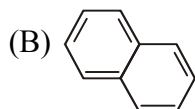
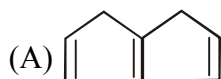
**Column-II**

- (P) -OH
- (Q) -NO<sub>2</sub>
- (R) -CH<sub>2</sub>-CH<sub>3</sub>
- (S) — $\overset{+}{N}H_3$
- (T) -NH<sub>2</sub>

GC0138

9. Match the column I with column II.

**Column-I**



**Column-II**

(P) Aromatic

(Q) Non-aromatic

(R) Anti-aromatic

(S) Cyclic structure

GC0139

10. **Statement-I** :  $\text{—}\overset{\text{a}}{\underset{\text{O}}{\parallel}}{\text{C}}\text{—OEt}$        $\text{—}\overset{\text{b}}{\underset{\text{O}}{\parallel}}{\text{C}}\text{—O—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$  bond length  $a < b$

**Because**

**Statement-II** : More is the double bond character less is the bond length.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

GC0140

11. **Statement-I** :  $\text{Me}_3\overset{+}{\text{C}}$  is more stable than  $\text{Me}_2\overset{+}{\text{C}}\text{H}$  and  $\text{Me}_2\overset{+}{\text{C}}\text{H}$  is more stable than the  $\text{Me}\overset{+}{\text{C}}\text{H}_2$ .

**Because**

**Statement-II** : Greater the number of hyperconjugative structures, more is the stability of carbocation.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

GC0141

12. **Statement-I** : The potential energy barrier for rotation about C = C bond in 2-butene is much higher than that in ethylene.

**Because**

**Statement-II** : Hyperconjugation effect decreases the double bond character.

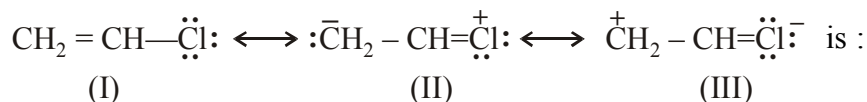
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

GC0142

Paragraph for Question 13 to 15

The intramolecular delocalisation of  $\pi$  and non-bonding electrons without any change in the position of atoms is called resonance. Delocalisation may occur in conjugated system involving carbon atom and atom other than carbon. Delocalisation makes system stable. More is the number of resonating structures, more is the stability of the system. A resonating structure is less stable when a higher electronegative atom has positive charge and when identical charges are present on adjacent atoms.

13. The decreasing order of stability of the following resonating structures



(I)

(II)

(III)

- (A) I > II > III      (B) II > III > I      (C) III > II > I      (D) I > III > II

GC0143

14. If A is  $\text{PhCH}_2^+$  and B is  $\text{CH}_2 = \text{CH} - \text{CH}_2^+$ , the greater number of resonating structure is of -

- (A) A      (B) B      (C) both A and B      (D) None of these

GC0144

15. Which of the following pairs represent resonance ?

- (A)  $\text{CH}_2 = \text{CHOH}$  ;  $\text{CH}_3\text{CHO}$       (B)  $\overset{\ominus}{\text{C}}\text{H}_2 - \text{CHO}$  ;  $\text{H}_2\text{C} = \text{CH} - \overset{\ominus}{\text{O}}$

- (C)  $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_3$  ;  $\text{CH}_3 - \overset{\text{OH}}{\text{C}} = \text{CH}_2$       (D)  $\text{CH}_3 - \overset{\text{OH}}{\parallel}{\text{C}} - \text{CH}_3$  ;  $\text{CH}_3 - \overset{\text{OH}}{\underset{\text{H}}{\text{C}}} - \text{CH}_3$

GC0145

Paragraph for Question 16 to 18

Carbocation is a specie with positively charged carbon atom having six electrons in the valence shell after sharing. Carbocations are formed in the heterolysis of a bond and are planar species. Stability of carbocation is determined by inductive effect, hyperconjugation and resonance effect. Greater the number of contributing structures, more is the stability of a Carbocation. Electron releasing groups (+I effect) increases the stability of a carbocation whereas the electron withdrawing groups (-I effect) have an opposite effect.

16. Which of the following is most stable carbocation ?

- (A)  $\overset{+}{\text{C}}\text{H}_3$       (B)  $\text{CH}_3 - \overset{+}{\text{C}}\text{H} - \text{CH}_3$       (C)  $\text{CH}_3 - \overset{+}{\text{C}}\text{H}_2$       (D)  $\text{CH}_3 - \overset{+}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_3$

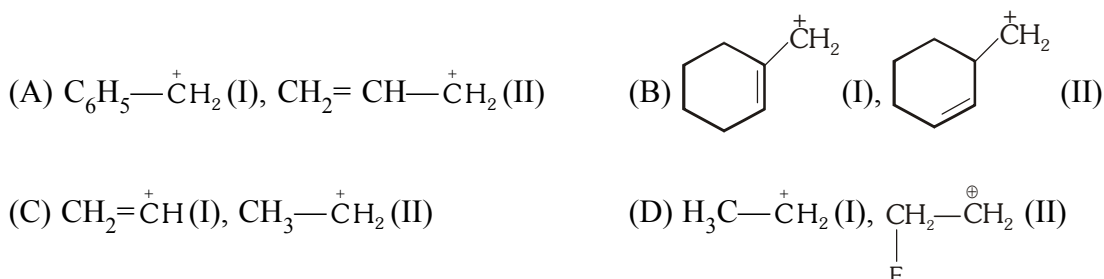
GC0146

17. The most stable carbocation among the following :



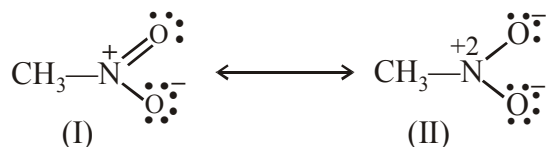
GC0147

18. In which of the following cases, the carbocation (I) is less stable than the carbocation (II) ?



GC0148

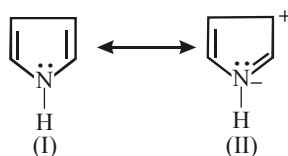
19. Examine the structures I and II for nitromethane and choose the statement correctly :



- (A) Structure II is unlikely representation because electrons have shifted to oxygen  
 (B) Structure II is unlikely representation because nitrogen has sextet of electrons  
 (C) Structure II is acceptable and important  
 (D) None of these

GC0149

20. Examine the following two structures for pyrrole and choose the correct statement given below



- (A) II is not an acceptable resonating structure because carbonium ions is less stable than nitride ion  
 (B) II is not an acceptable resonating structure because there is charge separation  
 (C) II is not an acceptable resonating structure because nitrogen has ten valance electrons  
 (D) II is an acceptable resonating structure

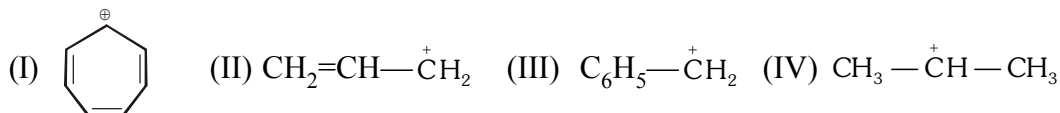
GC0150

21. Delocalization of electrons increases molecular stability because :

- (A) Potential energy of the molecule decreases (B) Electron-electron repulsion decreases  
 (C) Both (A) and (B) (D) Electron-electron repulsion increases

GC0151

22. The most stable and the least stable carbocation among



are respectively :

- (A) II, I (B) III, IV (C) I, II (D) I, IV

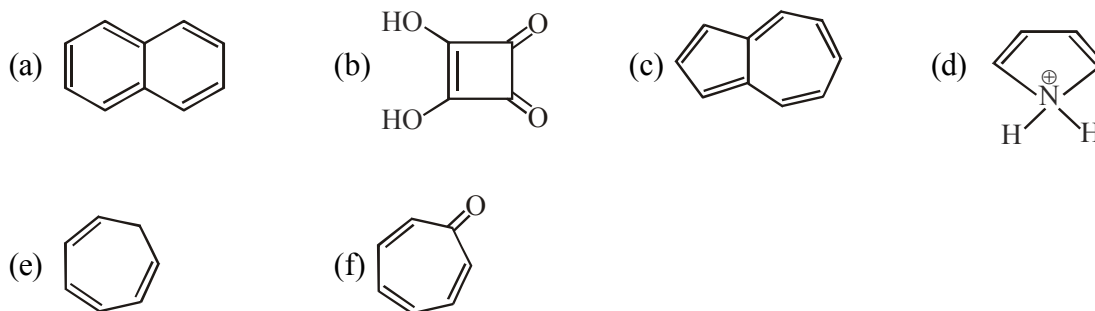
GC0152

23. Most stable carbocation is formed by the heterolysis of :

- (A)  $(\text{CH}_3)_3\text{CBr}$  (B)  $(\text{C}_6\text{H}_5)_3\text{CBr}$  (C)  $(\text{C}_6\text{H}_5)_2\text{CHBr}$  (D)  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$

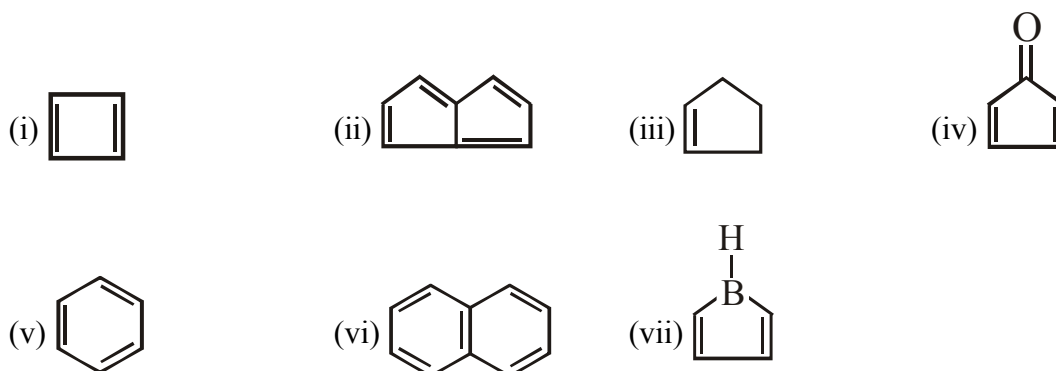
GC0153

24. Total number of aromatic compounds



GC0154

25. Identify total number of compounds which are unstable at room temperature ?



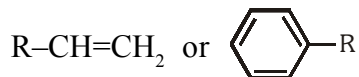
GC0155



## EXERCISE # J-MAIN

1. In the following benzyl/allyl system

[AIEEE-2002]



(R is alkyl group)

decreasing order of inductive effect is-

- (1)  $(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2-$       (2)  $CH_3-CH_2- > (CH_3)_2CH- > (CH_3)_3C-$   
 (3)  $(CH_3)_2CH- > CH_3CH_2- > (CH_3)_3CH-$       (4) None of these

GC0156

2. In the anion  $HCOO^-$  the two carbon-oxygen bonds are found to be of equal length. What is the reason for it- [AIEEE-2003]

- (1) Electronic orbits of carbon atoms are hybridised  
 (2) The C=O bond is weaker than the C-O bond  
 (3) The anion  $HCOO^-$  has two resonating structure  
 (4) The anion is obtained by removal of a proton form the acid molecule

GC0157

3. Which one of the following does not have  $sp^2$  hybridised carbon

[AIEEE-2004]

- (1) Acetamide      (2) Acetic acid      (3) Acetonitrile      (4) Acetone

GC0158

4. Due to the presence of an unpaired electron, free radicals are -

[AIEEE-2005]

- (1) Chemically inactive      (2) Chemically reactive  
 (3) Cations      (4) Anions

GC0159

5. The increasing order of stability of the following free radicals is

[AIEEE-2006]

- (1)  $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$   
 (2)  $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$   
 (3)  $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$   
 (4)  $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

GC0160

6. Arrange the carbanions,  $(\text{CH}_3)_3\bar{\text{C}}$ ,  $\bar{\text{CCl}}_3$ ,  $(\text{CH}_3)_2\bar{\text{C}}\text{H}$ ,  $\text{C}_6\text{H}_5\bar{\text{C}}\text{H}_2$ , in order of their decreasing stability [AIEEE-2009]

- (1)  $\bar{\text{CCl}}_3 > \text{C}_6\text{H}_5\bar{\text{C}}\text{H}_2 > (\text{CH}_3)_2\bar{\text{C}}\text{H} > (\text{CH}_3)_3\bar{\text{C}}$   
 (2)  $(\text{CH}_3)_3\bar{\text{C}} > (\text{CH}_3)_2\bar{\text{C}}\text{H} > \text{C}_6\text{H}_5\bar{\text{C}}\text{H}_2 > \bar{\text{CCl}}_3$   
 (3)  $\text{C}_6\text{H}_5\bar{\text{C}}\text{H}_2 > \bar{\text{CCl}}_3 > (\text{CH}_3)_3\bar{\text{C}} > (\text{CH}_3)_2\bar{\text{C}}\text{H}$   
 (4)  $(\text{CH}_3)_2\bar{\text{C}}\text{H} > \bar{\text{CCl}}_3 > \text{C}_6\text{H}_5\bar{\text{C}}\text{H}_2 > (\text{CH}_3)_3\bar{\text{C}}$

GC0161

7. The non aromatic compound among the following is :- [AIEEE-2011]



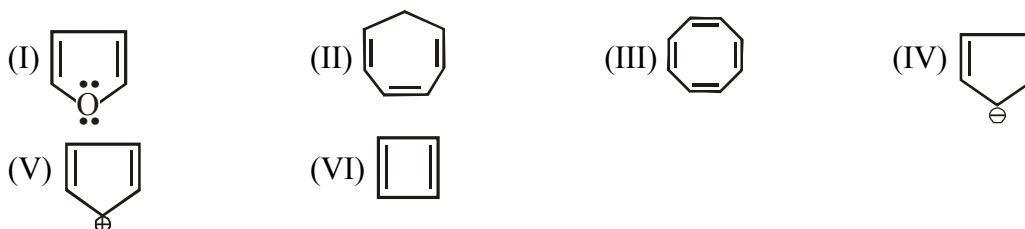
GC0162

8. ortho-Nitrophenol is less soluble in water than p- and m- Nitrophenols because :-

- (1) Melting point of o-Nitrophenol is lower than those of m- and p- isomers [AIEEE-2012]  
 (2) o-Nitrophenol is more volatile in steam than those of m- and p- isomers  
 (3) o-Nitrophenol shows Intramolecular H-bonding  
 (4) o-Nitrophenol shows Intermolecular H-bonding

GC0163

9. Which of the following compounds are antiaromatic :- [AIEEE-2012(Online)]



- (1) (III) and (VI) (2) (II) and (V) (3) (I) and (V) (4) (V) and (VI)

GC0164

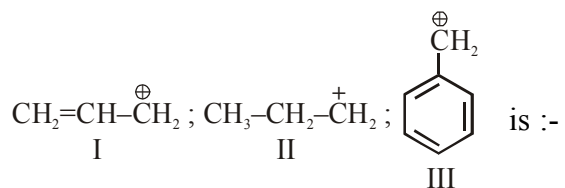
10. Among the following the molecule with the lowest dipole moment is :- [AIEEE-2012(Online)]

- (1)  $\text{CHCl}_3$  (2)  $\text{CH}_2\text{Cl}_2$  (3)  $\text{CCl}_4$  (4)  $\text{CH}_3\text{Cl}$

GC0165

11. The order of stability of the following carbocations

[JEE-MAIN-2013]

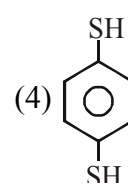
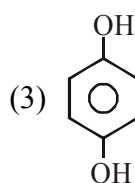
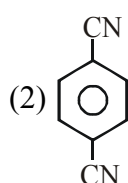
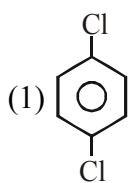


- (1) III > II > I      (2) II > III > I      (3) I > II > III      (4) III > I > II

GC0166

12. For which of the following molecule significant  $\mu \neq 0$

[JEE-MAIN-2014]

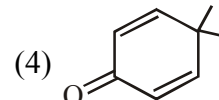
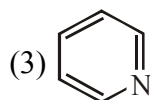
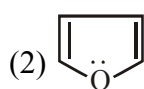
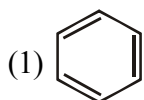


- (1) Only (3)      (2) (3) and (4)      (3) Only (1)      (4) (1) and (2)

GC0167

13. Which of the following molecules is least resonance stabilized ?

[JEE-MAIN-2017]



GC0168

## EXERCISE # J-ADVANCED

1. Which one of the following has the smallest heat of hydrogenation per mole of  $H_2$ ? [IIT-93]  
 (A) 1-Butene (B) trans-2-Butene  
 (C) cis-2-Butene (D) 1, 3-Butadiene

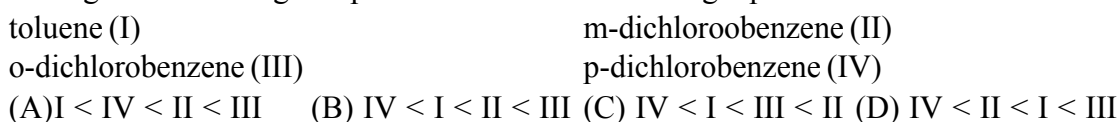
GC0176

2. Most stable carbonium ion is [IIT-95]



GC0177

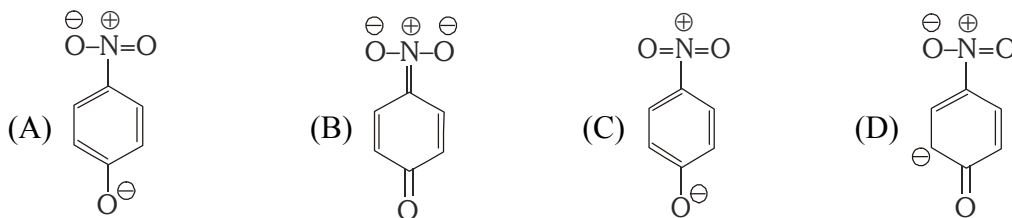
3. Arrange the following compounds in order of increasing dipole moment :



[IIT-96]

GC0178

4. The most unlikely representation of resonance structure of p-nitrophenoxide ion is - [IIT-99]



GC0179

5. An aromatic molecule will not [IIT-99]



GC0180

6. **Statement-I** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.

**Because**

**Statement-II** : o-Hydroxybenzoic acid has intramolecular hydrogen bonding. [IIT 2003]

- (A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I  
 (B) Statement-I is True, Statement-II is True ; Statement-II is NOT a correct explanation for Statement-I  
 (C) Statement-I is True, Statement-II is False.  
 (D) Statement-I is False, Statement-II is True.

GC0181

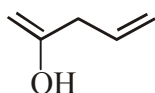
7. Among the following, the molecule with the highest dipole moment is [IIT-2003]



GC0182

8. Give resonating structures of following compound.

[IIT 2003]



9. Which of the following is least stable :

GC183

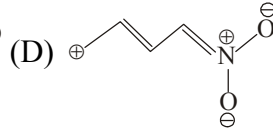
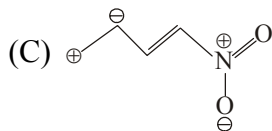
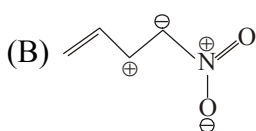
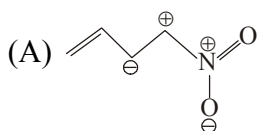
[IIT-2005]



10. Among the following, the least stable resonance structure is -

GC184

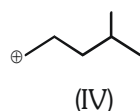
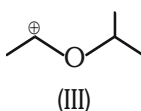
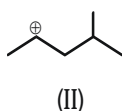
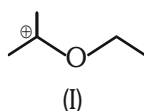
[IIT-2007]



11. The correct stability order for the following species is :

GC185

[IIT-2008]

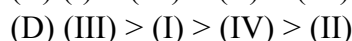
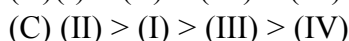
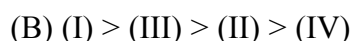
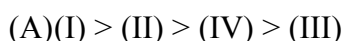
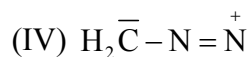
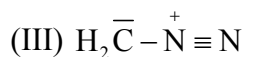
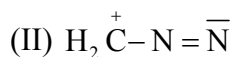
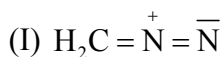


- (A) II > IV > I > III (B) I > II > III > IV (C) II > I > IV > III (D) I > III > II > IV

GC186

[IIT-2009]

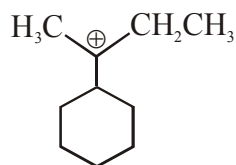
12. The correct stability order of the following resonance structures is



GC187

13. The total number of contributing structures showing hyperconjugation (involving C-H bonds) for the following carbocation is.

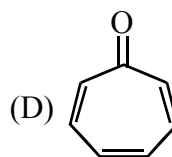
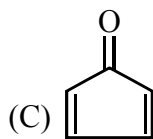
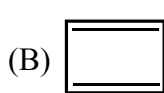
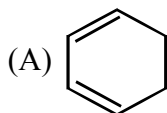
[IIT-2011]



GC188

14. Which of the following molecules, in pure form, is (are) **unstable** at room temperature ?

[IIT-2012]



GC189

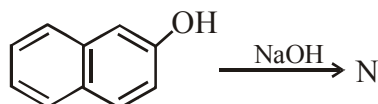
15. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to  
 (A)  $\sigma \rightarrow p$  (empty) and  $\sigma \rightarrow \pi$  electron delocalisations [IIT-2013]  
 (B)  $\sigma \rightarrow \sigma$  and  $\sigma \rightarrow \pi$  electron delocalisations  
 (C)  $\sigma \rightarrow p$  (filled) and  $\sigma \rightarrow \pi$  electron delocalisations  
 (D)  $p$  (filled)  $\rightarrow \sigma$  and  $\sigma \rightarrow \pi$  electron delocalisations

GC0190

16. The total number of lone-pairs of electrons in melamine is [IIT-2013]

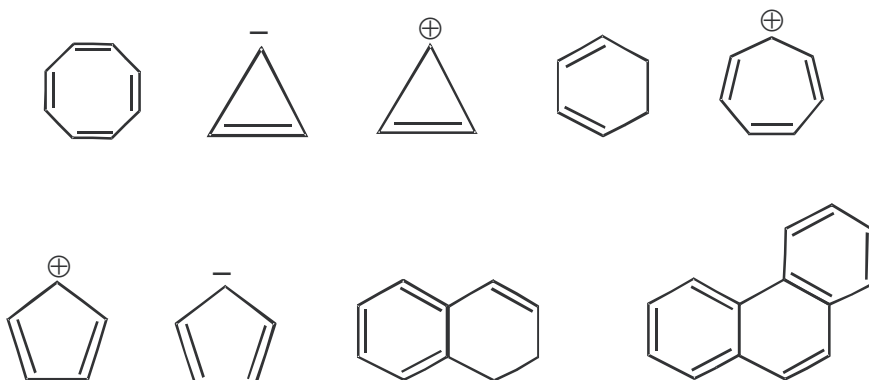
GC0191

17. The number of resonance structures for N is : [IIT-2015]



GC0192

18. Among the following, the number of aromatic compound (s) is- [JEE - Adv. 2017]



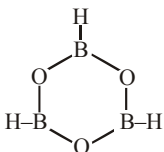
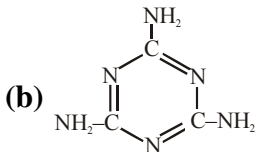
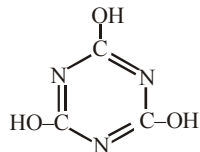
GC0193

## ANSWER-KEY

## EXERCISE # O-I

1. (D)      2. (C)      3. (B)      4. (A,B,D)      5. 4(b, d, f, g)  
 6. (a), (c), (d), (g), (j), (l), (m)      7. (A)      8. (A)      9. (A)  
 10. A,D      11. (D)      12. b, d, e      13. b d e      14. (d)      15. c, f  
 16. a, b, c, d, f      17. b, c, f      18.      19. a-I, b-II, c-II, d-II, e-I  
 20. a-I, b-I, c-I, d-I, e-II, f-II      21. a, e, f, g  
 22. (a) Resonance forms, (b) A, (c) C, (d) A & B, (e) B & C, (f) 0, (g) B, (h) B  
 23. (a) II; (b) II; (c) II      24. (A)      25. a-II, b-II, c-II, d-II      26. a & b  
 27. (i)-I, (ii)-II, (iii)-II, (iv)-I, (v)-I, (vi)-II, (vii)-I, (viii)-II, (ix)-II, (x)-II, (xi)-II, (xii)-I, (xiii)-I, (xiv)-I, (xv)-I  
 28. a-II, b-I, c-I, d-II, e-I      29. (B)      30. (D)      31. (B)      32. (C)  
 33. (C)      34. (C)      35. (D)      36. (A,B,C)      37. (B)      38. (B)  
 39. (C)      40. (D)      41. (D)      42. (A)      43. (B,C,D)      44. (B)  
 45. (A)      46. (A,C,D)      47. a-I, b-I, c-II, d-I, e-I, f-I  
 48. a-II, b-I, c-I, d-I, e-II, f-II      49. (D)      50. C>B>A      51. (A)

## EXERCISE # O-II

1. (i) a, b; (ii) a, c; (iii) b, c, d; (iv) a, b, c, d, e, f  
 2. Aromatic → a, b, d, e, g; Non-aromatic → c, f      3. (C)      4. (C)      5. (B)
6. (A)      7. (a)  (b)  (c) 
8. (D)  
 9. (i) c > b > a      (ii) c > b > a      (iii) b > c > a      (iv) d > c > b > a      (v) c > b > a  
 (vi) b > c > a      (vii) c > b > a      (viii) c > a > d > b      (ix) b > c > a      (x) c > a > b  
 (xi) c > a > b      (xii) a > b > c > d      (xiii) b > a > c > d      (xiv) d > e > b > a > c  
 (xv) a > c > b      (xvi) b > c > a  
 10. (C)      11. (a) I; (b) I; (c) II; (d) II;      12. (C)      13. (A)      14. (A)  
 15. (D)      16. (B)  
 17. (i) a < b      (ii) d < a < c < b      (iii) b < a      (iv) c < b < a      (v) c < a < b      (vi) a < c < b  
 (vii) c < b < a      (viii) c < b < a      (ix) b < a      (x) a < c < b < d

18. (A)            19. (D)            20. (B)            21. (D)
22. (a)  $IV < I < II < III < V$  (b)  $III < IV < I < II$             23. (B)            24. (A)
25. (a) -I ; (b) - I ; (c) - II            26. (a) 4658 ; (b) 4638 (c) 4632 ; (d) 4650 ; (e) 5293
27. (A)            28. (B)            29. (D)
30. (i)  $d > c > b > a$  ; (ii)  $e > c > d > b > a$  ; (iii)  $b > a$  (iv)  $a > b$  (v)  $b > a$  ; (vi)  $a > b$
31. (i)  $a < b$  ; (ii)  $e < d < c < b < a$  ; (iii)  $a < c < b$  ; (iv)  $a > b > c$
32. (i)  $c > b > a$  ; (ii)  $a > b > c > d$  ; (iii)  $a > b$  ; (iv)  $c > b > a$
33. a - I ; b - I ; c - II, d - I            34. Stability order :  $d > c > b > a$  ; HOH order :  $a > b > c > d$
35. (C)            36. (D)            37. (B)            38. (C)
39. (i)  $c > b > a$     (ii)  $a > b > c$     (iii)  $a > b$

**EXERCISE # S-I**

1. (C)            2. (A,D)            3. (D)            4. (C)            5. (A,B,D)
6. (A)  $\rightarrow$  P, S ; (B)  $\rightarrow$  Q,R ; (C)  $\rightarrow$  Q,S ; (D)  $\rightarrow$  P,S
7. (A)  $\rightarrow$  P, Q, S ; (B)  $\rightarrow$  R ; (C)  $\rightarrow$  P, S ; (D)  $\rightarrow$  Q, S
8. (A)  $\rightarrow$  R ; (B)  $\rightarrow$  S ; (C)  $\rightarrow$  P, T ; (D)  $\rightarrow$  Q
9. (A)  $\rightarrow$  Q,S ; (B)  $\rightarrow$  P,S ; (C)  $\rightarrow$  P,S ; (D)  $\rightarrow$  R,S
10. (D)            11. (A)            12. (D)            13. (A)            14. (A)            15. (B)
16. (D)            17. (C)            18. (C)            19. (B)            20. (C)            21. (C)
22. (D)            23. (B)            24. (4)            25. (4)

**EXERCISE # J-MAIN**

1. (1)            2. (3)            3. (3)            4. (2)            5. (4)            6. (1)
7. (1)            8. (3)            9. (4)            10. (3)            11. (4)            12. (2)
13. (4)

**EXERCISE # J-ADVANCED**

1. (D)            2. (D)            3. (B)            4. (C)            5. (A)            6. (D)
7. (A)            9. (D)            10. (A)            11. (D)            12. (B)            13. (6)
14. (B,C)            15. (A)            16. (6)            17. (9)            18. (5)







# Chapter Contents

## 03

### ACIDIC STRENGTH AND BASIC STRENGTH

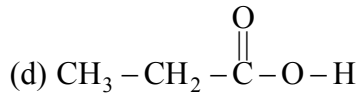
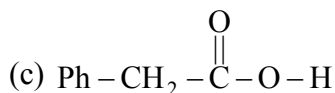
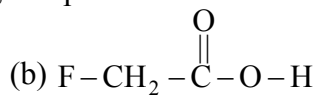
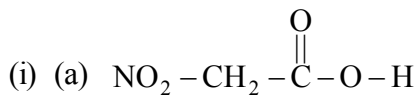
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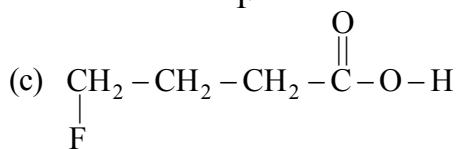
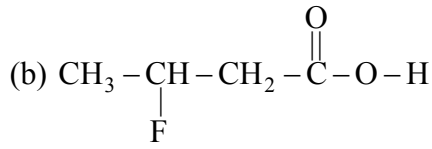
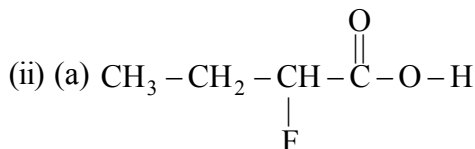
ACID STRENGTH & BASIC STRENGTH

EXERCISE # O-I

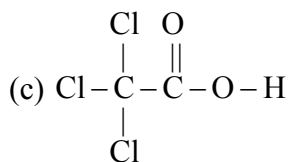
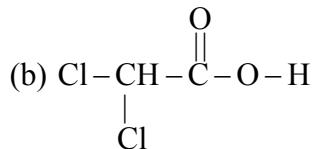
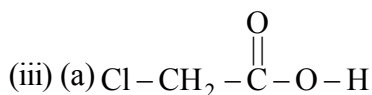
1. Write correct order of acidic strength of following compounds :



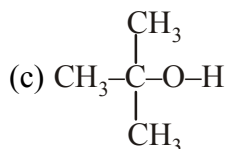
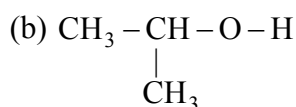
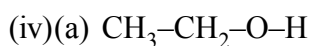
AB0001



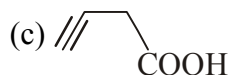
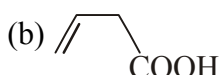
AB0002



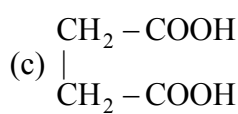
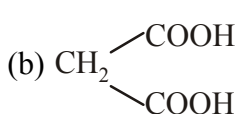
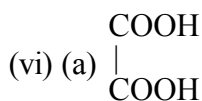
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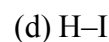
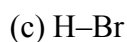
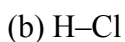
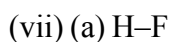
AB0004



AB0005



AB0006



AB0007

(viii) (a)  $\text{CH}_4$  (b)  $\text{NH}_3$  (c)  $\text{H}_2\text{O}$  (d)  $\text{H-F}$  **AB0008**

(ix) (a)  $\text{F-CH}_2\text{-CH}_2\text{-O-H}$  (b)  $\text{NO}_2\text{-CH}_2\text{-CH}_2\text{-O-H}$   
 (c)  $\text{Br-CH}_2\text{-CH}_2\text{-O-H}$  (d)  $\text{NH}_3^+\text{-CH}_2\text{-CH}_2\text{-O-H}$  **AB0009**

(x) (a)  $\text{CH}_3\text{COOH}$  (b)  $\text{CH}_3\text{CH}_2\text{OH}$  (c)  $\text{C}_6\text{H}_5\text{OH}$  (d)  $\text{C}_6\text{H}_5\text{SO}_3\text{H}$  **AB0010**

2. Explain which is a stronger acid.

(a)  $\text{CH}_3\text{CH}_3$  or  $\text{BrCH}_2\text{NO}_2$  **AB0011**

(b)  $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-CH}_3$  or  $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-CH}_2\text{CN}$  **AB0012**

(c)  **AB0013**

(d)  **AB0014**

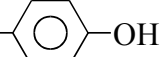
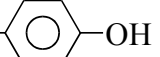
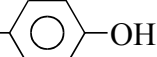
3. Which of the following would you predict to be the stronger acid ?

(a) Benzoic acid or para-nitrobenzoic acid **AB0015**

(b)  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}$  or  $\text{CH}_3\text{-CH}=\text{CH}-\text{OH}$  **AB0016**

(c)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{OH}$  or  $\text{CH}_3-\text{CH}=\text{CH}-\text{OH}$  **AB0017**




4. Arrange the given phenol & its derivative in their decreasing order of acidity :

(I)  $\text{C}_6\text{H}_5\text{-OH}$  (II)  (III)  (IV) 

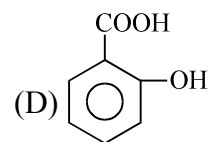
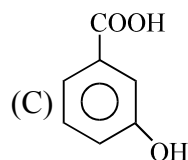
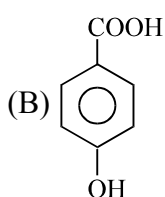
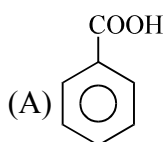
Select the correct answer from the given code:

(A)  $\text{IV} > \text{III} > \text{I} > \text{II}$  (B)  $\text{IV} > \text{II} > \text{III} > \text{I}$  (C)  $\text{IV} > \text{III} > \text{II} > \text{I}$  (D)  $\text{IV} > \text{I} > \text{III} > \text{II}$  **AB0018**

5. Which one of the following is the most acidic?

(A)  (B)  (C)  (D)  $\text{CH}_2=\text{CH-CH}_3$  **AB0019**

6. Which of the following is weakest acid?



AB0020

7. Arrange pH of the given compounds in decreasing order:

(1) Phenol                      (2) Ethyl alcohol              (3) Formic acid              (4) Benzoic acid

(A)  $1 > 2 > 3 > 4$               (B)  $2 > 1 > 4 > 3$               (C)  $3 > 2 > 4 > 1$               (D)  $4 > 3 > 1 > 2$

AB0021

8. Arrange acidity of given compounds in decreasing order:

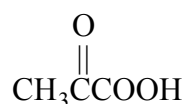
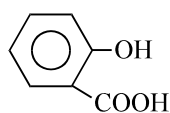
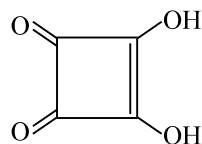
(I)  $\text{CH}_3\text{-NH-CH}_2\text{-CH}_2\text{-OH}$                       (II)  $\text{CH}_3\text{-NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$

(III)  $(\text{CH}_3)_3\text{N}^{\oplus}\text{-CH}_2\text{-CH}_2\text{-OH}$

(A)  $\text{III} > \text{I} > \text{II}$               (B)  $\text{III} > \text{II} > \text{I}$               (C)  $\text{I} > \text{II} > \text{III}$               (D)  $\text{II} > \text{I} > \text{III}$

AB0022

9. Consider the following compound



I

II

III

Which of the above compounds reacts with  $\text{NaHCO}_3$  giving  $\text{CO}_2$

(A) I, II and III              (B) I and III              (C) II and III              (D) I and II

AB0023

10. Say which  $\text{pK}_a$  belong to which functional group in case of following amino acids :

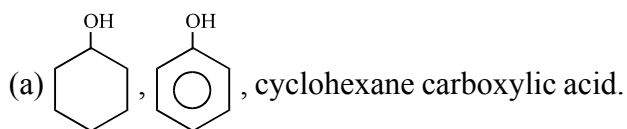
(i) cysteine : 1.8, 8.3 & 10.8

AB0024

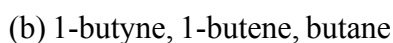
(ii) glutamic acid : : 2.19, 4.25, 9.67

AB0025

11. Record the following sets of compounds according to increasing  $pK_a$  ( $= -\log K_a$ )



AB0026



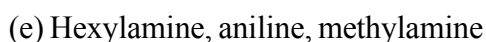
AB0027



AB0028

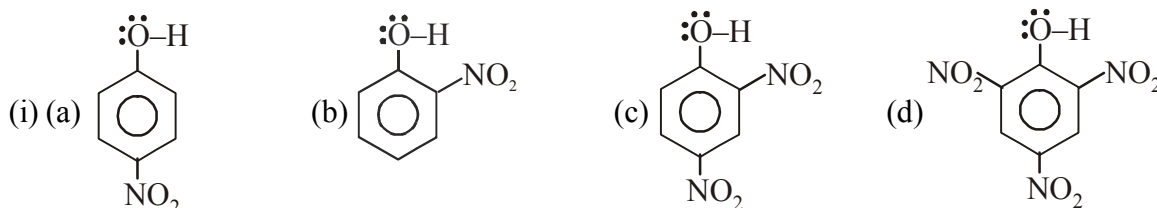


AB0029

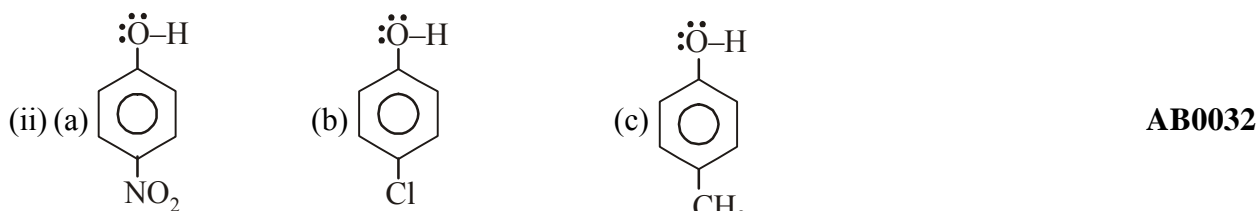


AB0030

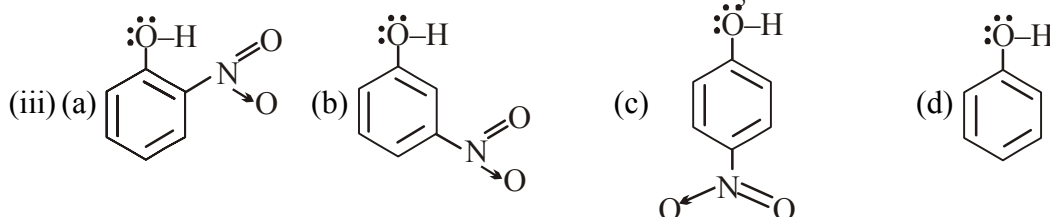
12. Write correct order of acidic strength of following compounds:



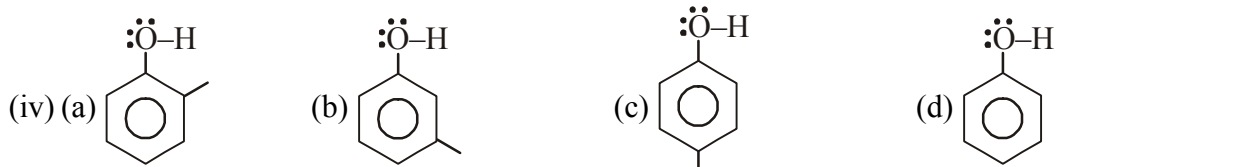
AB0031



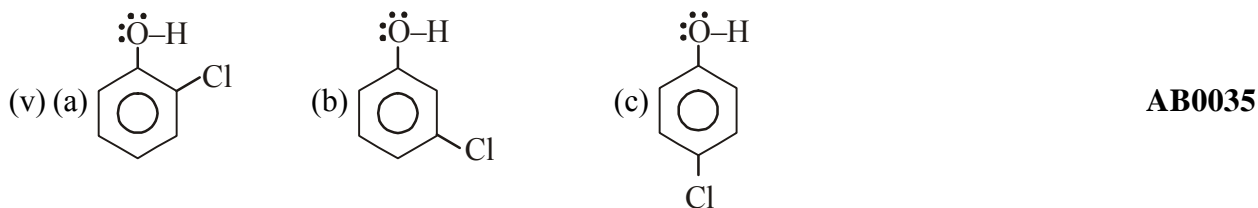
AB0032



AB0033



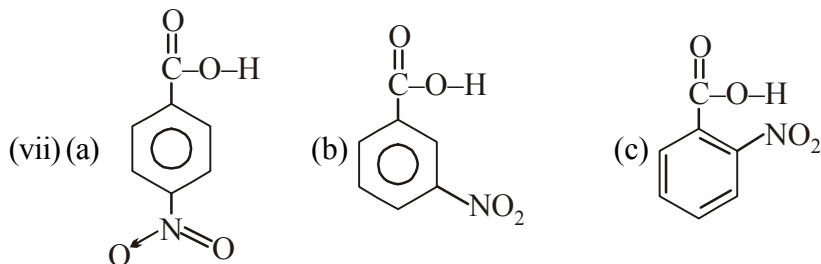
AB0034



AB0035

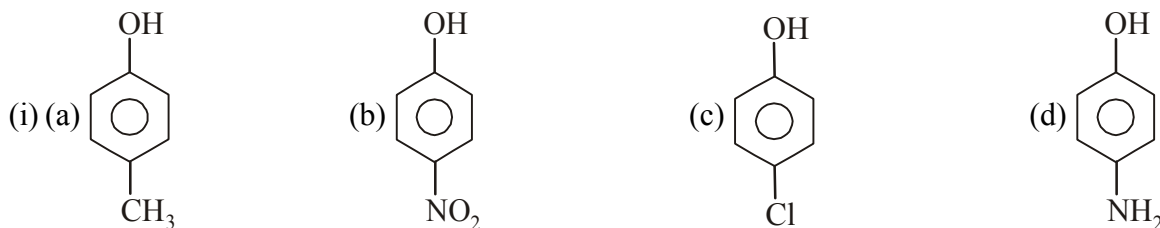


AB0036

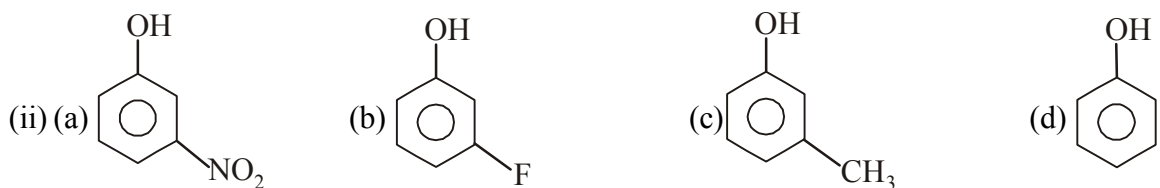


AB0037

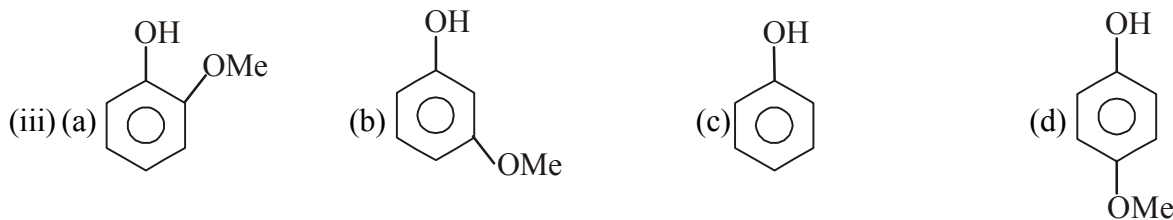
13. Select the strongest acid in each of the following sets :



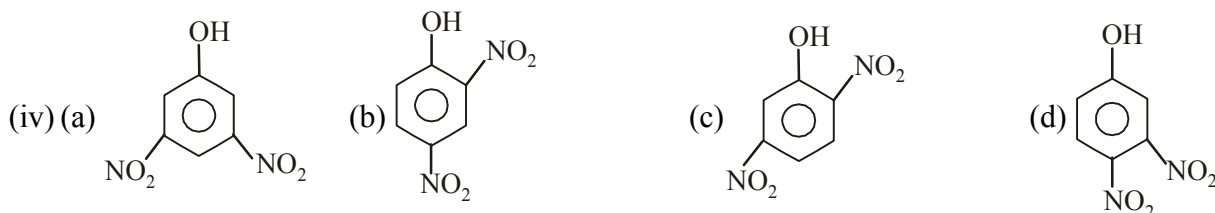
AB0038



AB0039

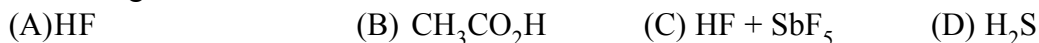


AB0040



AB0041

14. The strongest acid is :



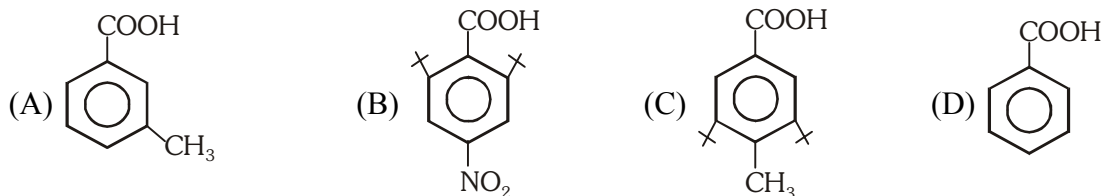
AB0042

15. The weakest acid (does not show acidic character) is :



AB0043

16. Which of the following is most acidic :



AB0044

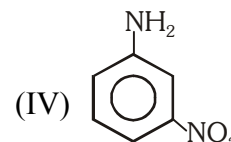
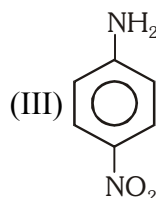
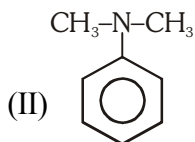
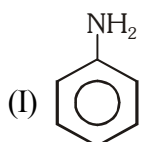


### Paragraph for Question 17 to 18

The most important condition for resonance to occur is that the involved atoms in resonating structure must be coplanar or nearly coplanar for maximum delocalisation. If this condition does not fulfil, involved orbitals cannot be parallel to each other and as a consequence delocalisation cannot occur. Bulky groups present on adjacent atoms inhibit the planarity of atoms involved in resonance. This phenomenon is known as steric inhibition of resonance. Steric inhibition of resonance has profound effect on

(1) Physical properties (2) Acidity and basicity (3) Reactivity of organic compounds

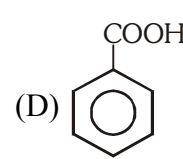
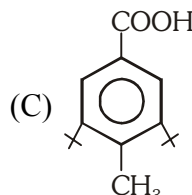
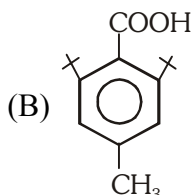
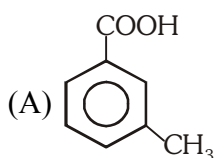
17. Arrange the following in the decreasing order of basicity :



(A) I > II > III > IV (B) IV > III > II > I (C) II > I > IV > III (D) I > IV > III > II

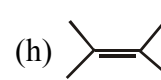
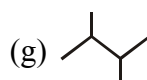
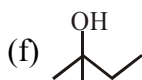
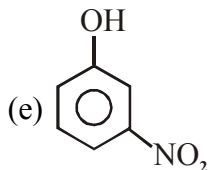
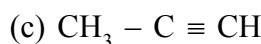
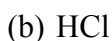
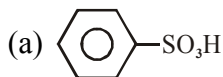
AB0045

18. Which of the following is most acidic :



AB0046

19. How many following compounds are more acidic than water ?



(i) NaOH

AB0047

20. Select correct order regarding acidic strength of given compounds :

(1) o-methylbenzoic acid

(2) m-methylbenzoic acid

(3) p-methylbenzoic acid

(4) benzoic acid

(A) 1 > 2 > 3 > 4

(B) 4 > 3 > 2 > 1

(C) 1 > 4 > 2 > 3

(D) 3 > 2 > 4 > 1

AB0048

EXERCISE # O-II

1. Write decreasing order of basic strength of following :



AB0049



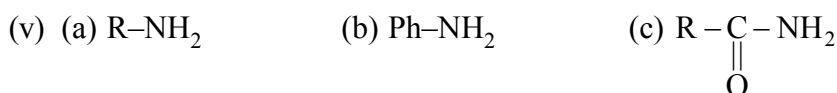
AB0050



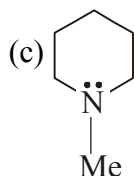
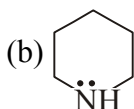
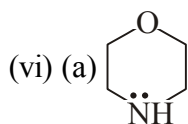
AB0051



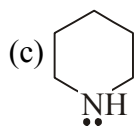
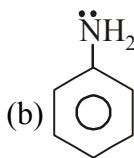
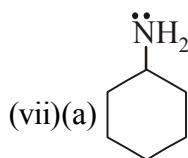
AB0052



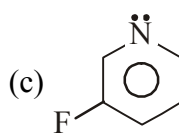
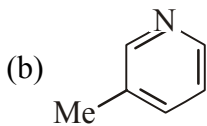
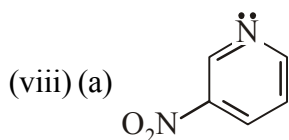
AB0053



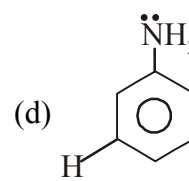
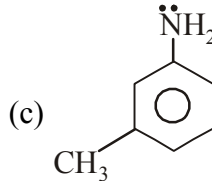
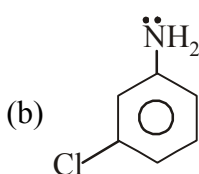
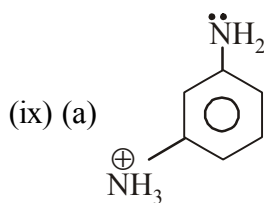
AB0054



AB0055

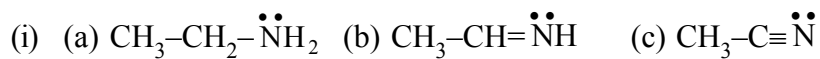


AB0056

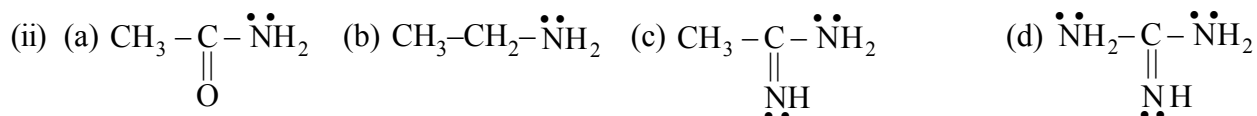


AB0057

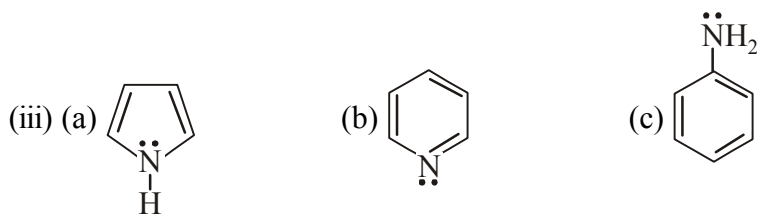
2. Write decreasing order of basic strength of following :



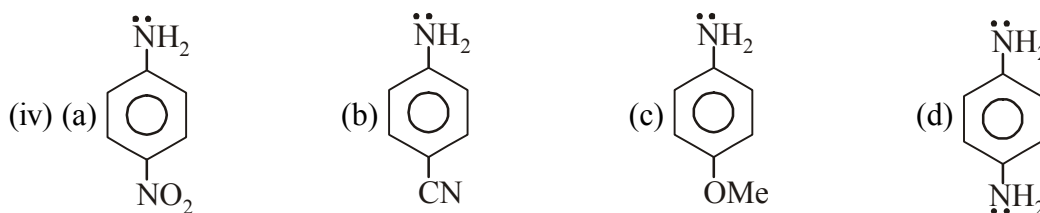
AB0058



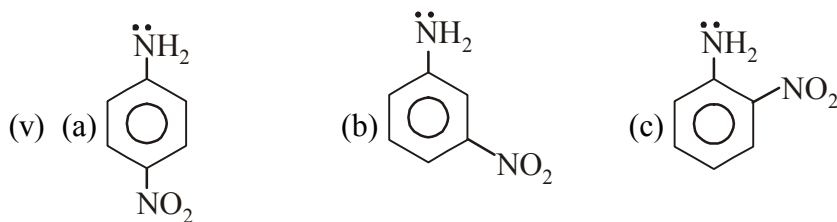
AB0059



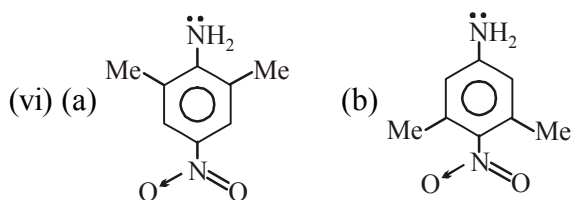
AB0060



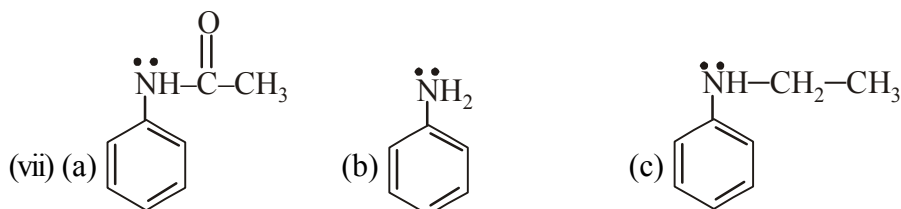
AB0061



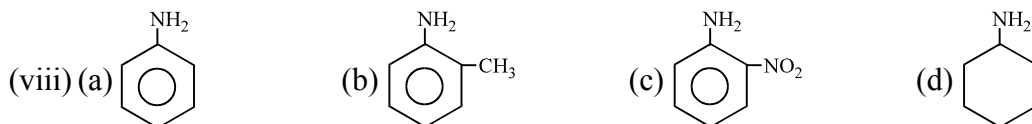
AB0062



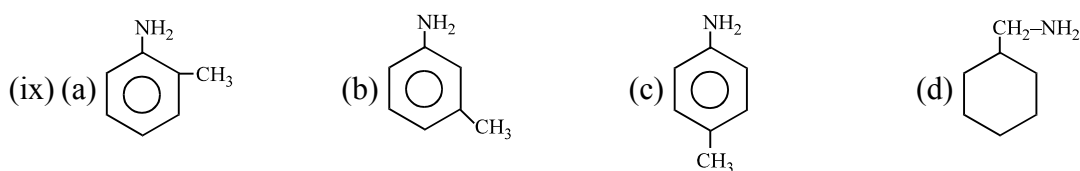
AB0063



AB0064

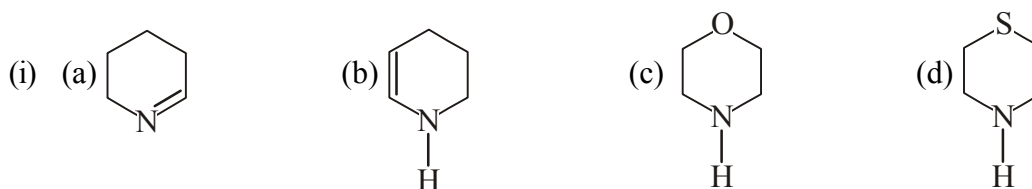


AB0065

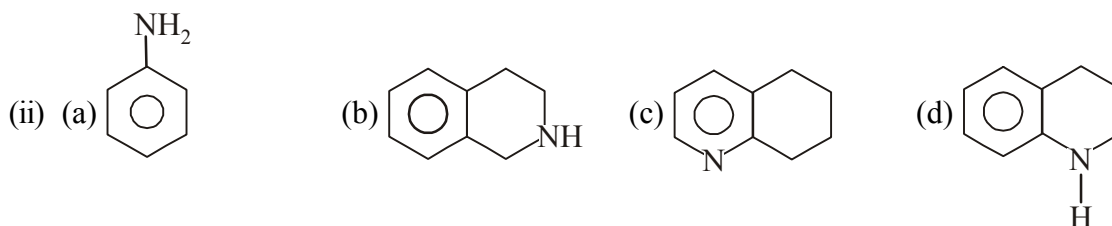


AB0066

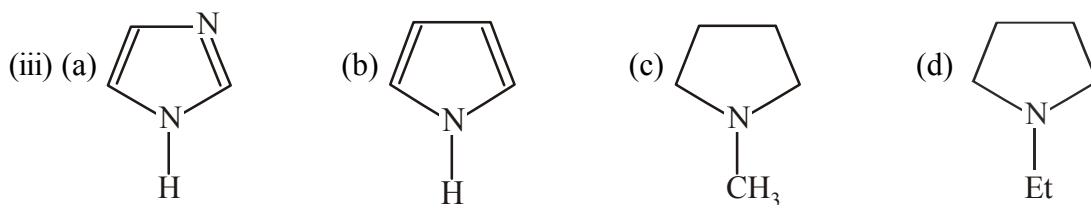
3. Select the strongest base in following compound :



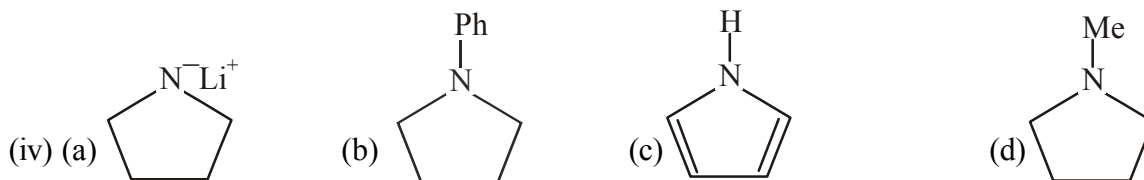
AB0067



AB0068



AB0069

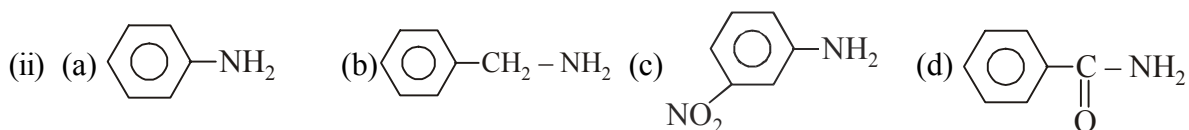


AB0070

4. Arrange the following compound in decreasing order of their basicity.

- (i) (a)  $\text{H}_2\text{C} = \text{CHNa}$     (b)  $\text{CH}_3\text{CH}_2\text{Na}$     (c)  $\text{CH}_3\text{CH}_2\text{ONa}$     (d)  $\text{HC} \equiv \text{CNa}$

AB0071

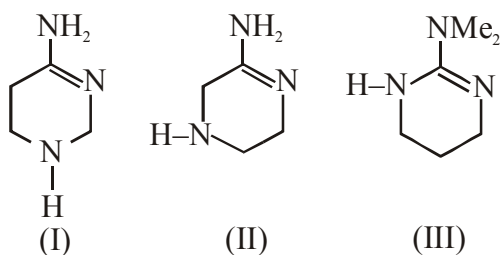


AB0072

- (iii) (a)  $\text{HO}^-$     (b)  $\text{NH}_3$     (c)  $\text{H}_2\text{O}$     (d)  $\text{HSO}_4^-$

AB0073

5. Correct decreasing order of basic strength -



Of following compound -

- (A)  $\text{III} > \text{II} > \text{I}$     (B)  $\text{II} > \text{I} > \text{III}$     (C)  $\text{I} > \text{II} > \text{III}$     (D)  $\text{III} > \text{I} > \text{II}$

AB0074

6. Consider the following bases:

- (I) o-nitroaniline    (II) m-nitroaniline    (III) p-nitroaniline

The decreasing order of basicity is:

- (A)  $\text{II} > \text{III} > \text{I}$     (B)  $\text{II} > \text{I} > \text{III}$     (C)  $\text{I} > \text{II} > \text{III}$     (D)  $\text{I} > \text{III} > \text{II}$

AB0075

7. Consider the basicity of the following aromatic amines:

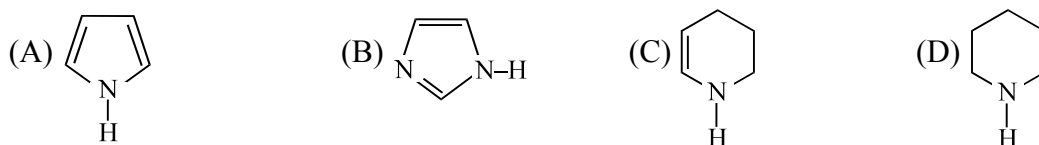
- (I) aniline    (II) p-nitroaniline    (III) p-methoxyaniline    (IV) p-methylaniline

The correct order of decreasing basicity is:

- (A)  $\text{III} > \text{IV} > \text{I} > \text{II}$     (B)  $\text{III} > \text{IV} > \text{II} > \text{I}$     (C)  $\text{I} > \text{II} > \text{III} > \text{IV}$     (D)  $\text{IV} > \text{III} > \text{II} > \text{I}$

AB0076

8. Which one of the following is least basic in character?



AB0077

9. In each of the following pair of compounds, which is more basic in aqueous solution?  
Give an explanation for your choice:

(a)  $\text{CH}_3\text{NH}_2$  or  $\text{CF}_3\text{NH}_2$  **AB0078**

(b)  $\text{CH}_3\text{CONH}_2$  or  $\text{H}_2\text{N}-\overset{\text{NH}}{\parallel}-\text{NH}_2$  **AB0078**

(c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  or  $\text{CH}_3\text{CN}$  **AB0078**

(d)  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$  or 2,6-dimethyl-N-N-dimethylaniline **AB0078**

10. Choose the member of each of the following pairs of compounds that is likely to be the weaker base.

(a)  $\text{H}_2\text{O}$  or  $\text{H}_3\text{O}^+$  **AB0079**

(b)  $\text{Cl}^-$ ,  $\text{SH}^-$  **AB0079**

(c)  $\text{F}^-$ ,  $\text{OH}^-$ ,  $\text{NH}_2^-$ ,  $\text{CH}_3^-$  **AB0079**

(d)  $\text{HF}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  **AB0079**

(e)  $\text{OH}^-$ ,  $\text{SH}^-$ ,  $\text{SeH}^-$  **AB0079**

11. Explain which compound is the weaker base.

(a)  or  **AB0080**

(b)  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH}_2^-$  or  $\text{CH}_2 = \text{CH} - \text{CH}_2^-$  **AB0080**

(c)  or  **AB0080**

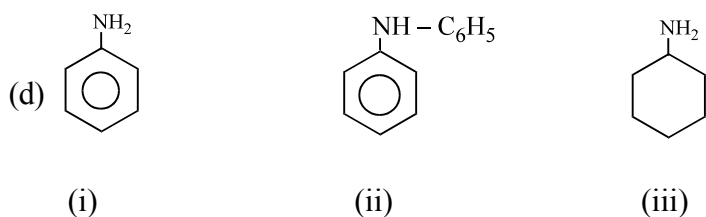
(d)  or  **AB0080**

12. Arrange the basic strength of the following compounds.

(a)  $\text{OH}^-$   $\text{CH}_3\text{COO}^-$   $\text{Cl}^-$   
(i) (ii) (iii) **AB0081**

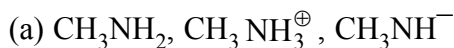
(b)  $\text{CH} \equiv \text{C}^-$   $\text{CH}_2 = \text{CH}^-$   $\text{CH}_3\text{CH}_2^-$   
(i) (ii) (iii) **AB0082**

(c)  $\text{CH}_2 = \text{CHCH}_2\text{NH}_2$   $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$   $\text{CH} \equiv \text{C} - \text{CH}_2\text{NH}_2$   
(i) (ii) (iii) **AB0083**

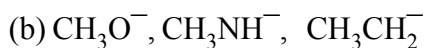


AB0084

13. Arrange the following compounds in order of increasing basicity.

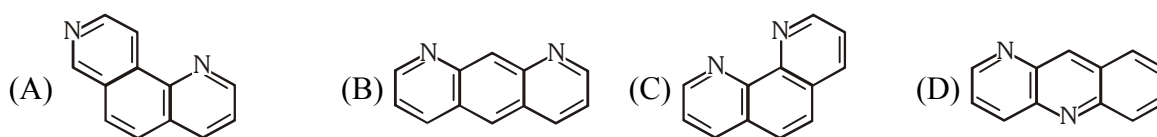


AB0085



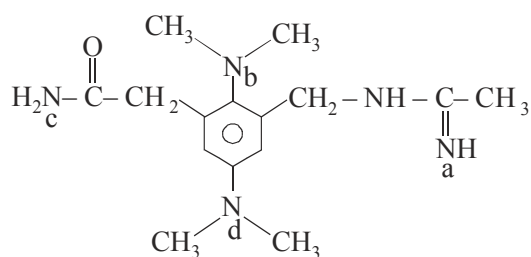
AB0085

14. Which of the following is most basic :



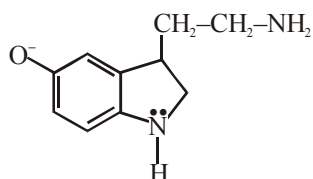
AB0086

15. Basicity order of N in following compound is :

(A)  $b > d > a > c$ (B)  $a > b > d > c$ (C)  $a > b > c > d$ (D)  $a > c > b > d$ 

AB0087

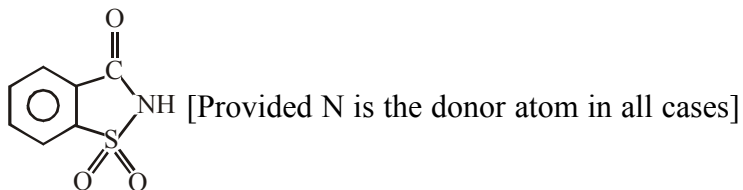
16. The conjugate base of serotonin (used as tranquilisers) is given as follows :



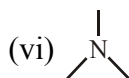
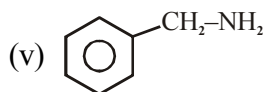
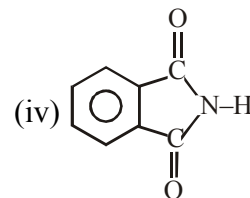
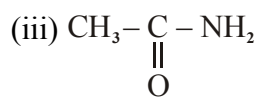
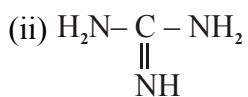
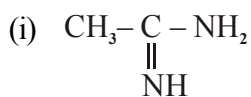
How many basic groups present in following compound ?

AB0088

17. The structure of saccharin is given as follows :



How many following compounds are more basic than saccharin ?

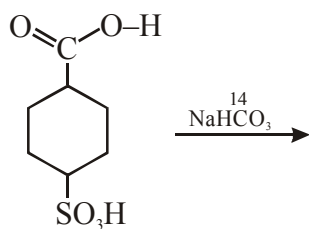


AB0089



## EXERCISE # S-I

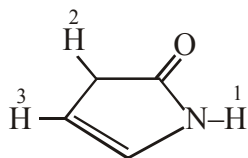
1. In given reaction Gas liberated is/are



- (A)  $\text{CO}_2$  &  $\text{SO}_3$       (B)  $\text{SO}_3$  &  $^{14}\text{CO}_2$       (C)  $^{14}\text{CO}_2$  only      (D)  $\text{SO}_2$  only

AB0090

2. Arrange marked atom in decreasing order of acidic strength

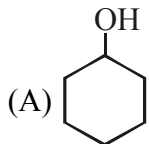


- (A)  $1 > 2 > 3$       (B)  $3 > 2 > 1$       (C)  $2 > 1 > 3$       (D)  $2 > 3 > 1$

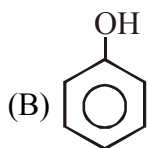
AB0091

3. Column - I

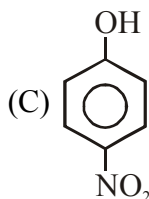
Column-I



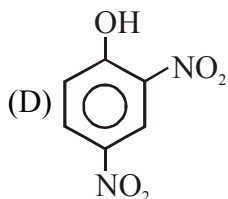
(P) React with NaOH



(Q) React with  $\text{NaHCO}_3$



(R) React with NaH

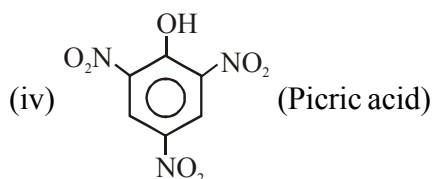
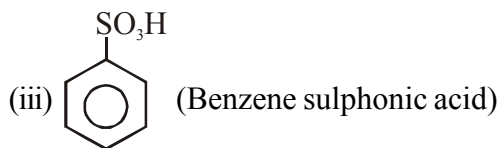
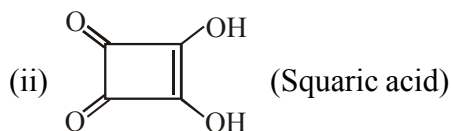
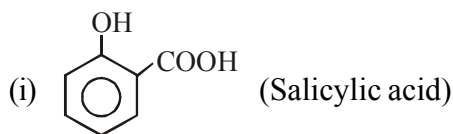


(S) React with Na

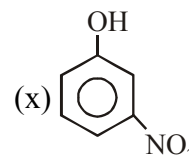
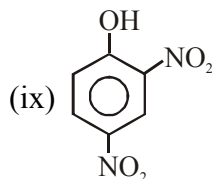
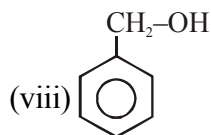
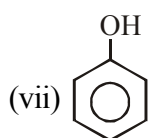
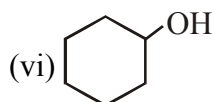
(T) React with  $\text{NaNH}_2$

AB0092

4. Compound which can give effevescences with  $\text{NaHCO}_3$

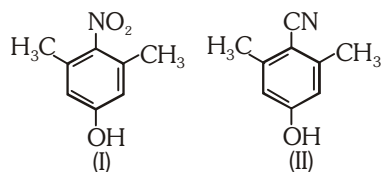


(v)  $\text{Ph-CH=CH-COOH}$  (cinnamic acid)



AB0093

5. **Statement-1** : For the given two compounds-I is more acidic than compounds-II.



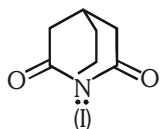
and

**Statement-2** : Due to presence of  $-\text{CH}_3$  group at ortho positions to  $-\text{NO}_2$  ; the plane of  $-\text{NO}_2$  deviates, w.r.t plane of ring.

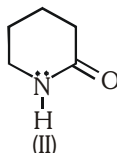
- (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.

AB0094

6. **Statement 1 :**



is more basic than



and

**Statement 2 :** Lone pair electrons on nitrogen in compound (I) does not participate in resonance.

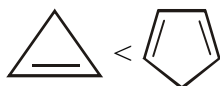
- (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.

AB0095

7. Match Column-I with Column-II.

**Column - I (Facts)**

- (A) Guanidine  $\text{H}_2\text{N}-\text{C}(\text{NH}_2)=\text{NH}$  is example of strong base  
 (B) Carbanion stability  $\bar{\text{C}}\text{Cl}_3 > \bar{\text{C}}\text{F}_3$   
 (C) Alkyne is more acidic than alkene  
 (D) Acidity :



**Column - II (Reasons)**

- (P) Resonance stabilisation of conjugate acid of strong base.  
 (Q) Due to s-character of central atoms  
 (R) Due to d-orbital resonance  
 (S) Due to formation of aromatic anion  
 (T) Stability of conjugate acid / base due to more number of identical resonating structure

AB0096

8. Match Column-I with Column-II.

**Column - I (Compounds)**

- (A)   
 (B)   
 (C)   
 (D)

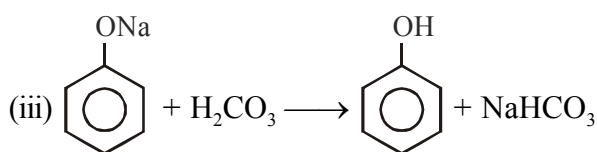
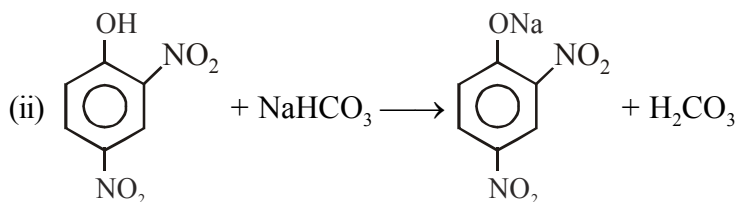
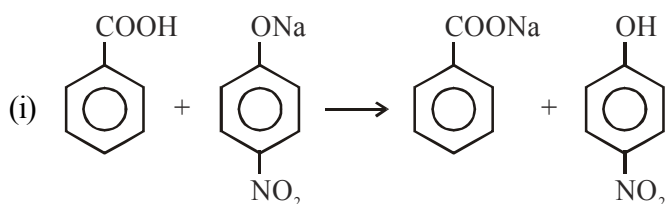
**Column - II (pKa)**

- (P) 7.15  
 (Q) 10.14  
 (R) 9.98  
 (S) 9.38  
 (T) pKa is more than phenol

AB0097

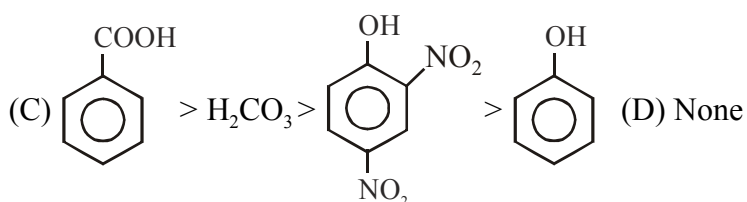
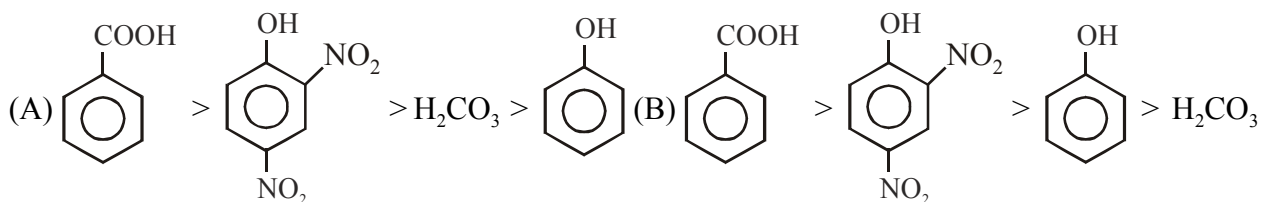
(Comprehension) (Q.9 to Q.11)

Observe the following feasible reactions :



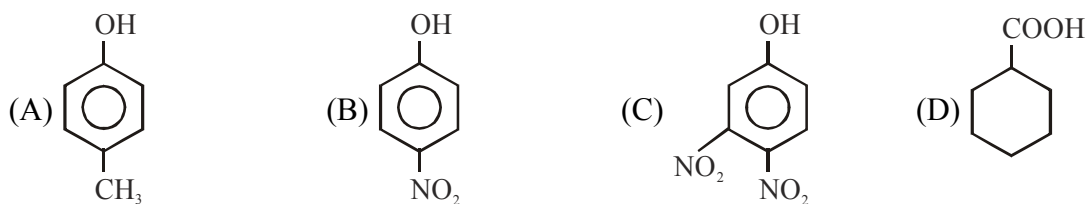
Answer the following question :

9. Which of the following is the correct order of acidic strength.



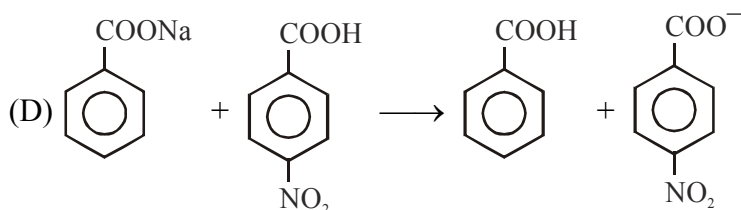
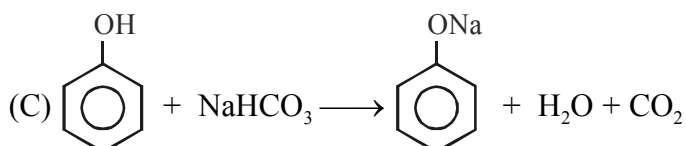
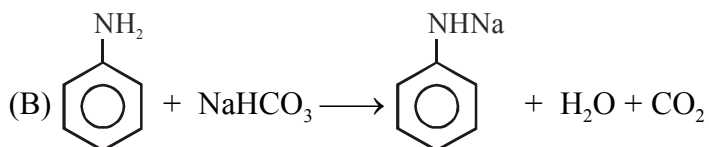
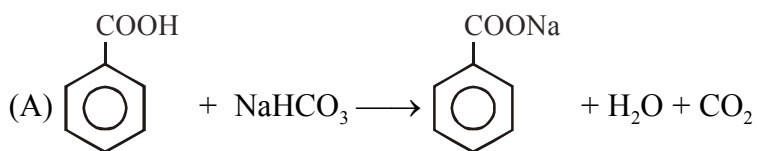
AB0098

10. Which of the following compound does not react with NaHCO<sub>3</sub>



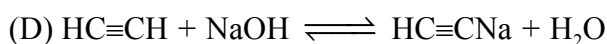
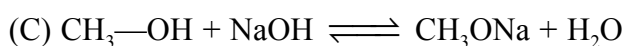
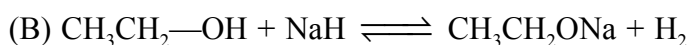
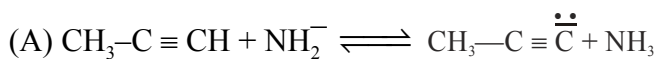
AB0099

11. Identify the feasible reactions



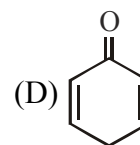
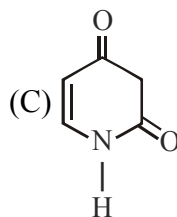
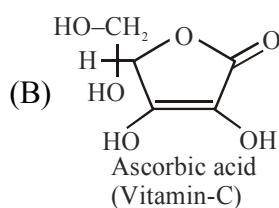
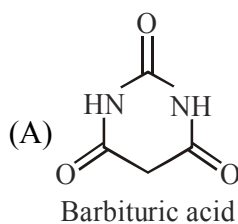
AB0100

12. Identify the non-feasible reaction



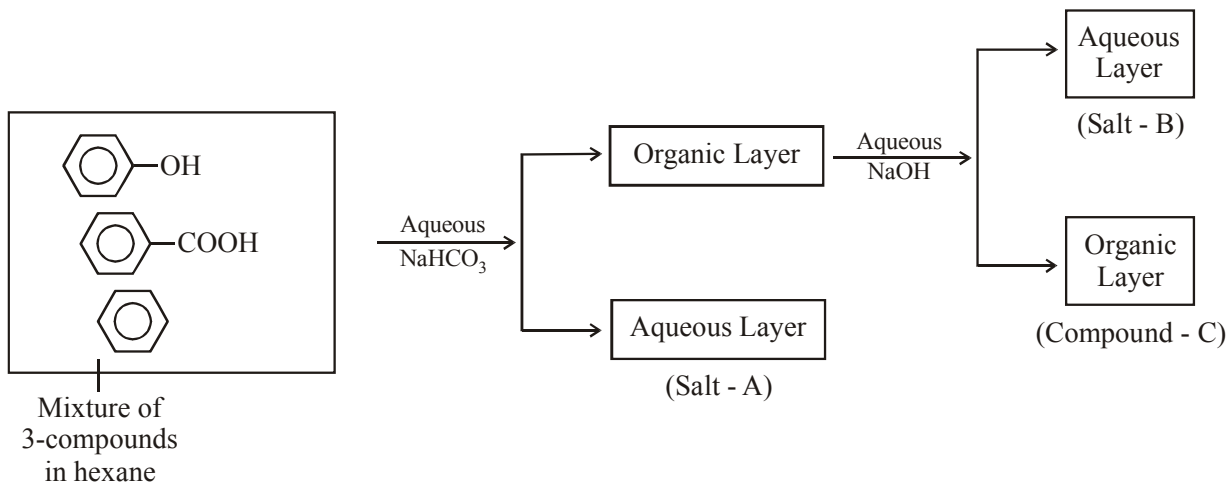
AB0101

13. Select the number of compounds in which deprotonation gives aromatic anion :

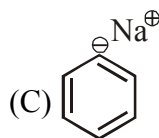
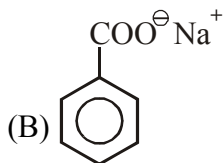
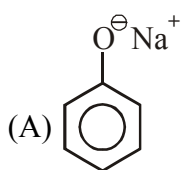


AB0102

Paragraph for Questions 14 and 15



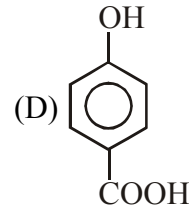
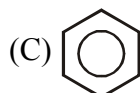
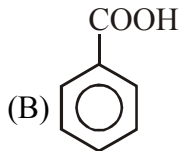
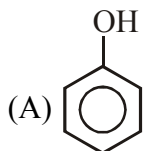
14. Identify salt 'A' ?



(D) All of these

AB0103

15. Identify compound 'C' ?

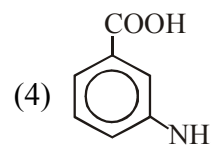
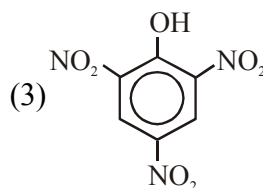
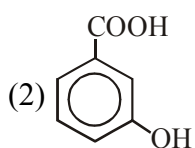
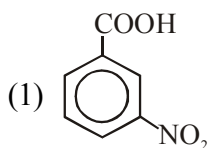


AB0103

## EXERCISE # JEE-MAIN

1. Picric acid is -

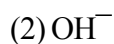
[AIIEEE-2002]



AB0104

2. Which of the following species acts both as bronsted acid &amp; base -

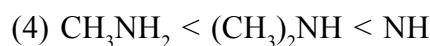
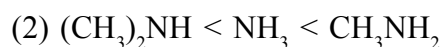
[AIIEEE-2002]



AB0105

3. The correct order of increasing basic nature for the bases  $\text{NH}_3$ ,  $\text{CH}_2\text{NH}_2$  and  $(\text{CH}_3)_2\text{NH}$  is-

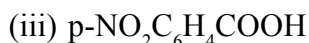
[AIIEEE-2003]



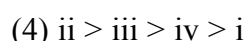
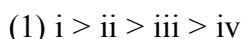
AB0106

4. Consider the acidity of the carboxylic acids-

[AIIEEE-2004]



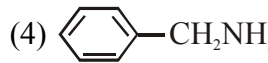
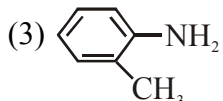
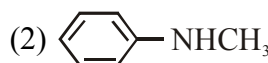
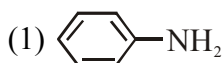
which of the following is the correct order of acidity-



AB0107

5. Which of the following is the strongest base -

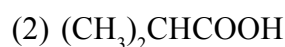
[AIIEEE-2004]



AB0108

6. Among the following acids which has the lowest  $\text{p}K_a$  value-

[AIIEEE-2005]



AB0109

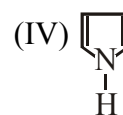
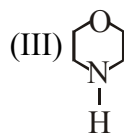
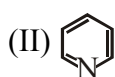
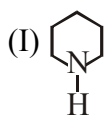
7. Amongst the following the most basic compound is- [AIEEE-2005]  
 (1) p-nitro aniline (2) Acetanilide  
 (3) Aniline (4) Benzylamine  
 AB0110
8. What is the conjugate base of  $\text{OH}^-$ ? [AIEEE-2005]  
 (1)  $\text{H}_2\text{O}$  (2)  $\text{O}_2$  (3)  $\text{O}^{2-}$  (4)  $\text{O}^-$   
 AB0111
9. Among the following acids which has the lowest  $\text{pK}_a$  value? [AIEEE-2005]  
 (1)  $\text{HCOOH}$  (2)  $\text{CH}_3\text{COOH}$   
 (3)  $\text{CH}_3\text{CH}_2\text{COOH}$  (4)  $(\text{CH}_3)_2\text{CH-COOH}$   
 AB0112
10. The correct order of increasing acid strength of the compounds is [AIEEE-2006]  
 (a)  $\text{CH}_3\text{CO}_2\text{H}$  (b)  $\text{MeOCH}_2\text{CO}_2\text{H}$   
 (c)  $\text{CF}_3\text{CO}_2\text{H}$  (d)  $\begin{array}{c} \text{Me} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{Me} \end{array} \text{CO}_2\text{H}$   
 (1)  $d < a < c < b$  (2)  $d < a < b < c$   
 (3)  $a < d < c < b$  (4)  $b < d < a < c$   
 AB0113
11. Which one of the following is the strongest base in aqueous solution? [AIEEE-2007]  
 (1) Trimethylamine (2) Aniline  
 (3) Dimethylamine (4) Methylamine  
 AB0114
12. The correct order of increasing basicity of the given conjugate base ( $\text{R}=\text{CH}_3$ ) is :- [AIEEE-2010]  
 (1)  $\text{RCO}\bar{\text{O}} < \text{HC} \equiv \bar{\text{C}} < \bar{\text{N}}\text{H}_2 < \bar{\text{R}}$  (2)  $\text{RCO}\bar{\text{O}} < \text{HC} \equiv \bar{\text{C}} < \bar{\text{R}} < \bar{\text{N}}\text{H}_2$   
 (3)  $\bar{\text{R}} < \text{HC} \equiv \bar{\text{C}} < \text{RCO}\bar{\text{O}} < \bar{\text{N}}\text{H}_2$  (4)  $\text{RCO}\bar{\text{O}} < \bar{\text{N}}\text{H}_2 < \text{HC} \equiv \bar{\text{C}} < \bar{\text{R}}$   
 AB0115
13. The strongest acid amongst the following compounds is? [AIEEE-2011]  
 (1)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$  (2)  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$   
 (3)  $\text{CH}_3\text{COOH}$  (4)  $\text{HCOOH}$   
 AB0116
14. The correct order of acid strength of the following compounds :-  
 A. Phenol B. p-Cresol  
 C. m-Nitrophenol D. p-Nitrophenol  
 is :- [AIEEE-2011]  
 (1)  $\text{C} > \text{B} > \text{A} > \text{D}$  (2)  $\text{D} > \text{C} > \text{A} > \text{B}$   
 (3)  $\text{B} > \text{D} > \text{A} > \text{C}$  (4)  $\text{A} > \text{B} > \text{D} > \text{C}$

AB0117

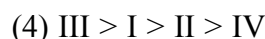
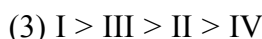


15. In the following compounds :

[JEE(Main)-2012]



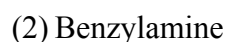
the order of basicity is as follows :



AB0118

16. The most basic compound among the following is :-

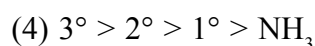
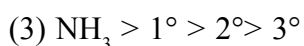
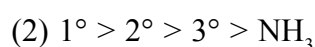
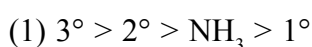
[JEE(Main)-2012]



AB0119

17. The order of basicity of amines in gaseous state is :-

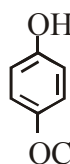
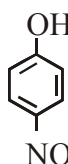
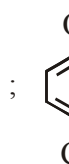
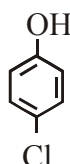
[JEE(Main)-2013]



AB0120

18. Arrange the following compounds in order of decreasing acidity :

[JEE(Main)-2013]

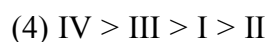
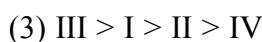
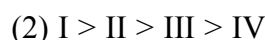


(I)

(II)

(III)

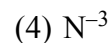
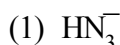
(IV)



AB0121

19. The conjugate base of hydrazoic acid is :-

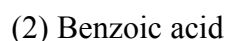
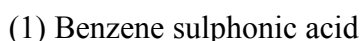
[JEE(Main)-2014]



AB0122

20. Which one of the following compounds will not be soluble in sodium bicarbonate ?

[JEE(Main)-2014]



AB0123

21. Considering the basic strength of amines in aqueous solution, which one has the smallest  $pK_b$  value ?

[JEE(Main)-2014]

- (1)  $(\text{CH}_3)_3\text{N}$       (2)  $\text{C}_6\text{H}_5\text{NH}_2$       (3)  $(\text{CH}_3)_2\text{NH}$       (4)  $\text{CH}_3\text{NH}_2$

AB0124

22. Among the following oxoacids, the correct decreasing order of acid strength is : [JEE(Main)-2014]

- (1)  $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$       (2)  $\text{HClO}_2 > \text{HClO}_4 > \text{HClO}_3 > \text{HOCl}$   
 (3)  $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$       (4)  $\text{HClO}_4 > \text{HOCl} > \text{HClO}_2 > \text{HClO}_3$

AB0125

23. Among the following compounds, the increasing order of their basic strength is:-

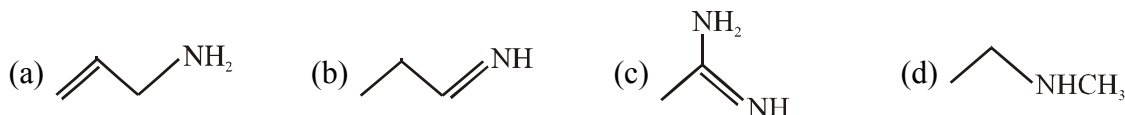


- (1) (II) < (I) < (III) < (IV)      (2) (I) < (II) < (IV) < (III)      [JEE(Main)-On-Line 2017]  
 (3) (II) < (I) < (IV) < (III)      (4) (I) < (II) < (III) < (IV)

AB0126

24. The increasing order of basicity of the following compounds is :

[JEE(Main)-2018]



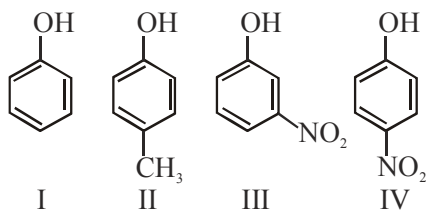
- (1) (b) < (a) < (c) < (d)      (2) (b) < (a) < (d) < (c)  
 (3) (d) < (b) < (a) < (c)      (4) (a) < (b) < (c) < (d)

AB0127

## EXERCISE # J-ADVANCED

1. In the following compounds

[IIT-JEE-1996]



The order of acidity is -

- (A) III>IV>I>II      (B) I>IV>III>II      (C) II>I>III>IV      (D) IV>III>I>II

AB0137

2. Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why? [IIT-JEE-1997]

AB0138

3. Amongst the following, the most basic compound is -

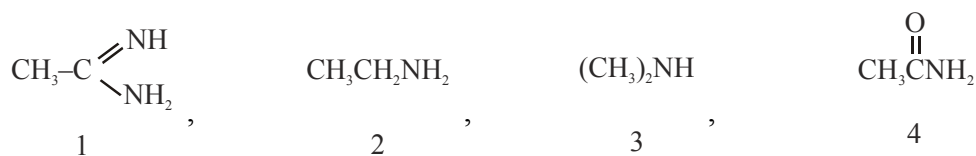
[IIT-JEE-2000]

- (A)  $C_6H_5NH_2$       (B)  $p\text{-NO}_2\text{-C}_6\text{H}_4\text{NH}_2$       (C)  $m\text{-NO}_2\text{-C}_6\text{H}_4\text{NH}_2$       (D)  $C_6H_5CH_2NH_2$

AB0139

4. The correct order of basicities of the following compounds is :

[IIT-JEE-2001]



- (A) 2 > 1 > 3 > 4      (B) 1 > 3 > 2 > 4      (C) 3 > 1 > 2 > 4      (D) 1 > 2 > 3 > 4

AB0140

5. **Statement-I** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.**Because****Statement-II** : o-Hydroxybenzoic acid has intramolecular hydrogen bonding. [IIT-JEE-2003]

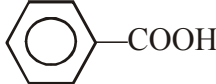
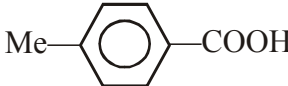
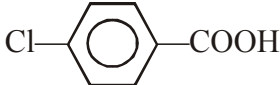


- (A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I  
 (B) Statement-I is True, Statement-II is True; Statement-II is NOT a correct explanation for Statement-I  
 (C) Statement-I is True, Statement-II is False.  
 (D) Statement-I is False, Statement-II is True.

AB0141

6. Match  $K_a$  values with suitable acid :

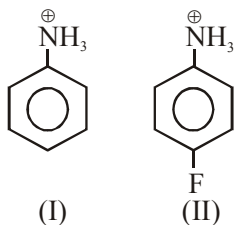
[IIT-JEE-2003]

- $K_a$
- (A)  $3.3 \times 10^{-5}$
- (B)  $4.2 \times 10^{-5}$
- (C)  $6.3 \times 10^{-5}$
- (D)  $6.4 \times 10^{-5}$
- (E)  $30.6 \times 10^{-5}$

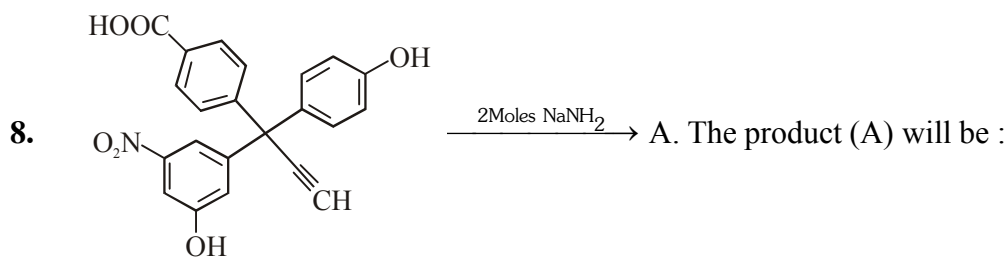
- Acid
- (p) 
- (q) 
- (r) 
- (s) 
- (t) 

7. (a) Which of the following is more acidic and why ?

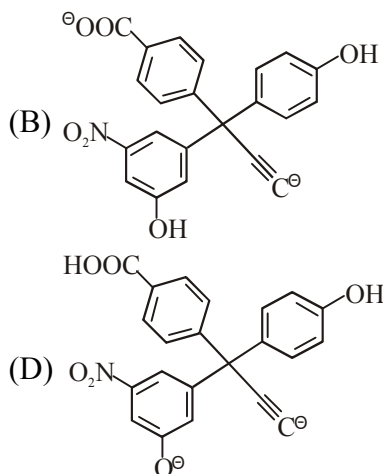
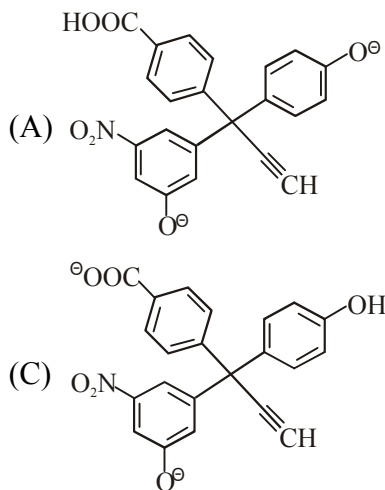
AB0142  
[IIT-JEE-2004]



AB0143



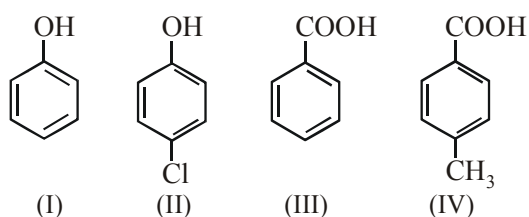
[IIT-JEE-2007]



AB0144

9. The correct acidity order of the following is :

[IIT-JEE-2009]

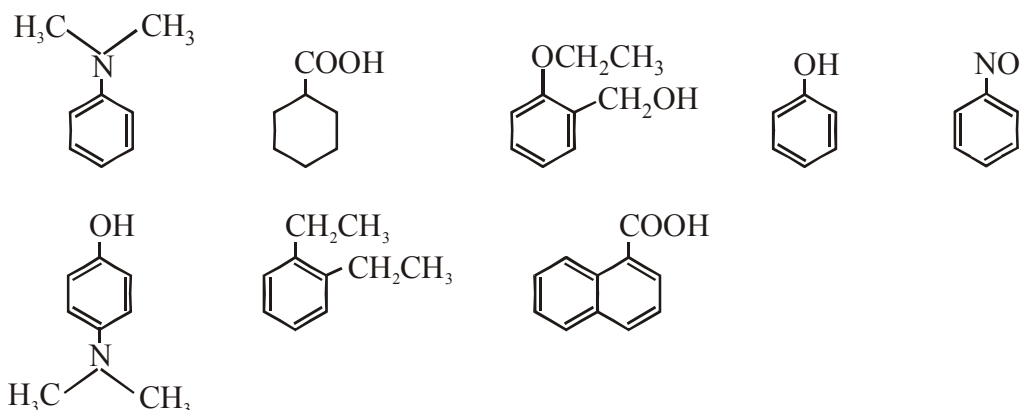


- (A) (III) > (IV) > (II) > (I)                      (B) (IV) > (III) > (I) > (II)  
 (C) (III) > (II) > (I) > (IV)                      (D) (II) > (III) > (IV) > (I)

AB0145

10. Amongst the following, the total number of compounds soluble in aqueous NaOH is:

[IIT-JEE-2010]



AB0146

11. Among the following compounds, the most acidic is

[IIT-JEE-2011]

- (A) p-nitrophenol                                      (B) p-hydroxybenzoic acid  
 (C) o-hydroxybenzoic acid                        (D) p-toluic acid

AB0147

12. The carboxyl functional group ( $-\text{COOH}$ ) is present in -

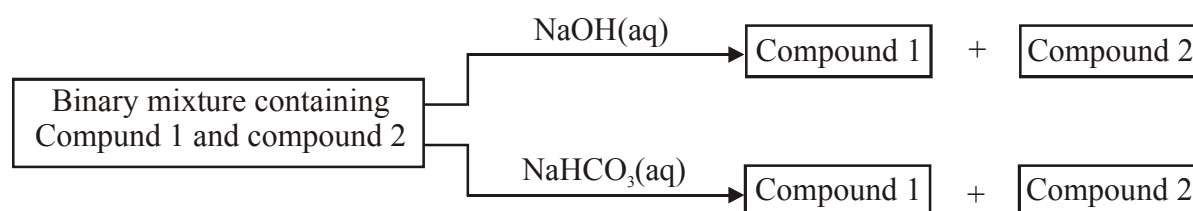
[IIT-JEE-2012]

- (A) picric acid                      (B) barbituric acid      (C) ascorbic acid      (D) aspirin

AB0148

13. Identify the binary mixtures (s) that can be separated into the individual compounds, by differential extraction, as shown in the given scheme -

[IIT-JEE-2012]



- (A)  $\text{C}_6\text{H}_5\text{OH}$  and  $\text{C}_6\text{H}_5\text{COOH}$                       (B)  $\text{C}_6\text{H}_5\text{COOH}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$   
 (C)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  and  $\text{C}_6\text{H}_5\text{OH}$                       (D)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$

AB0149

14. The compound that does NOT liberate  $\text{CO}_2$ , on treatment with aqueous sodium bicarbonate solution, is - [JEE-ADVANCED-2013]

- (A) Benzoic acid (B) Benzenesulphonic acid (C) Salicylic acid (D) Carboic acid (phenol)

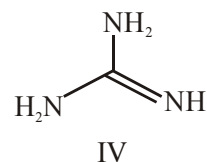
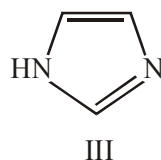
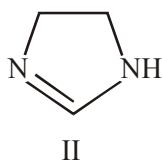
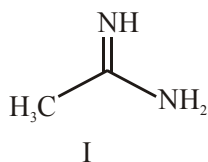
AB0150

15. Hydrogen bonding plays a central role in the following phenomena [JEE-ADVANCED-2014]

- (A) Ice floats in water  
 (B) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions  
 (C) Formic acid is more acidic than acetic acid  
 (D) Dimerisation of acetic acid in benzene

AB0151

16. The order of basicity among the following compounds is [JEE-ADVANCED-2017]



- (A) II > I > IV > III

- (B) IV > II > III > I

- (C) I > IV > III > II

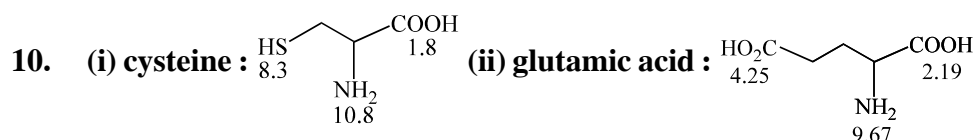
- (D) IV > I > II > III

AB0152

## ANSWER-KEY

## EXERCISE # O-I

1. (i)  $a > b > c > d$ , (ii)  $a > b > c$ , (iii)  $c > b > a$ , (iv)  $a > b > c$ ,  
 (v)  $c > b > a$ , (vi)  $a > b > c$  (vii)  $d > c > b > a$ , (viii)  $d > c > b > a$ ,  
 (ix)  $d > b > a > c$ , (x)  $d > a > c > b$
2. (a) 2; (b) 2; (c) 1; (d) 1      3. (a) 2; (b) 2; (c) 2      4. (C)      5. (B)  
 6. (B)      7. (B)      8. (A)      9. (A)



11. (a)  $3 < 2 < 1$ ; (b)  $1 < 2 < 3$ ; (c)  $3 < 2 < 1$ ; (d)  $2 < 1 < 3$ ; (e)  $2 < 3 < 1$
12. (i)  $d > c > a > b$ , (ii)  $a > b > c$ , (iii)  $c > a > b > d$ , (iv)  $d > b > c > a$ ,  
 (v)  $a > b > c$ , (vi)  $b > a$  (vii)  $c > a > b$
13. (i) b, (ii) a, (iii) b, (iv) b      14. (C)      15. (C)      16. (B)  
 17. (C)      18. (B)      19. (4)      20. (C)

## EXERCISE # O-II

1. (i)  $a > b > c > d$ , (ii)  $a > b > c > d$ , (iii)  $c > b > d > a$ , (iv)  $d > c > b > a$   
 (v)  $a > b > c$ , (vi)  $c > b > a$  (vii)  $c > a > b$ , (viii)  $b > c > a$ , (ix)  $c > d > b > a$
2. (i)  $a > b > c$ , (ii)  $d > c > b > a$ , (iii)  $b > c > a$ , (iv)  $d > c > b > a$ ,  
 (v)  $b > a > c$ , (vi)  $b > a$ , (vii)  $c > b > a$ , (viii)  $d > a > b > c$   
 (ix)  $d > c > b > a$
3. (i) d, (ii) b, (iii) a, (iv) a
4. (i)  $b > a > d > c$ , (ii)  $b > a > c > d$ , (iii)  $a > b > c > d$
5. (A)      6. (A)      7. (A)      8. (A)
9. (a) i, (b) ii, (c) i, (d) ii      10. (a) 2; (b) 1; (c) 1; (d) 1; (e) 3
11. (a) 2; (b) 1; (c) 2; (d) 2      12. (a)  $1 > 2 > 3$ ; (b)  $1 < 2 < 3$ ; (c)  $3 < 1 < 2$ ; (d)  $2 < 1 < 3$
13. (a)  $2 < 1 < 3$ ; (b)  $1 < 2 < 3$       14. (C)      15. (B)
16. 3, 3 basic groups are  $\ddot{\text{N}}\text{H}_2$ ;  $-\text{NH}-$ ;  $\text{O}^-$       17. (6)

## EXERCISE # S-I

1. (C)    2. (C)
3. (A) – R, S, T ; (B) – P, R, S, T ; (C) – P, Q, R, S, T ; (D) – P, Q, R, S, T
4. (i), (ii) (iii) (iv), (v) (ix)    5. (D)    6. (A)
7. (A) – P, T ; (B) – R ; (C) – Q ; (D) – S, T    8. (A) – R ; (B) – S ; (C) – P ; (D) – Q, T
9. (A)    10. (A)    11. (A, D)    12. (D)
13. (A, B, C, D)                                  14. (B)    15. (C)

## EXERCISE # JEE-MAIN

1. (3)    2. (4)    3. (3)    4. (4)    5. (4)
6. (3)    7. (4)    8. (3)    9. (1)    10. (2)
11. (3)    12. (1)    13. (1)    14. (2)    15. (3)
16. (2)    17. (4)    18. (3)    19. (2)    20. (3)
21. (3)    22. (1)    23. (3)    24. (2)

## EXERCISE # J-ADVANCED

1. (D)    2. Benzoate has equivalent resonating structures    3. (D)
4. (B)    5. (D)    6. A-(s) ; B-(q) ; C-(p) ; D-(r) ; E-(t)
7. (II is most acidic)                                  8. (C)    9. (A)    10. (4)    11. (C)
12. (D)    13. (B, D)    14. (D)    15. (A, B, D)
16. (D)







# Chapter Contents

## 04

## ISOMERISM

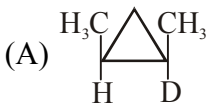
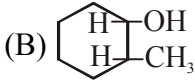
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02. EXERCISE-II (JEE-MAIN)	116
03. EXERCISE-III (J-ADVANCED)	118
04. ANSWER KEY	120



## ISOMERISM

## EXERCISE # I (MAINS ORIENTED)

## Single Correct Type :

1. Minimum number of carbon atom required by a Hydrocarbon alkane, alkene and alkyne to show chain isomerism respectively are :  
 (A) 4, 4, 4 (B) 4, 3, 3 (C) 4, 4, 3 (D) 4, 4, 5
2.  $C_7H_7Cl$  shows how many benzenoid aromatic isomers ?  
 (A) 4 (B) 3 (C) 5 (D) 6
3. How many structural isomers of primary amines are possible for the formula  $C_4H_{11}N$  ?  
 (A) 2 (B) 3 (C) 4 (D) 5
4. How many benzenoid structure are possible for molecular form  $C_7H_8O$  :  
 (A) 3 (B) 4 (C) 5 (D) 6
5. Which of the following compound give geometrical isomerism ?  
 (A)  $CH_2Cl_2$  (B)  $CH_2Cl-CH_2Cl$  (C)  $CHBr = CHCl$  (D)  $CH_2Cl-CH_2Br$ .
6. Maximum potential energy is associated with which of the following conformers of n-butane :  
 (A) Anti (B) Gauche (C) Eclipsed (D) Partial eclipsed
7. Which among the following compounds will show geometrical isomerism :  
 (A)  $CH_3-CH=CH_2$  (B)  $CH_3-\underset{\text{CH}_3}{\text{C}}=CH_2$  (C)  $CH_3-\underset{\text{CH}_3}{\text{C}}=CHD$  (D)  $CH_3-CH=CHD$
8. Which among the following will show geometrical isomerism :  
 (A)  (B)  (C)  $C_6H_5-CH=N-OH$  (D) All of these
9. Which one of the following is Z isomer :  
 (A)  $\begin{matrix} CH_3 & & Br \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ H & & Cl \end{matrix}$  (B)  $\begin{matrix} CH_3 & & Cl \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ H & & Br \end{matrix}$  (C)  $\begin{matrix} CH_3 & & Cl \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ Br & & H \end{matrix}$  (D)  $\begin{matrix} CH_3 & & H \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ H & & CH_3 \end{matrix}$

SR0001

SR0002

SR0003

SR0004

SR0005

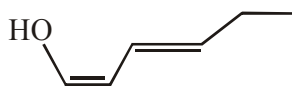
SR0006

SR0007

SR0008

SR0009

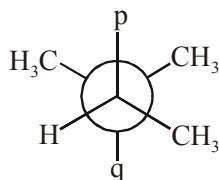
10. The correct stereochemical descriptions for the structure given below are :



- (A) 1 Z, 3Z (B) 1Z, 3E (C) 1E, 3E (D) 1E, 3Z

SR0010

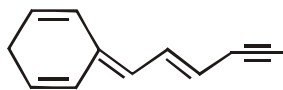
11. What is the value of p & q of following conformer of 2,3-dimethyl butane ?



- (A) p = H, q = H (B) p = CH<sub>3</sub>, q = CH<sub>3</sub> (C) p = CH<sub>3</sub>, q = H (D) p = H, q = CH<sub>3</sub>

SR0011

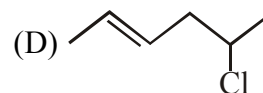
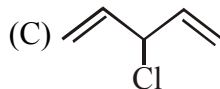
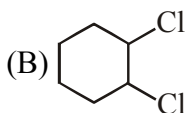
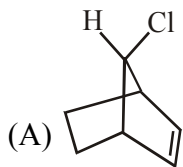
12. The number of cis-trans isomer possible for the following compound.



- (A) 2 (B) 4 (C) 6 (D) 8

SR0012

13. Which of the following can not show geometrical isomerism :



SR0013

14. How many structural formula are possible when one of the hydrogen is replaced by a chlorine atom in benzene & naphthalene respectively ?

- (A) 1, 1 (B) 1, 2 (C) 2, 2 (D) 2, 1

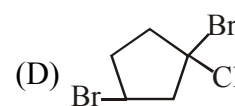
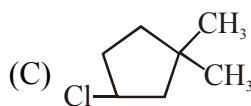
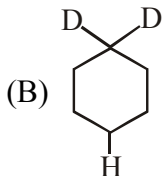
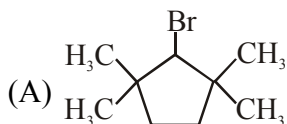
SR0076

15. The number of structural isomers of C<sub>5</sub>H<sub>10</sub> is :-

- (A) 10 (B) 11 (C) 12 (D) 13

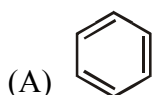
SR0015

16. Which of the following compounds will show geometrical isomerism.

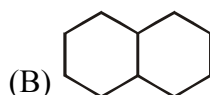


SR0016

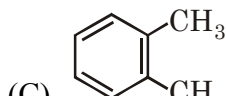
17. Which of the following will show geometrical isomerism?



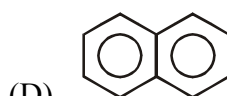
Benzene



Decalin



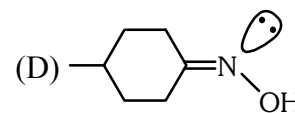
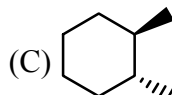
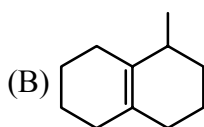
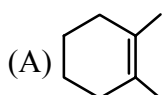
o-Xylene



Naphthalene

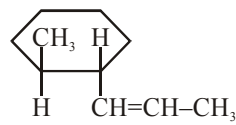
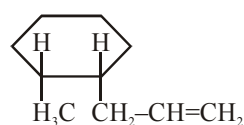
SR0077

18. Which of the following cannot be represent in E or Z



SR0018

19.



(A) Geometrical isomer

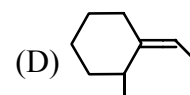
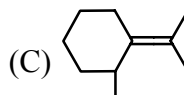
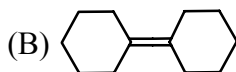
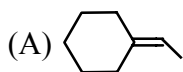
(B) Ring chain isomer

(C) Position isomer

(D) Chain isomer

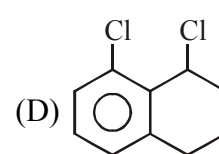
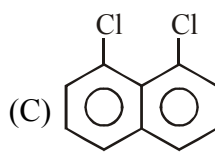
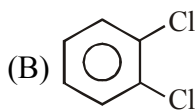
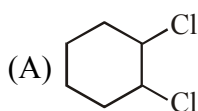
SR0019

20. Which of the following can show geometrical isomerism :



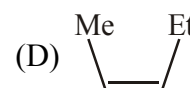
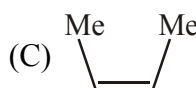
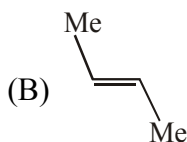
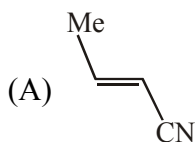
SR0020

21. Which of the following will show Geometrical isomerism.



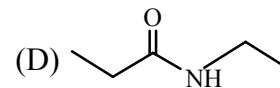
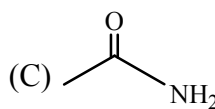
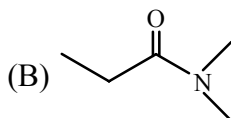
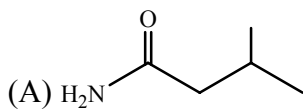
SR0021

22. Which of the following will have lowest dipole moment?



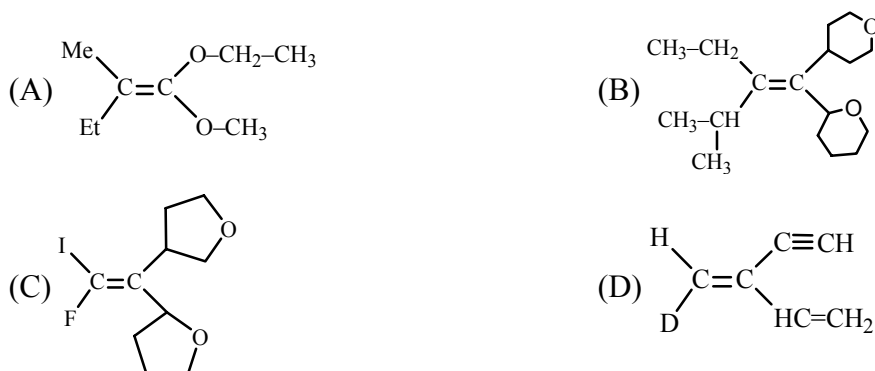
SR0022

23. Which of the following compounds can show geometrical isomerism in its resonating structure.



SR0023

24. Which of the following represent Z-isomer ?



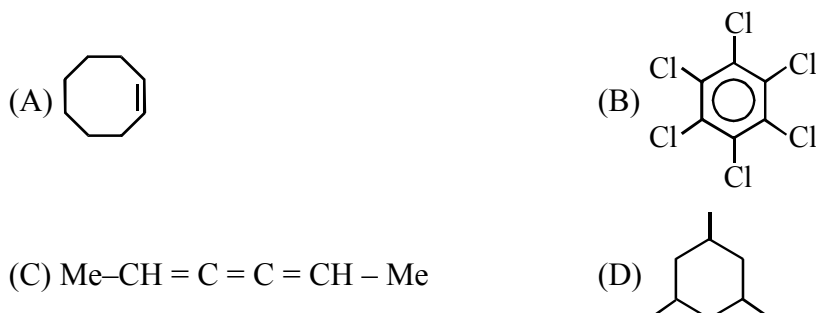
SR0024

25. Which of the following statement is not correct :-

- (A) Cyclobutane is a planar compound  
 (B) Trans cyclohexadecene is relatively more stable than its cis form  
 (C) Cis form of 1,3,5-trimethylcyclohexane is relatively more stable than its trans form  
 (D) Cis 1,2-dichloroethene is relatively more stable than its trans form.

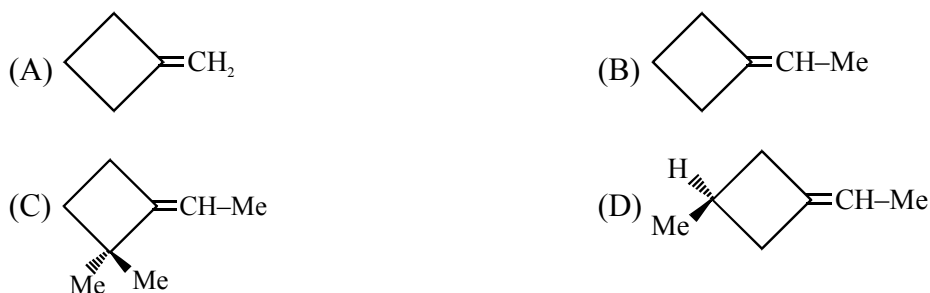
SR0025

26. Select which one of the following can not show geometrical isomerism



SR0026

27. Which one of the following is capable of showing geometrical isomerism.



SR0027

More than one correct Type :

28. Which of the following statements is/are not correct :

- (A) Metamerism belongs to the category of structural isomerism
- (B) Tautomeric structures are the resonating structures of a molecule
- (C) Keto form is always more stable than the enol form
- (D) Geometrical isomerism is shown only by alkenes

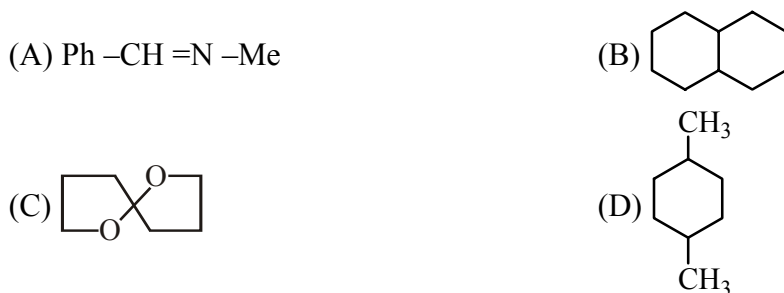
SR0028

29. Which of the following will show geometrical isomerism :

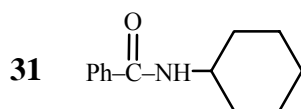


SR0029

30. Which of the following compound will shows geometrical isomerism ?



SR0030



- (A) This molecule shows geometrical isomerism.
- (B) One of the resonating structure of this molecule shows geometrical isomerism
- (C) One of the tautomer of this molecule shows geometrical isomerism
- (D) In acidic medium this molecule shows geometrical isomerism.

SR0031



**Assertion / Reasoning Type :**

**32. Statement-1 :** All double bond containing compounds show geometrical isomerism.

and

**Statement-2 :** Alkenes have restricted rotation about the carbon-carbon double bond.

- (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.

SR0032

**33. Statement-1 :** According to CIP sequence rule the priority of the groups is



and

**Statement-2 :** Priority of the given groups are based on molecular mass of groups.

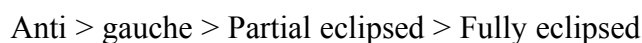
- (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1  
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1  
 (C) Statement-1 is True, Statement-2 is False  
 (D) Statement-1 is False, Statement-2 is True

SR0033

**Comprehension Type :**

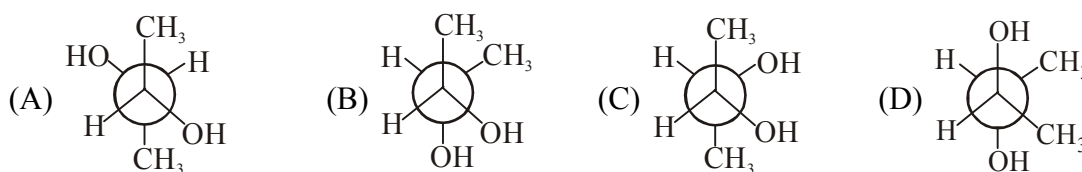
**Paragraph for Q. 34 to 35**

Different spatial arrangements of the atoms that result from rotation about a single bond are conformers. n-Butane has four conformers eclipsed, partial eclipsed, gauche and anti. The stability order of these conformers are as follows :



Although anti is more stable than gauche but in some cases gauche is more stable than anti.

**34.** Which one of the following is the most stable conformer ?



SR0034

35. Number of possible conformations of n-butane is :

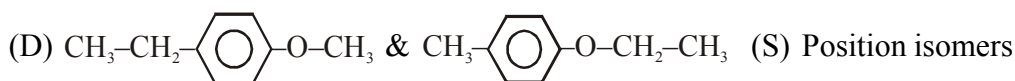
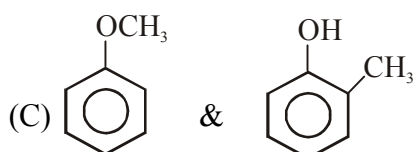
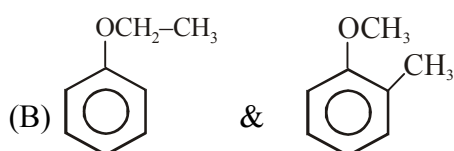
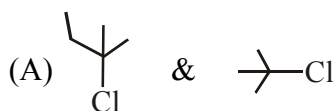
- (A) 2 (B) 4 (C) 6 (D) infinite

SR0034

Matrix Match Type :

36. Match the column I with column II.

Column-I (reaction)



Column-II (stereoisomers)

(P) Homologs

(Q) Functional isomers

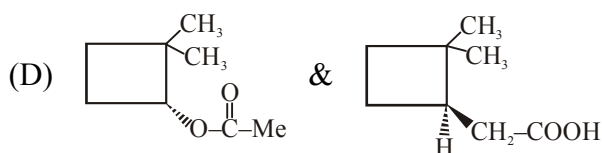
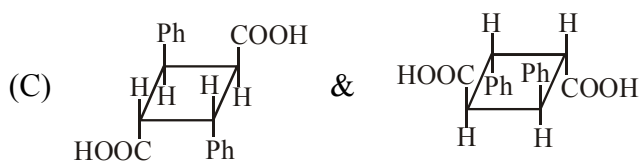
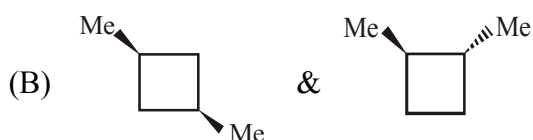
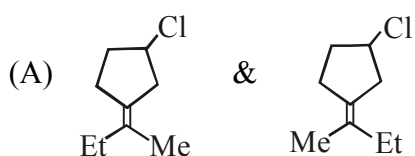
(R) Metamer

(S) Position isomers

SR0035

37. Match the column I with column II.

Column-I



Column-II

(P) Identical

(Q) Functional isomers

(R) Geometrical Isomers

(S) Positional Isomers

SR0036

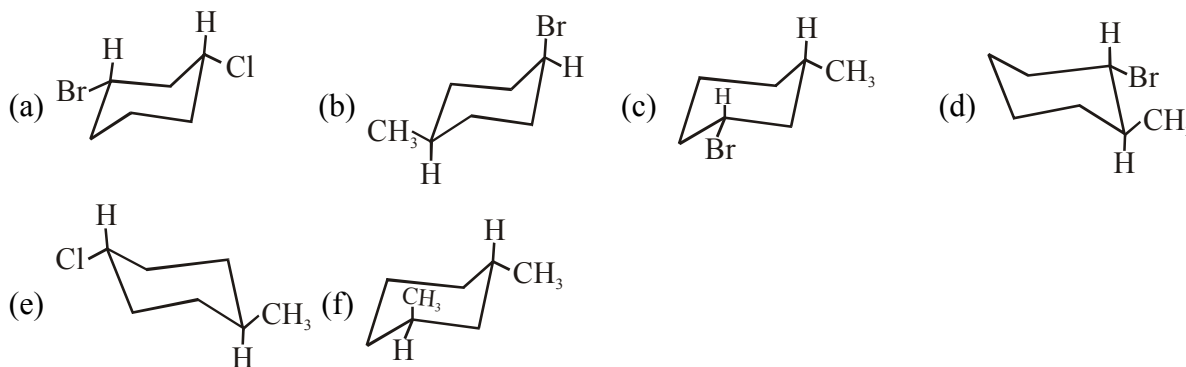
**Subjective Type :**

38. Considering rotation about the  $C_3-C_4$  bond of 2-methylhexane :

- (a) Draw the Newman projection of the most stable conformer  
 (b) Draw the Newman projection of the least stable conformer

SR0037

39. Determine whether each of the following compounds is a cis isomer or a trans isomer.



SR0038

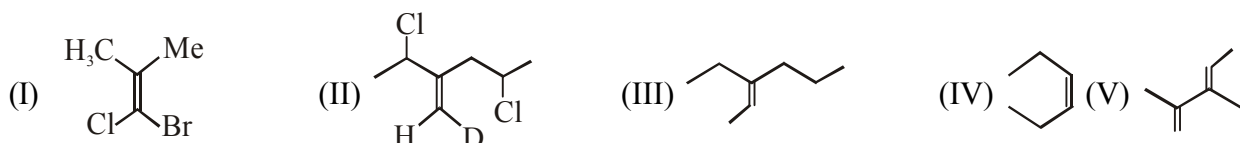
40. Draw the most stable conformer of N-methylpiperidine.

SR0039

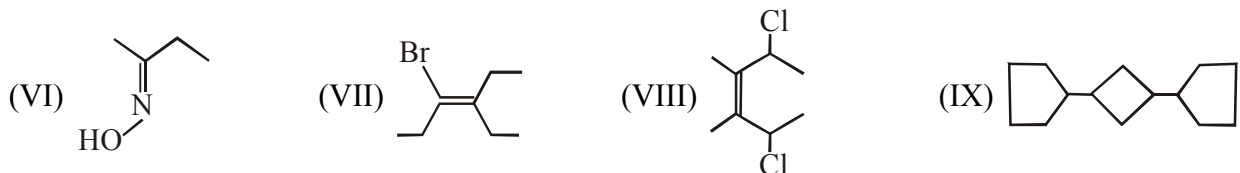
41. How many pair(s) of geometrical isomers are possible with  $C_6H_{12}$  (only in open chain structures)

SR0040

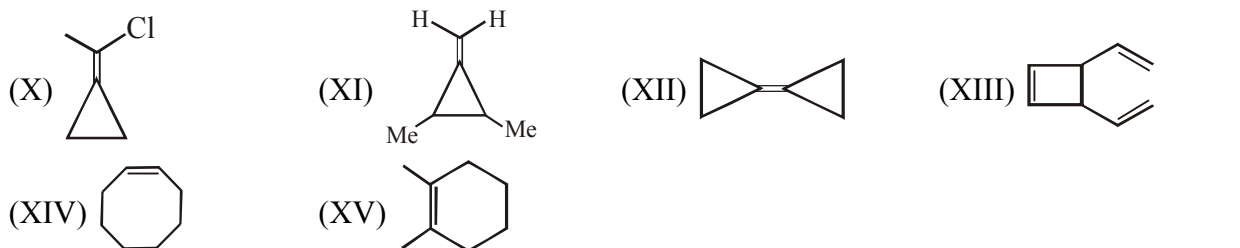
42. Identify molecules which usually can show geometrical isomerism (at room temperature):



SR0041



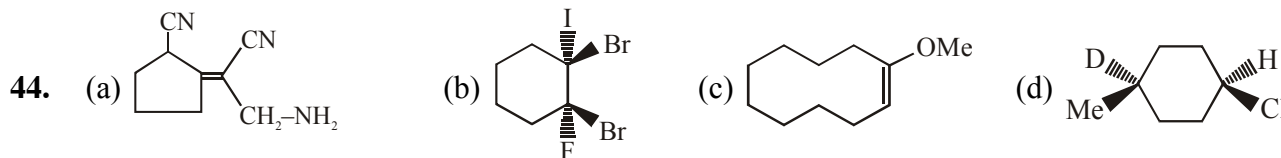
SR0042



SR0043

43. Calculate the number of Benzenoid isomers possible for  $C_6H_3ClBrI$ .

SR0044

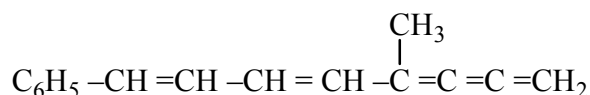


Assign E or Z to the following compounds and write 1 for E and 2 for Z.

Write answer of part (a), (b), (c) & (d) in the same order and present the four digit number as answer in OMR sheet. For example: If all these answer are 9 then fill 9999 in OMR sheet.

SR0045

45. (a) Number of geometrical isomers of the following compound.



(b) Total number  $2^\circ$  and  $3^\circ$  Alcohols possible for  $C_5H_{11}OH$ . without counting stereo isomers.

Write answer of part (a) & (b) in the same order and present the four digit number as answer in OMR sheet. For example: If your Answer for (a) is 9 & (b) is 9 then fill 0909 in OMR sheet.

SR0046

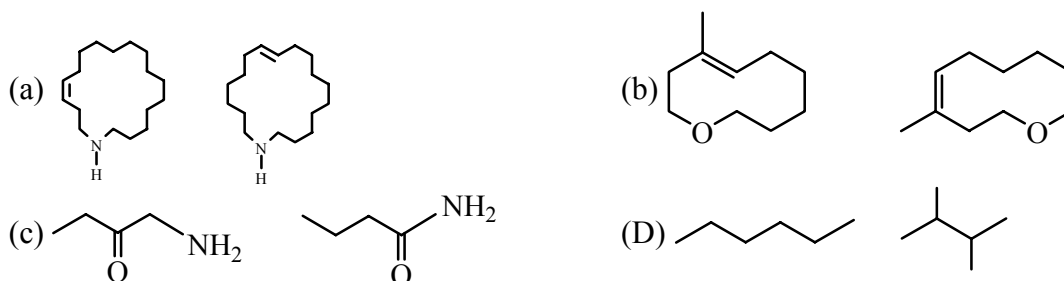
46. Analyse the following pairs of compounds.

Write 1 if they are Geometrical isomers.

Write 2 if they are Chain isomers.

Write 3 if they are position isomers.

Write 4 if they are Functional group isomers.



Write answer of part (a), (b), (c) & (d) in the same order and present the four digit number as answer in OMR sheet. For example: If all these answers are 9 then fill 9999 in OMR sheet.

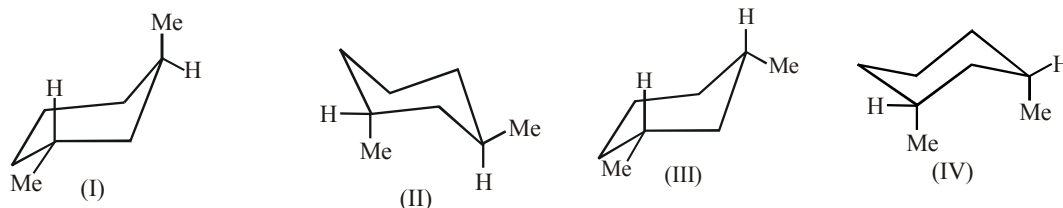
SR0047

## EXERCISE # II (J-MAINS)

1. Geometrical isomerism is not shown by- [AIEEE-2002]  
 (A) 1,1-dichloro-1-pentene (B) 1,2-dichloro-1-pentene  
 (C) 1,3-dichloro-2-pentene (D) 1,4-dichloro-2-pentene
- SR0048
2. Increasing order of stability among the three main conformations (i.e. Eclipse, Anti, Gauche) of 2-fluoroethanol is [AIEEE-2006]  
 (A) Gauche, Eclipse, Anti (B) Eclipse, Anti, Gauche  
 (C) Anti, Gauche, Eclipse (D) Eclipse, Gauche, Anti
- SR0049
3. The alkene that exhibits geometrical isomerism is :- [AIEEE-2009]  
 (A) 2-butene (B) 2-methyl-2-butene  
 (C) Propene (D) 2-methyl propene
- SR0051
4. Identify the compound that exhibits tautomerism :- [AIEEE-2011]  
 (A) 2-Pentanone (B) Phenol (C) 2-Butene (D) Lactic acid
- SR0052
5. The IUPAC name of the following compounds is : [JEE-MAIN-2012]
- 
- (A) (Z) - 5 hepten - 3 - yne (B) (Z) - 2 hepten - 4 - yne  
 (C) (E) - 5 hepten - 3 - yne (D) (E) - 2 hepten - 4 - yne
- SR0053
6. Dipole moment is shown by :- [JEE-MAIN 2012]  
 (A) trans-2, 3-dichloro- 2-butene (B) 1, 2-dichlorobenzene  
 (C) 1, 4-dichlorobenzene (D) trans-1, 2-dinitroethene
- SR0054
7. Maleic acid and fumaric acids are :- [JEE-MAIN 2012]  
 (A) Tautomers (B) Chain isomers  
 (C) Geometrical isomers (D) Functional isomers
- SR0055
8. Monocarboxylic acids are functional isomers of : [JEE-MAIN 2013]  
 (A) Esters (B) Amines  
 (C) Ethers (D) Alcohols
- SR0056

9. Arrange in the correct order of stability (decreasing order) for the following molecules:

[JEE-MAIN 2013]

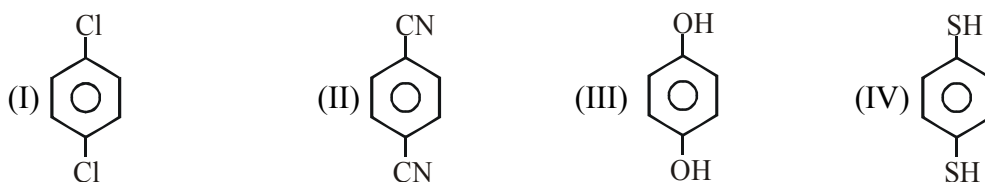


- (A) (I) > (II) > (III) > (IV)                      (B) (IV) > (III) > (II) ≈ (I)  
 (C) (III) > (I) ≈ (II) > (IV)                      (D) (I) > (II) ≈ (III) > (IV)

SR0057

10. For which of the following molecule significant  $\mu \neq 0$

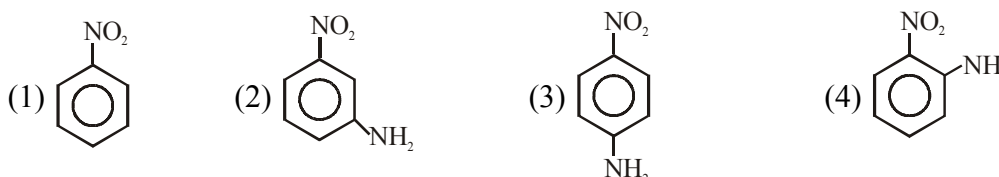
[JEE-MAIN 2014]



- (A) Only (III)                      (B) (III) and (IV)                      (C) Only (I)                      (D) (I) and (II)

SR0058

11. Which compound exhibits maximum dipole moment among the following :-[JEE-MAIN 2015]



SR0059

12. The number of structural isomers for  $C_6H_{14}$  is:

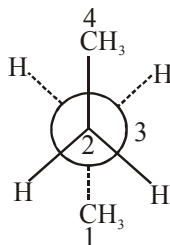
[JEE-MAIN 2015]

- (1) 6                      (2) 4                      (3) 3                      (4) 5

SR0060

## EXERCISE # III (J-ADVANCED OBJECTIVE)

1. When cyclohexane is poured on water, it floats, because : [IIT-1997]  
 (A) cyclohexane is in 'boat' form  
 (B) cyclohexane is in 'chair' form  
 (C) cyclohexane is in 'crown' form  
 (D) cyclohexane is less dense than water
- SR0063
2. Which of the following compounds will show geometrical isomerism : [IIT-1998]  
 (A) 2-butene (B) propene  
 (C) 1-phenylpropene (D) 2-methyl-2-butene
- SR0064
3. Which of the following compound will exhibits geometrical isomerism : [IIT-2000]  
 (A) 1-phenyl-2-butene (B) 3-phenyl-1-butene  
 (C) 2-phenyl-1-butene (D) 1, 1-diphenyl-1-propene
- SR0065
4. The number of isomers for the compound with molecular formula  $C_2BrClFI$  is : [IIT-2000]  
 (A) 3 (B) 4 (C) 5 (D) 6
- SR0066
5. Which of the following has the lowest dipole moment : [IIT-2000]  
 (A)  $\begin{array}{c} CH_3 \\ \diagdown \\ C=C \\ \diagup \\ H \end{array}$  (B)  $CH_3-C\equiv C-CH_3$   
 (C)  $CH_3CH_2C\equiv CH$  (D)  $CH_2=CH-C\equiv CH$
- SR0067
6. In the given conformation, If  $C_2$  is rotated about  $C_2-C_3$  bond anticlockwise by an angle of  $120^\circ$  then the conformation obtained is : [IIT-2004]



- (A) Fully eclipsed conformation (B) Partially eclipsed conformation  
 (C) Gauche conformation (D) Staggered conformation

SR0068

7. (i)  $\mu_{\text{obs}} = \sum \mu_i x_i$

where  $\mu_i$  is the dipole moment of a stable conformer of the molecule,  $Z\text{-CH}_2\text{-CH}_2\text{-Z}$  and  $x_i$  is the mole fraction of the stable conformer. [IIT- 2005]

Given :  $\mu_{\text{obs}} = 1.0 \text{ D}$  and  $x(\text{Anti}) = 0.82$

Draw all the stable conformers of  $Z\text{-CH}_2\text{-CH}_2\text{-Z}$  and calculate the value of  $\mu_{(\text{Gauche})}$ .

(ii) Draw the stable conformer of  $Y\text{-CHD-CHD-Y}$  (meso form), when  $Y = \text{CH}_3$  (rotation about  $\text{C}_2\text{-C}_3$ ) and  $Y = \text{OH}$  (rotation about  $\text{C}_1\text{-C}_2$ ) in Newmann projection.

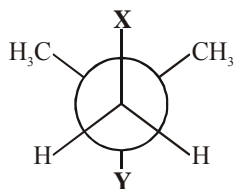
SR0069

8. The number of structural isomers of  $\text{C}_6\text{H}_{14}$  is : [IIT-2007]

- (A) 3 (B) 4 (C) 5 (D) 6

SR0070

9. In the Newman projection for 2,2-dimethylbutane [IIT-2010]

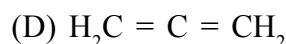
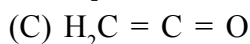
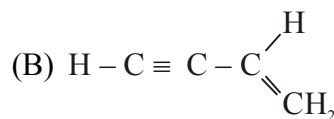
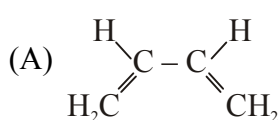


X and Y can respectively be –

- (A) H and H (B) H and  $\text{C}_2\text{H}_5$  (C)  $\text{C}_2\text{H}_5$  and H (D)  $\text{CH}_3$  and  $\text{CH}_3$

SR0071

10. Amongst the given option, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are) - [IIT-2011]



SR0072



## ANSWER KEY

## EXERCISE # I (MAINS ORIENTED)

## Single Correct Type :

- |              |              |              |              |              |
|--------------|--------------|--------------|--------------|--------------|
| 1. Ans. (D)  | 2. Ans. (A)  | 3. Ans. (C)  | 4. Ans. (C)  | 5. Ans. (C)  |
| 6. Ans. (C)  | 7. Ans. (D)  | 8. Ans. (D)  | 9. Ans. (A)  | 10. Ans. (B) |
| 11. Ans. (C) | 12. Ans. (A) | 13. Ans. (C) | 14. Ans. (B) | 15. Ans. (A) |
| 16. Ans. (D) | 17. Ans. (B) | 18. Ans. (D) | 19. Ans. (C) | 20. Ans. (D) |
| 21. Ans. (A) | 22. Ans. (B) | 23. Ans. (D) | 24. Ans. (B) | 25. Ans. (A) |
| 26. Ans. (B) | 27. Ans. (C) |              |              |              |

## More than one correct Type :

28. Ans. (B,C,D)    29. Ans. (A,C,D)    30. Ans. (A,B,D)    31. Ans. (B,C,D)

## Assertion / Reasoning Type :

32. Ans. (D)    33. Ans. (C)

## Comprehension Type :

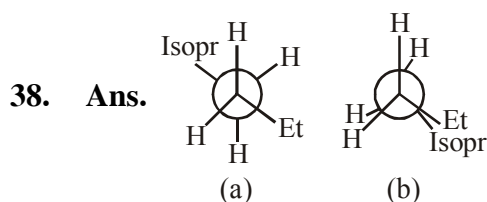
34. Ans. (C)    35. Ans. (D)

## Matrix Match Type :

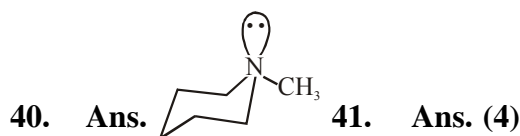
36. Ans. (A)→P ; (B)→R ; (C)→Q ; (D)→R

37. Ans. (A)→R ; (B)→S ; (C)→P ; (D)→Q

## Subjective Type :



39. Ans. (a) cis (b) cis (c) cis (d) trans (e) trans (f) trans



42. Ans. II, III, IV, V, VI, VIII, IX, XI, XIII, XIV,

43. Ans. (10)    44. Ans. (2112)    45. (a) Ans. (4) ; (b) Ans. (0404)

46. Ans. (a) Position isomers so (3)    (b) Geometrical isomers so (1)  
(c) Functional isomers so (4)    (d) Chain isomers so (2)

**EXERCISE # II (J-MAINS)**

- 
- |              |              |             |             |              |
|--------------|--------------|-------------|-------------|--------------|
| 1. Ans. (A)  | 2. Ans. (B)  | 3. Ans. (A) | 4. Ans. (A) | 5. Ans. (D)  |
| 6. Ans. (B)  | 7. Ans. (C)  | 8. Ans. (A) | 9. Ans. (C) | 10. Ans. (B) |
| 11. Ans. (3) | 12. Ans. (4) |             |             |              |

**EXERCISE # III (J-ADVANCED OBJECTIVE)**

- 
- |             |  |                |             |             |
|-------------|--|----------------|-------------|-------------|
| 1. Ans. (D) | 2. Ans. (A,C)  | 3. Ans. (A)    | 4. Ans. (D) | 5. Ans. (B) |
| 6. Ans. (C) | 7. Ans. (i) $\frac{1}{0.18}D$ , (ii) Anti form when $Y = CH_3$ & Gauche when $Y = -OH$ |                |             |             |
| 8. Ans. (C) | 9. Ans. (B,D)  | 10. Ans. (B,C) |             |             |



# Chapter Contents

## 05

### Purification & characterisation of organic compounds

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**PURIFICATION & CHARACTERISATION OF ORGANIC COMPOUNDS****METHODS OF PURIFICATION OF ORGANIC COMPOUNDS :**

Organic compounds obtained either from natural source (or) synthesized in laboratory are contaminated with impurities. Various methods are used for removal of impurities from an organic compound depends on the nature of compound and type of impurities present in it. The following methods are commonly used for purification

- |                     |  |
|---------------------|--|
| (1) Sublimation     | (2) Crystallisation                              |
| (3) Distillation    | (4) Solvent extraction (differential extraction) |
| (5) Chromatography. |  |

**Note: Most of the pure compounds contain sharp Melting point & Boiling points.**

**Sublimation :**

The process of conversion of sublimable solid to vapour state directly by heating without passing through liquid state is called sublimation.

**Solid vapour**

- This method is used for purification of solids
- Sublimation process is used for separation of sublimable volatile compounds from non sublimable impurities.
- Sublimation is generally used for purification of camphor, naphthalene, Anthracene, Benzoic acid, phthalic anhydride, Anthraquinone, Indigo and Iodine  $HgCl_2$ , solid  $SO_3$

**Crystallisation :**

- It is used for purification of solid organic compounds.
- Crystallisation is based on the difference in solubilities of the compound and impurities in a suitable solvent.
- The principle involved in this method is impure compound dissolved in a solvent is sparingly soluble at low temperature, but appreciably soluble at high temperature. Insoluble impurities are separated by filtration. The filtrate on cooling saturated solution, pure compound crystallises out. If a compound is highly soluble in one solvent and too little soluble in another solvent then crystallisation is carried out by using mixture of these solvents.
- Impurities, which impart colour are removed by adsorbing over activated charcoal.
- Repeated crystallisation is required if organic compound contains impurities of comparable solubilities.
- The process of separation of different components of a mixture by repeated crystallisation is called fractional crystallisation.
- Fractional crystallisation is used for separation of two or more soluble substances which have different solubilities in the same solvent.
- Most commonly used solvents for crystallisation are water, alcohol, ether, chloroform, carbontetrachloride, acetone, benzene, petroleum ether.

- Sugar having an impurity of common salt can be crystallised from hot ethanol. since sugar dissolves in hot ethanol but common salt does not.
- Fractional crystallisation can be used to separate a mixture of  $\text{KClO}_3$  (less soluble) and  $\text{KCl}$  (more soluble).

### DISTILLATION :

Distillation is an important method used to separate

- i) Volatile liquids from non volatile impurities.
- ii) Liquids having sufficient difference in boiling points.

### Simple Distillation :

- This process is used for purification of liquids which does not undergo decomposition at their boiling points
- The vapourisation of a liquid by heating and subsequent condensation of vapours by cooling is known as distillation.
- Liquid mixture is taken in a round bottom flask and heated carefully, the vapour component with lower boiling point distills first, the vapour formed is condensed by using condenser and the liquid is collected in a receiver. The vapours of component with higher boiling point distills later.
- The liquids that have boiling point difference greater than  $40^\circ\text{C}$  can be purified by this method,

**e.g:**

- (i) Chloroform (BP. 334 K) & Aniline (B.P. 457 K)
- (ii) Ether (B.P. 308 K)& Toluene (B.P. 384 K)
- (iii) Benzene (B.P. 353 K)& Aniline(B.P. 457 K)

### Fractional Distillation :

- Fractional distillation is used if the difference in boiling point of two liquids is less than  $40^\circ\text{C}$ .
- Vapours of liquid mixture are passed through fractionating column before condensation, which is fitted over mouth of the round bottom flask.
- Vapours of liquid with higher boiling point condense before the vapours of liquid with lower boiling point the vapours raising up in the fractionating column is richer in more volatile component.
- Fractionating column provides many surfaces for heat exchange between ascending vapours and descending condensed liquid.
- Each successive condensation and vapourisation unit in the fractionating column is called a theoretical plate.
- Liquids forming a constant boiling mixture (azeotropic mixture) can not be separated by this method.
- Fractional distillation is used to separate different fractions of crude oil in petroleum industry.
- This method is used for separation of mixture of acetone(B.P. 330K) and methyl alcohol (B.P. 338K)
- Mixture of benzene and toluene can be separated by fractional distillation.

**Ex.1** How is ethyl alcohol purified from methylated spirit.

**Sol:** Methylated spirit is ethyl alcohol contaminated mainly with methyl alcohol. Ethyl alcohol is purified by fractional distillation since the difference in boiling point is less.

**DISTILLATION UNDER REDUCED PRESSURE (Vacuum Distillation)**

- This method is used to purify liquids having very high boiling points, which decompose at or below their boiling points.
- These liquids are made to boil at a temperature lower than their normal boiling point by reducing pressure on their surface with the help of vacuum pump.
- Glycerine,  $H_2O_2$ , formaldehyde are purified by vacuum distillation.
- Glycerol can be separated from spent-lye in soap industry by using vacuum distillation.
- Sugar cane juice is concentrated in sugar industry by evaporation under reduced pressure which saves lot of fuel.

**Steam Distillation :**

- This method is used for separation and purification of organic compounds (solids or liquids) which
  - i) are steam volatile
  - ii) are insoluble in water.
  - iii) Process high vapour pressure (10-15 mm of Hg at 373 K)
  - iv) Contains non volatile impurities.
- Steam distillation is based on Dalton's law of partial pressure i.e.,  $P = P_1 + P_2$ , where  $P$  = Atmospheric pressure.
  - $P_1$  = Partial pressure of organic liquid
  - $P_2$  = Vapour pressure due to water.
- Compounds which can be purified by steam distillation are aniline, nitrobenzene, bromobenzene, o-nitrophenol, o-hydroxy benzaldehyde (salicylaldehyde), o-hydroxy acetophenone, turpentine oil, essential oils.

**Ex.2** Mention about the purification of (a) aniline and (b) naphthalene

- Sol.** (a) Aniline can be purified by steam distillation because it is immiscible with water and steam volatile.  
 (b) Naphthalene can be purified by sublimation because it changes on heating directly to vapour state and on cooling, it changes back into solid form.

**Solvent Extraction (Differential Extraction) :**

- **Definition:** The process of isolating an organic compound from its aqueous solution by shaking with a suitable solvent is called differential extraction. It is also called solvent extraction
- When an organic compound is present in an aqueous medium, then it is separated by shaking it with an organic solvent in which it is more soluble than in water.
- Solvent should be immiscible with water and organic compound to be separated should be highly soluble in it
- Organic solvent and aqueous solution are immiscible with each other, so they can form two distinct layers (which can be separated by separator funnel).
- Organic solvent is distilled or evaporated to get organic compound.
- If organic compound is less soluble in organic solvent then large quantity of solvent is required to extract small quantity of compound, which is said to be continuous extraction.
- Benzoic acid can be extracted from its aqueous solution using benzene as solvent.



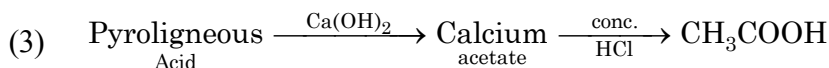
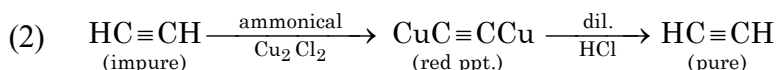
- Ether is a better solvent in differential extraction due to:
  - its less polarity
  - less reactivity
  - Less Boiling Point
  - higher solubility of organic compounds

### SEPARATION BY CHEMICAL METHODS :

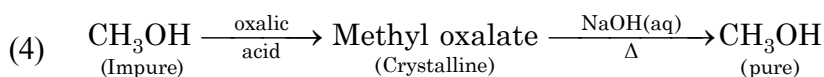
- It is used for mixture of substances which are chemically different.

e.g :

(1) Separation of acidic and basic compounds of coal-tar.



(from wood distillation industry)  $\rightarrow \text{CH}_3\text{COOH} + \text{MeCoMe} + \text{MeOH}$



### Chromatography :

- This method is used for separation of mixtures into their components, purification of compounds and also to test the purity of compounds.
- Chromatography is obtained from the greek word "Chroma" means colour and "graphy" means writing.
- This method was first used for separation of coloured substances found in plants.
- This method was described by Tswett.
- This Technique consists of two phases one is stationary phase of large surface area while the second is moving phase which is allowed to move slowly over the stationary phase.
- Stationary phase is either liquid or solid, while moving phase may be liquid or gas.
- The technique of chromatography is based on the rates at which the components of the mixture moves through a porous medium (called stationary phase) under the influence of some solvent (or) gas (called mobile phase).
- Mixture of substances is applied on a stationary phase which may be solid or liquid A pure solvent, a mixture of solvents or a gas is allowed to move slowly over the stationary phase, the components of the mixture get gradually separated from one another.
- Recovery of separated substances by using suitable solvent is known as elution. The solvent used is known as eluant.

S.No.	Chromatography process	Stationary Phase	Mobile Phase
1.	Column chromatography (Adsorption)	Solid	Liquid
2.	Liquid-liquid partition chromatography	Liquid	Liquid
3.	Paper chromatography	Liquid	Liquid
4.	Thin layer chromatography (TLC)	Liquid (or) solid	Liquid
5.	Gas-liquid chromatography (GLC)	Liquid	Gas
6.	Gas-solid chromatography (GSC)	Solid	Gas
7.	Ionic exchange chromatography	Solid	Liquid

- Based on the principle involved chromatography is classified in to

- Adsorption chromatography and
- partition chromatography.

(a) **Adsorption Chromatography :**

- Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees.
- Commonly used adsorbents are silica gel, alumina, magnesium oxide, cellulose powder, activated animal charcoal.
- When a mobile phase is allowed to move over stationary phase, the components of the mixture move by varying distances over stationary phase.
- There are two main types of chromatographic techniques based on principle of differential adsorption
  - Column chromatography and
  - Thin layer chromatography (TLC)

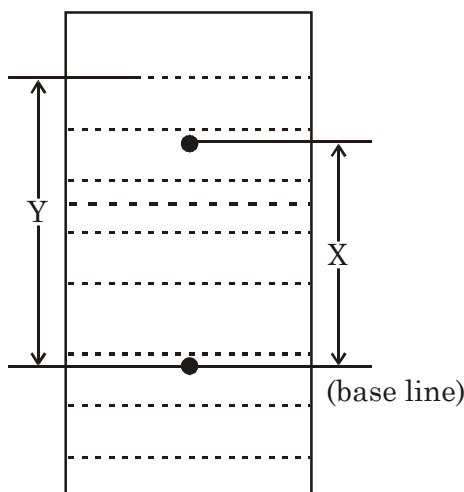
**i) Column Chromatography**

- It involves separation of a mixture over a column of adsorbent packed in a glass tube, which is fitted with stop cock at its lower end.
- The mixture to be separated on the adsorbent is placed at the top of the stationary phase.
- An appropriate eluant, which is a liquid or a mixture of liquids is allowed to flow down the column slowly.
- The strongly adsorbed substances are retained near the top and others come down to various distances in the column,

**(ii) Thin layer chromatography (TLC)**

- It involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate.
- The glass plate is coated with adsorbent (ex: silica gel, alumina) as a thin layer (about 0.2mm thick) is called chromatography plate or chroma plate .
- The solution of mixture to be separated is applied as small spot about 2cm above from one end of the TLC plate.

- The glass plate is placed in a closed jar containing the eluant. As the eluant rises up, the components of the mixture move up along the eluant to different distances depending on their degree of adsorption and separation takes place.
- The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e,  $R_f$  value.



$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

- The spots of coloured compounds are visible on TLC plate due to their original colour.
- The colourless compound which fluoresce are detected with ultraviolet light
- Spots of compounds are even detected by allowing them to adsorb iodine, will show up as brown spots.
- Some times an appropriate reagent is sprayed on the plate.

**eg :** Amino acids are detected by spraying the plate with ninhydrin solution.

#### Partition Chromatography :

- Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases.
- Paper chromatography is a type of partition chromatography.
- In paper chromatography a special quality known as chromatography paper is used.
- In Chromatography paper, cellulose helps as support, and water absorbed from air on to hydroxyl groups of cellulose acts as stationary phase.
- The chromatography paper spotted with the solution of mixture at the base is suspended in a suitable solvent or mixture of solvents, this solvent (s) act as mobile phase.
- The solvent rises up the paper by capillary action and flows over the spot.
- The paper selectively retains different component according to their differing partition in the two phases. The paper strip so developed is called chromatogram.
- The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram.

- The spots of the separated colourless compound may be observed either under ultraviolet or by the use of appropriate spraying agent

**Additional Information : Applications of Chromatography:**

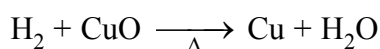
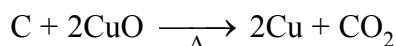
- I. i) In Chemical Industry column chromatography is used for separation of required components obtained after synthesis.  
ii) TLC is useful for monitoring large scale column chromatography.
- II **Pharmaceutical industry** : Chromatography is used for separation of chiral compounds to obtain pharmaceutically active optical isomer.
- III **Food Industry** : Chromatography techniques are used for quality control in food industry. It is used to determine presence and to separate additives, flavours etc. It is also used to detect presence of contaminants like mould, bacteria in food.
- IV **Environment-Testing lab** : Presence and quality of pollutants in air and drinking water can be determined by chromatography technique.
- V) **Diagnostic Technique**: Presence of certain drugs and the marker compounds for medical diagnosis in blood and urine are determined.

**Qualitative Analysis of Organic Compounds ( Detection of Elements):**

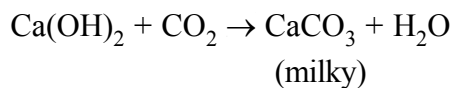
- The qualitative analysis of an organic compound involves detection of all elements present in it

**Detection of Carbon and Hydrogen :**

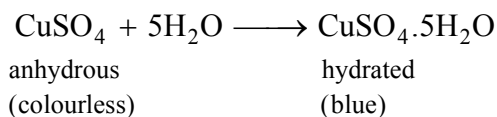
- Carbon and hydrogen are detected by heating the compound with cupric oxide (CuO).
- Carbon present in the compound is oxidised to carbon dioxide, which turns lime water milky.
- Hydrogen present in the compound is converted into water, which turns anhydrous copper sulphate into blue.



- Carbondioxide turns lime water milky.



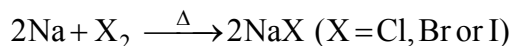
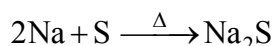
- Water vapours turn anhydrous copper sulphate into blue.



**Detection of Nitrogen, Sulphur Halogens & Phosphorus :**

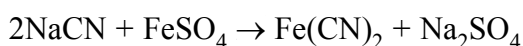
- Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by Lassaigne's test.
- Organic compounds are fused with dry sodium in fusion tube and fused mass after extraction with water is boiled and filtered, the filtrate is called sodium fusion extract
- During preparation of sodium fusion extract covalent compound is converted into ionic compound.

- The following reactions takes place



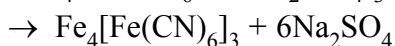
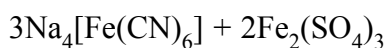
### Test for Nitrogen :

Sodium fusion extract is boiled with freshly prepared ferrous sulphate (  $\text{FeSO}_4$  ) solution and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.



sodium hexacyanoferrate(II)

On heating with concentrated sulphuric acid some Iron(II) ions are oxidised to Iron(III) ion, which reacts with sodium hexacyanoferrate(II) to produce Iron (III) hexacyanoferrate(II) (ferri ferrocyanide) which is Prussian blue in colour.



ferriferrocyanide

(prussianblue)

- This test fails in case of diazo compounds.
- If the amount of nitrogen present is less, then Prussian blue is present in collaidal form and the solution looks green.

**Ex.3** Hydrazine does not give Lassaigne's test, Why?

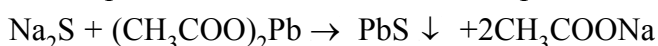
**Sol.** In the Lassaigne's test, nitrogen is converted to cyanide by combining with carbon of the compound Hydrazine does not contain carbon and hence cyanide cannot form.

**Ex.4** Why diazonium salts do not show positive Lassaigne's test for nitrogen ?

**Sol:** Diazonium salts are unstable and lose nitrogen as  $\text{N}_2$  gas on heating. Hence during fusion, no sodium cyanide is formed in Lassaigne's extract due to the loss of nitrogen.

### Test for Sulphur:

- a) Sodium fusion extract is acidified with acetic acid and lead acetate is added to it, a black precipitate of lead sulphide is formed, which indicates presence of sulphur.



black

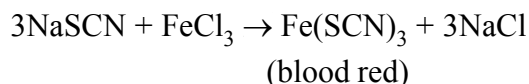
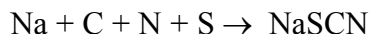
- b) Sodium fusion extract is treated with freshly prepared sodium nitroprusside, appearance of violet colour (purple) indicates presence of sulphur.



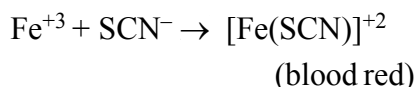
(sodium nitro prusside)

(violet)

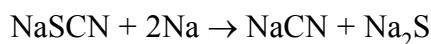
- In case both nitrogen and sulphur are present in an organic compound sodium thiocyanate is formed, which gives blood red colour with neutral  $\text{FeCl}_3$  solution.



(or)



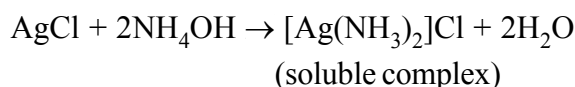
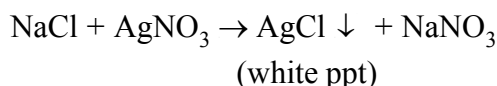
- If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide, these ions give their usual tests.



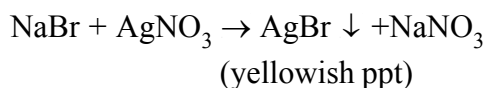
### Test for Halogens:

- Sodium fusion extract is acidified with nitric acid and then treated with silver nitrate solution.

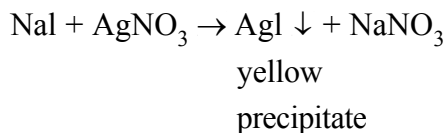
(i) White precipitate, soluble in ammonium hydroxide indicates presence of chlorine.



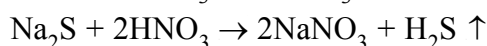
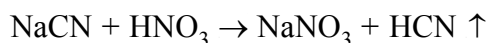
(ii) Yellowish precipitate, sparingly soluble in ammonium hydroxide indicates presence of bromine.



(iii) Yellow precipitate, insoluble in ammonium hydroxide indicates presence of Iodine.



- Nitrogen and sulphur are also present in the compound, the sodium fusion extract is boiled with concentrated nitric acid to decompose sodium cyanide & sodium sulphide formed during Lassaigne's test, otherwise they interfere with silver nitrate test for halogens.



- If NaCN and Na<sub>2</sub>S are not decomposed, then white and black precipitates of AgCN and Ag<sub>2</sub>S are formed respectively with silver nitrate solution.

### Beilstein's Test:

A copper wire flattened at one end is heated in an oxidising flame of Bunsen burner. The heating is continued till it does not impart blue colour flame. The hot end of copper wire is now touched with the organic substance and is once again kept in flame, the appearance of green or blue colour indicates the presence of halogens in the organic compound.

### Limitations :

- Substances such as urea, thiourea do not contain halogens but give this test
- It does not tell which halogen is present in organic compound.

**Chlorine Water Test for Bromine and Iodine :**

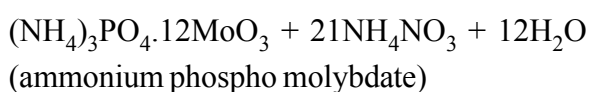
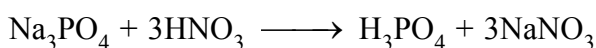
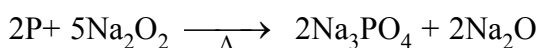
- Both AgBr and AgI are yellow precipitates, it is a little bit difficult to identify given halogen in bromine or iodine, to confirm it chlorine water test is used.
- Sodium fusion extract is acidified with dilute  $\text{H}_2\text{SO}_4$  (or)  $\text{HNO}_3$ , to this 1(or) 2ml of chloroform (or) Carbon tetrachloride is added and then excess of chlorine water is added with constant shaking.
- (i) If chloroform (or) carbon tetrachloride layer becomes yellow (or) brown indicates presence of bromine.  

$$2\text{NaBr} + \text{Cl}_2 \rightarrow 2\text{NaCl} + \text{Br}_2$$
 $\text{Br}_2$  dissolves in chloroform (or) carbontetrachloride gives yellow (or) brown colour
- (ii) If chloroform (or) carbon tetrachloride layer becomes violet indicates presence of iodine  

$$2\text{NaI} + \text{Cl}_2 \rightarrow 2\text{NaCl} + \text{I}_2$$
 $\text{I}_2$  dissolves in chloroform (or) carbontetrachloride gives violet colour.
- Presence of NaCN (or)  $\text{Na}_2\text{S}$  in sodium fusion extract does not interfere in this test.

**Test for Phosphorus :**

The compound is heated with oxidising agent (sodium peroxide) or with fusion mixture (sodium carbonate and potassium nitrate) phosphorus present in the compound is oxidised to sodium phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate, a canary yellow (ammonium phospho molybdate) precipitate formation (or) yellow colouration indicates presence of phosphorus.

**Test for Oxygen :**

- There is no direct test for oxygen.
- If organic compound is heated in a dry test tube in nitrogen atmosphere, if water droplets are formed on the walls of the test tube indicates presence of oxygen.
- Presence of oxygen can be known by testing functional groups containing oxygen.

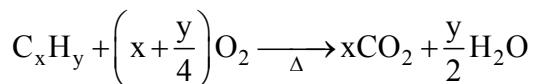
**eg:**  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CHO}$ ,  $-\text{NO}_2$  etc

**QUANTITATIVE ANALYSIS**

It involves the estimation of percentage composition of various elements by suitable methods.

**Estimation of Carbon and Hydrogen**

- Carbon and hydrogen are estimated by Liebig's combustion method.
- A known mass of an organic compound is burnt in the presence of excess of oxygen (free from  $\text{CO}_2$ ) and Cupric oxide ( $\text{CuO}$ )
- Carbon and hydrogen present in the compound are oxidised to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively



- $CO_2$  and  $H_2O$  produced are weighed by absorbing in concentrated solution of potassium hydroxide and anhydrous calcium chloride (or) magnesium perchlorate respectively

$$\%C = \frac{12}{44} \times \frac{\text{weight of } CO_2 \text{ formed}}{\text{weight of organic compound}} \times 100$$

$$\%H = \frac{2}{18} \times \frac{\text{weight of } CO_2 \text{ formed}}{\text{weight of organic compound}} \times 100$$

**Ex.5** On complete combustion, 0.246g of an organic compound gave 0.198 g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

**Sol.**  $\% \text{ of carbon} = \frac{12 \times 0.198 \times 100}{44 \times 0.246} = 21.95$

$$\% \text{ of hydrogen} = \frac{2 \times 0.1014 \times 100}{18 \times 0.246} = 4.58$$

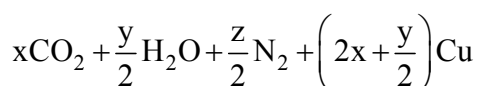
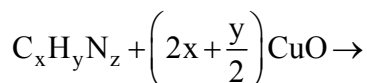
### ESTIMATION OF NITROGEN

Nitrogen present in organic compound is estimated by

- Dumas method
- Kjeldahl's method

#### (a) Dumas method

- In this method nitrogen present in the organic compound is converted in to  $N_2$  (molecular nitrogen)
- A weighed amount of organic compound is heated with cupric oxide in an atmosphere of carbondioxide.
- Carbon and hydrogen present in the compound are oxidised to  $CO_2$  and  $H_2O$ , while  $N_2$  is at free.
- Some oxides of nitrogen formed are reduced to free nitrogen by passing over heated copper gauze



- Oxides of nitrogen + Cu  $\rightarrow$   $N_2$  + CuO
- The mixture of gases produced is collected over caustic potash solution (KOH solution) which absorbs  $CO_2$ .
- Nitrogen is collected in the upper part of nitro meter.

$$\%N = \frac{28}{22400} \times \frac{\text{Volume of nitrogen in ml at STP}}{\text{Weight of organic compound}} \times 100$$



**Ex.6.** 0.25g of an organic compound gave 30 cm<sup>3</sup> of moist dinitrogen at 288 K and 745 mm pressure. Calculate the percentage of nitrogen. (Aqueous tension at 288 K = 12.7 mm)

**Sol.** Mass of the substance = 0.25 g

Volume of moist dinitrogen = 30 cm<sup>3</sup>

Temperature = 288 K

Pressure = 745 – 12.7 = 732.3 mm

Volume of dinitrogen at STP :

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{732.3 \times 30 \times 273}{288 \times 760} = 27.4 \text{ cm}^3$$

$$\text{Percentage of nitrogen in organic compound} = \frac{28}{22400} \times \frac{\text{vol of N}_2 \text{ at STP}}{\text{wt of organic compound}} \times 100$$

$$\frac{28}{22400} \times \frac{27.4}{0.25} \times 100 = 13.6$$

**Ex.7** 0.3g of an organic compound gave 50 ml nitrogen at 27°C and 715 mm pressure. If the aqueous tension at 27°C is 15 mm, calculate the percentage composition of nitrogen in the compound.

**Sol.** Mass of the substance = 0.3 g

Volume of the moist dinitrogen = 50 ml

Temperature = 27°C = 27 + 273 = 300 K

Pressure = 715 – 15 = 700 mm

Volume of dinitrogen at STP :

$$v_2 = \frac{P_1 V_1}{T_1} = \frac{T_2}{P_2} = \frac{700 \times 50 \times 273}{760 \times 300} = 41.9 \text{ ml}$$

$$\frac{28}{22400} \times \frac{\text{vol of N}_2 \text{ STP}}{\text{wt of organic compound}} \times 100 = \frac{28}{22400} \times \frac{41.9}{0.3} \times 100 = 17.46$$

22400 ml of dinitrogen at STP weight = 28 g

$$41.9 \text{ ml dinitrogen at STP weight} = \frac{28 \times 41.9}{22400} \text{ g}$$

0.3 g of organic compound contains  $\frac{28 \times 41.9}{22400}$  g of N<sub>2</sub>

$$100 \text{ g of organic compound contain } \frac{28 \times 41.9}{22400} \times \frac{100}{0.3} = 17.46$$

percentage of nitrogen = 17.46

**Kjeldahl's Method :**

- In this method nitrogen in the organic compound is converted into ammonia ( $\text{NH}_3$ )
- A known mass of organic compound containing nitrogen is heated with concentrated sulphuric acid in presence of  $\text{K}_2\text{SO}_4$  and  $\text{CuSO}_4$  then nitrogen present in the compound is converted into ammonium sulphate.  $\text{K}_2\text{SO}_4$  increases boiling point of  $\text{H}_2\text{SO}_4$  and  $\text{CuSO}_4$  acts as catalyst.
- Organic compound +  $\text{H}_2\text{SO}_4 \longrightarrow (\text{NH}_4)_2\text{SO}_4$
- The resulting solution is distilled with excess of sodium hydroxide  
 $(\text{NH}_4)_2\text{SO}_4 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{NH}_3 + 2\text{H}_2\text{O}$
- Ammonia evolved is absorbed in a known but excess volume of standard  $\text{HCl}$  (or)  $\text{H}_2\text{SO}_4$  solution.
- The acid left unreacted is estimated by titration against standard solution of sodium hydroxide.


$$\text{Percentage of Nitrogen} = \frac{14}{1000} \times \frac{V \times N}{\text{wt. of organic compound}} \times 100$$

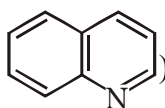
$$\%N = \frac{1.4 \times V \times N}{\text{Weight of organic compound}}$$

Where  $V$  = volume of acid in ml neutralised by ammonia

$N$  = Normality of acid.

- This method is simpler and more convenient
- It is mainly used to find percentage of nitrogen present in food stuffs, soils, fertilizers and various agricultural products.
- This method is not applicable to compounds containing nitro ( $-\text{NO}_2$ ), Nitroso ( $\text{NO}$ ), azo group

( $-\text{N}=\text{N}-$ ), azoxy compounds  $\left[ \begin{array}{c} \text{O} \\ \uparrow \\ -\text{N} = \text{N}- \end{array} \right]$  and nitrogen present in the ring (pyridine , quinoline



) because nitrogen present in these compounds is not quantitatively converted in to ammonium sulphate.

**Ex.8** In Kjeldahl's estimation of nitrogen, the ammonia evolved from 0.5 g of an organic compound neutralised 10 ml of 1M  $\text{H}_2\text{SO}_4$ . Calculate the percentage of nitrogen in the compound?

**Sol.** 10 ml of 1M  $\text{H}_2\text{SO}_4 = 20\text{ml}$  of 1M  $\text{NH}_3$   
 1000 ml of 1M ammonia contains 14 g nitrogen

20 ml of 1M ammonia contains  $\frac{14 \times 20}{1000}$  g  $\text{N}_2$

$$\% \text{ of nitrogen} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0$$

**Ex.9** In Kjeldahl's estimation of nitrogen, the ammonia obtained from 0.5 g of an organic substance was passed

into 100 cm<sup>3</sup> of  $\frac{M}{10}$  NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.

**Sol.** m eq. of H<sub>2</sub>SO<sub>4</sub> taken = molarity x basicity x volume (ml)

$$= \frac{1}{10} \times 2 \times 100 = 20$$

$$\text{m.eq of NaOH} = \frac{1}{10} \times 1 \times 154 = 15.4$$

$$\text{m. eq of H}_2\text{SO}_4 \text{ unused} - 20 - 15.4 = 4.6$$

$$\% \text{ of nitrogen} = \frac{1.4 \times \text{meq of H}_2\text{SO}_4 \text{ unused}}{\text{wt of organic compound}} = \frac{1.4 \times 4.6}{0.5} = 12.88\%$$

### ESTIMATION OF HALOGENS CARIUS METHOD

- A weighed amount of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as carius tube.
- Carbon and hydrogen present in the compound is converted into CO<sub>2</sub> and H<sub>2</sub>O.
- Halogen present in the organic compound is converted into silver halide.
- The precipitate is washed, dried and weighed

$$\text{Percentage of halogen} = \frac{\text{Atomic weight of halogen}}{\text{Mwt of silver halide}} \times \frac{\text{Weight of silver halide formed}}{\text{Weight of organic compound}} \times 100$$

$$\% \text{Cl} = \frac{35.5}{143.5} \times \frac{\text{wt of AgCl formed}}{\text{wt of organic compound}} \times 100$$

$$\% \text{Br} = \frac{80}{188} \times \frac{\text{wt. of AgBr formed}}{\text{Wt. of organic compound}} \times 100$$

$$\% \text{I} = \frac{127}{235} \times \frac{\text{Wt. of AgI formed}}{\text{Wt. of organic compound}} \times 100$$

**Ex.10** In Carius method, 0.1890g of an organic compound gave 0.2870g of silver chloride. Calculate the percentage of chlorine in the compound

**Sol:** Weight of substance = 0.1890g

Weight of silver chloride = 0.2870g

$$\% \text{ of chlorine} = \frac{\text{weight of AgCl} \times 35.5 \times 100}{\text{weight of substance} \times 143.5} = \frac{0.2870 \times 35.5 \times 100}{0.1890 \times 143.5} = 37.8$$

**Ex.11** One gram of bromoalkane on heating with excess silver nitrate in Carius tube method gave 0.94g of yellow precipitate. What is the percent weight of halogen ?

**Sol.** Weight of substance = 1g Yellow precipitate is AgBr ; Weight of AgBr = 0.94g

$$\% \text{ of bromine} = \frac{0.94 \times 80 \times 100}{1 \times 188} = 40$$

**Ex.12** In carius method of estimation of halogen 0.15g of an organic compound gave 0.12g of AgBr. Find out the percentage of bromine in the compound

**Sol.**  $\% \text{ of bromine} = \frac{80 \times 0.12 \times 100}{188 \times 0.15} = 34.04$

#### Estimation of Sulphur Carius method:

- A weighed amount of organic compound is heated in a carius tube with sodium peroxide or fuming nitric acid.
- Sulphur present in the compound is oxidised into sulphuric acid, which is treated with  $\text{BaCl}_2$  solution gives precipitate of  $\text{BaSO}_4$ .
- It is filtered, the precipitate is washed, dried and weighed.

$$\% \text{S} = \frac{\text{Atomic wt of sulphur}}{\text{Mol. wt of BaSO}_4} \times \frac{\text{wt of BaSO}_4 \text{ formed}}{\text{wt of organic compound}} \times 100$$

$$\% \text{S} = \frac{32}{233} \times \frac{\text{wt of BaSO}_4 \text{ formed}}{\text{wt. of organic compound}} \times 100$$

**Ex.13** In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

**Sol.** 233 g  $\text{BaSO}_4$  contain 32g sulphur

$$0.4813 \text{ g BaSO}_4 \text{ contain } \frac{32 \times 0.4813}{233} \text{ g sulphur}$$

$$\% \text{ of sulphur} = \frac{32 \times 0.4813 \times 100}{233 \times 0.157} = 42.10$$

**Ex.14** On heating 0.2g of an organic compound with a mixture of barium chloride and nitric acid, 0.466g of barium sulphate was obtained. Calculate the percentage of sulphur.

**Sol.** Weight of substance = 0.2 g

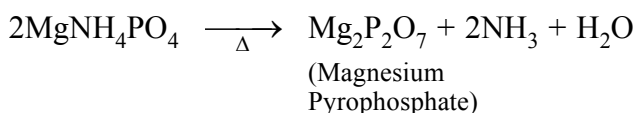
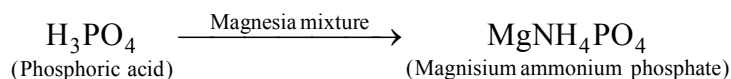
Weight of barium sulphate = 0.466 g

$$\text{Weight percentage of sulphur} = \frac{0.466 \times 32 \times 100}{0.2 \times 233} = 32$$

**Estimation of Phosphorus Carius Method :**

A weighed amount of organic compound is heated with fuming nitric acid, then phosphorus present in the compound is oxidised to phosphoric acid. Phosphoric acid is precipitated as magnesium ammonium phosphate ( $\text{Mg NH}_4 \text{PO}_4$ ), by addition of magnesia mixture ( $\text{MgCl}_2 + \text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ )

- Magnesium ammonium phosphate is washed, dried and it is heated strongly to get magnesium pyrophosphate ( $\text{Mg}_2\text{P}_2\text{O}_7$ ).



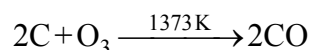
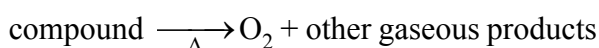
$$\% \text{P} = \frac{62}{222} \times \frac{\text{wt. of } \text{Mg}_2\text{P}_2\text{O}_7 \text{ formed}}{\text{wt. of organic compound}} \times 100$$

- Phosphoric acid is precipitated as ammonium phospho molybdate ( $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ ) by adding ammonia and ammonium molybdate. (Molecular mass of  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 = 1877$ )

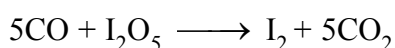
$$\% \text{P} = \frac{31}{1877} \times \frac{\text{wt of } (\text{NH}_4)_3 \text{PO}_4 \cdot 12\text{MoO}_3 \text{ formed}}{\text{wt of organic compound}} \times 100$$

**Estimation of oxygen .**

- Usually percentage of oxygen in organic compound is determined by method of difference % of oxygen = 100 – (sum of the percentages of all other elements)
- Oxygen present in the organic compound is estimated by Aluisse's method.
- A known amount of organic compound is subjected to pyrolysis in a stream of nitrogen.
- The mixture of gaseous products containing oxygen is passed over red-hot coke, then all the oxygen is converted in to carbon monoxide.



- CO formed is quantitatively converted in to  $\text{CO}_2$  by passing over warm Iodine pentoxide ( $\text{I}_2\text{O}_5$ )



The resulting gaseous mixture ( $\text{CO}_2$  and  $\text{I}_2$ ) is passed through potassium iodide solution, which absorbs iodine, and then passed over KOH to absorb  $\text{CO}_2$ .

$$\% \text{ of oxygen} = \frac{16}{44} \times \frac{\text{wt. of } \text{CO}_2 \text{ formed}}{\text{wt. of organic compound}} \times 100$$

**Ex.15** 0.2g of an organic compound on analysis gave 0.147g of carbondioxide, 0.12g of water and 74.6 c.c of nitrogen at S.T.P. Calculate the weight percentages of constituents.

**Sol.** Weight of compound = W = 0.2g

Weight of  $\text{CO}_2 = W_1 = 0.147\text{g}$

Weight of  $\text{H}_2\text{O} = W_2 = 0.12\text{g}$

Volume of  $N_2$  at STP = 74.6 c.c.

$$\% \text{ of carbon} = \frac{W_1 \times 12 \times 100}{W \times 44} = \frac{0.147 \times 12 \times 100}{0.2 \times 44} = 20.04\%$$

$$\% \text{ of Hydrogen} = \frac{W_2 \times 2 \times 100}{W \times 18} = \frac{0.12 \times 2 \times 100}{0.2 \times 18} = 6.66\%$$

$$\% \text{ of Nitrogen} = \frac{W_3 \times 28 \times 100}{W \times 22400} = \frac{74.6}{8 \times 0.2} = 46.63\%$$

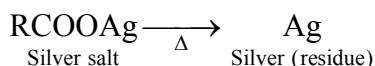
Remaining is oxygen.

$$\% \text{ of Oxygen} = 100 - (\%C + \%H + \%N) = 100 - 73.33 = 26.67\%$$

**Note :** Presently estimation of elements (C,H and N) in organic compound is estimated by using CHN elemental analyser by taking very small amount of substance (1-3 mg), results are displayed on screen with in short time.

#### Chemical Methods used to Find Molecular Mass Silver Salt Method for Acids :

Organic acid form insoluble silver salts, which on heating undergoes decomposition to leave a residue of metallic silver.



$$\frac{\text{Equivalent of silver salt}}{\text{Equivalent wt. of silver}} = \frac{\text{mass of silver salt}}{\text{Mass of silver}}$$

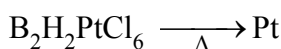
$$\frac{E + 108 - 1}{108} = \frac{\text{Mass of silver salt}}{\text{Mass of silver}}$$

$$E = \left[ \frac{\text{Mass of silver salt}}{\text{Mass of silver}} \times 108 \right] - 107$$

Molecular weight of acid = Equivalent weight of acid (E) × basicity.

#### Platinic Chloride Method for Base

- Organic bases combines with chloroplatinic acid ( $H_2PtCl_6$ ) to form insoluble platinichloride, which on ignition gives metallic platinum.
- If 'B' is mono acidic base then formula of salt will be  $B_2H_2PtCl_6$ .



$$\frac{\text{Molecular mass of platinum salt}}{\text{Atomic mass of platinum}} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$$

If E is equivalent weight of base then

$$\frac{2E + 410}{195} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$$

$$E = \frac{1}{2} \left[ \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}} \times 195 - 410 \right]$$

Molecular mass of base = Equivalent mass of base x acidity

### Empirical formula

- The simplest whole number ratio between the atoms of various elements present in one molecule of a substance is called empirical formula.

### Calculation of Empirical Formula

The steps involved are

- Divide mass percentage of each element by its atomic mass, gives relative number of atoms.
- Simplest ratio is obtained when the figures obtained is divided by lowest number.
- If the simplest ratio obtained is not a whole number ratio, then multiply all the figures with suitable integer to get simplest whole number ratio.
- Write symbols of various elements side by side with above numbers at the lower right corner of each, which is empirical formula of compound.

### Molecular formula

The actual number of atoms present in one molecule of a substance is called molecular formula.

Molecular formula = (Empirical formula)<sub>n</sub>

where

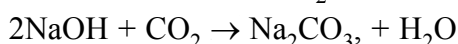
$$n = \frac{\text{Molecular wt of the compound}}{\text{Empirical formula weight of the compound}}$$

- If vapour density is given then molecular weight = 2 × vapour density.

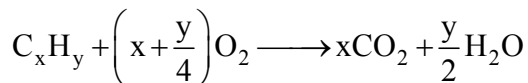
### Determination of molecular formula of Gaseous Hydrocarbons (Eudiometry) :

- Eudiometry is a direct method used to find molecular formula of gaseous hydrocarbon without finding percentage composition of elements and its molecular weight.
- A known volume of gaseous hydrocarbon is mixed with excess of pure and dry oxygen in eudiometer tube placed inverted in a trough of mercury.
- The mixture is exploded by passing an electric spark between platinum electrodes. As a result carbon and hydrogen of hydrocarbon are oxidised to CO<sub>2</sub> and H<sub>2</sub>O vapour respectively.
- The tube is allowed to cool to room temperature, then water vapour is condensed in to liquid water, whose volume occupied is almost negligible. Thus the gaseous mixture left in eudiometer tube is CO<sub>2</sub> and O<sub>2</sub>.
- Caustic potash solution is then introduced in to eudiometer tube which absorbs CO<sub>2</sub> completely.

The gas left is unused O<sub>2</sub> -



- Decrease in volume on introducing KOH solution gives volume of  $\text{CO}_2$  used.
- Some times volume of  $\text{O}_2$  left unused is found by introducing pyrogallol and noting the decrease in volume.
- Let molecular formula of gaseous hydrocarbon is  $\text{C}_x\text{H}_y$ . On combustion one volume of it forms  $x'$  volumes of  $\text{CO}_2$  & ' $y/2$ ' volumes of water vapour.



- For 1 volume of hydrocarbon

$$\text{Volume of O}_2 \text{ used} = \left(x + \frac{y}{4}\right) \text{ vol}$$

$$\text{Volume of CO}_2 \text{ produced} = x \text{ vol.}$$

$$\text{Contraction on explosion and cooling} = 1 + \frac{y}{4} \text{ (volume of liquid water is neglected)}$$

#### Determination of Molecular mass by Victor Meyer's Method

- A known mass of the volatile substance is vapourised in victor meyer's method.
- The vapours obtained displaces an equal volume of air in to graduated tube.
- The volume of air displaced is calculated at STP condition by using  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\text{Mol. mass of volatile substance} = \frac{\text{Mass of substance taken}}{\text{Volume of air displaced in ml at STP}} \times 22400$$



## EXERCISE # O-1

1. For the Separation of two immiscible liquids which method (or apparatus) is used?  
(1) Chromatography (2) Fractionating column  
(3) Fractional distillation (4) Separating funnel **PO0001**
2. A mixture of benzene and chloroform is separated by  
(1) Sublimation (2) Separating funnel (3) Crystallization (4) Distillation **PO0002**
3. Which of the following has molecular weight of 92 ?  
(1) Toluene (2) Benzene (3) Methylene (4) Propene **PO0003**
4. Aniline is usually purified by  
(1) Chromatographic technique (2) Steam distillation  
(3) By addition of oxalic acid (4) Fractional crystallization **PO0004**
5. The most suitable method for separation of 1:1 mixture of ortho- and para- nitrophenols is  
(1) Sublimation (2) Chromatography (3) Crystallization (4) Steam distillation  
**PO0005**
6. Distillation under reduced pressure is employed for  
(1) Benzene (2) Petrol  
(3) Glycerol (4) Organic compounds used in medicine **PO0006**
7. Impure glycerine is purified by  
(1) Steam distillation (2) Simple distillation  
(3) Vacuum distillation (4) None of the above **PO0007**
8. Absolute alcohol is prepared by  
(1) Fractional distillation (2) Kolbe's method  
(3) Azotropic distillation (4) Vacuum distillation  
**PO0008**
9. The latest technique used for purification for organic compounds in  
(1) Chromatography (2) Vacuum distillation  
(3) Fractional distillation (4) Crystallisation **PO0009**
10. In paper chromatography  
(1) Moving phase is liquid and stationary phase is solid  
(2) Moving phase is liquid and stationary phase is liquid  
(3) Moving phase is solid and stationary phase is solid  
(4) Moving phase is solid and stationary phase is liquid **PO0010**

11. A is a lighter phenol and B is an aromatic carboxylic acid. Separation of mixture A and B can be carried out easily by using a solution of  
(1) Sodium hydroxide (2) Sodium sulphate (3) Calcium chloride (4) Sodium bicarbonate  
**PO0011**
12. In sodium fusion test of organic compounds the nitrogen of the organic compound is converted into  
(1) Sodamide (2) Sodium cyanide (3) Sodium nitrite (4) Sodium nitrate  
**PO0012**
13. The Lassaigne's extract is boiled with dil.  $\text{HNO}_3$  before testing for halogens because  
(1) Silver halides are soluble in  $\text{HNO}_3$  (2)  $\text{Na}_2\text{S}$  and  $\text{NaCN}$  are decomposed by  $\text{HNO}_3$   
(3)  $\text{Ag}_2\text{S}$  is soluble in  $\text{HNO}_3$  (4)  $\text{AgCN}$  is soluble in  $\text{HNO}_3$  **PO0013**
14. In a Lassaigne's test for nitrogen, the blue colour is due to the formation of  
(1) Potassium ferricyanide (2) Sodium cyanide  
(3) Sodium ferrocyanide (4) Ferri-ferro cyanide **PO0014**
15. Which of the following compounds does not show Lassaigne test for nitrogen?  
(1) Urea (2) Hydrazine (3) Phenyl hydrozene (4) Azo benzene  
**PO0015**
16. When piece of human hair are heated strongly with soda lime smell of ammonia can be detected. which one of the following conclusion can be drawn from this observation.  
(1) Ammonia is present in human hair (2) Ammonium salt is present in hair  
(3) Hair contains amino acids (4) None of the above **PO0016**
17. The Beilstein test for organic compounds is used to detect  
(1) Nitrogen (2) Sulphur (3) Carbon (4) Halogen **PO0017**
18. Which of the following is the best scientific method to test presence of water in liquid?  
(1) Smell (2) Taste  
(3) Use of litmus paper (4) Use of anhydrous copper sulphate **PO0018**
19. Liebig's method is used for the estimation of  
(1) Nitrogen (2) Sulphur  
(3) Carbon and hydrogen (4) Halogens **PO0019**
20. 0.765 gm of an acid gives 0.535 gm of  $\text{CO}_2$  and 0.138 gm of  $\text{H}_2\text{O}$ . Then the ratio of percentage of carbon and hydrogen is  
(1) 19:2 (2) 18:11 (3) 20:17 (4) 1:7 **PO0020**

21. Nitrogen is an organic compound can be estimated by  
 (1) Kjeldahl's method only (2) Duma's method only  
 (3) Both the methods (4) none of these methods **PO0021**
22. Dumas method involves the determination of nitrogen content in the organic compound in form of  
 (1)  $\text{NH}_3$  (2)  $\text{N}_2$  (3)  $\text{NaCN}$  (4)  $(\text{NH}_4)_2\text{SO}_4$  **PO0022**
23. In Kjeldahl's method, nitrogen present is estimated as  
 (1)  $\text{N}_2$  (2)  $\text{NO}$  (3)  $\text{NH}_3$  (4)  $\text{NO}_2$  **PO0023**
24. The percentage of sulphur in an organic compound whose 0.32g produces 0.233g of  $\text{BaSO}_4$  [At.wt.Ba=137, S=32] is  
 (1) 1.0 (2) 10.0 (3) 23.5 (4) 32.1 **PO0024**
25. If 0.2 gram of an organic compound containing carbon, hydrogen and oxygen on combustion, yielded 0.147 gram carbon dioxide and 0.12 gram water. What will be the content of oxygen in the substance?  
 (1) 73.29% (2) 78.45% (3) 83.23% (4) 89.50% **PO0025**
26. If a compound on analysis was found to contain C=18.5%, H= 1.55 %, Cl=55.04% and Oxygen =24.81%, Then the empirical formula is  
 (1)  $\text{CHClO}$  (2)  $\text{CH}_2\text{ClO}$  (3)  $\text{C}_2\text{H}_2\text{OCl}$  (4)  $\text{ClCH}_2\text{O}$  **PO0026**
27. An organic compound contains C=40 %, H= 1 3.33% and N=46.6 %. Its empirical formula would be  
 (1)  $\text{CHN}$  (2)  $\text{C}_2\text{H}_2\text{N}$  (3)  $\text{CH}_4\text{N}$  (4)  $\text{C}_3\text{H}_7\text{N}$  **PO0027**
28. Two elements X (atomic weight =75) and Y (atomic weight=16) combine to give a compound having 75.8% X. The formula of the compound is  
 (1)  $\text{XY}$  (2)  $\text{X}_2\text{Y}$  (3)  $\text{X}_2\text{Y}_2$  (4)  $\text{X}_2\text{Y}_3$  **PO0028**
29. On analysis a saturated hydrocarbon is found to contain 83.70% carbon and 16.30% hydrogen. The empirical formula will be (at wt. of C=12, at. wt. of H=1)  
 (1)  $\text{C}_3\text{H}_6$  (2)  $\text{C}_3\text{H}_8$  (3)  $\text{C}_3\text{H}_4$  (4)  $\text{C}_6\text{H}_{12}$  **PO0029**
30. Empirical formula of a hydrocarbon containing 80% carbon and 20% hydrogen is  
 (1)  $\text{CH}$  (2)  $\text{CH}_2$  (3)  $\text{CH}_3$  (4)  $\text{CH}_4$  **PO0030**
31. An organic compound with C= 40% and H= 6.7% will have the empirical formula  
 (1)  $\text{CH}_4$  (2)  $\text{CH}_2\text{O}$  (3)  $\text{C}_3\text{H}_6\text{O}_3$  (4)  $\text{C}_2\text{H}_4\text{O}_2$  **PO0031**
32. In a hydrocarbon, mass ratio of hydrogen and carbon 1:3, the empirical formula of hydrocarbon is  
 (1)  $\text{CH}_4$  (2)  $\text{CH}_2$  (3)  $\text{C}_2\text{H}$  (4)  $\text{CH}_3$  **PO0032**
33. 8.24 g of a volatile liquid on vaporization gives 45 ml of vapours at NTP. What will be the vapour density of the substance? (Density of  $\text{H}_2=0.089 \text{ g L}^{-1}$ )  
 (1) 95.39 (2) 39.95 (3) 99.53 (4) 59.93 **PO0033**

34. 0.1914 g of an organic acid is dissolved in about 20 ml of water. 25 ml of 0.12 N. NaOH is required for the complete neutralization of the acid solution. The equivalent weight of the acid is  
 (1) 65.0 (2) 64.0 (3) 63.8 (4) 62.5 **PO0034**
35. The equivalent weight of an acid is equal to  
 (1) Molecular weight x acidity (2) Molecular weight x basicity  
 (3) Molecular weight /basicity (4) Molecular weight /acidity **PO0035**
36. Simple distillation can be used to separate liquids which differ in their boiling points at least by  
 (1) 5°C (2) 10°C (3) 35 - 50°C (4) 100°C **PO0036**
37. Empirical formula of a compound is  $\text{CH}_2\text{O}$ . If its vapour density is 90, then the molecular formula of the compound is  
 (1)  $\text{C}_5\text{H}_{10}\text{O}_5$  (2)  $\text{C}_3\text{H}_6\text{O}_3$  (3)  $\text{C}_6\text{H}_{12}\text{O}_6$  (4)  $\text{C}_4\text{H}_8\text{O}_4$  **PO0037**
38. The empirical formula of an acid is  $\text{CH}_2\text{O}_2$ , the probable molecular formula of the simplest acid may be  
 (1)  $\text{CH}_2\text{O}$  (2)  $\text{CH}_2\text{O}_2$  (3)  $\text{C}_2\text{H}_4\text{O}_4$  (4)  $\text{C}_3\text{H}_6\text{O}_6$  **PO0038**
39. A gaseous hydrocarbon has 85% carbon and vapour density of 28. The possible formula of the hydrocarbon will be  
 (1)  $\text{C}_3\text{H}_6$  (2)  $\text{C}_2\text{H}_4$  (3)  $\text{C}_2\text{H}_2$  (4)  $\text{C}_4\text{H}_8$  **PO0039**
40. a hydrocarbon has C=85.72% and remaining H. The hydrocarbon is  
 (1)  $\text{C}_2\text{H}_4$  (2)  $\text{C}_2\text{H}_6$  (3)  $\text{C}_2\text{H}_2$  (4)  $\text{CH}_4$  **PO0040**
41. An organic compound containing carbon, hydrogen and oxygen contains 52.2 % carbon 13.04% hydrogen. Vapour density of the compound is 23. Its molecular formula will be  
 (1)  $\text{C}_2\text{H}_6\text{O}$  (2)  $\text{C}_3\text{H}_8\text{O}$  (3)  $\text{C}_4\text{H}_8\text{O}$  (4)  $\text{C}_5\text{H}_{10}\text{O}$  **PO0041**
42. percentage of Se(at.wt 78.4) in peroxidase anhydrase enzyme is 0.5% by weight, then minimum molecular weight of peroxidase anhydrase enzyme is  
 (1)  $1.568 \times 10^4$  (2)  $1.568 \times 10^3$   
 (3) 15.68 (4)  $2.136 \times 10^4$  **PO0042**
43. The empirical formula of a compound is  $\text{CH}_2$ . One of the compound has a mass of 42 g. its molecular formula is  
 (1)  $\text{CH}_2$  (2)  $\text{C}_2\text{H}_2$  (3)  $\text{C}_3\text{H}_6$  (4)  $\text{C}_3\text{H}_8$  **PO0043**
44. In a compound C, H and N atoms are present in 9:1:3.5 by weight. If molecular weight of the compound is 108, then the molecular formula of the compound is  
 (1)  $\text{C}_2\text{H}_6\text{N}_2$  (2)  $\text{C}_3\text{H}_4\text{N}$  (3)  $\text{C}_6\text{H}_8\text{N}_2$  (4)  $\text{C}_9\text{H}_{12}\text{N}_3$  **PO0044**

45. the following is the percentage composition of a compound. Na=16.08%, C=4.19% , O=16.78% , and  $H_2O = 62.95\%$ . Its molecular formula is  
(1)  $Na_2CO_3$                       (2)  $Na_2CO_3 \cdot H_2O$                       (3)  $Na_2CO_3 \cdot 10H_2O$                       (4)  $Na_2CO_3 \cdot 5H_2O$  **PO0045**
46. An organic compound contains 49.3% carbon, 6.84% hydrogen and its vapour density is 73. Empirical Formula of the compound is  
(1)  $C_3H_5O_2$                       (2)  $CH_{10}O_4$                       (3)  $C_3H_{10}O_2$                       (4)  $C_4H_{10}O_4$  **PO0046**
47. Molecular mass of a volatile substance may be obtained by  
(1) Kjeldahl's method                      (2) Duma's method  
(3) Victor meyer's method                      (4) Liebig's method **PO0047**
48. The most suitable method of separation of 1:1 mixture of ortho and para nitro phenol is  
(1) Distillation                      (2) Crystallization                      (3) Sublimation                      (4) Chromatography **PO0048**
49. Kjeldahl's method can not be used for the estimation of Nitrogen in  
(1) Pyridine                      (2) Nitro compounds                      (3) Azo compounds                      (4) All **PO0049**
50. In Kjeldahl's method nitrogen present is estimated as  
(1)  $N_2$                       (2)  $NH_3$                       (3)  $NO_2$                       (4) None **PO0050**

## ANSWER-KEY

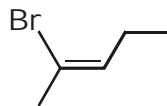
## PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS

1. Ans. 4	11. Ans. 4	21. Ans. 3	31. Ans. 2	41. Ans. 1
2. Ans. 4	12. Ans. 2	22. Ans. 2	32. Ans. 1	42. Ans. 1
3. Ans. 1	13. Ans. 2	23. Ans. 3	33. Ans. 4	43. Ans. 3
4. Ans. 2	14. Ans. 4	24. Ans. 2	34. Ans. 3	44. Ans. 3
5. Ans. 4	15. Ans. 2	25. Ans. 1	35. Ans. 3	45. Ans. 3
6. Ans. 3	16. Ans. 3	26. Ans. 1	36. Ans. 3	46. Ans. 1
7. Ans. 3	17. Ans. 4	27. Ans. 3	37. Ans. 3	47. Ans. 3
8. Ans. 3	18. Ans. 4	28. Ans. 4	38. Ans. 2	48. Ans. 1
9. Ans. 1	19. Ans. 3	29. Ans. 2	39. Ans. 4	49. Ans. 4
10. Ans. 2	20. Ans. 1	30. Ans. 3	40. Ans. 1	50. Ans. 2

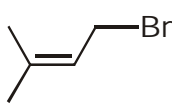
STEREO ISOMERISM

EXERCISE # I (MAINS ORIENTED)

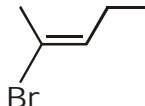
1. Which one of the following statements concerning compounds V–Z is true :



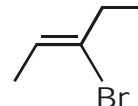
(V)



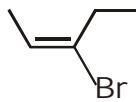
(W)



(X)



(Y)



(Z)

- (A) V and X are conformational isomers
- (B) Y and Z are constitutional isomers
- (C) X and Y are constitutional isomers
- (D) V and Y are stereoisomers

SE0001

2. Which of the following compound has no isomer?

- (A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
- (B)  $\text{CH}_3\text{CHO}$
- (C)  $\text{CH}_2=\text{CH}-\text{Cl}$
- (D)  $\text{ClCH}_2\text{CH}_2\text{Cl}$

SE0002

3. Compound  $\text{CH}_2\text{Cl}_2$  contain :

- (A) Plane of symmetry
- (B) Centre of symmetry
- (C) Axis of symmetry
- (D) Both (A) & (C)

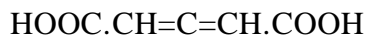
SE0003

4. Number of POS present in  $\text{CH}_4$  :

- (A) 3
- (B) 4
- (C) 5
- (D) 6

SE0004

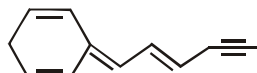
5. How many stereoisomers of the following molecule are possible ?



- (A) Two optical isomers
- (B) Two geometrical isomers
- (C) Two optical and two geometrical isomers
- (D) None

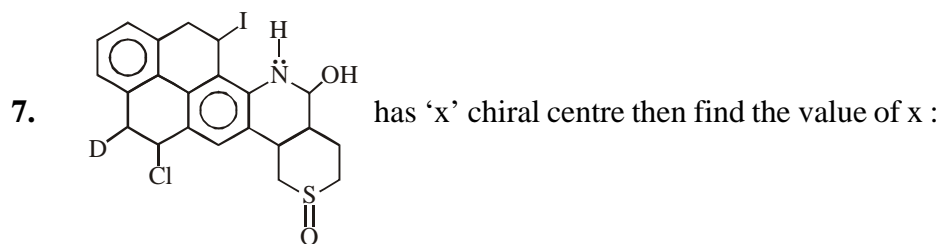
SE0005

6. The number of cis-trans isomer possible for the following compound.



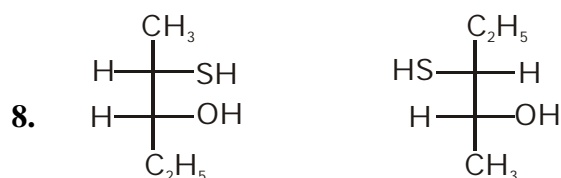
- (A) 2
- (B) 4
- (C) 6
- (D) 8

SE0006



- (A) 7 (B) 8 (C) 6 (D) 5

SE0007



- (A) Diastereomers (B) Enantiomers (C) Identical (D) Constitutional isomers

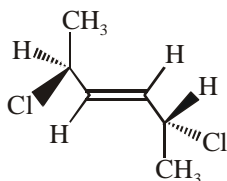
SE0008

9. The number of optically active compounds in the isomers of  $C_4H_9Br$  is :

- (A) 1 (B) 2 (C) 3 (D) 4

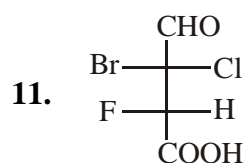
SE0009

10. Compound have :



- (A) Plane of symmetry (B) Centre of symmetry  
(C) Axis of symmetry (D) None

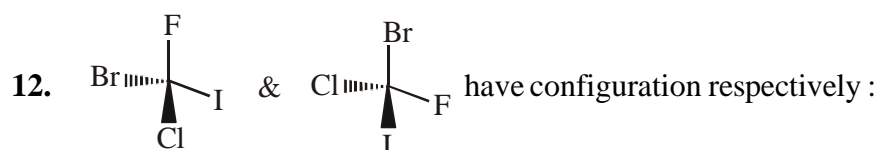
SE0010



Configuration of compound is :

- (A) 2S, 3S (B) 2R, 3S (C) 2R, 3R (D) 2S, 3R

SE0011



- (A) R, S (B) S, S (C) S, R (D) R, R

SE0012

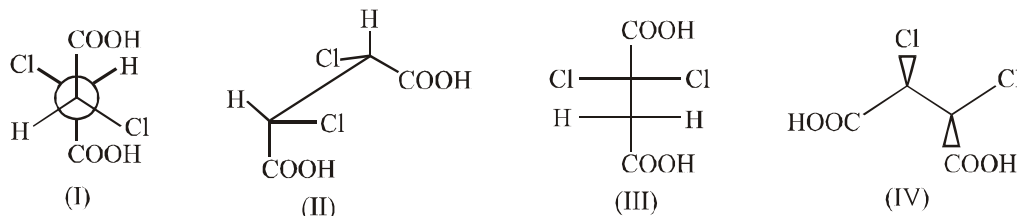


13. Minimum molecular weight of a hydrocarbon containing minimum number of C-atom to show optical isomerism :

- (A) 100 (B) 80 (C) 68 (D) 70

SE0013

14. For the given configuration :



Which of the compound/configuration are optically active :

- (A) I (B) II (C) III (D) IV

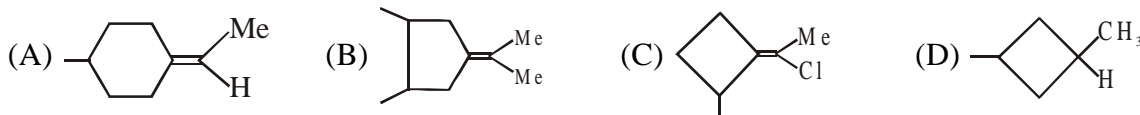
SE0014

15. Compounds which can show both optical as well as geometrical isomerism :



SE0015

16. Which of the following will not show optical isomerism :



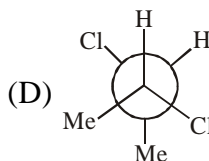
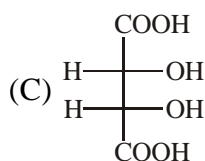
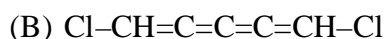
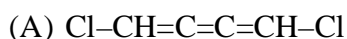
SE0016

17. Optical & geometrical isomerism both can be shown by :-



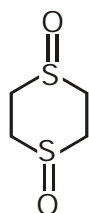
SE0017

18. Which of the following will not show optical isomerism :



SE0018

19. The correct statement for the given compound is



(A) It can show geometrical isomerism

(B) It can show optical isomerism

(C) It contains chiral centre

(D) None of these

SE0019

20. Meso-tartaric acid and d-tartaric acid are :-

(A) Positional isomers

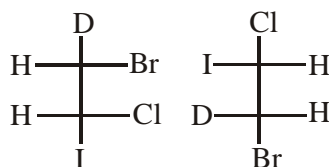
(B) Enantiomers

(C) Diastereomers

(D) Racemic mixture

SE0020

21. The two compounds given below are :



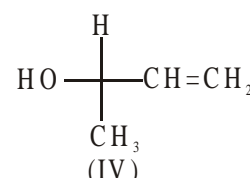
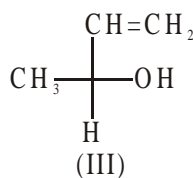
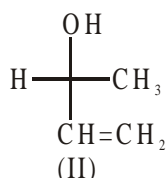
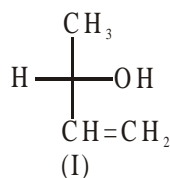
(A) Enantiomers

(B) Diastereomers

(C) Optically inactive (D) Identical

SE0021

22. Which of the following combinations amongst the four Fischer projections represents the same absolute configurations ?



(A) (II) and (III)

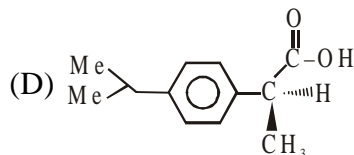
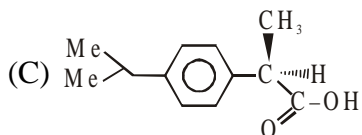
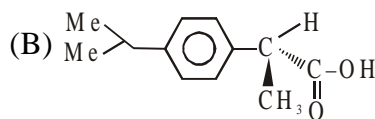
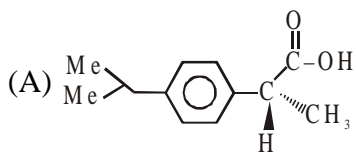
(B) (I) and (IV)

(C) (II) and (IV)

(D) (III) and (IV)

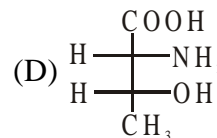
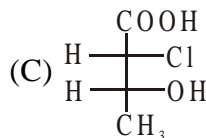
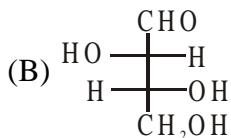
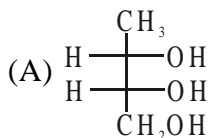
SE0022

23. The S-ibuprofen is responsible for its pain relieving property. Which one of the structure shown is S-ibuprofen :



SE0023

24. Which of the following is a 'threo' isomer :



SE0024

25. Number of possible stereoisomers of glucose are :-

(A) 10

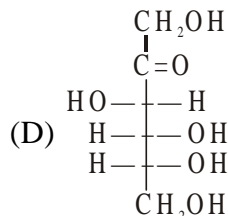
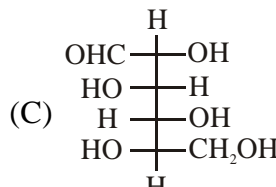
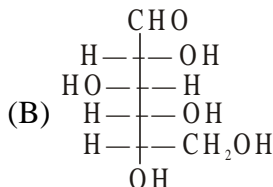
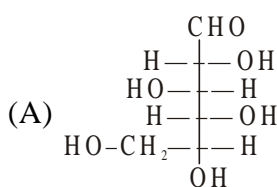
(B) 8

(C) 16

(D) 20

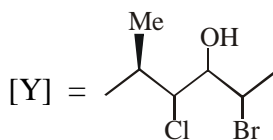
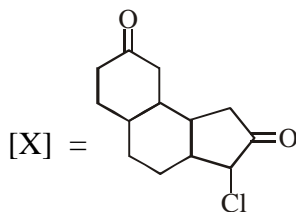
SE0025

26. Which of the following is not D sugar :



SE0026

27. Number of chiral centres in [X] & [Y] is a & b respectively. The value of (a-b) is :



(A) 1

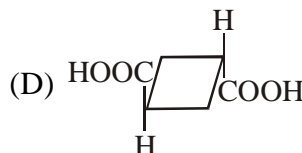
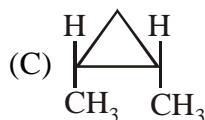
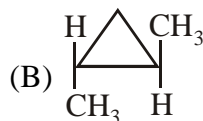
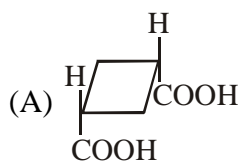
(B) 2

(C) 3

(D) 4

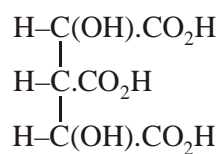
SE0027

28. Which one of the following is resolvable :



SE0028

29. How many stereoisomers can exist for the following acid.



(A) Two

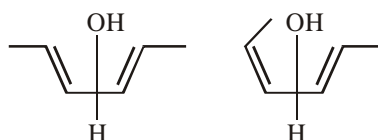
(B) Four

(C) Eight

(D) Six

SE0029

30. Incorrect relationship between given compounds are



(A) Both are geometrical isomers

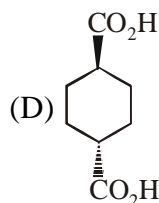
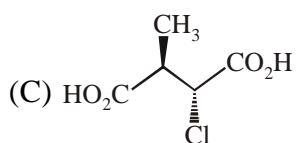
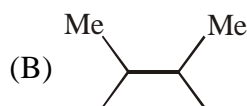
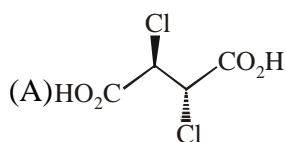
(B) Both are stereo isomers

(C) Both are enantiomers

(D) Both are diastereomers

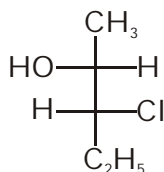
SE0030

31. Identify meso compound.

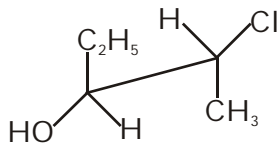


SE0031

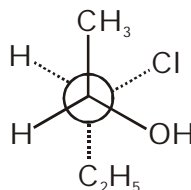
32. The two projection formulae that represent a pair of enantiomers are :-



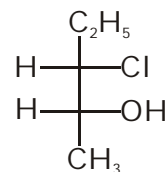
(I)



(II)



(III)



(IV)

- (A) I and II  
(C) I and III

- (B) III and IV  
(D) II and IV

SE0032

33. A pure sample of 2-chlorobutane shows rotation of PPL by  $30^\circ$  in standard conditions. When above sample is made impure by mixing its opposite form, so that the composition of the mixture becomes 87.5% d-form and 12.5% l-form, then what will be the observed rotation for mixture.

- (A)  $-22.5^\circ$                       (B)  $+22.5^\circ$                       (C)  $+7.5^\circ$                       (D)  $-7.5^\circ$

SE0033

34. When an optically active compound is placed in a 10 dm tube is present 20 gm in a 200 ml solution rotates the PPL by  $30^\circ$ . Calculate the angle of rotation & specific angle of rotation if above solution is diluted to 1 Litre.

- (A)  $16^\circ$  &  $36^\circ$                       (B)  $6^\circ$  &  $30^\circ$                       (C)  $3^\circ$  &  $30^\circ$                       (D)  $6^\circ$  &  $36^\circ$

SE0034

35. Identify % optical purity if 6 gm (+)-2-butanol is mixed with 2 gm (-)-2-butanol.

- (A) 50 %                      (B) 66.6 %                      (C) 33.3 %                      (D) 75 %

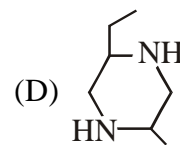
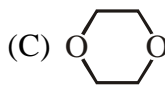
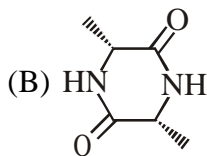
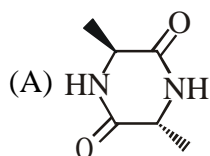
SE0035

36. A mixture of d and l, 2-bromobutane contain 75% d-2-bromobutane. Calculate enantiomeric excess.

- (A) 75%                      (B) 25%                      (C) 50%                      (D) 100%

SE0036

37. Which of the following is example of meso compound?



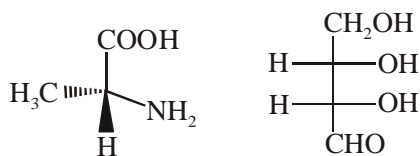
SE0037

38. Which of the following has  $C_2$  &  $C_3$  axis of symmetry ?



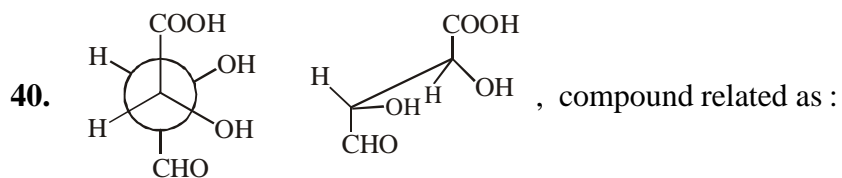
SE0038

39. Configuration of I & II respectively will be :



- (A) D, D (B) L, D (C) D, L (D) L, L

SE0039



- (A) Enantiomers (B) Conformation (C) Identical (D) Diastereomers

SE0040

EXERCISE # II (JEE-ADVANCE ORIENTED LEVEL-I)

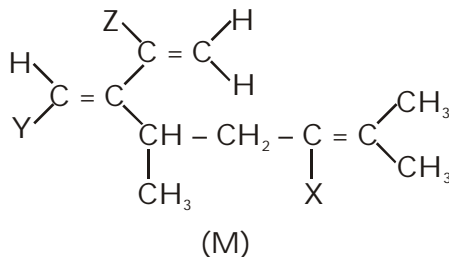
Single correct Option Type :

1. Molecular formula  $C_5H_{10}O$  can have :

- (A) 6-Aldehyde, 4-Ketone (B) 5-Aldehyde, 3-Ketone  
 (C) 4-Aldehyde, 3-Ketone (D) 5-Aldehyde, 2-Ketone

SE0041

2. In the given halogenoalkene M, atoms X, Y and Z represents hydrogen or bromine or chlorine. To show cis-trans isomerism, what could be the identities of atoms X, Y and Z?



	X	Y	Z
1	Cl	H	Br
2	H	Br	Cl
3	Cl	Br	H

- (A) 1, 2 and 3 (B) 1 and 2 only (C) 2 and 3 only (D) 1 and 3 only

SE0042

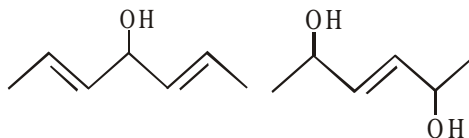
3. **Statement-1** :  $H-\overset{\text{Me}}{\underset{\text{Cl}}{\text{C}}}-\text{Et}$  is a chiral resolvable molecule.

**Statement-2** :  $H-\overset{\text{Me}}{\underset{\text{Cl}}{\text{C}}}-\text{Et}$  is non-superimposable on its mirror image.

- (A) Statement-1 is true, Statement-2 is true; Statement-2 is not the correct explanation of Statement-1  
 (B) Statement-1 is true, Statement-2 is true ; Statement-2 is the correct explanation of Statement-1  
 (C) Statement-1 is true, Statement-2 is false  
 (D) Statement-1 is false, Statement-2 is true

SE0043

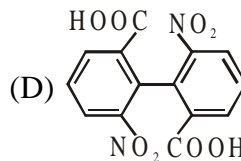
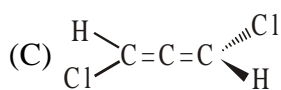
4. Total number of stereoisomer of following compounds are respectively :-



- (A) 4, 6 (B) 8 (C) 6, 6 (D) 8, 8

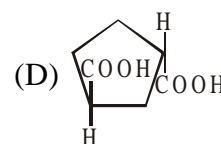
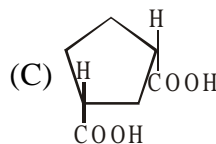
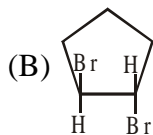
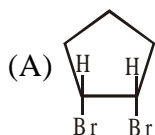
SE0044

5. Which of the following compounds are optically active ?



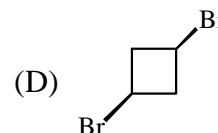
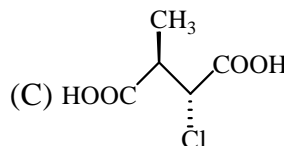
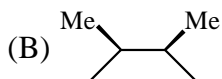
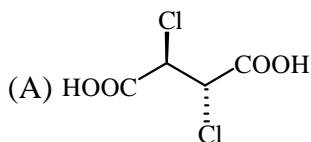
SE0045

6. Which out the following are Non-resolvable :



SE0046

7. Identify compound(s) which is/are not meso :



SE0047

8. Which of the following statements for a meso compound is/are correct :

(A) The meso compound has either a plane or centre of symmetry

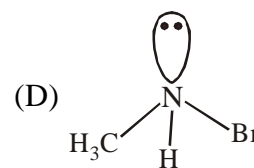
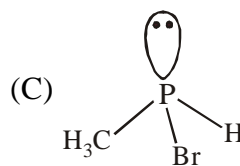
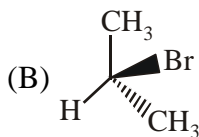
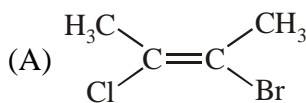
(B) The meso compound is optically inactive due to internal compensation.

(C) The meso compound is achiral

(D) The meso compound is formed when equal amounts of two enantiomers are mixed

SE0048

9. Among the following the non-resolvable compound is/are :



SE0049

10. Compound is/are ?

(A) (2R, 3S), L

(B) L, Erythro

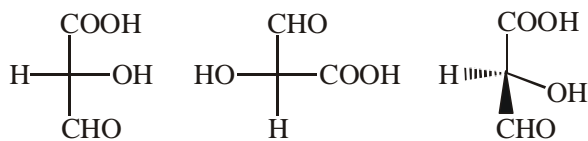
(C) Threo , D

(D) (2R, 3S), D

SE0050



11. Relation between compounds are :

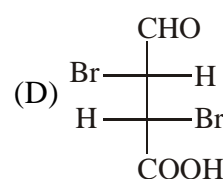
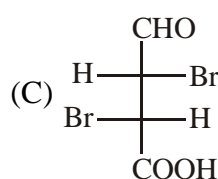
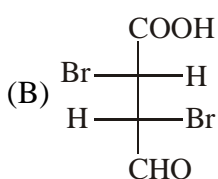
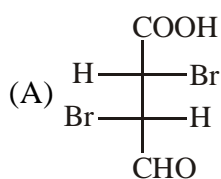


- (A) I & II = Enantiomers  
(C) I & II = Identical

- (B) II & III = Enantiomers  
(D) II & III = Identical

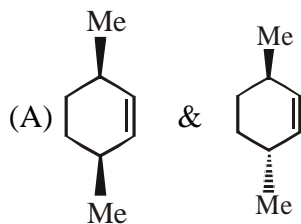
SE0051

12. has fisher diagram ?

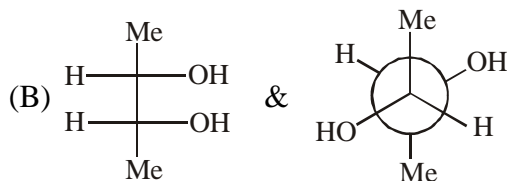


SE0052

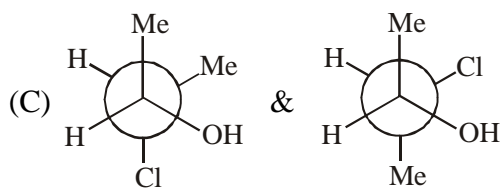
13. Identify correct relation between pair of compounds ?



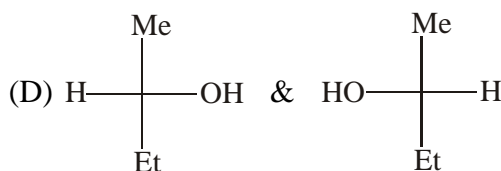
Diastereomers



Identical



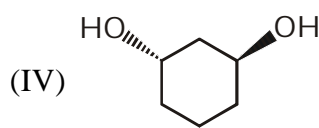
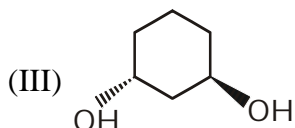
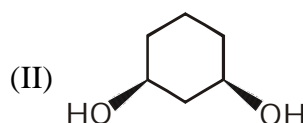
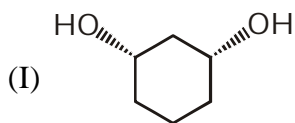
Diastereomers



Enantiomers

SE0053

14. Which two of the following compounds represents a pair of enantiomers?



(A) I & II

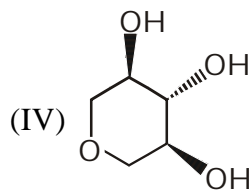
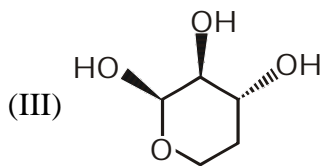
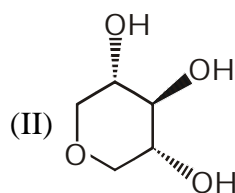
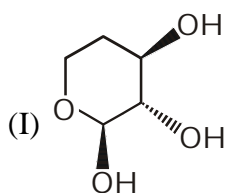
(B) II & III

(C) III & IV

(D) II & IV

SE0054

15. Which two of the following compounds are diastereomers?



(A) I & II

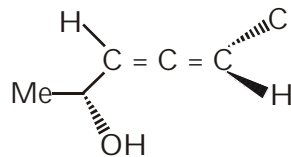
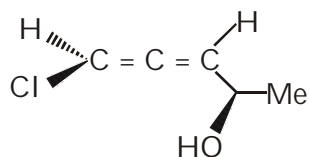
(B) II & IV

(C) III & IV

(D) I & III

SE0055

16. The correct relation between the following compounds is :



(A) Enantiomers

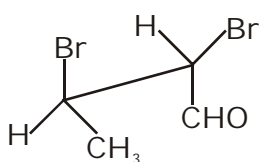
(B) Diastereomers

(C) Homomers (Identical)

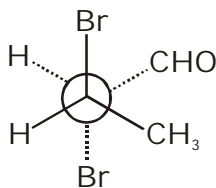
(D) Constitutional isomers

SE0056

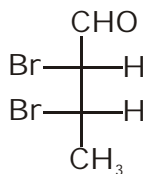
17. Identify the correct statement regarding following molecules?



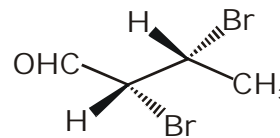
(M)



(N)



(O)



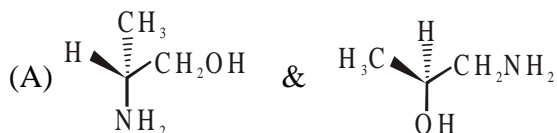
(P)

- (A) M and O are diastereomers
- (B) N and P are enantiomers
- (C) M and N are identical
- (D) O and P are diastereomers

SE0057

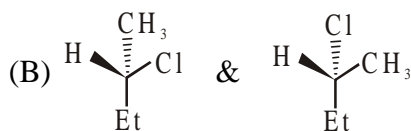
Matrix Match Type :

18. Column I

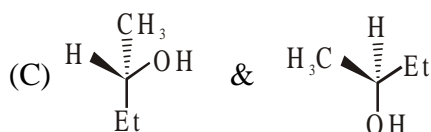


Column II

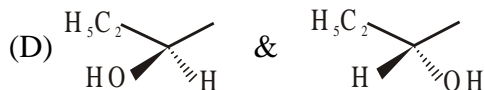
(P) Structural



(Q) Identical



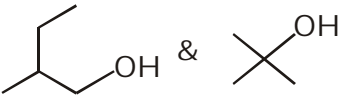
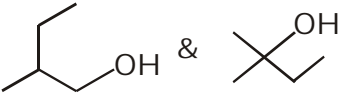
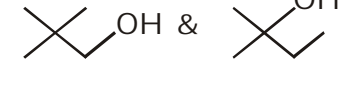
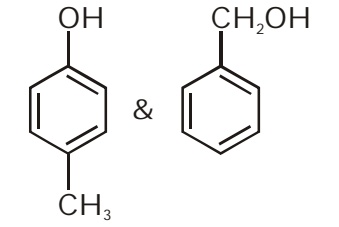
(R) Enantiomers



(S) Diastereomers

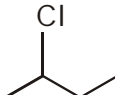
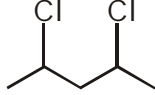
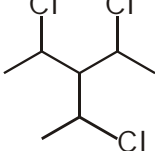
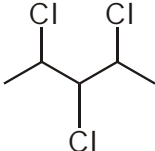
SE0058

## 19. Match the column :-

	Column-I		Column-II
(1)		(P)	Position isomers
(2)		(Q)	Chain isomers
(3)		(R)	Homologues
(4)		(S)	Functional isomers

SE0059

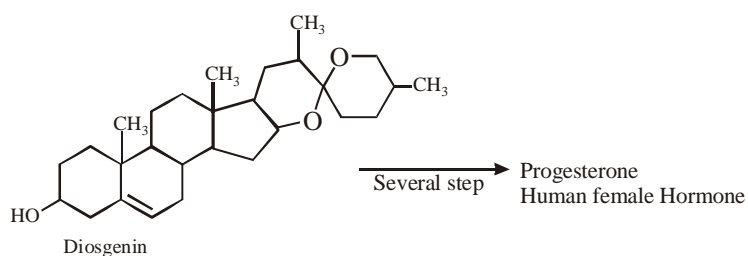
## 20. Match the column-I :-

	Column-I (Compounds)		Column-II (Total number of stereoisomers)
(1)		(P)	8
(2)		(Q)	4
(3)		(R)	3
(4)		(S)	2

SE0060

Subjective Type :

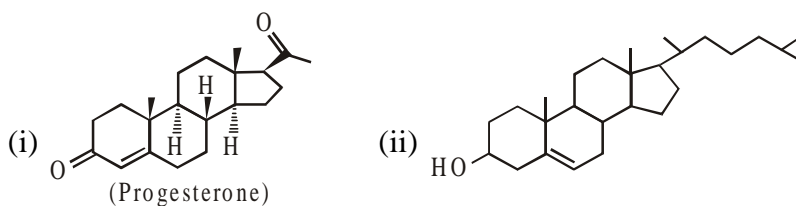
21.



What is number of chiral centres present in Diosgenin is :

SE0061

22. Calculate the total number of chiral carbon atoms in.

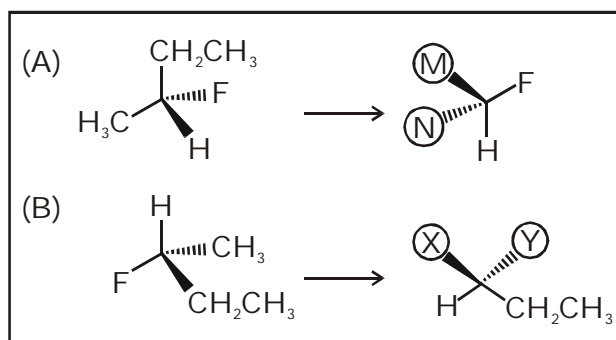


SE0062

23. Total number of isomeric (including stereo) bromochlorofluoriodo propadiene.

SE0063

24. Re-orient the molecule at the left to match the partially drawn perspective at the right. Find the two missing substituents at their correct positions.



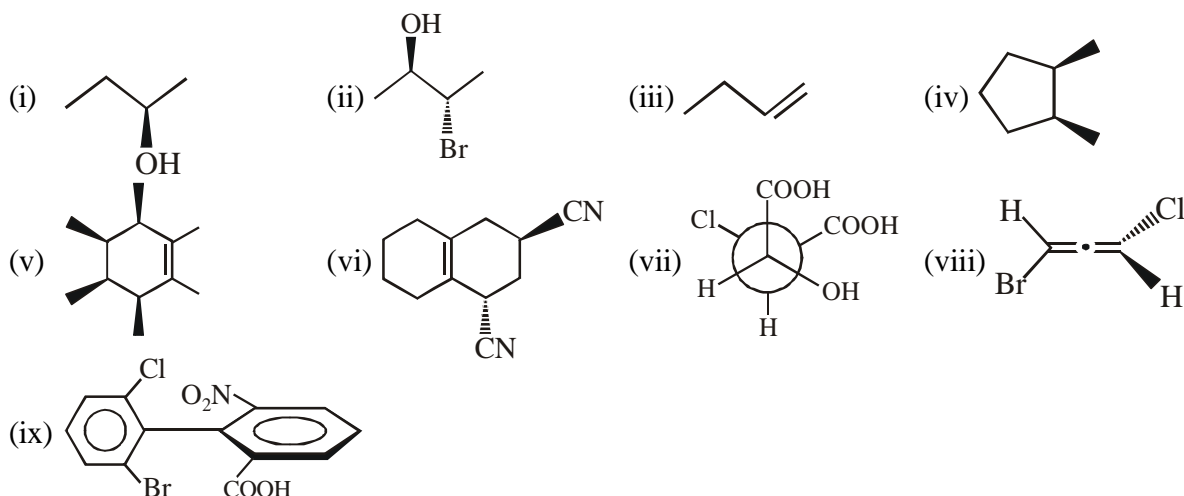
- (A)  $M = \text{CH}_3\text{CH}_2-$       (B)  $X = \text{CH}_3-$       (C)  $M = \text{CH}_3-$       (D)  $X = \text{F}-$   
 $N = \text{CH}_3-$        $Y = \text{F}-$        $N = \text{CH}_3\text{CH}_2-$        $Y = \text{CH}_3-$

SE0064

25. Find out the total number of cyclic isomers of  $\text{C}_6\text{H}_{12}$  which are optically active ?

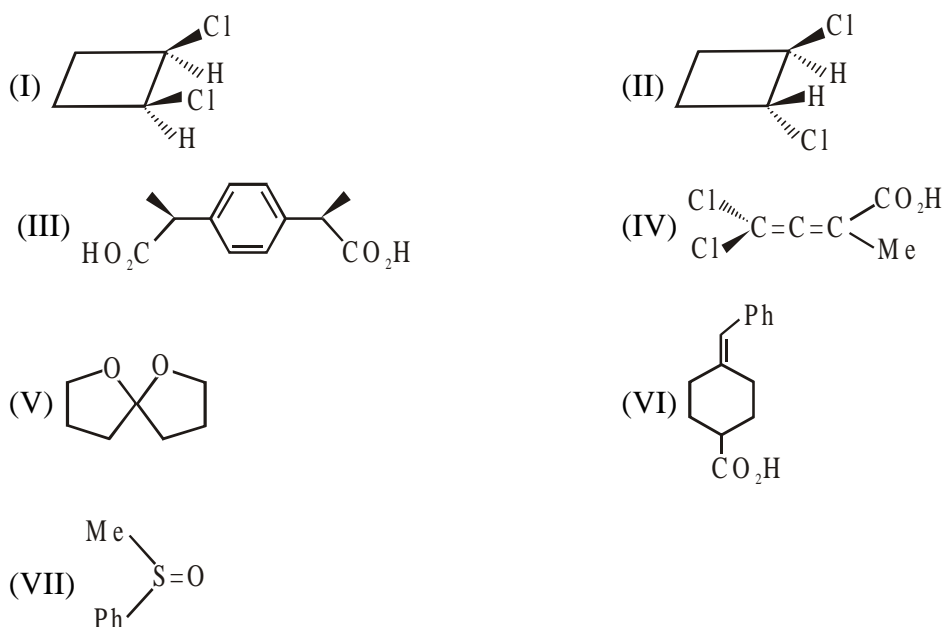
SE0065

26. How many of the given compounds are chiral :



SE0066

27. With reasons, state whether each of the following compounds I to VIII is chiral



SE0067

28. How many cyclopentane structures (including stereo) are possible for  $C_7H_{14}$ .

SE0068

29. The number of diastereoisomers (excluding enantiomers) for 1-bromo-2-chloro-3-iodocyclopropane.

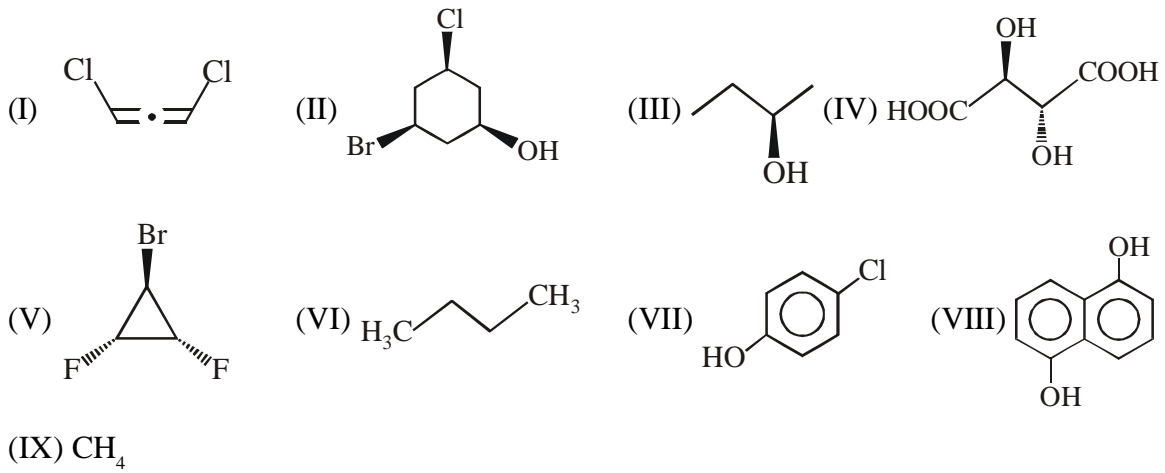
SE0069

30. Identify total number of stereoisomers for the following compound :



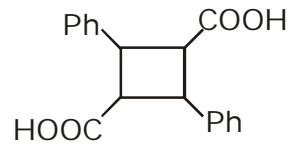
SE0070

31. How many of the given molecule / species are chiral :



SE0071

32. Total geometrical isomers possible for :



(A) 3

(B) 4

(C) 5

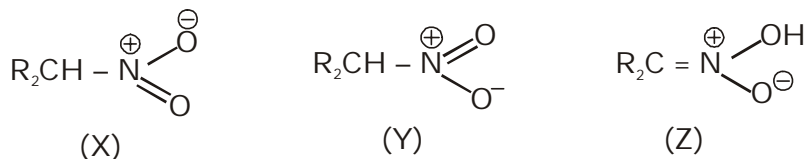
(D) 8

SE0072

## EXERCISE # III (JEE-ADVANCE ORIENTED LEVEL # II)

## Single Correct Type :

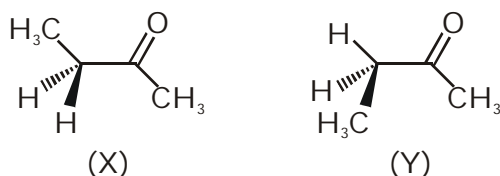
1. The correct statements describing the relationship between :



- (A) **X** and **Y** are resonance structures and **Z** is a tautomer  
 (B) **X** and **Y** are tautomers and **Z** is resonance structure  
 (C) **X**, **Y** and **Z** are all resonance structures  
 (D) **X**, **Y** and **Z** all are tautomers

SE0073

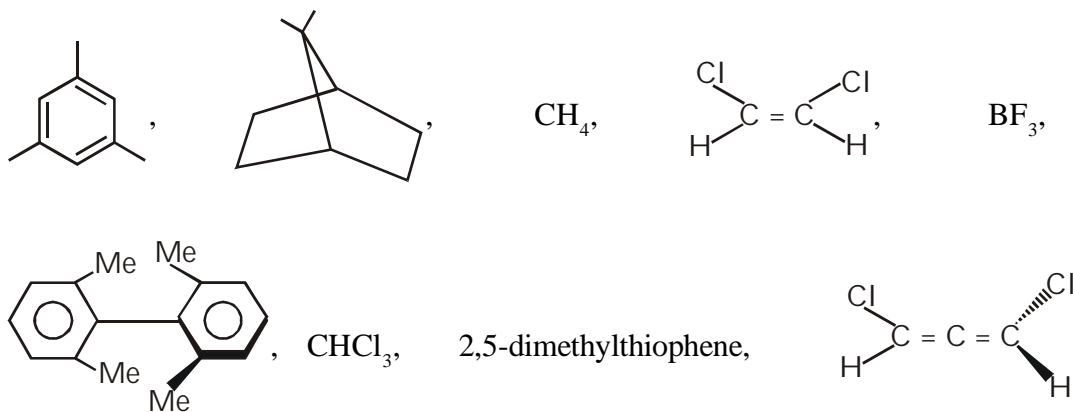
2. The correct statements about conformations **X** and **Y** of 2-butanone are :



- (a) **X** is more stable than **Y**                      (b) **Y** is more stable than **X**  
 (c) Methyl groups in **X** are anti              (d) Methyl groups in **Y** are gauche  
 (A) a and d                      (B) a and c                      (C) b and c                      (D) a, c and d

SE0074

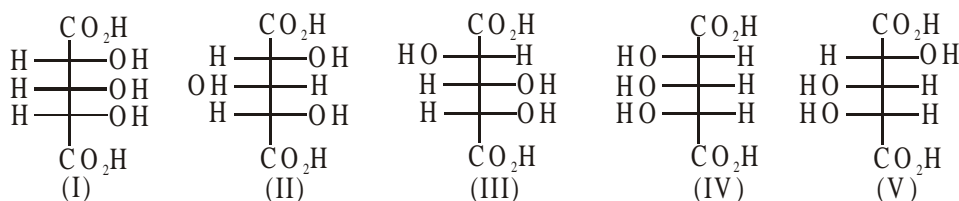
3. Among the following, the number of molecules that possess  $C_2$ -axis of symmetry is :



SE0075



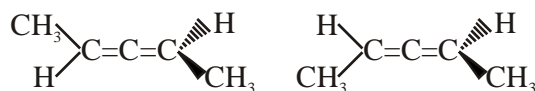
4. Observe the given compounds and answer the following questions.



- (i) Which of the above formulae represent identical compounds ?  
 (A) I and II                      (B) I and IV                      (C) II and IV                      (D) III and IV
- (ii) Which of the above compounds are enantiomers ?  
 (A) II and III                      (B) III and IV                      (C) III and V                      (D) I and V

SE0076

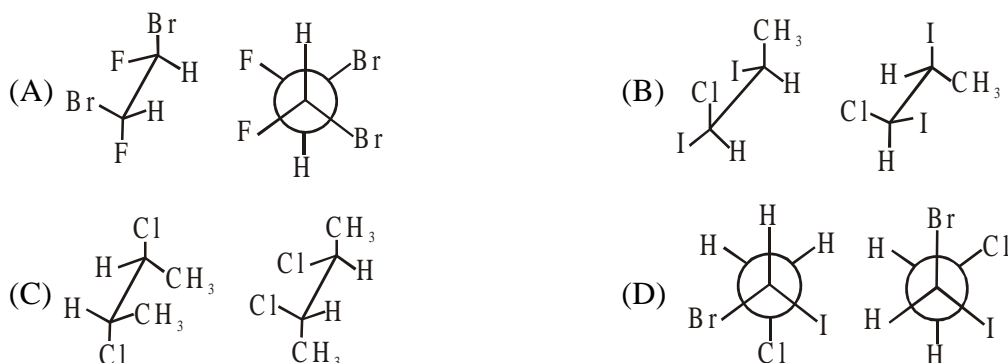
5. Which of the following option is correct regarding the given compounds :



- (A) Both are identical                      (B) Both are optically inactive  
 (C) Both are enantiomers                      (D) Geometrical isomer

SE0077

6. Which of the following pairs of compound is/are identical ?



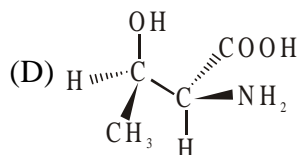
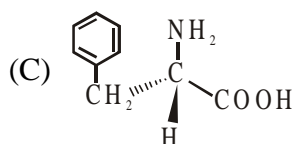
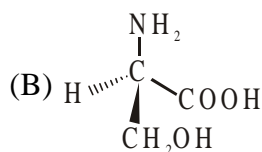
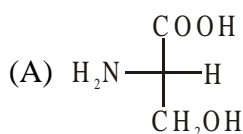
SE0078

**Multiple Correct Type :**

7. Which of the following statements is/are not correct for D-(+) glyceraldehyde :
- (A) The symbol D indicates the dextrorotatory nature of the compound  
 (B) The sign(+) indicates the dextrorotatory nature of the compound  
 (C) The symbol D indicates that (–OH) group lies left to the chiral centre in the conventionally correct Fischer projection diagram  
 (D) The symbol D indicates that (–OH) group lies right to the chiral centre in the conventionally correct Fischer projection diagram

SE0079

8. Which of the following are correct representation of L-amino acids :



SE0080

9. Identify relation between these two compounds :



(A) Homomers

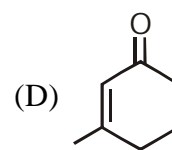
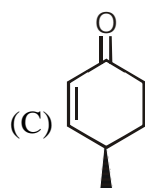
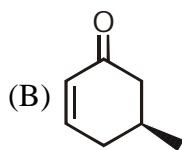
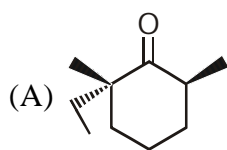
(B) Enantiomers

(C) Diastereomers

(D) Positional Isomers

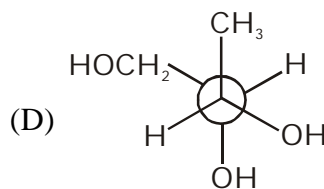
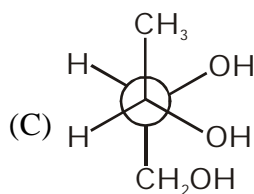
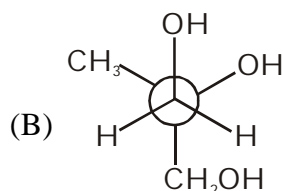
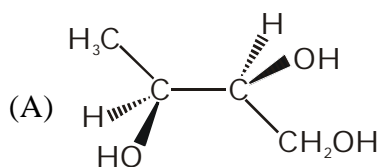
SE0081

10. Which of the following undergoes racemisation in alkaline medium?

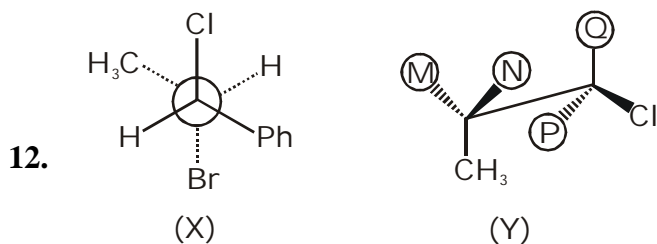


SE0082

11. Which compound is different from the others?



SE0083



What would be the correct match to get (Y) as a diastereomers of (X)?

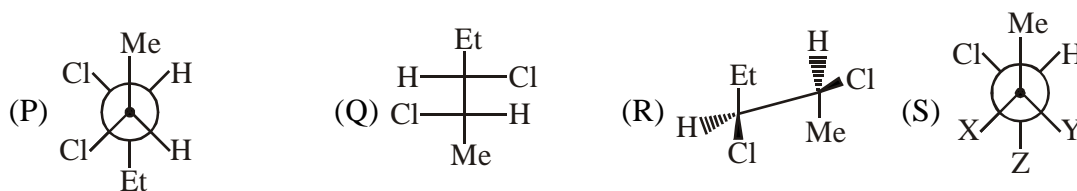
- |             |         |             |         |
|-------------|---------|-------------|---------|
| (A) M = -H  | Q = -Ph | (B) M = -H  | Q = -H  |
| N = -Br     | P = -H  | N = -Br     | P = -Ph |
| (C) M = -Br | Q = -Ph | (D) M = -Br | Q = -H  |
| N = -H      | P = -H  | N = -H      | P = -Ph |

SE0084

Comprehension Type :

Paragraph for Question 13 and 14

Four compounds are given below 'S' is a stereoisomer of P.



13. P & Q are related as :

- (A) Identical                      (B) Enantiomer                      (C) Diastereomer                      (D) Positional isomerism

SE0085

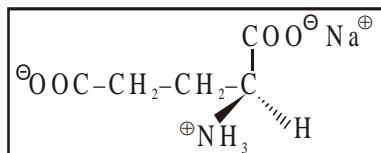
14. Which of the above structures represented is Sawhorse projection :-

- (A) P                      (B) Q                      (C) R                      (D) S

SE0086

Paragraph for Question 15 to 17

S(+) Mono sodium Glutamate (MSG) is a flavour enhancer used in many foods. Fast foods often contain substantial amount of MSG and is widely used in Chinese food. If one mole of above MSG was placed in 845 ml solution and passed through 200 mm tube, the observed rotation was found to be + 9.6°.



15. Find out the specific rotation of (-) MSG :

- (A) + 24°                      (B) +56.8°                      (C) -48°                      (D) None of these

SE0087

16. Find out the approximate percentage composition of (–) MSG in a mixture containing (+) MSG and (–) MSG whose specific optical rotation is  $-20^\circ$  :
- (A) 83.3%                      (B) 16.7%                      (C) 91.6%                      (D) 74%

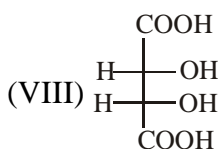
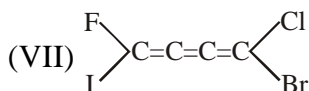
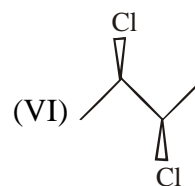
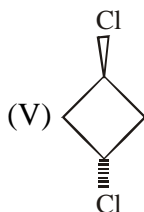
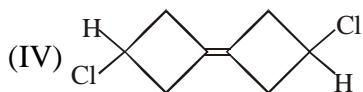
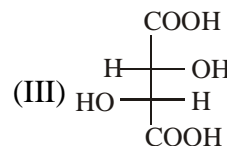
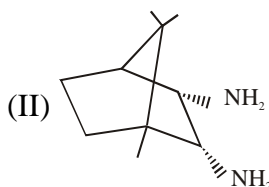
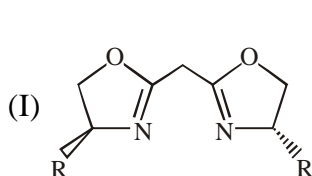
SE0088

17. If 33.8 g of (+) MSG was put in 338 ml solution and was mixed with 16.9g of (–) MSG put in 169 ml solution and the final solution was passed through 400 mm tube. Find out observed rotation of the final solution :
- (A)  $+1.6^\circ$                       (B)  $+4.8^\circ$                       (C)  $+3.2^\circ$                       (D) None of these

SE0089

*Paragraph for Q.18 and Q.19*

Among the following structures ?



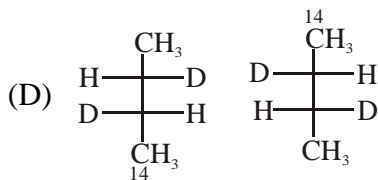
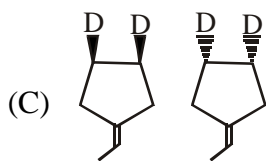
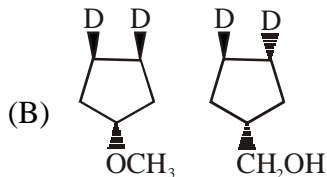
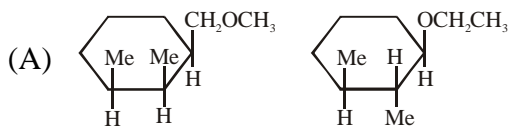
18. Optically active compound is -
- (A) III                      (B) IV                      (C) V                      (D) VII
19. Which of the following will not show optical isomerism -
- (A) I                      (B) II                      (C) V                      (D) VIII

SE0090

SE0091

Matrix Match Type :

20. Column-I  
(Compounds)



Column-II  
(Relation)

(P) Metamers

(Q) Functional Isomer

(R) Geometrical isomer

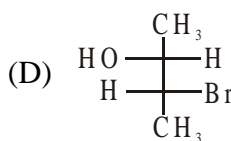
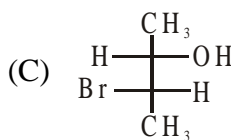
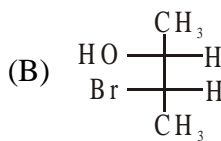
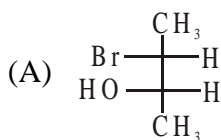
(S) Enantiomer

(T) Diastereomer

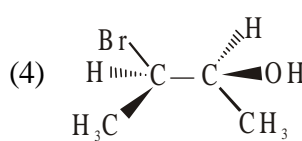
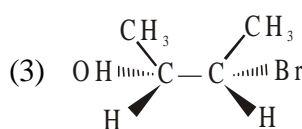
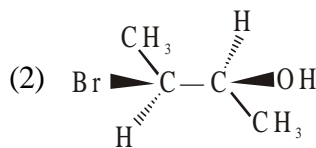
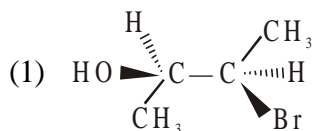
SE0092

21. Match List-I, II, III with each other :

List - I



List - II



List - III

(i) (2R, 3R)

(ii) (2S,3S)

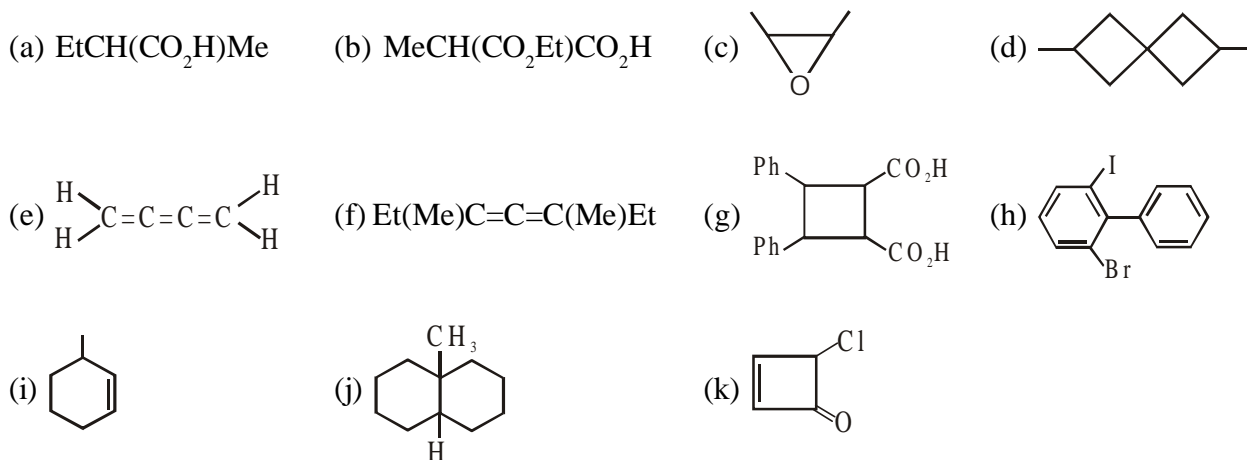
(iii) (2S,3R)

(iv) (2R,3S)

SE0093

## Subjective Type :

22. In what stereoisomeric forms would you expect the following compounds to exist ?

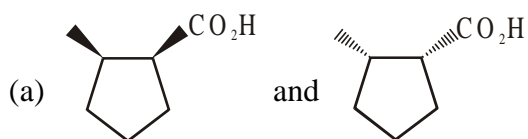


SE0094

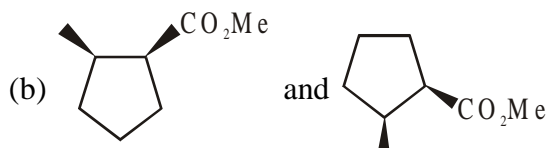
23. Calculate the number of Benzenoid isomers possible for  $\text{C}_6\text{H}_3\text{ClBrI}$ .

SE0095

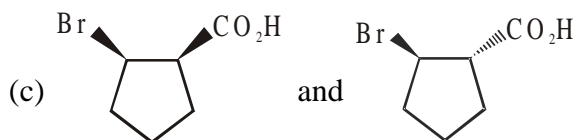
24. What are the relationships between the following pairs of isomers ?



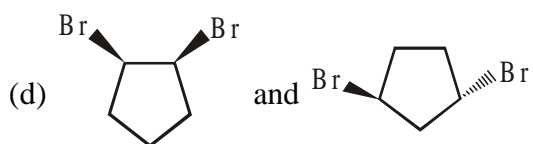
SE0096



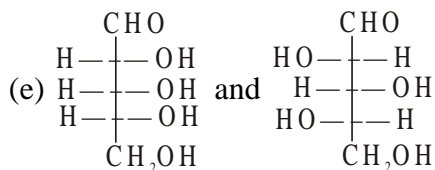
SE0096



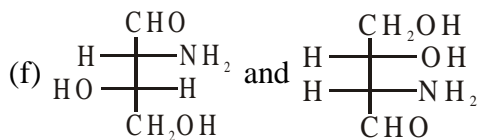
SE0096



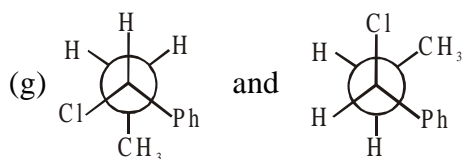
SE0096



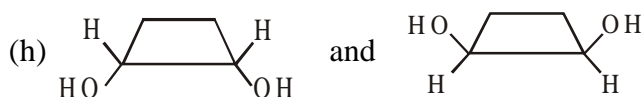
SE0097



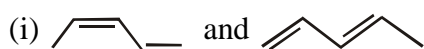
SE0097



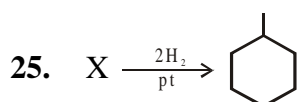
SE0098



SE0098



SE0098



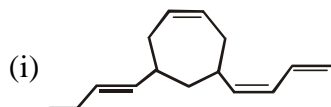
Find out total number of structures of X.

SE0099

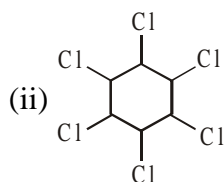
26. Calculate the number of chiral center in the molecule Ethyl 2,2-dibromo-4-ethyl-6-methoxy cyclohexane carboxylate.

SE0100

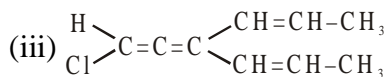
27. Calculate the total number of stereoisomers possible for



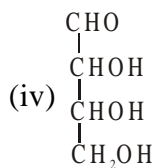
SE0101



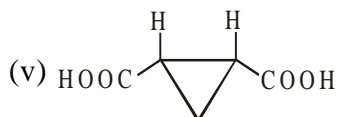
SE0102



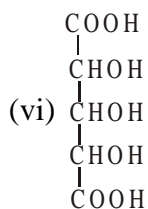
SE0103



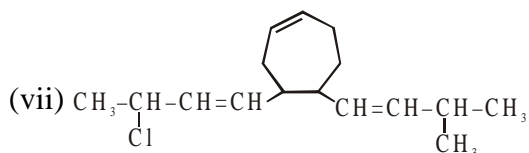
SE0104



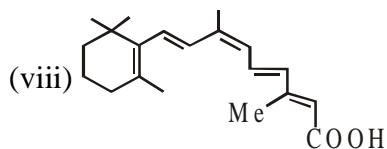
SE0105



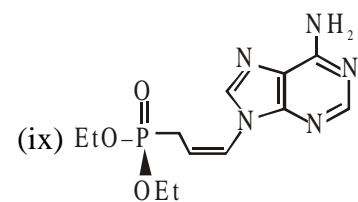
SE0105



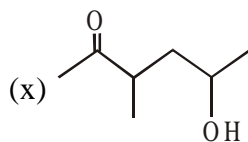
SE0105



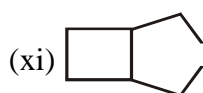
SE0105



SE0106



SE0106



SE0106

28. How many different chloroethanes are there from the formula  $\text{C}_2\text{H}_{6-n}\text{Cl}_n$  (where n can be any integer from 1 to 6)?

SE0107



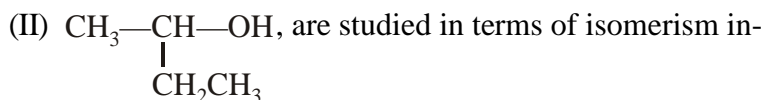
## EXERCISE # IV (A) (J-MAINS)

1. Racemic mixture is formed by mixing two : [AIEEE-2002]

- (1) Isomeric compounds (2) Chiral compounds  
(3) Meso compounds (4) Enantiomers with chiral carbon

SE0108

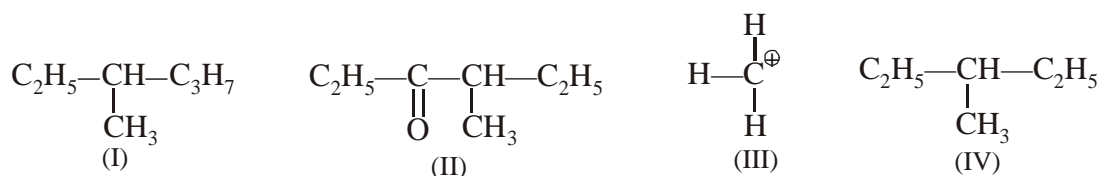
2. Following types of compounds I and II [AIEEE-2002]



- (1) Chain isomerism (2) Position isomerism  
(3) Conformers (4) Stereo isomerism

SE0109

3. Among the following four structures I to IV [AIEEE-2003]



It is true that-

- (1) All four are chiral compounds (2) Only I and II are chiral compounds  
(3) Only III is a chiral compound (4) Only II and IV are chiral compounds

SE0110

4. Which of the following will have a meso-isomer also- [AIEEE-2004]

- (1) 2-chlorobutane (2) 2,3-dichlorobutane  
(3) 2,3-dichloropentene (4) 2-hydroxy propanoic acid

SE0111

5. Amongst the following compounds, the optically active alkane having lowest molecular mass is

- (1)  $\text{CH}_3-\text{CH}_2-\text{C} \equiv \text{CH}$  (2)  $\text{CH}_3-\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{CH}_3$  [AIEEE-2004]  
(3)  $\text{CH}_3-\underset{\text{C}_2\text{H}_5}{\overset{\text{H}}{\text{C}}}-\text{Cyclopropyl}$  (4)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$

SE0112

6. Which of following compounds is not chiral [AIEEE-2005]

- (1) 1-chloropentane (2) 2-chloropentane  
(3) 1-chloro-2-methyl pentane (4) 3-chloro-2-methyl pentane

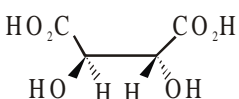
SE0113

7. Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is :  
 (1) 2-methyl pentane (2) 2,2-dimethyl butane [AIEEE-2005]  
 (3) 2,3-dimethyl butane (4) n-hexane

SE0114

8. Which types of isomerism is shown by 2,3-dichloro butane-  
 (1) Structural (2) Geometric (3) Optical (4) Diastereo [AIEEE-2005]

SE0115

9. The absolute configuration of  is : [AIEEE-2008]

- (1) S, S (2) R, R (3) R, S (4) S, R

SE0116

10. The number of stereoisomers possible for a compound of the molecular formula  $\text{CH}_3\text{-CH=CH-CH(OH)-Me}$  is :- [AIEEE-2009]

- (1) 4 (2) 6 (3) 3 (4) 2

SE0117

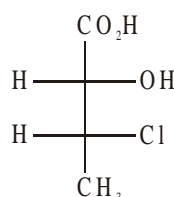
11. Out of the following, the alkene that exhibits optical isomerism is :- [AIEEE-2010]  
 (1) 2-methyl-2-pentene (2) 3-methyl-2-pentene  
 (3) 4-methyl-1-pentene (4) 3-methyl-1-pentene

SE0118

12. The optically inactive compound from the following is :- [JEE-MAIN-2015]  
 (1) 2-chloropropanal (2) 2-chlorobutane  
 (3) 2-chloro-2-methylbutane (4) 2-chloropentane

SE0119

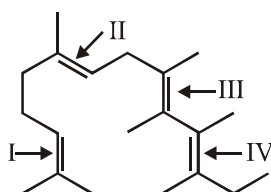
13. The absolute configuration of : [JEE-MAIN-2016]



- (1) (2R, 3R) (2) (2R, 3S) (3) (2S, 3R) (4) (2S, 3S)

SE0120

14. In the following structure, the double bonds are marked as I, II, III and IV [JEE-MAIN-2017]

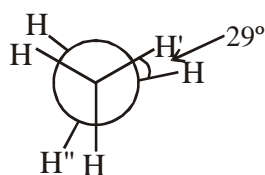


Geometrical isomerism is **not** possible at site (s)

- (1) III (2) I (3) III and IV (4) I and III

SE0121

15. Which of the following compounds will show the maximum enol content?  
 (1)  $\text{CH}_3\text{COCH}_2\text{COCH}_3$  (2)  $\text{CH}_3\text{COCH}_3$  [JEE-MAIN-April 2019]  
 (3)  $\text{CH}_3\text{COCH}_2\text{CONH}_2$  (4)  $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$   
 SE0122
16. Which of these factors does not govern the stability of a conformation in acyclic compounds?  
 (1) Torsional strain (2) Angle strain [JEE-MAIN-April 2019]  
 (3) Steric interactions (4) Electrostatic forces of interaction  
 SE0123
17. In the following skew conformation of ethane,  $\text{H}'\text{-C-C-H}''$  dihedral angle is :



[JEE-MAIN-April 2019]

- (1)  $120^\circ$  (2)  $58^\circ$  (3)  $149^\circ$  (4)  $151^\circ$

SE0124

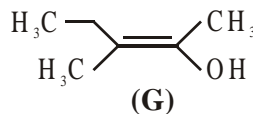
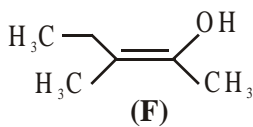
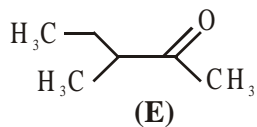
## EXERCISE # IV (B) (J-ADVANCE OBJECTIVE)

1. The  $\begin{array}{c} \text{H}_3\text{C} \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H}_3\text{C} \quad \text{C} \quad \text{H} \\ | \quad \diagdown \\ \text{CH}_3 \quad \text{COOH} \end{array}$  shows : [IIT-1995]
- (A) Geometrical isomerism (B) Optical isomerism  
(C) Geometrical & optical isomerism (D) tautomerism
- SE0125
2. How many optically active stereoisomers are possible for butane -2,3-diol : [IIT-1997]
- (A) 1 (B) 2 (C) 3 (D) 4
- SE0126
3. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methyl butane is : [IIT-1997]
- (A) 2 (B) 3 (C) 4 (D) 1
- SE0127
4. Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III
- $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{CH}_3 \\ \text{I} \end{array}$

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{CH}_3 \\ \text{II} \end{array}$

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{CH}_3 \\ \text{III} \end{array}$
- [IIT-2000]
- SE0128
5. Which of the following compounds exhibits stereoisomerism- [IIT-2002]
- (A) 2-Methylbutene-1 (B) 3-Methylbutyne-1  
(C) 3-Methylbutanoic acid (D) 2-Methylbutanoic acid
- SE0129
6. On monochlorination of 2-methylbutane, the total number of chiral compounds formed is : [IIT-2004]
- (A) 2 (B) 4 (C) 6 (D) 8
- SE0130
7. **Statement-I** : Molecules that are not superimposable on their mirror images are chiral  
**Because**
- Statement-II** : All chiral molecules have chiral centres. [IIT-2007]
- (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1  
(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1  
(C) Statement-1 is True, Statement-2 is False.  
(D) Statement-1 is False, Statement-2 is True.
- SE0131

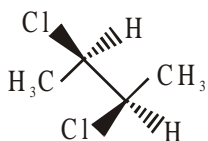
8. The correct statement(s) concerning the structures E, F and G is (are) [IIT-2008]



- (A) E, F and G are resonance structures  
 (B) E, F and E, G are tautomers  
 (C) F and G are geometrical isomers  
 (D) F and G are diastereomers

SE0132

9. The correct statement(s) about the compound given below is (are) : [IIT-2008]



- (A) The compound is optically active  
 (B) The compound possesses centre of symmetry  
 (C) The compound possesses plane of symmetry  
 (D) The compound possesses axis of symmetry

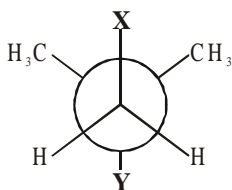
SE0133

10. The correct statement(s) about the compound  $\text{H}_3\text{C}(\text{HO})\text{HC} - \text{CH} = \text{CH} - \text{CH}(\text{OH})\text{CH}_3$  (X) is (are) :

- (A) The total number of stereoisomers possible for X is 6 [IIT-2009]  
 (B) The total number of diastereomers possible for X is 3  
 (C) If the stereochemistry about the double bond in X is trans, the number of enantiomers possible for X is 4  
 (D) If the stereochemistry about the double bond in X is cis, the number of enantiomers possible for X is 2

SE0134

11. In the Newman projection for 2,2-dimethylbutane [IIT-2010]



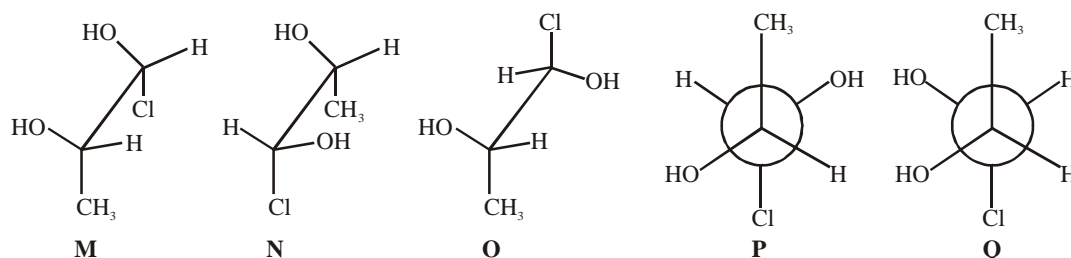
X and Y can respectively be –

- (A) H and H  
 (B) H and  $\text{C}_2\text{H}_5$   
 (C)  $\text{C}_2\text{H}_5$  and H  
 (D)  $\text{CH}_3$  and  $\text{CH}_3$

SE0135

12. Which of the given statement(s) about N,O,P and Q with respect to M is (are) correct ?

[JEE-2012]

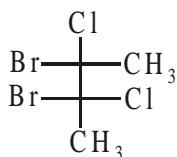


- (A) M and N are non-mirror image stereoisomers  
 (B) M and O are identical  
 (C) M and P are enantiomers  
 (D) M and Q are identical

SE0136

13. The total number(s) of **stable** conformers with **non-zero** dipole moment for the following compound is (are)

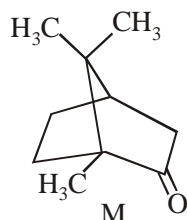
[JEE-2014]



SE0137

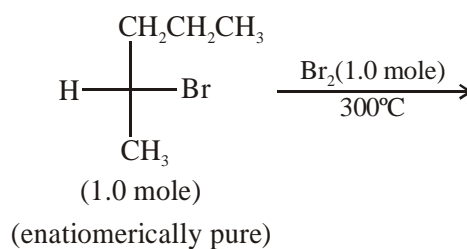
14. The total number of stereoisomers that can exist for M is :

[JEE-2015]



SE0138

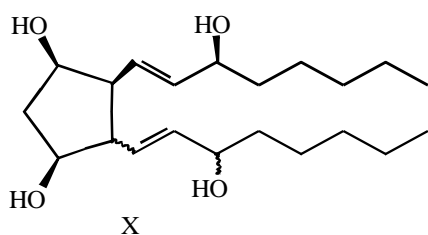
15. In the following monobromination reaction, the number of possible chiral products is : [JEE-2016]



SE0139

16. For the given compound X, the total number of optically active stereoisomers is \_\_\_\_.

[IIT-JEE 2018]



▶ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed

⋯ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is NOT fixed

SE0140

17. Total number of isomers, considering both structural and stereoisomers, of cyclic ethers with the molecular formula  $C_4H_8O$  is \_\_\_\_

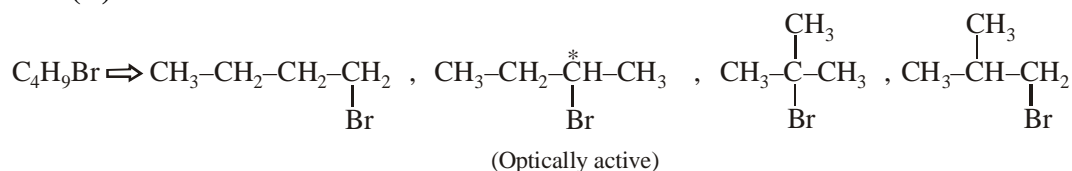
[IIT-JEE 2019]

SE0141

## ANSWER - KEY

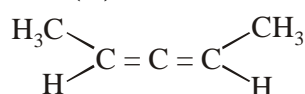
## EXERCISE # I (MAINS ORIENTED)

1. Ans.(C)                      2. Ans.(C)                      3. Ans.(D)                      4. Ans.(D)  
 5. Ans.(A)                      6. Ans.(A)                      7. Ans.(A)                      8. Ans.(D)  
 9. Ans.(B)



Optically active isomers  $\Rightarrow$  2

10. Ans.(B)                      11. Ans.(D)                      12. Ans.(A)  
 13. Ans.(C)



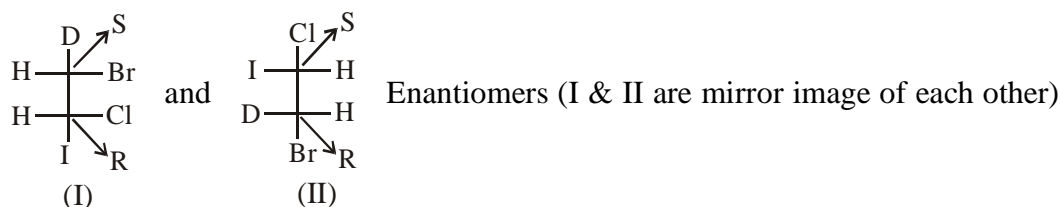
14. Ans.(B)                      15. Ans.(C)                      16. Ans.(D)  
 17. Ans.(C)  
 18. Ans.(A)

Cl-CH=C=C-CH-Cl is a planar structure

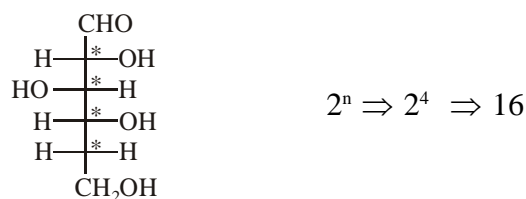
19. Ans.(A)  
 20. Ans.(C)

Meso tartaric acid and d-tartaric acid are not mirror image of each other so they are diastereomers.

21. Ans.(A)



22. Ans.(C)                      23. Ans.(D)                      24. Ans.(B)  
 25. Ans.(C)

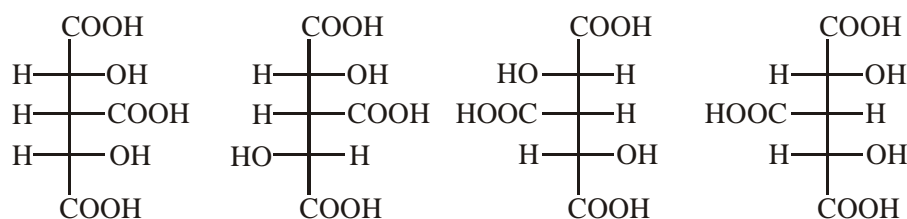


26. Ans.(B)                      27. Ans.(B)

28. Ans.(B)

Optically active compounds are resolvable.

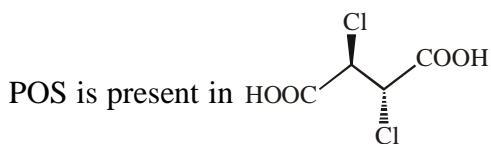
29. Ans.(B)



30. Ans.(C)



31. Ans.(A)



32. Ans.(C)

33. Ans.(B)

$$e.e = 87.5 - 12.5 \Rightarrow 75 \% \text{ of}$$

$$ee = \frac{\text{Rotation by mixture}}{\text{Rotation by pure isomer}} \times 100$$

$$75 = \frac{X}{30} \times 100$$

$$X = \frac{75 \times 30}{100} = +22.5^\circ$$

34. Ans.(B)

$$l = 10 \text{ dm}$$

$$c = 20 \text{ gm}/200 \text{ ml}$$

$$\alpha = 30^\circ$$

$$[\alpha]_{\text{specific}} = \frac{\alpha_{\text{obs}}}{c \cdot l} = \frac{30}{\frac{20}{200} \times 10} \Rightarrow 30^\circ$$

$\alpha_{\text{obs}}$  after dilution

$$\alpha_{\text{obs}} = \alpha_{\text{sp}} \cdot c.p.$$

$$\alpha_{\text{obs}} = 30 \times \frac{20}{1000} \times 10 \Rightarrow 6^\circ$$

35. Ans.(A)

$$\% \text{ optical purity} = \frac{|d - l|}{d + l} \times 100 = \frac{4}{8} \times 100 = 50\%$$

36. Ans.(C)

37. Ans.(A)

38. Ans.(D)

39. Ans.(C)

40. Ans.(A)

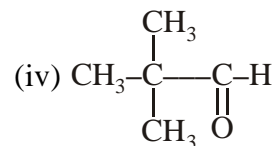
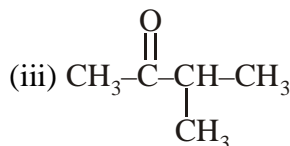
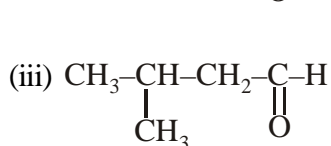
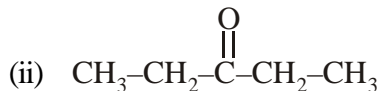
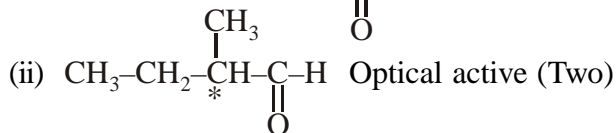
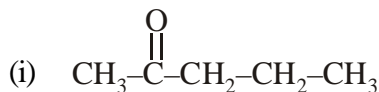
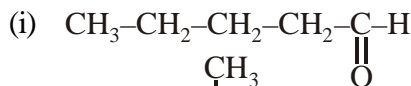
EXERCISE-II (JEE-ADVANCE ORIENTED LEVEL-I)

Single correct Option Type :

1. Ans.(B)



Ketones



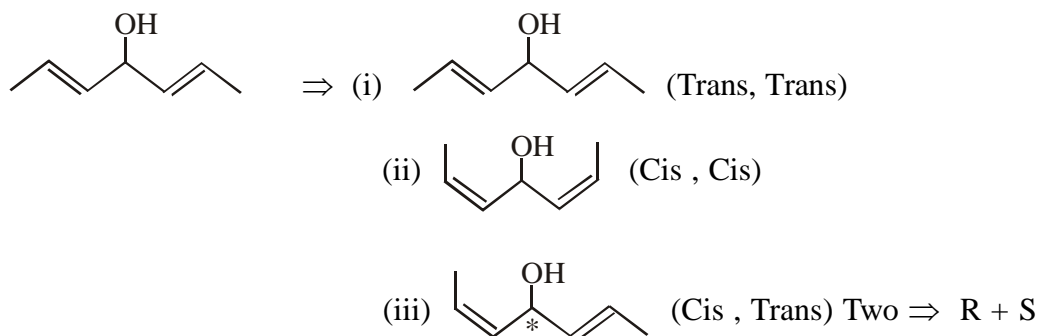
Total  $\Rightarrow$  5 aldehyde

Total  $\Rightarrow$  3 ketones

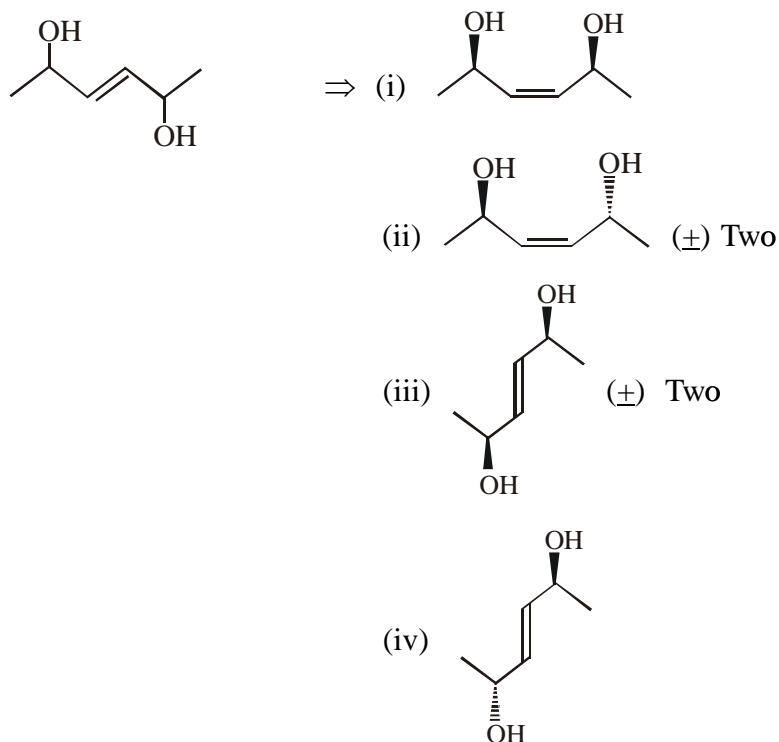
2. Ans.(C)

3. Ans.(D)

4. Ans.(A)



Total isomers = 4



Total = 6 isomer

5. Ans.(A,C,D)

6. Ans.(A,C)

Optically active compounds are resolvable and A &amp; C are optically inactive

7. Ans.(B,C,D)

8. Ans.(A,B,C)

9. Ans.(A,B,D)

10. Ans.(C,D)

11. Ans.(A,D)

12. Ans.(A,C)

13. Ans.(A,B,C,D)

14. Ans.(C)

15. Ans.(D)

16. Ans.(C)

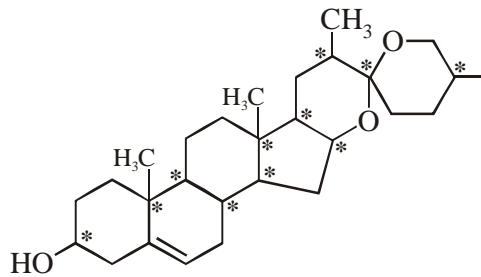
17. Ans.(D)

18. Ans.(A)→P ; (B)→R ; (C)→Q ; (D)→R

19. Ans.(1→R, 2→P, 3→Q, 4→S)

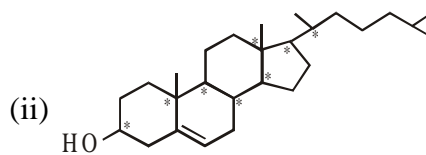
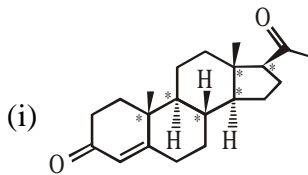
20. Ans.(1→S, 2→R, 3→Q, 4→Q)

21. Ans.(11)

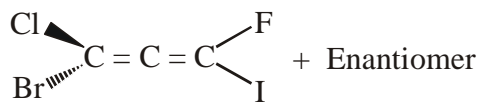
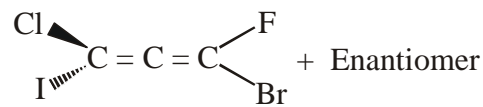
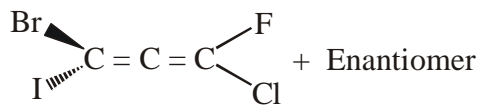


22. Ans. (i) 6, (ii) 8

Explanation

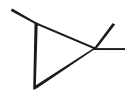


23. Ans.(6)



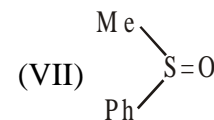
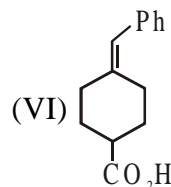
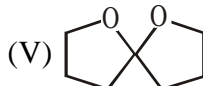
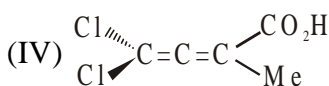
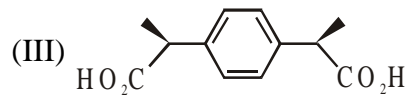
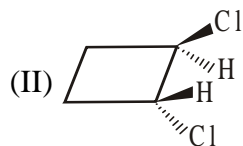
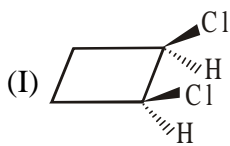
24. Ans.(A,B)

25. Ans.(8)



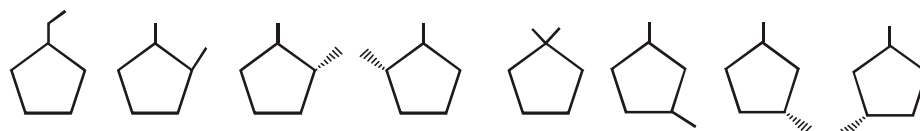
4 Optically Active Isomers    2 Optically Active    2 Optically Active  
 $2 + 2 + 4 = 8$

26. Ans.(6)

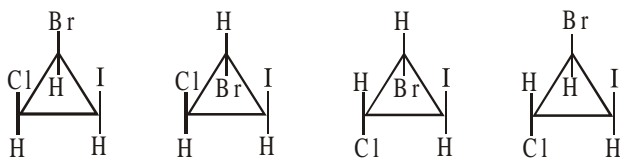


27. Ans. Achiral : I, III , IV ; Chiral : II,V, VI, VII

28. Ans.(8)



29. Ans.(4)



30. Ans.(8)



Stereogenic centre = 3

Total number of stereoisomer =  $2^3 = 8$ 

31. Ans.(3)

32. Ans.(C)

## EXERCISE#III (JEE-ADVANCE ORIENTED LEVEL # II)

Single Correct Type :

- |                           |            |            |
|---------------------------|------------|------------|
| 1. Ans.(A)                | 2. Ans.(D) | 3. Ans.(8) |
| 4. Ans.(i)-(B) ; (ii)-(C) | 5. Ans.(C) | 6. Ans.(C) |

Multiple Correct Type :

- |              |                |               |
|--------------|----------------|---------------|
| 7. Ans.(A,C) | 8. Ans.(A,C,D) | 9. Ans.(C)    |
| 10. Ans.(C)  | 11. Ans.(B)    | 12. Ans.(A,D) |

Comprehension Type :

- |             |             |
|-------------|-------------|
| 13. Ans.(B) | 14. Ans.(C) |
| 15. Ans.(D) |             |

M.W. of MSG = 169

$$C = \frac{169 \text{ gm}}{845 \text{ ml}}$$

$$l = 200 \text{ mm} = 2 \text{ dm}$$

$$\alpha_{\text{obs}} = +9.6^\circ$$

$$[\alpha]_{\text{sp}} = \frac{\alpha_{\text{obs}}}{C.l.} = \frac{9.6}{\frac{169}{845} \times 2} = -24^\circ$$

16. Ans.(C)

$$ee = \frac{[\alpha]_{\text{mixture}}}{[\alpha]_{\text{pure}}} \times 100 = \frac{-20^\circ}{-24^\circ} \times 100 = 83.3\%$$

$$\therefore \text{RM} = 100 - 83.3 \Rightarrow 16.7\% \begin{cases} \rightarrow d = 8.35 \\ \rightarrow l = 8.35 \end{cases}$$

$$\begin{aligned} \text{Total (-) MSG} &= 83.3 + 8.35 \\ &= 91.6\% \end{aligned}$$

17. Ans.(C)

$$C = \frac{33.8 - 16.9 \text{ g}}{338 + 169 \text{ ml}} = \frac{16.9 \text{ g}}{507 \text{ ml}}$$

$$l = 400 \text{ mm} = 4 \text{ dm}$$

$$\alpha_{\text{obs}} = [\alpha]_{\text{sp.}} \cdot c \cdot l = 24 \times \frac{16.9}{507} \times 4 = + 3.2^\circ$$

18. Ans.(A)

19. Ans.(C)

Matrix Match Type :

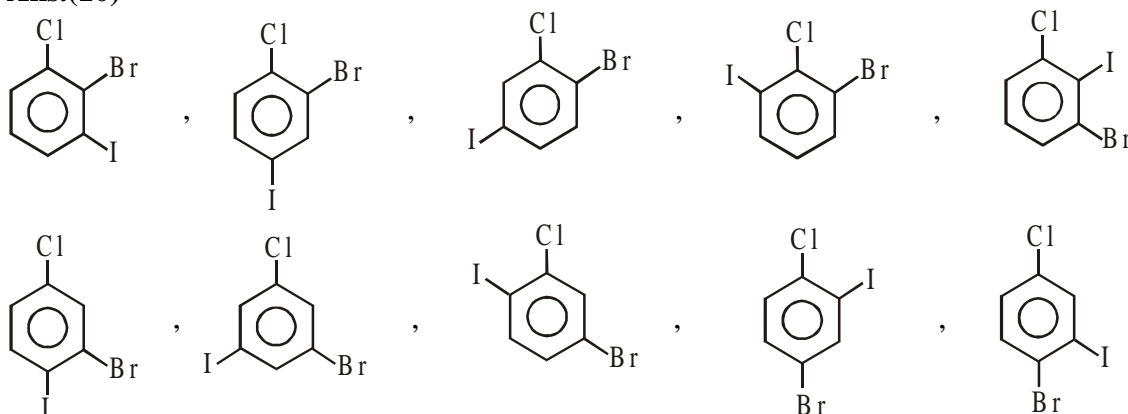
20. Ans.(A)→P ; (B)→Q ; (C)→R,S ; (D)→S

21. Ans.(A)→4→iii ; (B)→3→iv ; (C)→2→ii ; (D)→1→i

Subjective Type :

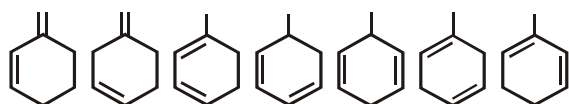
22. Ans. Optical : a, b, c, d, f, g, i, j, k ; Geometrical isomer : c, g, j ; None : e, h

23. Ans.(10)



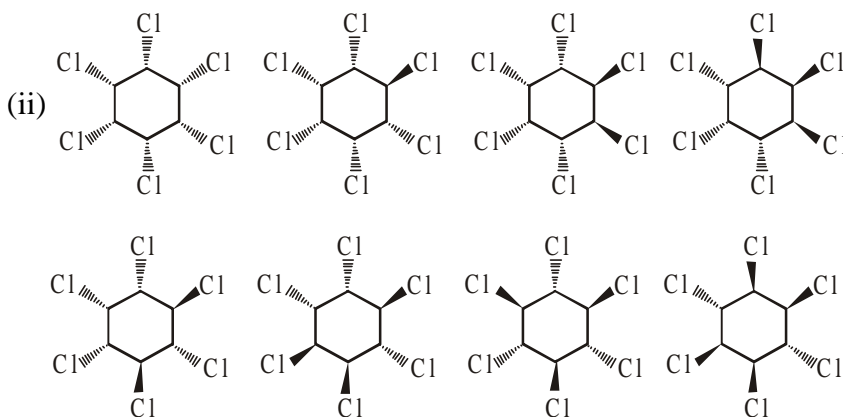
24. Ans. (a) Enantiomers, (b) Enantiomers, (c) Geometrical isomers & Diastereomers, (d) Positional, (e) Optical, (Diastereomers), (f) Diastereomers (g) Enantiomers, (h) Identical, (i) Geometrical isomers (Diastereomers)

25. Ans.(7)



26. Ans.(3)

27. Ans.(i) 2<sup>4</sup> (ii) 9 (iii) 4 (iv) 4 (v) 3, (vi) 4 (vii) 2<sup>5</sup>, (viii) 2<sup>4</sup>, (ix) 2, (x) 4, (xi) 3



28. Ans.(9)

## EXERCISE # IV (A) (J-MAINS)

1. Ans. (4)      2. Ans. (4)      3. Ans. (2)      4. Ans. (2)  
 5. Ans. (3)      6. Ans. (1)      7. Ans. (3)      8. Ans. (3)  
 9. Ans. (2)      10. Ans. (1)      11. Ans. (4)

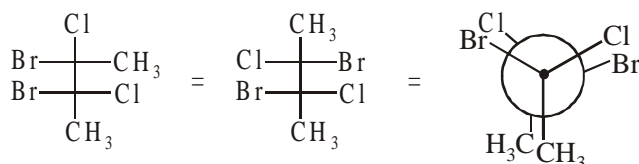


It achiral \ optically inactive

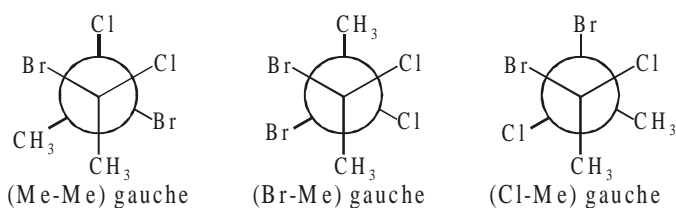
13. Ans. (3)      14. Ans. (2)      15. Ans. (1)      16. Ans. (2)      17. Ans. (4)

## EXERCISE # IV (B) (J-ADVANCE OBJECTIVE)

1. Ans. (B)      2. Ans. (B)      3. Ans. (A)  
 4. Ans. Enantiomers - I and III ; Diastereomers - I & II and II & III  
 5. Ans. (D)      6. Ans. (B)      7. Ans. (C)  
 8. Ans. (B,C,D)      9. Ans. (A,D)      10. Ans. (A,D)  
 11. Ans. (B,D)      12. Ans. (A,B,C)  
 13. Ans. (3)

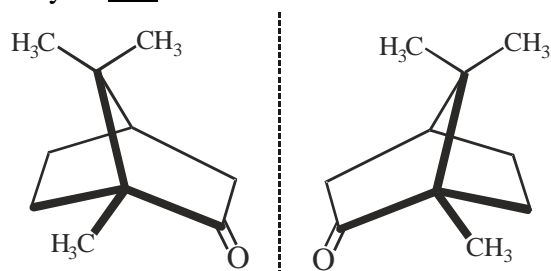


Stable conformer (with  $\mu \neq 0$ )



14. Ans. (2)

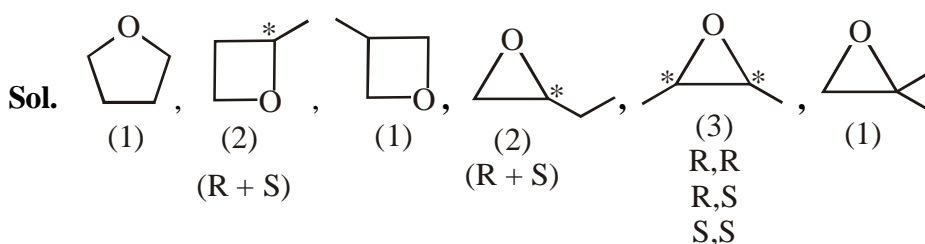
Sol. M is a organic compound known as camphor. M contains two **rigid** chiral centre so it can exist only in **two** enantiomeric forms.



15. Ans. (5)

16. Ans. (7)

17. Ans. (10.00)



## POLYMERS AND PRACTICAL ORGANIC CHEMISTRY NOTES

- The term polymer is used to describe a very large molecule that is made up of many small repeating molecular units. These small molecular units from which the polymer is formed are called monomers.
- The chemical reaction that joins the monomers together is called polymerisation.
- Starting from  $n$  molecules of a compound  $M$ , linking in a linear manner will form polymer  $x-M-(M)_{n-2}-M-y$ . The nature of linkages at the terminal units i.e.  $M-x$  and  $M-y$  depends upon the mode of reaction used in making the polymers.

### Homopolymers and Copolymers

Polymers which are formed by only one type of monomer are called homopolymers. Some examples of homopolymers and their monomers are given below :

Homopolymer	Monomer
Starch	Glucose
Cellulose	Glucose
Glycogen	Glucose
Dextrin	Glucose
Inulin	Fructose
Polyethylene	Ethylene
Polyvinyl chloride	Vinyl chloride
Teflon	Tetrafluoro ethylene
Nylon-6	Caprolactam
Polystyrene	Styrene
Orlon (Acrilan)	Acrylonitrile
Plexiglas (Lucite)	Methyl methacrylate
Polyvinyl acetate	Vinyl acetate

Polymers, which are formed by more than one type of monomers are known as copolymers. Some examples are given below in the table :

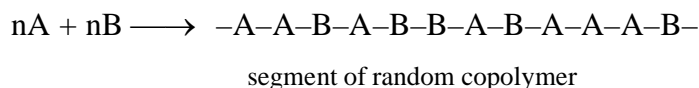
Copolymer	Monomers
Saran	Vinyl chloride and vinylidene chloride
SAN	Styrene and acrylonitrile
ABS	Acrylonitrile, butadiene and styrene
Butyl rubber	Isobutylene and Isoprene
Buna-S, SBR	Styrene and Butadiene
Buna-N, NBR	Acrylonitrile and Butadiene
Nylon-66	Hexamethylenediamine and Adipic acid
Terylene	Terephthalic acid and ethylene glycol

**Types of copolymers**

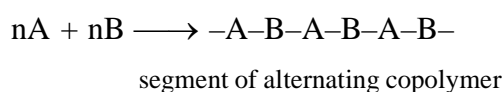
Depending upon the distribution of monomer units, the following types of copolymers are possible.

**(1) Random Copolymer**

If the monomer units have random distribution throughout the chain, it is called random copolymer. For example, if the monomer A and monomer B undergo copolymerisation then the structure of the random copolymer is

**(2) Alternating Copolymer**

If the two monomer units present alternatively throughout the polymer chain, it is said to be alternating copolymer. For example,

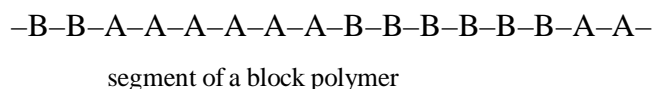


The exact distribution depends upon the proportion of the two reactant monomers and their relative reactivities. In practice neither perfectly random nor perfectly alternating copolymers are usually formed. However, most copolymers tend more towards alternating type but have many random imperfections.

**(3) Block copolymer**

Polymers in which different blocks of identical monomer units alternate with each other are called block copolymers.

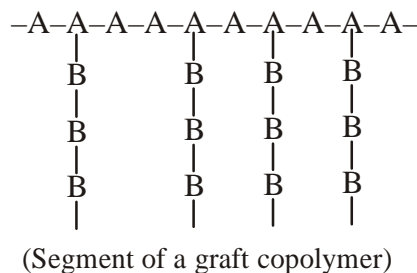
For example,



Block copolymer can be prepared by initiating the radical polymerisation of one monomer to grow homopolymer chains, followed by addition of an excess of the second monomer.

**(4) Graft copolymer**

Polymers in which homopolymer branches of one monomer unit are grafted onto a homopolymer chain of another monomer unit are called graft co-polymers. For example:



Graft copolymers are prepared by  $\gamma$ -irradiation of a homopolymer chain in the presence of a second monomer. The high energy radiation knock out H-atoms from the homopolymer chain at random points thus generating radical sites that can initiate polymerisation of the second monomer.



**CLASSIFICATION OF POLYMERS**

Polymers are classified in following ways :

**(I) CLASSIFICATION BASED UPON SOURCE****(1) Natural polymers**

Polymers which are obtained from animals and plants are known as natural polymers. Examples of natural polymers are given below.

**Natural polymer**

1. Polysaccharide
2. Proteins
3. Nucleic acid
4. Silk
5. Natural Rubber (cis polyisoprene)
6. Gutta purcha (trans polyisoprene)

**Monomers**

- Monosaccharide
- $\alpha$ -L-Amino acids
- Nucleotide
- Amino acids
- Isoprene (2-Methyl-1,3-butadiene)
- Isoprene

Natural polymers which take part in metabolic processes are known as biopolymers. Examples are polysaccharides, proteins, RNA and DNA.

**(2) Semisynthetic polymers**

Polymers which are prepared from natural polymers are known as semisynthetic polymers. Most of the semisynthetic polymers are prepared from cellulose. Examples are: cellulose acetate, cellulose nitrate, cellulose xanthate and Rayon.

**(3) Synthetic polymers**

Man-made polymers, i.e. polymers prepared in laboratory are known as synthetic polymers. Example are : PVC, polyethylene, polystyrene, nylon-6, nylon-66, nylon-610, terylene, synthetic rubbers etc.

**(II) CLASSIFICATION BASED UPON SHAPE****(1) Linear polymers**

Polymer whose structure is linear is known as linear polymer. The various linear polymeric chains are stacked over one another to give a well packed structure.



The chains are highly ordered with respect to one another. The structure is close packed in nature, due to which they have high densities, high melting point and high tensile (pulling) strength. Linear polymers can be converted into fibres.

**Note :**

- (i) All fibers are linear polymers. Examples are cellulose, silk, nylon, terylene etc.
- (ii) Linear polymers may be condensation as well as addition polymers. Examples are cellulose, polypeptide, nucleic acid, nylon, terylene etc.

**(2) Branched chain polymers**

Branched chain polymers are those in which the monomeric units constitute a branched chain. Due to the presence of branches, these polymers do not pack well. As a result branched chain polymers have lower melting points, low densities and tensile strength as compared to linear polymers. Branched chain polymers may be formed due to addition as well as condensation polymerisation. Examples are amylopectin, glycogen, low density polyethylene.

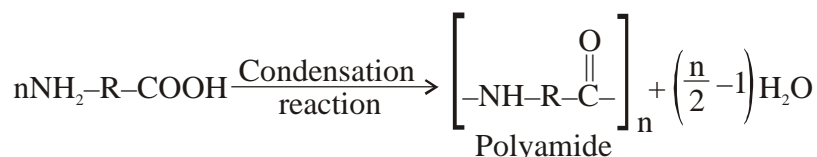
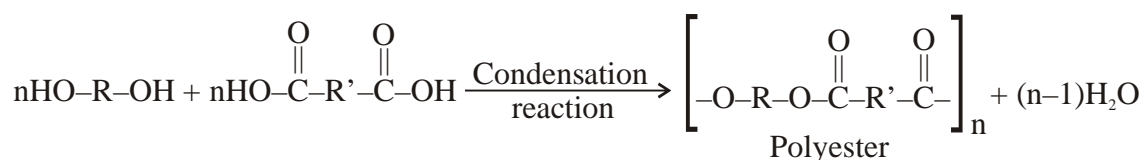
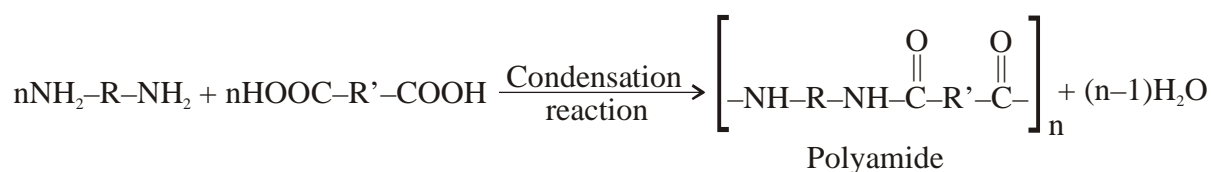
**(3) Cross-linked or Three Dimensional network polymers**

In these polymers the initially formed linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross-linked polymers are always condensation polymers. Resins are cross linked polymers, Urea-formaldehyde resin, phenol-formaldehyde resin.

**CLASSIFICATION BASED UPON SYNTHESIS****(1) Condensation polymerisation**

They are formed due to condensation reactions. Condensation polymerisation is also known as step growth polymerisation. For condensation polymerisation, monomers should have at least two functional groups. Both functional groups may be same or different. Monomers having only two functional group always give linear polymer.

For example,



Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules. Monomer having three functional groups always gives cross-linked polymer.

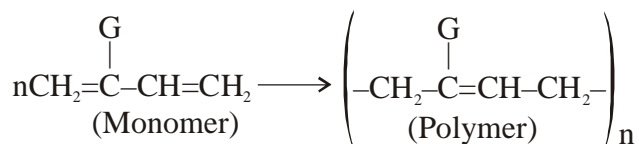
**Examples are :** Urea-formaldehyde resin, phenol-formaldehyde resin.

**(3) Addition polymerisation**

Polymers which are formed by addition reaction are known as addition polymers. If monomer is ethylene or its derivative, then addition polymer is either linear polymer or branch-chain polymer.

Examples are : polystyrene, polytetrafluoroethylene, polyacrylonitrile etc. If monomer is 1, 3-butadiene

or 2-substituted-1, 3-butadiene  $\left( \begin{array}{c} \text{CH}_2 = \text{C} - \text{CH} = \text{CH}_2 \\ | \\ \text{G} \end{array} \right)$ , then polymer is always branched chain polymer.

**(Monomer)****(Polymer)**

(i) G = H : 1,3 - Butadiene

(i) Polybutadiene

(ii) G = CH<sub>3</sub> ; 2 - Methyl-1,3-butadiene or isoprene

(ii) Polyisoprene

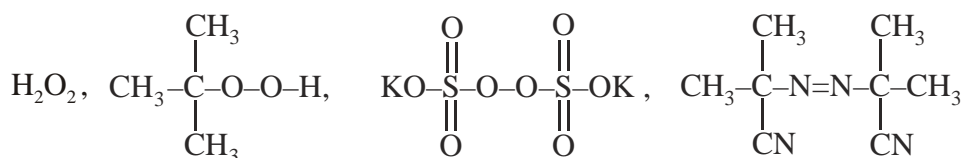
(iii) G = Cl ; 2 -Chloro-1,3-butadiene or chloroprene

(ii) Polychloroprene (Neoprene)

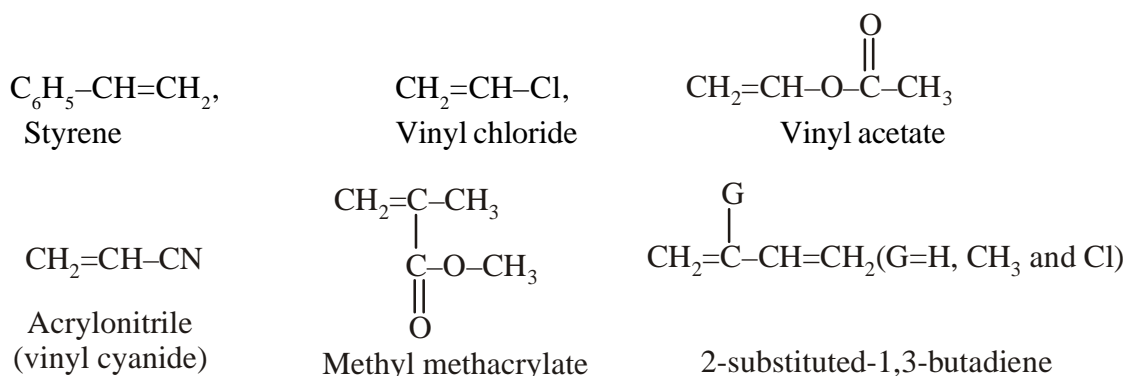
Addition polymers retain all the atoms of the monomer units in the polymer. Addition polymerisation takes place in three steps. Initiation, chain propagation and chain termination. Addition polymers are called as chain growth polymers.

**Types of Addition Polymerisation****(A) Radical Polymerisation :**

Radical polymerisation takes place in the presence of radical initiators. The radical initiator may be any of the following :



Reaction intermediate of radical polymerisation is a free radical. Radical polymerization has more chance for those monomers whose free radicals are more stable.

**Examples are :**

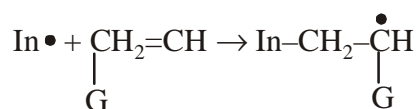
Radical polymer has linear as well as branched chain structure.

Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives  $\text{CH}_2=\underset{\text{G}}{\text{CH}}$  [G is H,  $\text{C}_6\text{H}_5$ , R etc.]. This type of polymerisation is performed by heating the

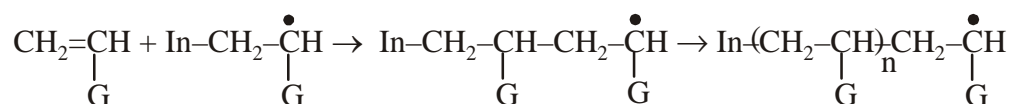
monomer with only a very small amount of the initiator or by exposing the monomer to light. the general mode of radical polymerisation of vinyl monomers is depicted below :

**Chain initiation step :**

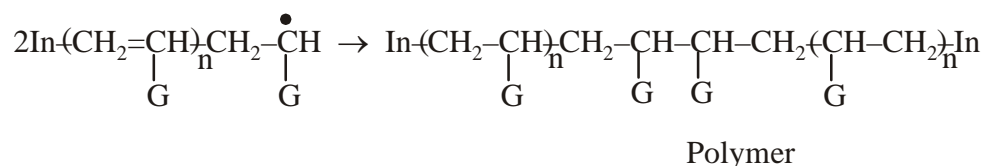
Initiator  $\rightarrow \text{In} \bullet$



**Chain propagating step :**

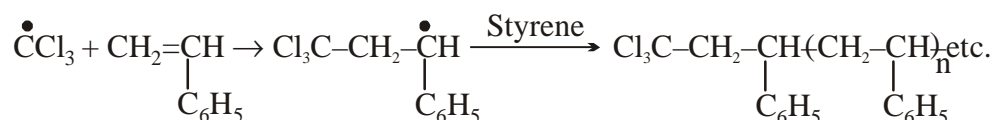
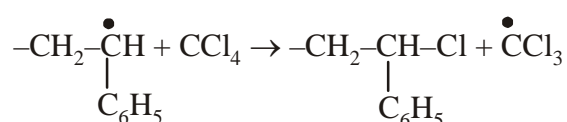


**Chain terminating step :**



In vinylic polymerisation, various other reaction of free radicals with some other compounds present may compete with the parent addition chain reactions. One such reaction takes place with molecules that can react with the growing chain to interrupt the further growth. This leads to the lowering of the average molecular mass of the polymer. Such reagents are called as chain transfer agents and include  $\text{CCl}_4$ ,  $\text{CBr}_4$  etc.

For example, in the presence of  $\text{CCl}_4$ , styrene polymerises to form polystyrene of a lower average molecular mass which also contains some chlorine what happens here is that growing polystyrene radical which normally would add on a monomer reacts with the chain transfer agent to end the original chain and produces a new radical. The latter initiates a new polymerisation chain and thereby forms a new polymer as depicted below.

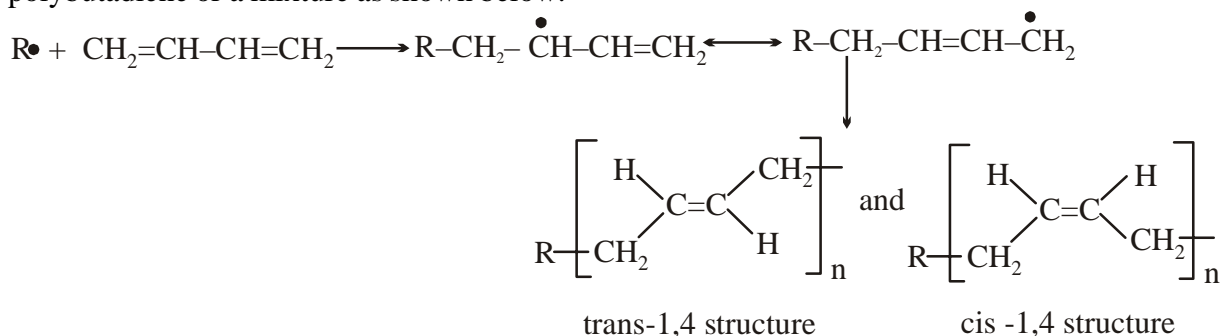


If the chain transfer agent a radical, which is highly unreactive, the reaction chain gets terminated such a compound thus inhibits or arrests polymerisation. Many amines, phenols, quinones etc. act as inhibitors. So, even traces of certain impurities, which can act as chain transfer agent or an inhibitor can interfere with the original polymerisation chain reaction. Hence, the monomers could be free from such inhibitors.

In case the alkene is a (diene), the following kinds of polymerisation is possible :

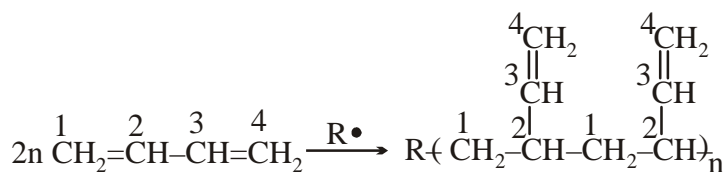
(1) **1,4 - polymerisation.**

When the polymerisation takes place at C<sub>1</sub> and C<sub>4</sub> of butadiene, an unbranched polymer is formed. This product is different from that formed from an alkene having a double bond, which at each of its carbons is substituted by different groups and hence can exist either as trans-polybutadiene or cis-polybutadiene or a mixture as shown below.



(2) **1,2-Polymerisation**

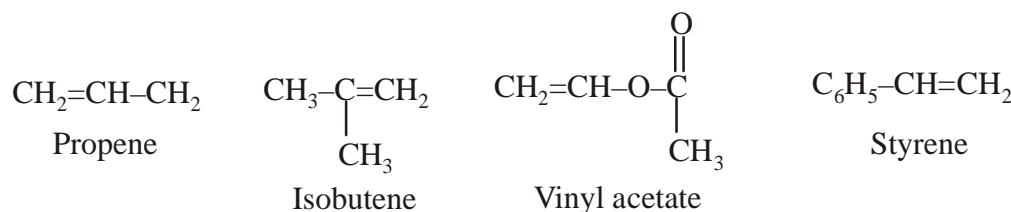
Alternatively, 1,3 -butadiene can undergo polymerisation at C<sub>1</sub> and C<sub>2</sub> to yield the polymeric product, polyvinyl polythene.



The double bonds in these initial polymers can be linked by further treatment with chemicals to modify the properties of the polymers. These reactions form the basis of the formation of rubber.

(B) **Cationic Polymerisation :**

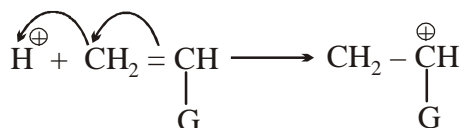
Polymerisation which is initiated by an electrophile is known as cationic polymerisation. Reaction intermediate of cationic polymerisation is a carbocation. Carbocations can undergo rearrangement leading to the formation of a more stable carbocation. The electrophile commonly used for initiation is BF<sub>3</sub>.OEt<sub>2</sub>. Monomers that are best able to undergo polymerisation by a cationic mechanism are those with electron - donating substituents that can stabilise the carbocation. Some examples are:



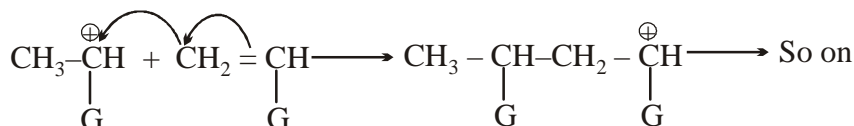
It is terminated by a base.

Thus, when the initiator is cationic in nature, it would generate a cationic intermediate on addition to the double bond for propagating the addition chain process and is termed as cationic addition polymerisation. The process is initiated by an acid. The stages of polymerisation are depicted below.

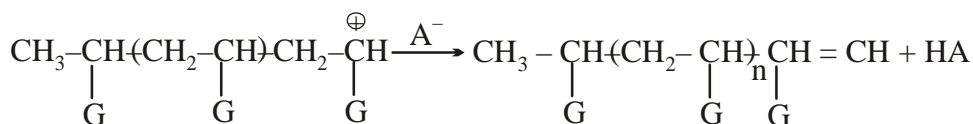
**Chain initiation step :**



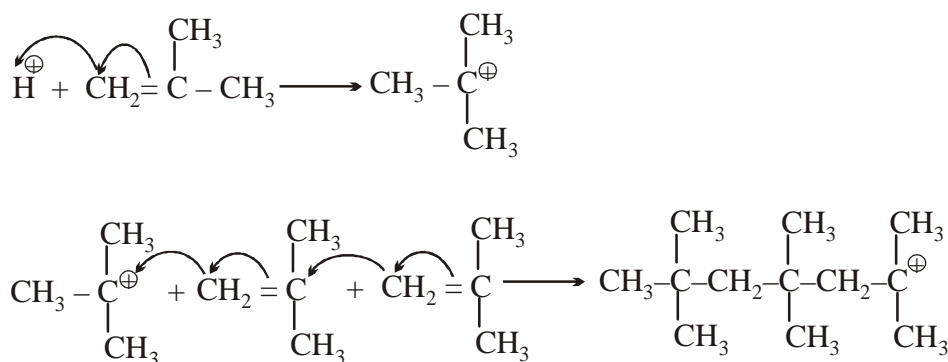
**Chain propagating step :**



**Chain terminating step :**



Cationic polymerisation is facilitated in monomers containing electron-releasing groups. Thus, isobutylene undergoes cationic polymerisation easily as it has two electron-releasing  $-\text{CH}_3$  groups that will stabilize the intermediate carbocation.

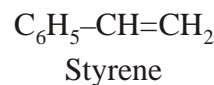
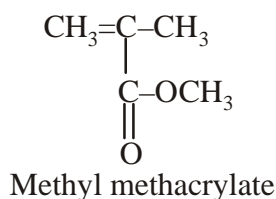
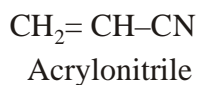
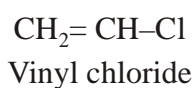


(Butyl Rubber)

**(C) Anionic Polymerisation :**

Anionic polymerisation takes place in the presence of base or nucleophile, which is initiator in this polymerization. Reaction intermediate in propagation steps are carboanion. The suitable initiator can be  $\text{NaNH}_2$  or  $\text{RLi}$ . Those monomers undergo anionic polymerisation reaction whose anion is stable.

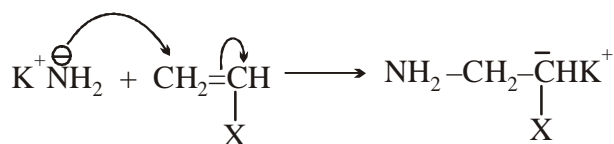
Example of monomers are :



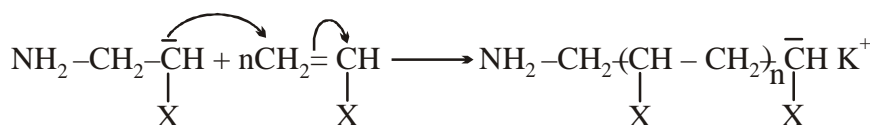
Anionic polymerisation always gives linear polymer. Anionic polymerisation terminated by an acid.

The formation of polystyrene from styrene in the presence of potassium amide is an important example of this category of polymerisation. The mode of anionic polymerisation is depicted below:

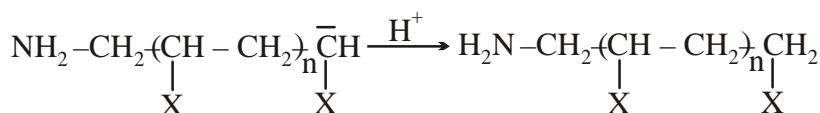
**Chain initiation step :**



**Chain propagating step :**



**Chain terminating step :**



**(D) Ziegler- Natta polymerisation :**

Addition polymerisation which takes place in the presence of Ziegler- Natta catalyst  $[(\text{C}_2\text{H}_5)_3\text{Al}$  and  $\text{TiCl}_4]$  is known as Ziegler- Natta polymerisation or coordination polymerisation. Ziegler- Natta polymerisation always gives linear, stereo-regular polymers. Ziegler- Natta catalyst revolutionised the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers (due to linear geometry) that have greater resistance to cracking and heat.

*High density polyethylene is prepared using a Ziegler- Natta catalyst.*

**CLASSIFICATION BASED ON INTERMOLECULAR FORCES**

**(SECONDARY FORCES)**

Intermolecular forces present between polymeric chains are (a) Van der waals forces (b) Hydrogen bonds and (c) Dipole - dipole attractions. Mechanical properties such as tensile strength, elasticity, toughness etc. depend upon the secondary forces present between the polymeric chains. Magnitude of secondary forces depends upon the size of the molecule and the number of functional groups along the polymeric chains. Magnitude of secondary forces is directly proportional to the length of the polymeric chain. On the basis of magnitude of secondary forces, polymers can be divided into the following following categories.

**(1) Elastomes**

An elastomer is a plastic that stretches and then reverts back to its original shape. It is randomly oriented amorphous polymer. It must have some cross-links so that the chains do not slip over one another. Very weak Vander Waal forces are present in between polymeric chains.

When elastomers are stretched, the random chains stretch out, but there are insufficient Vander Waal forces to maintain them in that configuration and position. When the stretching force is removed, they go back to their random shape. Elastomers have the ability to stretch out over ten times their normal length. Important examples are vulcanized rubbers.

**Note :** Addition polymers obtained from butadiene and its derivatives are elastomers.

**(2) Fibres**

Fibres are linear polymers in which the individual chains of a polymer are held together by hydrogen bonds or dipole-dipole attraction. In the fibres, the polymeric chains are highly ordered with respect to one another. Due to strong intermolecular forces of attraction and highly ordered geometry, fibres have high tensile strength and least elasticity. They have crystalline character and have high melting points and low solubility. Examples are cellulose, nylon, terylene, wool, silk etc.

**Note :**

(i) Condensation polymers formed from bifunctional monomers are fibres in character.

(ii) Addition polymers of alkene derivatives having strong -I group are fibres in character.

**(3) Thermoplastic Polymers**

Thermoplastic polymers are polymers that have both ordered crystalline regions (the regions of the polymer in which the chains are highly ordered with respect to one another) and amorphous, non-crystalline regions (the regions of the polymer in which the chains are randomly oriented). The intermolecular forces of attraction are in between elastomers and fibres. There are no cross links between the polymeric chains. Thermoplastic polymers are hard at room temperature, but when they are heated, the individual chains can slip past one another and the polymer become soft and viscous. This soft and viscous material become rigid on cooling. The process of heating softening and cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic. As a result, these plastics can be moulded into toys, buckets, telephone and television cases. Some common examples are : polyethene, polypropylene, polystyrene, polyvinyl chloride, teflon etc.

**Note :** Addition polymers obtained from ethylene and ethylene derivatives are thermoplastic polymers.

**(4) Thermosetting Polymers**

Polymers which become hard on heating are called thermosetting polymers. Thermosetting polymers can be heated only once when it permanently sets into a solid, which cannot be remelted by heating. Thermosetting polymers are cross-linked polymers. Greater the degree of cross-linking that exist, the more rigid is the polymer. Cross-linking reduces the mobility of the polymer chains, causing them to be relatively brittle materials. The hardening on heating is due to the extensive cross-linking between different polymer chains to give a three dimensional network solid. Examples are : phenol formaldehyde resin, urea-formaldehyde resin, melamine-formaldehyde resin.



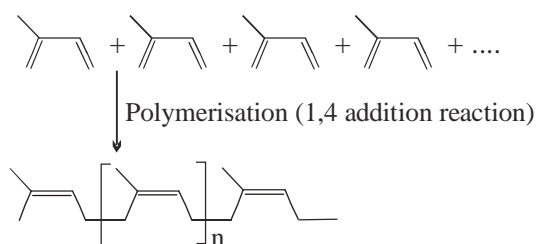
**DIFFERENCE BETWEEN THERMOPLASTIC AND THERMOSETTING POLYMERS**

S.No.	Thermoplastic polymers	Thermosetting polymers
1.	Soften and melt on heating and become hard on cooling i.e. process is reversible	Become hard on heating and process is irreversible.
2.	Can be moulded and remoulded and reshaped.	They can be moulded once and cannot be remoulded or reshaped.
3.	They are addition polymers	They are condensation polymers.
4.	Structure is generally linear	Structure is cross - linked.

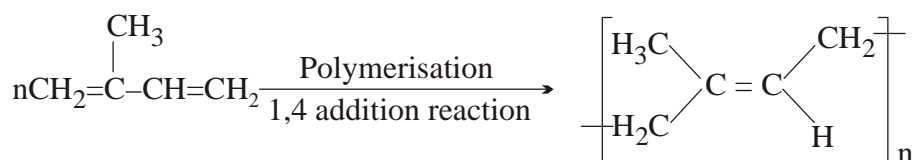
**RUBBER**
**1. Natural Rubber**

Natural rubber is obtained from nearly five hundred different plants but the main source is a brazilensis tree. It is obtained in the form of milky sap known as latex. This latex is coagulated with acetic acid and formic acid. The coagulated mass is then squeezed.

The raw natural rubber is a soft gummy and sticky mass. It is insoluble in water, dilute acids and alkalies but soluble in non-polar solvents. It has low elasticity and low tensile strength. Natural rubber is a polymer of 2-methyl-1,3-butadiene (isoprene). On average, a molecule of rubber contains 5000 isoprene units held together by head to tail. All the double bonds in rubber are cis, hence natural rubber is cis-polyisoprene.

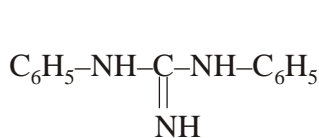


Gutta - percha is a naturally occurring isomer of rubber in which all the double bonds are trans. Thus, gutta-percha is trans-polyisoprene.

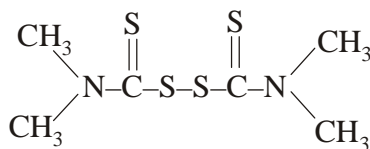


It is harder and more brittle than rubber. It is the filling material that dentists use in root canal treatment.

In order to give strength and elasticity to natural rubber, it is vulcanized. Heating of rubber with sulphur or sulphur containing compound at 150° C for few hours is known as vulcanisation. The essential feature of the vulcanisation is the formation of cross-linking between the polymeric chains. This cross-linking gives mechanical strength to the rubber. Vulcanisation process can be enhanced in the presence of certain organic compounds known as accelerators. The common accelerators are:



Diphenyl guanidine



Tetramethylthioureadisulph

In addition, fillers such as carbon black and zinc oxide are usually added to the crude rubber before vulcanisation in order to improve its wearing characteristics.

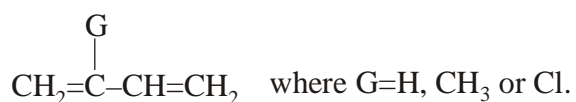
Natural rubber is used for making shoes, water - proof coats and golf balls. Vulcanised rubber is used for manufacture of rubber bands, gloves tubing and car tyres.

### SYNTHETIC RUBBER OR POLYMERISATION OF DIENES

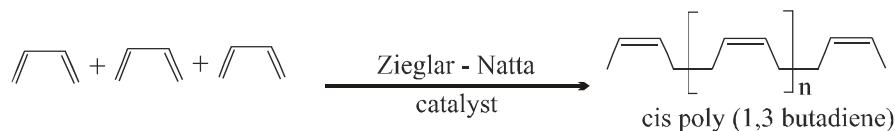
Polymers of 1,3 - butadienes are called synthetic rubbers because they have some of the properties of natural rubbers including the fact that they are water proof and elastic. Synthetic rubbers have some improved properties. They are more flexible, tougher and more durable than natural rubber.

#### 1. Homopolymers

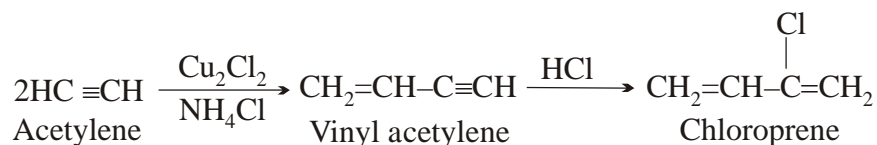
Monomer of this class is 2 - substituted - 1,3- butadienes.



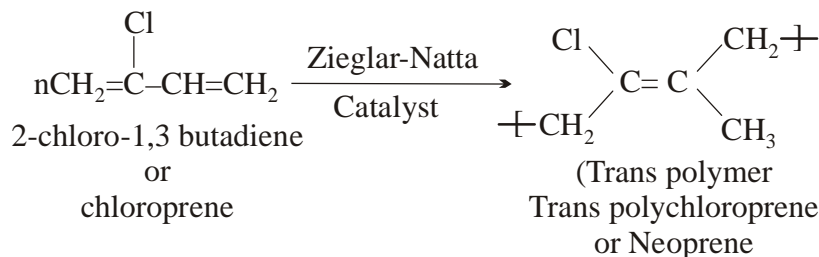
Polymerisation is always carried out in the presence of Ziegler-Natta catalyst which gives stereo regular polymers.



Neoprene was the first synthetic rubber manufactured on large scale. It is also called dieprene. Its monomer, chloroprene(2-chlorobutadiene) is prepared from acetylene.



Chloroprene undergoes free radical polymerisation to form neoprene (polychloroprene).



Many of the properties of neoprene are similar to natural rubber but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non - inflammable. It is used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

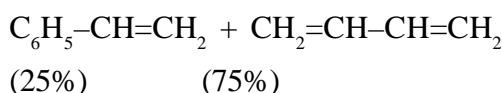
## 2. Copolymers

The following synthetic rubbers are example of copolymers.

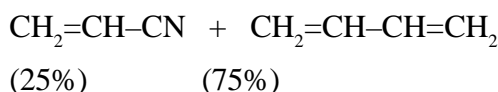
### Synthetic rubber

1. Buna-S, SBR (Styrene-butadiene rubber)

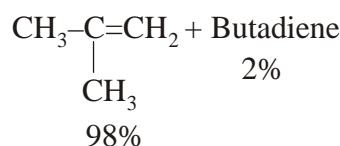
### Monomers



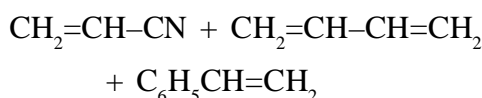
2. Buna-N, NBR (Nitrile-butadiene rubber)



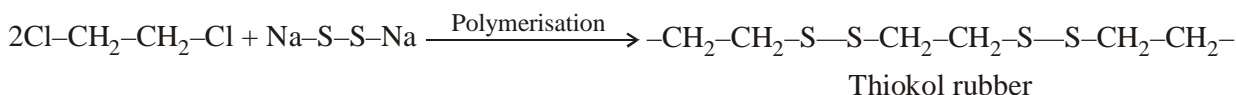
3. Butyl rubber



4. ABS; Acrylonitrile, Butadiene, Styrene

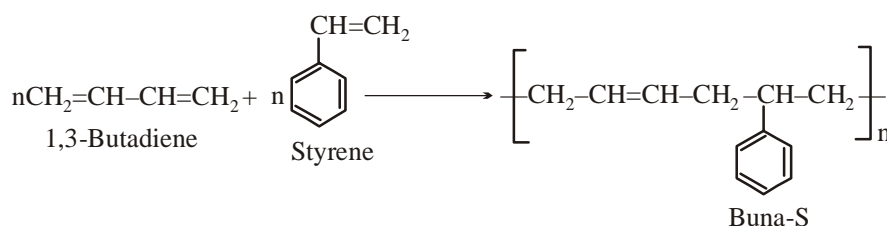


(a) **Thiokol** : Thiokol is made by polymerising ethylene chloride and sodium polysulphide.



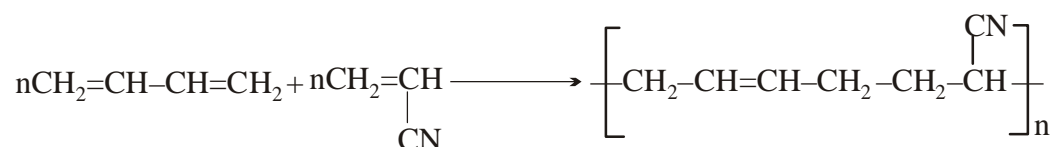
The repeating unit is  $-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-$ . Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

(b) **Buna -S (SBR : Styrene-butadiene rubber)** : Buna-S rubber is a copolymer of three moles of butadiene and one mole of styrene. In Buna-S, 'Bu' stands for butadiene, 'na' for symbol of sodium (Na) which is a polymerizing agent and 'S' stands for styrene. It is an elastomer (General purpose styrene Rubber or GRS).



Buna-S is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and therefore used in the manufacture of tyres and other mechanical rubber goods. It is obtained as a result of free radical copolymerisation of its monomers.

- (c) **Buna-N**: It is obtained by copolymerisation of butadiene and acrylonitrile (General Purpose Rubber acrylonitrile or GRA).



It is very rigid and is very resistant to action of petrol, lubricating oil and many organic solvents. It is mainly used for making fuel tanks.

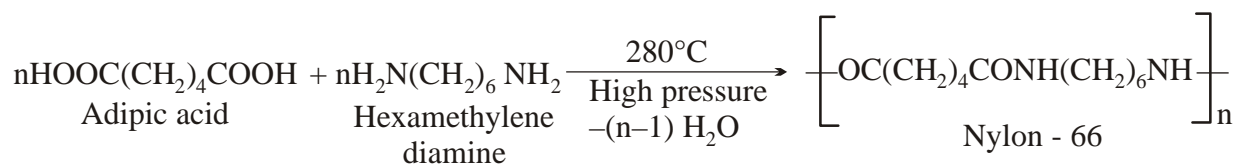
- (d) **Cold Rubber**: Cold rubber is obtained by polymerisation of butadiene and styrene at  $-18^\circ$  to  $5^\circ\text{C}$  temperature in the presence of redox system. Cold rubber has a greater tensile strength and greater resistance to abrasion than SBR.

## NYLON

Nylon is used as a general name for all synthetic fibres forming polyamides, i.e., having a protein like structure. A number is usually suffixed with the name 'nylon' which refers to the number of carbon atoms present in the monomers.

- (1) **NYLON - 66** (Nylon six, six)

It is obtained by the condensation polymerisation of hexamethylenediamine (a diamine with six carbon atoms) and adipic acid (a dibasic acid having 6 carbon atoms).



- (2) **NYLON-610** (Nylon six, ten)

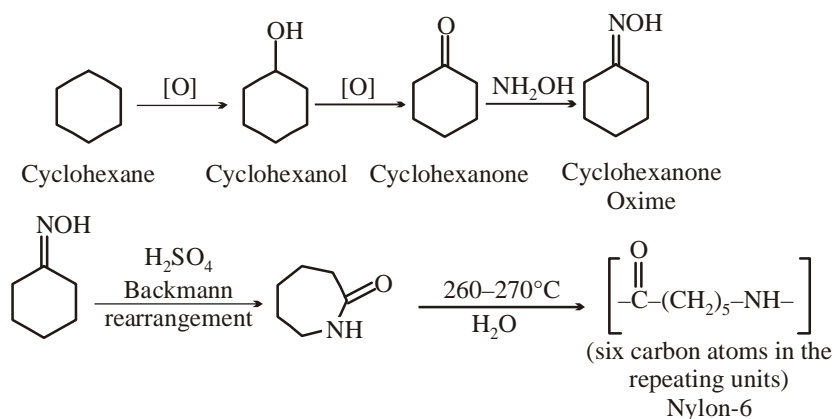
It is obtained by condensation polymerisation of hexamethylenediamine (six carbon atoms) and sebacic acid (a dibasic acid with 10 carbon atoms.)

Nylon fibres are stronger than natural fibres and so are used in making cords and ropes. The fibres are elastic, light, very strong and flexible. They have drip dry property and retain creases. It is inert towards chemicals and biological agents. It can be blended with wool. Nylon fibres are used in making garments, carpets, fabrics, tyre cords, ropes, etc.

- (3) **NYLON-6 (Perlon L)**

A polyamide closely related to nylon is known as perlon L (Germany) or Nylon - 6 (USA). It is prepared by prolonged heating of caprolactam at  $260-270^\circ\text{C}$ . It is formed by self condensation of a large number of molecules of amino caproic acid. Since, caprolactam is more easily available, it is used for polymerization, which is carried out in the presence of  $\text{H}_2\text{O}$  that first hydrolyses the lactam to amino acid. Subsequently, the amino acid can react with the lactam and the process goes on and on to form the polyamide polymer.

Carpolactam is obtained by Backmann rearrangement of cyclohexanone oxime.



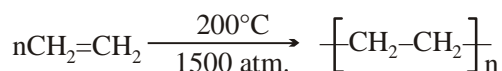
#### (4) NYON-2-NYLON-6

It is in alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.

#### POLYETHYLENE

Polyethylene is of two types :

- (a) **Low Density Poly Ethylene (LDPE)** : It is manufactured by heating ethylene at  $200^\circ C$  under a pressure of 1500 atmospheres and in the presence of traces of oxygen. This polymerisation is a free radical polymerisation.



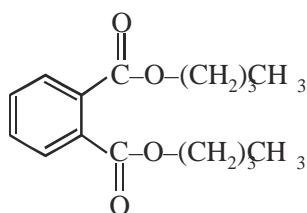
The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point ( $110^\circ C$ ). That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent polymer of moderate tensile strength and high toughness. It is widely used as a packing material and as insulation for electrical wires and cables.

- (b) **High Density Poly Ethylene (HDPE)** : It is prepared by the use of Ziegler - Natta catalyst at  $160^\circ C$  under pressure of 6 to 7 atmospheres.

The polymer is linear chain, hence it has high density (0.97) and has high melting point ( $130^\circ C$ ). That is why it is called high density polyethylene. It is a translucent polymer. It has greater toughness, hardness and tensile strength than low density polyethylene. It is used in the manufacture of containers (buckets, tubes), house wares, bottles and toys.

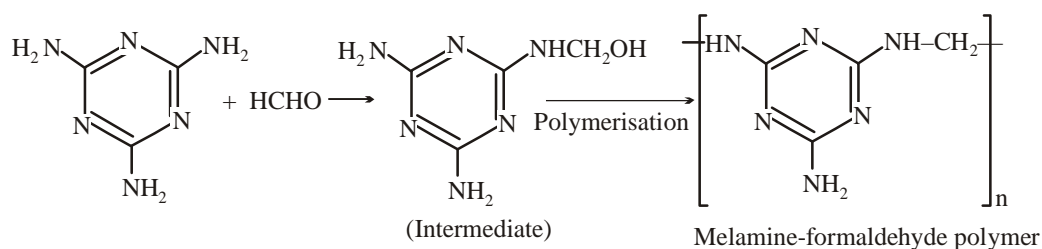
#### PLASTICISER

A plasticiser is an organic compound that dissolves in the polymer and allows the polymer chains to slide past one another. This makes polymer more flexible. Dibutylphthalate is a commonly used plasticiser.



### MELAMINE - FORMALDEHYDE RESIN

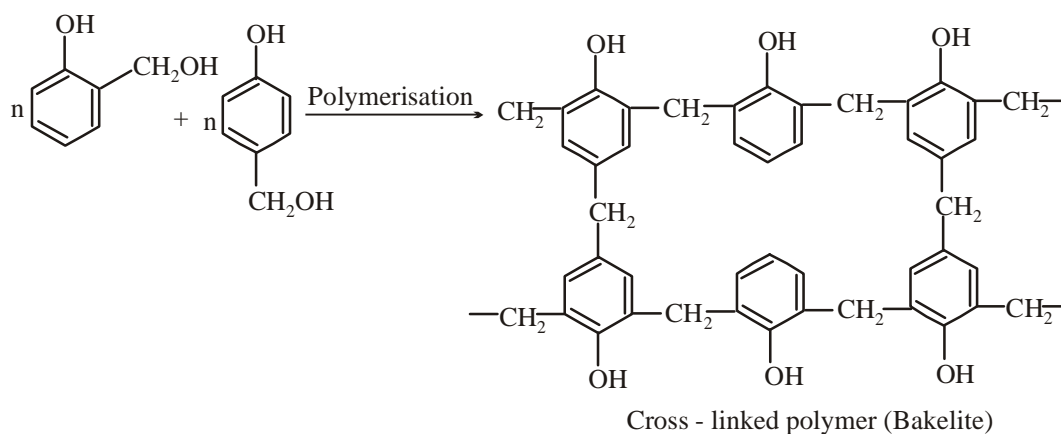
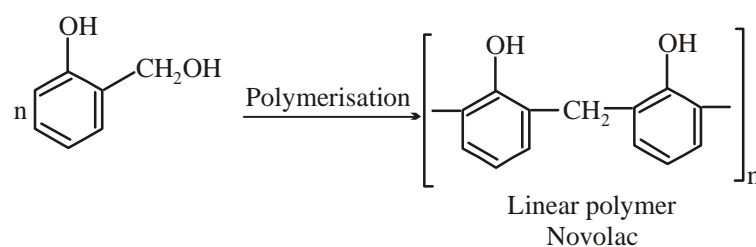
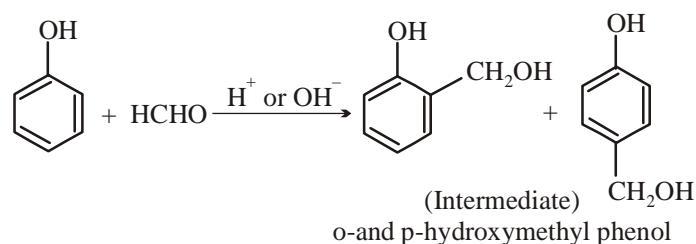
This resin is formed by condensation polymerisation of melamine and formaldehyde.



It is a quite hard polymer and is used widely for making plastic crockery under the name melamine. The articles made from this polymer do not break even when dropped from considerable height.

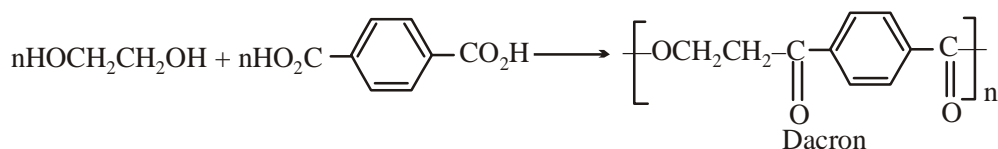
### BAKELITE

Phenol-formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of either an acid or a basic catalyst. The reaction starts with the initial formation of ortho and para-hydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with  $-\text{CH}_2$  groups. The reaction involves the formation of methylene bridges in ortho, para or both ortho and para positions. Linear or cross - linked materials are obtained depending on the conditions of the reaction.



## POLYESTERS

Dacron is a common polyester, prepared using ethylene glycol and terephthalic acid. The reaction is carried out at 140° to 180° C in the presence of zinc acetate and  $\text{Sb}_2\text{O}_3$  as catalyst.



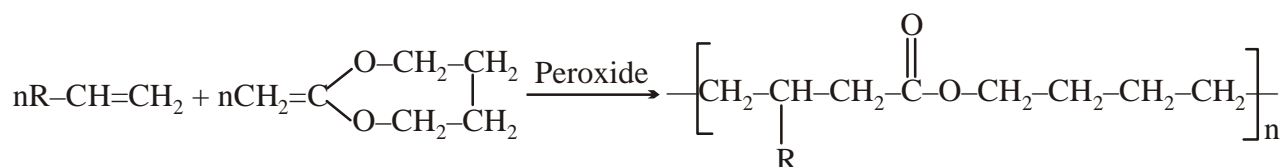
The terylene fibre (Dacron) is crease resistant and has low moisture absorption. It has high tensile strength. It is mainly used in making wash and wear garments, in blending with wool to provide better crease and wrinkle resistance.

## BIODEGRADABLE POLYMERS

By far the largest use of synthetic polymers is as plastic. A major portion of it is used as throwaway containers and packing materials. Since plastics do not disintegrate by themselves, they are not biodegradable over a period of time. Non-biodegradability is due to the carbon-carbon bonds of addition polymers which are inert to enzyme catalysed reaction. These polymers create pollution problem.

Biodegradable polymers are the polymers that can be broken into small segments by enzyme catalysed reactions using enzymes produced by microorganisms. In biodegradable polymers, bonds that can be broken by the enzymes are inserted into the polymers. Therefore, when they are buried as waste, enzymes present in the ground can degrade the polymer.

One method involves inserting hydrolysable ester group into the polymer. For example, when acetal (I) is added during the polymerization of alkene, ester group is inserted into the polymeric chains.

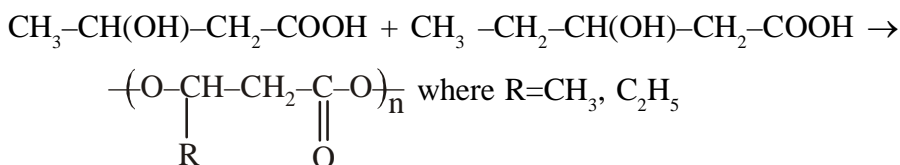


Ester linkage attacked by enzyme

Aliphatic polyesters are important class of biodegradable polymers. Some examples are described below:

### (1) Poly - Hydroxybutyrate-CO-β-Hydroxyvalerate (PHBV)

It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid, in which the monomer units are connected by ester linkages.



The properties of PHBV vary according to the ratio of both the acids. 3-Hydroxybutanoic acid provides stiffness and 3-hydroxypentanoic acid imparts flexibility to the co-polymer. It is used in specialty packaging, orthopaedic devices and even in controlled drug release. When a drug is put in a capsule of PHBV, It is released only after the polymer is degraded. PHBV also undergoes bacterial degradation in the environment.

## (2) POLY (GLYCOLIC ACID) AND POLY (LACTIC ACID)

They constitute commercially successful biodegradable polymers such as sutures. Dextron was the first bioadsorbable suture made for biodegradable polyesters for post - operative stitches.

## MOLECULAR MASS OF POLYMER

Normally, a polymer contains chains of varying lengths and therefore, its molecular mass is always expressed as an average. In contrast, natural polymers such as protein contains chain of identical length and hence, have definite molecular mass.

The molecular mass of a polymer is expressed as

- (a) Number average molecular mass ( $\overline{M}_n$ )

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

where  $N_i$  is the number of molecules of molecular mass  $M_i$

- (b) Weight average molecular mass ( $\overline{M}_w$ )

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

where  $N_i$  is the number of molecules of molecular mass  $M_i$ . Methods such as light scattering and ultracentrifuge depend on the mass of the individual molecules and yield weight average molecular masses.  $\overline{M}_n$  is determined by employing methods which depend upon the number of molecules present in the polymer sample viz. colligative properties like osmotic pressure.

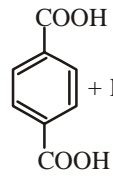
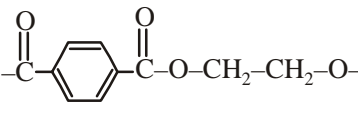
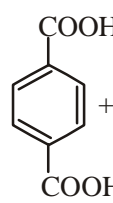
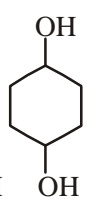
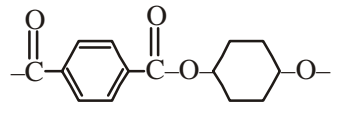
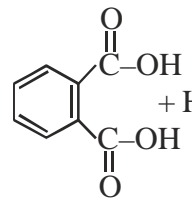
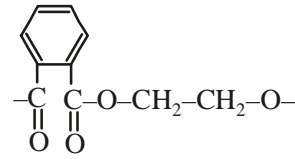
The ratio of the weight and number average molecular masses ( $\overline{M}_w / \overline{M}_n$ ) is called Poly Dispersity Index (PDI). Some natural polymers, which are generally monodispersed, the PDI is unity (i.e.  $\overline{M}_w = \overline{M}_n$ ).

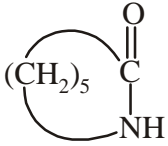
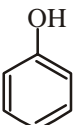
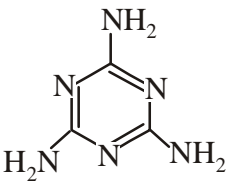
In synthetic polymers, which are always polydispersed,  $PDI > 1$  because  $\overline{M}_w$  is always higher than  $\overline{M}_n$ .



COMMON POLYMERS

Monomer	Repeatng unit	Polymer
1. $\text{CH}_2=\text{CH}_2$ Ethylene	$-\text{CH}_2-\text{CH}_2-$	Polyethylene
2. $\text{CH}_3-\text{CH}=\text{CH}_2$ Propene	$-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-$	Polypropene
3. $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$ Styrene	$-\text{CH}_2-\overset{\text{C}_6\text{H}_5}{\underset{ }{\text{CH}}}-$	Polystyrene
4. $\text{CF}_2=\text{CF}_2$ Tetrafluoroethylene	$-\text{CF}_2-\text{CF}_2-$	Polytetrafluoroethylene (PTFE), Teflon
5. $\text{CH}_2=\text{CH}-\text{Cl}$ Vinyl chloride	$-\text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{CH}}}-$	Polyvinyl Chloride(PVC)
6. $\text{CH}_2=\text{CH}-\text{CN}$ Vinyl cyanide or Acrylonitrile	$-\text{CH}_2-\overset{\text{CN}}{\underset{ }{\text{CH}}}-$	Polyvinyl cyanide, polyacrylonitrile, Orlon.
7. $\text{CH}_2=\overset{\text{H}_3\text{C}}{\underset{ }{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_3$ Methyl methacrylate	$-\text{CH}_2-\overset{\text{COOCH}_3}{\underset{\text{CH}_3}{\text{C}}}-$	Polymethyl metha acrylate, Plexiglas, Lucite
8. $\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ Vinyl acetate	$-\text{CH}_2-\overset{\text{OCOCH}_3}{\underset{ }{\text{CH}}}-$	Polyvinyl Acetate
9. $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ 1,3-butadiene	$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$	Polybutadiene, Buna rubber
10. $\text{CH}_2=\text{CH}-\text{Cl}$ (vinyl chloride) + $\text{CH}_2=\text{CCl}_2$ (Vinylidene chloride)	$-\text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{CH}}}-\text{CCl}_2-\text{CH}_2-$	Saran

11. $C_6H_5-CH=CH_2$ (Styrene) $+$ $CH_2=CH-CN$ (acrylonitrile)	$\begin{array}{c} C_6H_5 \quad CN \\   \quad   \\ -CH_2-CH-CH-CH_2- \end{array}$	SAN
12. $CH_2=CH-CN + CH_2=CH-CH=CH_2$ $+$ $C_6H_5-CH=CH_2$	—	ABS
13. $CH_2=C-CH_2 + CH_2=C-CH=CH_2$ $\quad   \quad \quad \quad  $ $\quad CH_3 \quad \quad \quad CH_3$	—	Butyl rubber
14. $C_6H_5-CH=CH_2 + CH_2=CH-CH=CH_2$	—	Buna -S, SBR
15. $CH_2=CH-CN + C_6H_5-CH=CH_2$	—	Buna-N, NBR
16. $CH_2=C-CH=CH_2$ $\quad  $ $\quad Cl$ Chloroprene	$\begin{array}{c} Cl \\   \\ -CH_2-C=CH-CH_2- \end{array}$	Neoprene
17.  + HO-CH <sub>2</sub> -CH <sub>2</sub> -OH		Poly(ethylene terephthalate, Terylene, Dacron or Mylar
18.  + 		Kodel Polyester
19.  + HO-CH <sub>2</sub> -CH <sub>2</sub> -OH		Polyethylene phthalate alkyd resin (Glyptal)

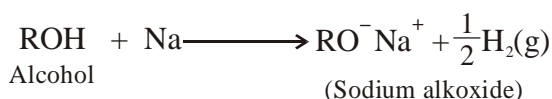
<p>20. </p> <p>Caprolactam</p>	$-\text{NH}(\text{CH}_2)_5-\overset{\text{O}}{\parallel}{\text{C}}-$	<p>Nylon-6</p>
<p>21. <math>\text{NH}_2(\text{CH}_2)_6-\text{NH}_2</math> Hexamethylenediamine + <math>\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}</math> Adipic Acid</p>	$-\text{NH}-(\text{CH}_2)_6-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-$	<p>Nylon - 66</p>
<p>22.  + HCHO</p>	<p>—</p>	<p>Bakelite or resol</p>
<p>23. <math>\text{NH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 + \text{HCHO}</math></p>	<p>—</p>	<p>Urea- formaldehyde resin</p>
<p>24.  + HCHO</p> <p>Melamine</p>	<p>—</p>	<p>Melamine formaldehyde resin</p>

## CHEMICAL TESTS FOR FUNCTIONAL GROUPS

- Elemental analysis, physical, spectral and solubility test give a reasonable idea regarding the identity of unknown compound.
- Despite the tremendous importance and ease of spectral analysis, chemical tests are indispensable to complete characterization.

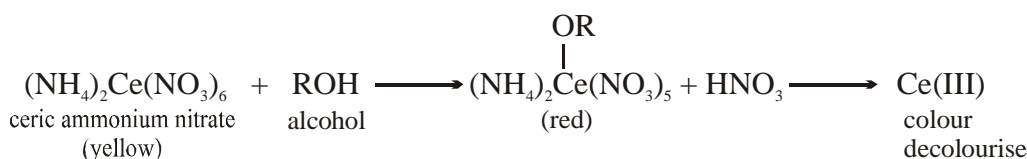
### 1. Test For Alcohols :

#### (i) Sodium Metal



- When Na-metal reacted with alcohol  $\text{H}_2(\text{g})$  evolve
- It occurs in  $1^\circ$ ,  $2^\circ$  &  $3^\circ$
- The rate is highly variable and depends upon the alcohol structure.
- Other Functional groups that evolve  $\text{H}_2(\uparrow)$   
 $\text{R}_2\text{NH}$ ,  $\text{RSH}$ ,  $\text{RC}\equiv\text{C-H}$ ,  $\text{RCO}_2\text{H}$  etc.

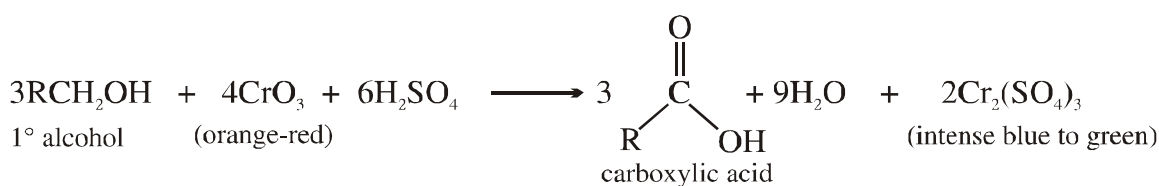
#### (ii) Ceric Ammonium Nitrate Oxidation (CAN Test)

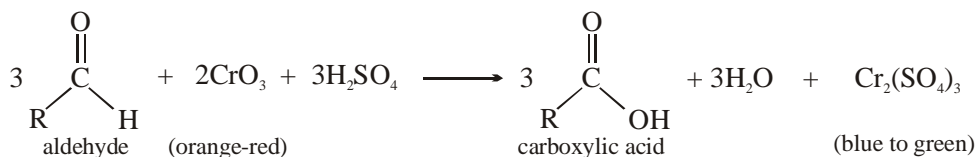
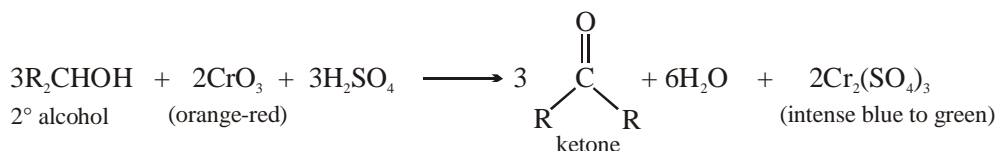


- Positive Test:** Color changes from yellow to red first then to colorless solution. (1 min. to 12 hrs)
- A positive test includes successively the formation, and then the disappearance of the red color.
- Very good test for  $1^\circ$ ,  $2^\circ$  alcohol, but slow for  $3^\circ$  alcohol
- Note:** Phenols gives brown or black colour.

#### (iii) Jones Oxidation: Chromic anhydride or Chromium Trioxide ( $\text{CrO}_3$ )

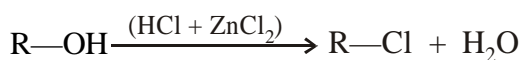
- A positive test for  $1^\circ$ , and  $2^\circ$  alcohols consists in the changes from an orange-red color ( $\text{Cr}^{6+}$ ) to opaque suspension with green to blue color ( $\text{Cr}^{3+}$ ) in 2 sec.
- $3^\circ$  alcohols give no visible reaction within 2 sec. remaining orange
- Note:** Aldehydes give positive result.





**(iv) Lucas Test**

- This test distinguishes 1°, 2° & 3° alcohol from each other
- It uses, anhydrous ZnCl<sub>2</sub> in conc. HCl (lucas reagent)



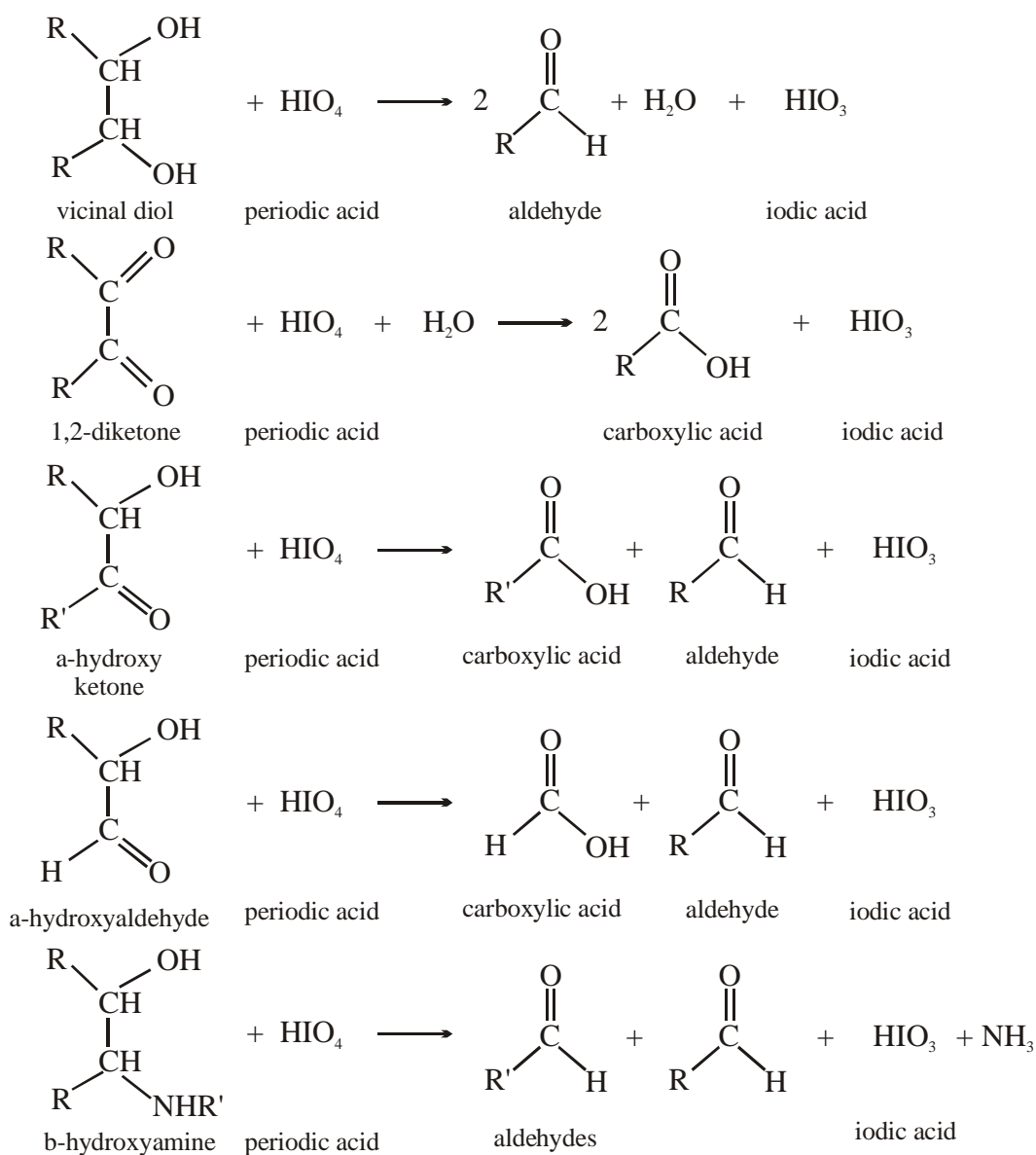
- 3° alcohols give white turbidity solution immediately
- 2° alcohols give white turbidity solution within 5 to 10 minutes
- 1° alcohols does not give white turbidity at room temperature

**Note :** Benzyl alcohol also react immediately

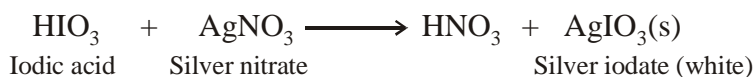
**(v) Victor-Mayer Test**

- This test also distinguishes 1°, 2° & 3° alcohol

1° - Alcohol	2° - Alcohol	3° - Alcohol
$R-CH_2-OH$ <p style="text-align: center;">↓ Red P + I<sub>2</sub></p> $R-CH_2-I$ <p style="text-align: center;">↓ NaNO<sub>2</sub></p> $R-CH_2-N \begin{array}{l} \diagup O \\ \diagdown \end{array}$ <p style="text-align: center;">↓ HNO<sub>2</sub></p> $R-C \begin{array}{l} \diagup N=O \\ \diagdown N-OH \end{array}$ <p style="text-align: center;">(Nitrolic Acid)</p> <p style="text-align: center;">↓ NaOH</p> $R-C \begin{array}{l} \diagup NO_2 \\ \diagdown N-O^- Na^+ \end{array}$ <p style="text-align: center;">(Red colour)</p>	$\begin{array}{c} R \\   \\ R-CH-OH \end{array}$ <p style="text-align: center;">↓ Red P + I<sub>2</sub></p> $\begin{array}{c} R \\   \\ R-CH-I \end{array}$ <p style="text-align: center;">↓ NaNO<sub>2</sub></p> $\begin{array}{c} R \\   \\ R-CH-NO_2 \end{array}$ <p style="text-align: center;">↓ HNO<sub>2</sub></p> $\begin{array}{c} R \\   \\ R-C \begin{array}{l} \diagup N=O \\ \diagdown N=O \end{array} \end{array}$ <p style="text-align: center;">(Pseudo nitrol)</p> <p style="text-align: center;">↓ NaOH</p> <p style="text-align: center;">(Blue colour)</p>	$\begin{array}{c} R \\   \\ R-C-OH \end{array}$ <p style="text-align: center;">↓ Red P + I<sub>2</sub></p> $\begin{array}{c} R \\   \\ R-C-I \end{array}$ <p style="text-align: center;">↓ NaNO<sub>2</sub></p> $\begin{array}{c} R \\   \\ R-C-NO_2 \end{array}$ <p style="text-align: center;">↓ HNO<sub>2</sub></p> <p style="text-align: center;">No Reaction</p>

(vi) Periodic Acid ( $\text{HIO}_4$ ) Test for detection of Vicinal Diols and Related Compounds

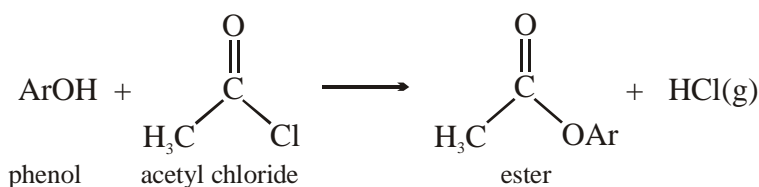
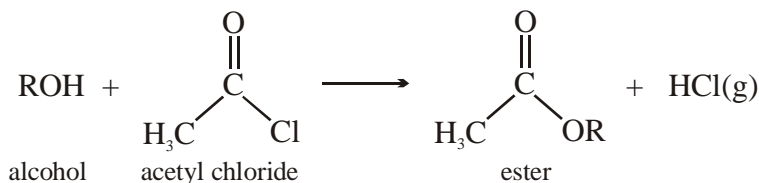
- The iodic acid is detected with 5%  $\text{AgNO}_3$  solution -an immediate precipitation of silver iodate occurs.



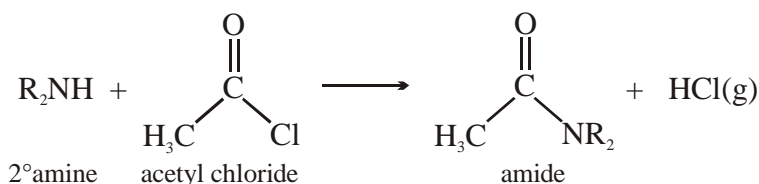
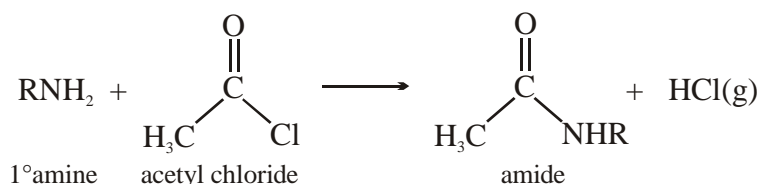
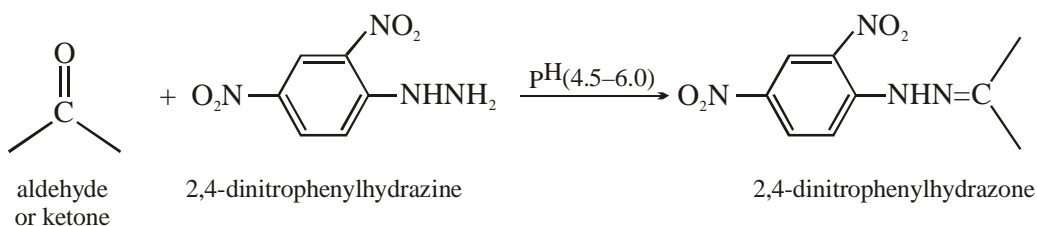
- Olefins, 2° alcohols, 1,3-glycols, ketones and aldehydes are not affected by  $\text{HIO}_4$  under the test condition.

**(vii) Acetyl Chloride**

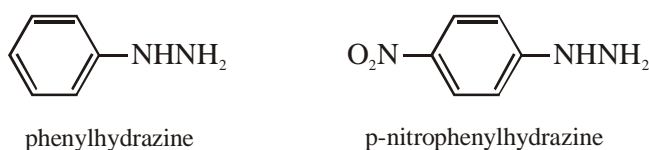
- Positive Test: Evolution of HCl gas and formation of ester as a top layer



- 3° alcohols form primarily alkyl chloride due to the reaction of the liberated HCl on another molecule of the alcohol.
- Other functional groups that give positive test: 1° and 2° amines

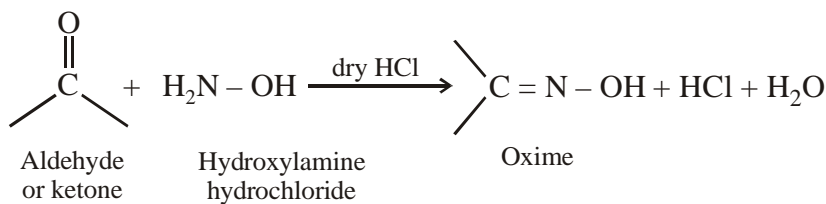
**2. Classification Tests For Aldehydes and Ketone****(i) 2,4-Dinitrophenyl Hydrazine**

- Positive Test:** formation of yellow, orange or red ppt.
- The precipitate may be oily at first and become crystalline on standing.

**(ii) Phenyl hydrazine and p-Nitrophenyl hydrazine.**

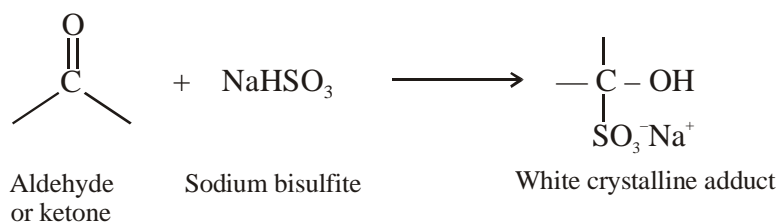
**Positive Test: formation of yellow ppt.**

**(iii) Hydroxylamine Hydrochloride**



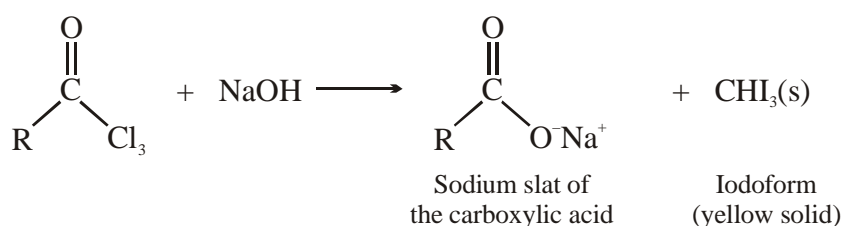
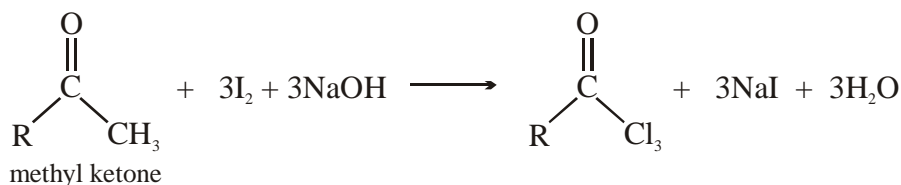
The liberation of hydrogen chloride can be detected by the change in colour from orange to red of a pH indicator.

**(iv) Sodium Bisulfite (NaHSO<sub>3</sub>)**

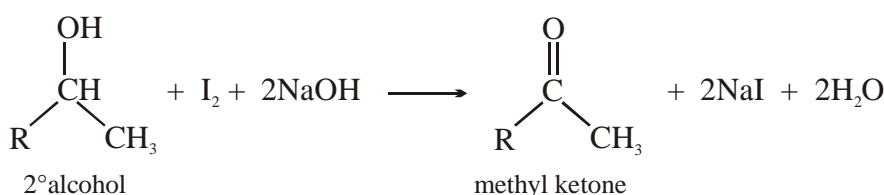


- **Positive Test:** By aldehydes and methyl ketone
- Only some cyclic ketones give positive results (ppt)
- This reaction is greatly inhibited by the steric constraints about the carbonyl group.

**(v) Iodoform Test (For Methyl Ketones)**

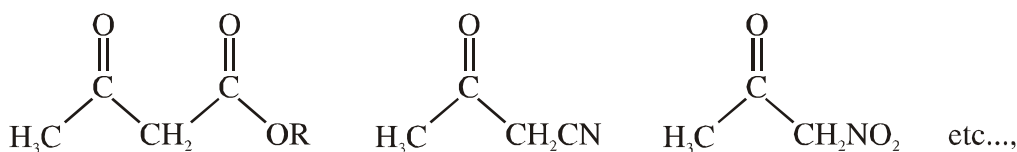


- **Positive Test:** Yellow ppt for methyl ketones
- **Disadvantages:** Some compounds that can be easily oxidized to methyl ketones give also positive results
- The principal types of compounds that give a positive test:



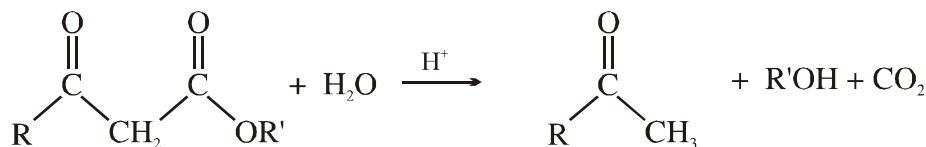
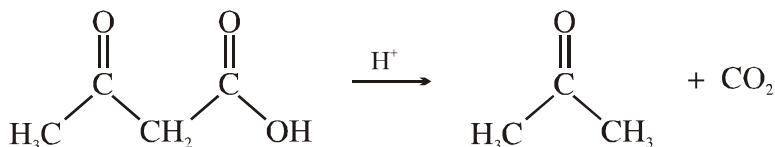


- The test is negative for the following type:



In such compounds the reagent removes the acetyl group and converts it to acetic acid, which resists iodination.

Acetoacetic acid is unstable, acidic aqueous solutions decompose to give  $\text{CO}_2$  and acetone.



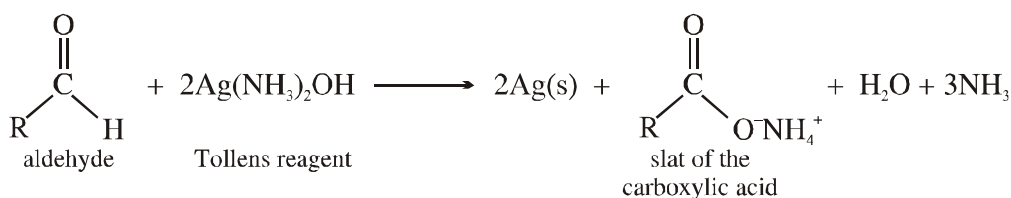
give positive iodoform test

### 3. Tests that give positive results with aldehydes and negative results with Ketones

- (i) **Jones Oxidation: Chromic anhydride or Chromium Trioxide ( $\text{CrO}_3$ )**

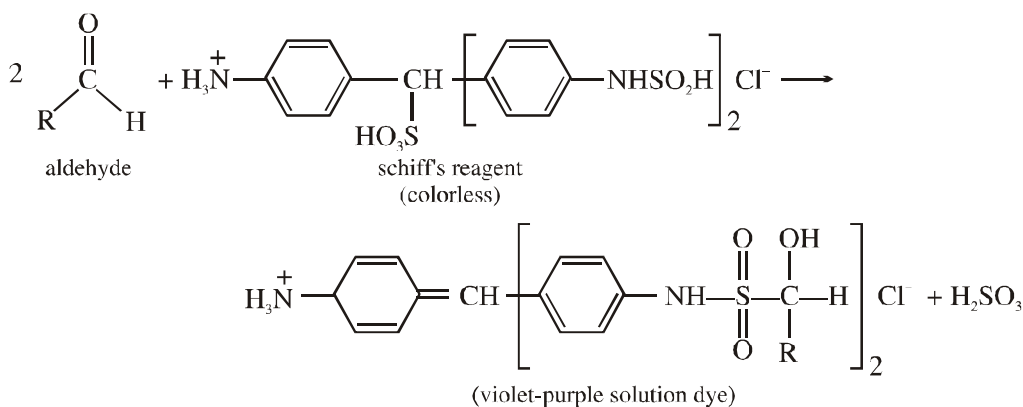
(Refer Jones Oxidation for alcohols at Page No. 22)

- (ii) **Tollens Reagents  $\text{Ag}(\text{NH}_3)_2\text{OH}$**



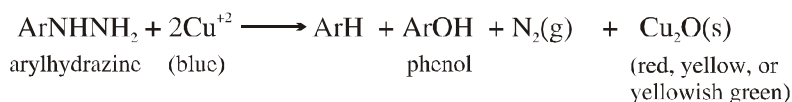
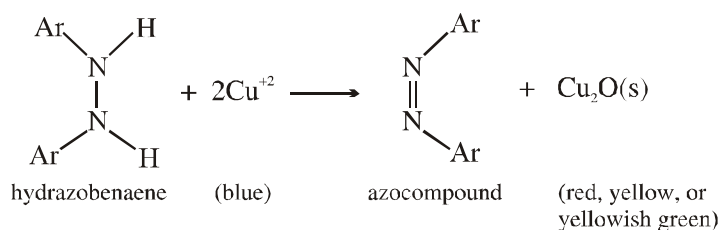
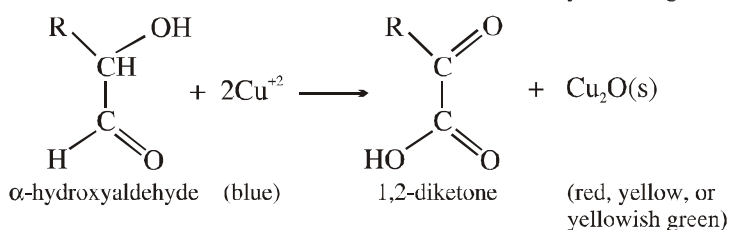
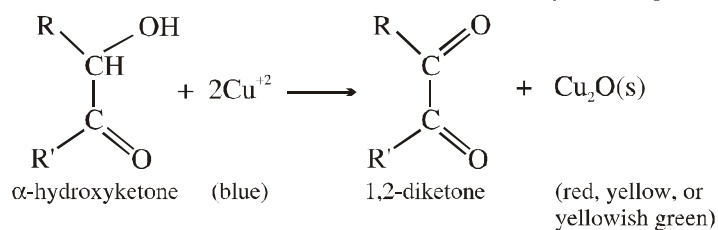
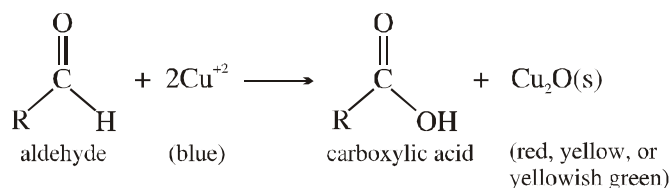
- Positive Test:** Formation of silver mirror (Ag) or colloidal (granular) gray or black Ag precipitate.

- (iii) **Schiff's Reagent**

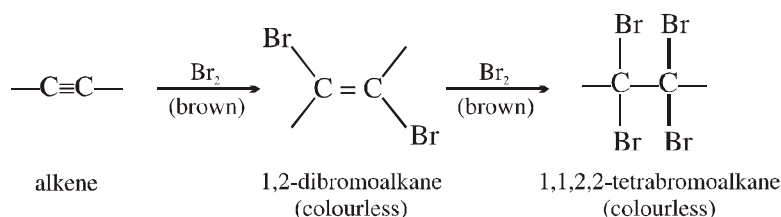
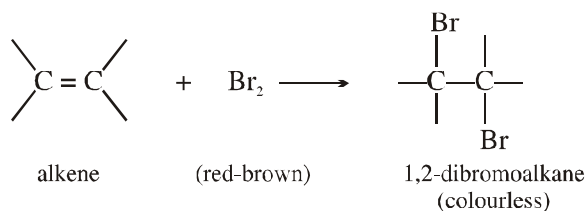


**(iv) Benedict's solution and Fehling's Solution**

- **Positive Test:** yellow or yellowish green ppt.
- All aldehydes give positive result except aromatic aldehydes (negative)

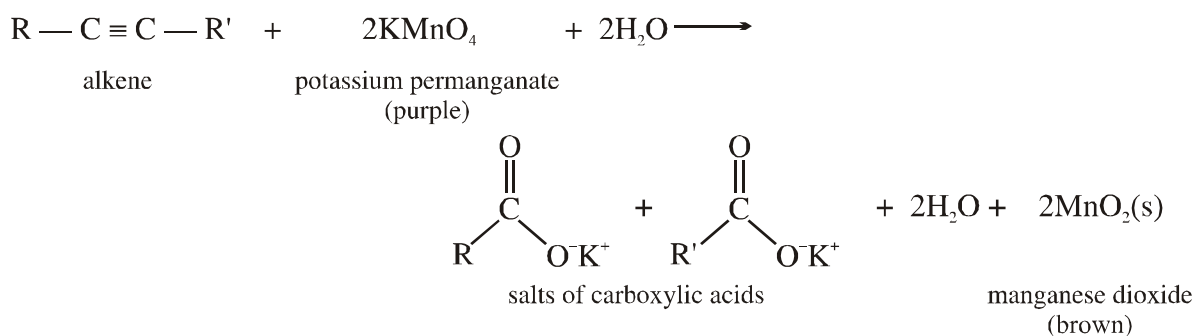
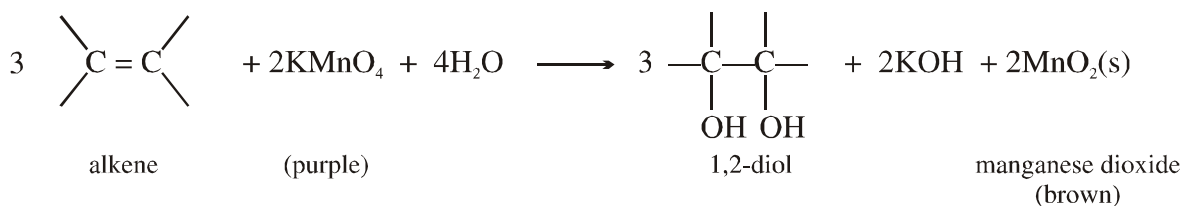
**4. Classification Tests for Unsaturation "alkenes & alkynes"**

- Alkanes are not usually characterized chemically because they are quite inert to most classification reactions

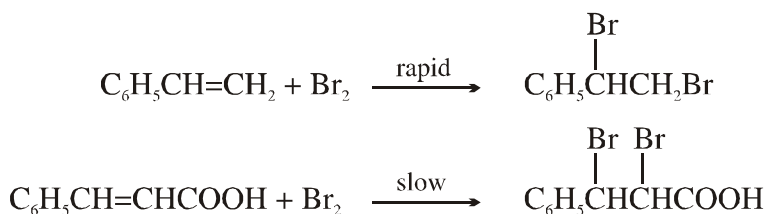
**(i) Bromine in CCl<sub>4</sub>**

- **Positive Test:** Bromine color discharged without evolution of gas (HBr)
- Alkenes & alkynes give positive results
- If HBr is evolved, it indicates phenols, enols & enolizable compounds, -,
- Bromine color is discharged by amines to produce a salt, which could be mistaken for addition.

(ii) Baeyer Test (KMnO<sub>4</sub> aqueous)



- **Positive Test:** Purple color discharges, and brown color ppt (MnO<sub>2</sub>) appears
- **Note :** Aldehydes and alcohols also give positive result
- Since the ionic characters of the Br<sub>2</sub> and KMnO<sub>4</sub> reactions are very different, there is some complementary character between the two tests.
- For example, some alkenes bearing electron-withdrawing groups undergo rapid reaction with KMnO<sub>4</sub> but often slow or negligible reaction with Br<sub>2</sub>.



- A few tetrasubstituted olefins such as C<sub>6</sub>H<sub>5</sub>CBr=CBrC<sub>6</sub>H<sub>5</sub> and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C=C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> fail to give positive tests with Br<sub>2</sub> in CCl<sub>4</sub> or KMnO<sub>4</sub> solution.

## 5. Tests for Alkyl Halides

- Aliphatic halides are often detected initially by qualitative by halogen analysis **halogen analysis**.

### (i) Ethanolic Silver Nitrate & (ii) Sodium Iodide in Acetone

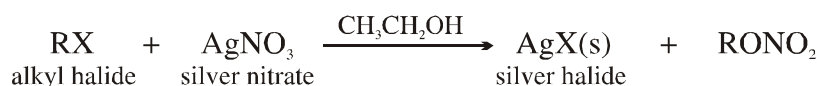
- Both tests involve displacement of halogen:
- $\text{AgNO}_3$ /ethanol test proceeds by a carbocation ( $\text{S}_{\text{N}}1$ ) process &  $\text{NaI}$  / acetone test proceeds by a direct displacement ( $\text{S}_{\text{N}}2$ )

$\text{AgNO}_3$ /ethanol test :  $\text{R}_3\text{CX} > \text{R}_2\text{CHX} > \text{RCH}_2\text{X}$

$\text{NaI}$ /acetone test:  $\text{R}_3\text{CX} < \text{R}_2\text{CHX} < \text{RCH}_2\text{X}$

### (i) Ethanolic Silver Nitrate Solution

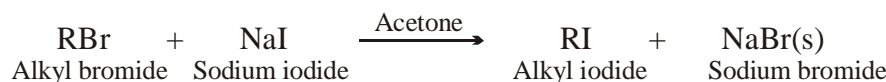
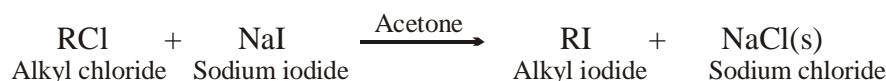
- The reaction of alkyl halide with silver nitrate yields a silver halide precipitate



- Positive Test:** formation of ppt. indicates  $2^\circ$  and  $3^\circ$  RX
- $1^\circ$  RX, Ar-X, and vinyl halides give negative Result.
- Note:** allylic and benzylic RX give positive result
- The identity of the halogen can sometimes be determined from the color of the silver halide:  $\text{AgCl}$  (white);  $\text{AgBr}$  (pale yellow);  $\text{AgI}$  (yellow)

### (ii) Sodium Iodide in Acetone Test

- The  $\text{NaI}$  test can be used to test for the presence of bromine or chlorine.
- Sodium halide ( $\text{NaX}$ ) precipitates from the solution.

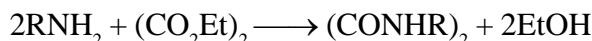


- Positive Test:** precipitate forms
- Indications :  $1^\circ$ ,  $2^\circ$  RX, allylic and benzylic halides. Not good for ArX, vinyl halides,  $\text{HCCl}_3$ , and  $3^\circ$  RX.
- Since reactivity toward alcoholic silver nitrate is often very different from reactivity toward sodium iodide in acetone, both tests should be used with any halogen compound.

## 6. Tests for Amines and Amine Salts

### (i) Diethyl oxalate test :

- This method helps in the separation of primary, secondary and tertiary amines.
- Primary amines on reaction with diethyl oxalate gives solid oxamide, secondary amine gives liquid oxamic ester and tertiary amine remains unreacted in gaseous form.

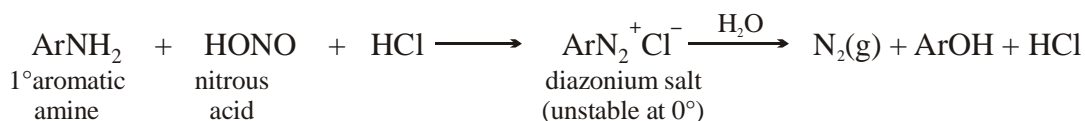
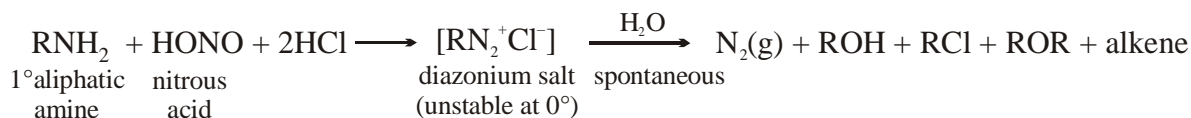


- The gaseous tertiary amine is separated out.
- The solid oxamide is filtered out of the liquid oxamic ester.
- These products are added to the alkaline solution of NaOH.

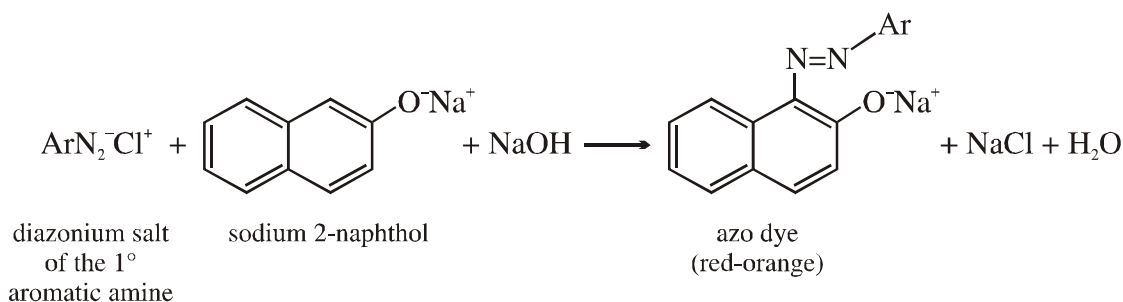
In this way, Primary, secondary and tertiary amines are separated by Hoffmann's Method

### (ii) Nitrous Acid

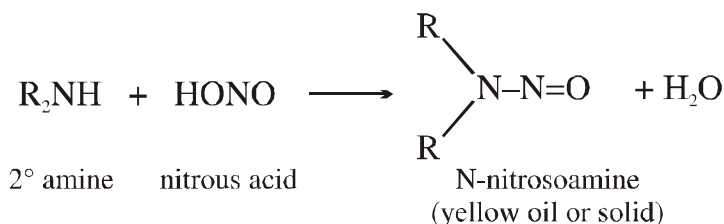
- Reaction of amines with nitrous acid (HONO) classifies the amine not only as 1°, 2°, or 3°, but also as aliphatic or aromatic.



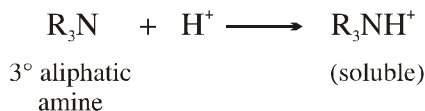
- The diazonium salt of the primary aromatic amine reacts with sodium 2-naphthol to produce a red-orange azo dye.



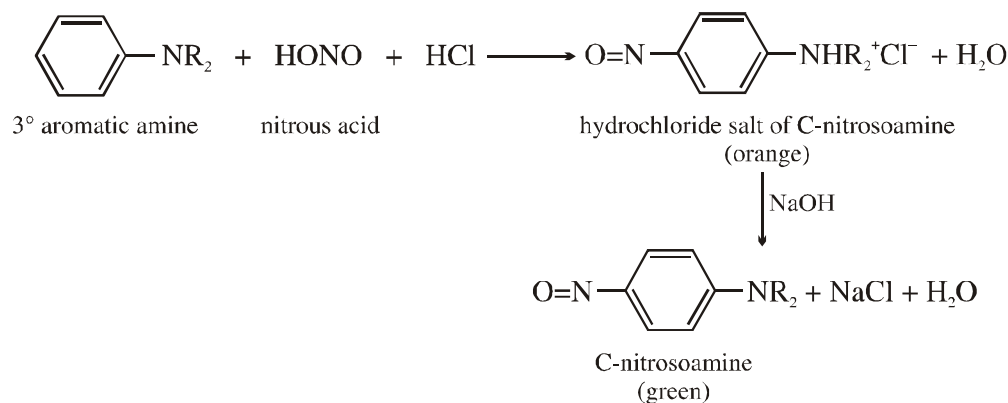
- 2° amines undergo a reaction with nitrous acid to form N-nitrosoamine, which are usually yellow solids.



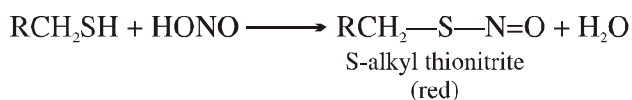
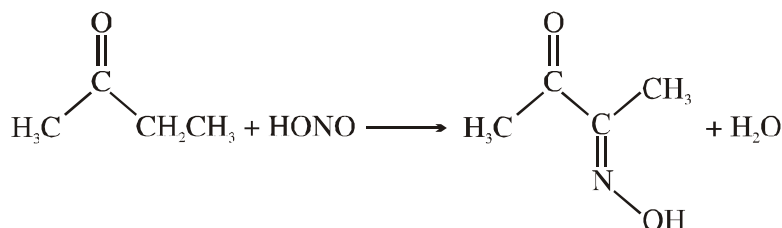
- 3° aliphatic amines do not react with nitrous acid, but they form a soluble salt. The reaction mixture gives an immediate positive test on the starch-iodide paper for nitrous acid.



- 3° aromatic amines react with nitrous acid to form the orange-colored hydrochloride salt of the C-nitrosoamine. Treating the solution with base liberates the blue or green C-nitrosoamine.

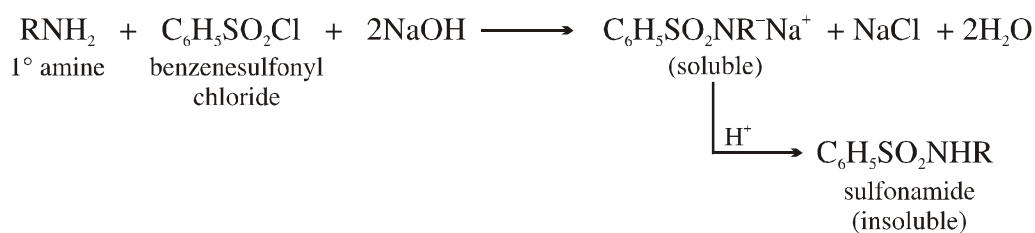


- Although nitrous acid is useful for characterizing amines, other functional groups also react.
- A methylene group adjacent to a keto group is converted to an oximino group and alkyl mercaptans yield red S-alkyl thionitrites.

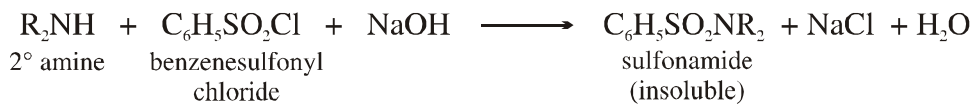


### (iii) Hinsberg Test

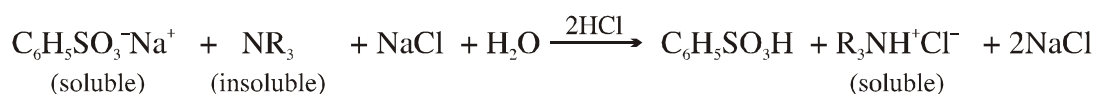
- Based on the reaction of the amine with benzenesulfonyl chloride (Hinsberg reagent), it can be used to separate 1°, 2°, and 3° amines.
- 1° amines: give solution that produce ppt after addition of HCl



2° amines: give ppt - acidification of the solution does not dissolve the sulfonamide (i.e., the PPT is not soluble in NaOH or HCl)



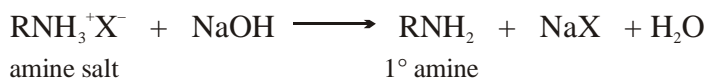
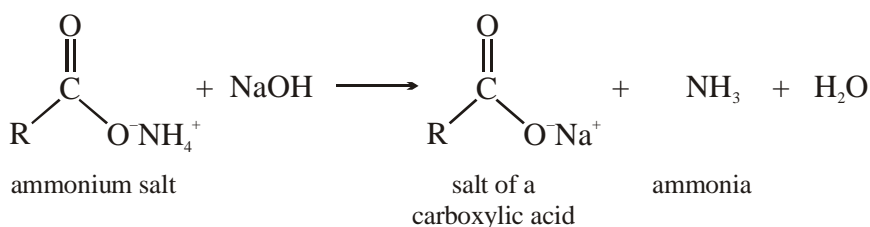
- 3° amines: undergo reaction with benzenesulfonyl chloride to produce quaternary ammonium sulfonate salts, which yield sodium sulfonate and insoluble 3° amines in basic solution.
- Acidification of the reaction mixture results in the formation of sulfonic acids and soluble amine salts



- The results of the Hinsberg test must not be used alone in classifying amines. The solubility of the original compounds must also be considered.
- If the original compound is amphoteric, which means that it is soluble in both acids and alkalis, the Hinsberg method fails to distinguish among the types of amines.

#### (iv) Sodium Hydroxide Treatment of Ammonium Salt and Amine Salts

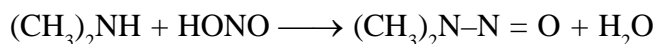
- Amine salts can be detected by treating the salt with NaOH to liberate ammonia or amine.



- Moistened pink litmus paper placed in the vapor above the solution will turn blue if ammonia or a volatile amine is present.

#### (v) Libermann's nitroso test :

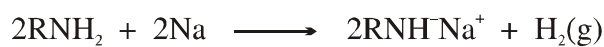
It is used as a test for secondary amines. Secondary amines (aliphatic as well as aromatic) reacts with nitrous acid to form N-nitrosoamines.



- Nitrosoamines are water soluble yellow oils and when warmed with phenol and few drops of conc.  $\text{H}_2\text{SO}_4$  produce a green colour solution which turns blue on adding alkali. This reaction is called Libermann's nitroso reaction.
- Tertiary amine do not react with nitrous acid.

### Sodium Metal :

- The active hydrogen on 1° and 2° amines undergo reaction with sodium to form salt and liberate hydrogen gas



1° amine

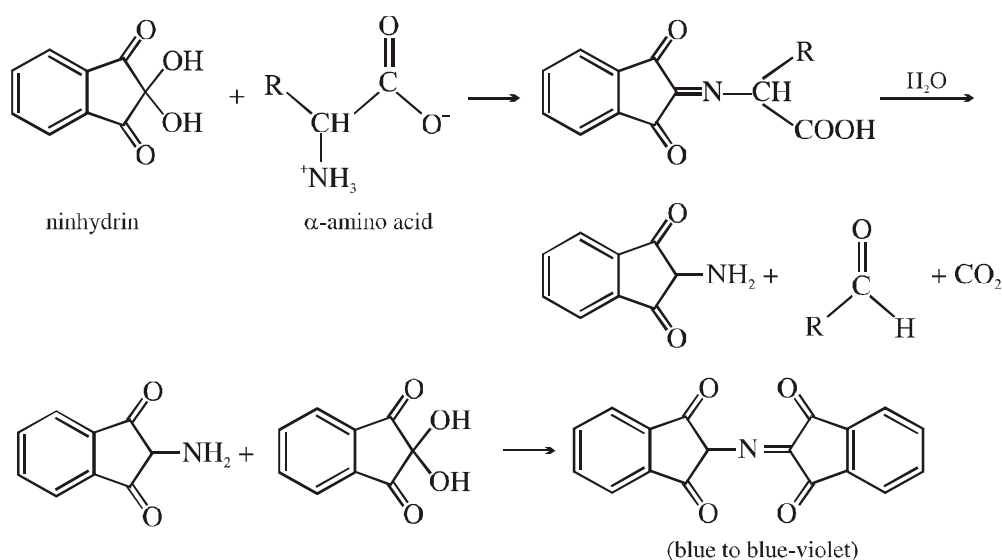


2° amine

## 7. Tests for Amino Acids

### (i) Ninhydrin Test :

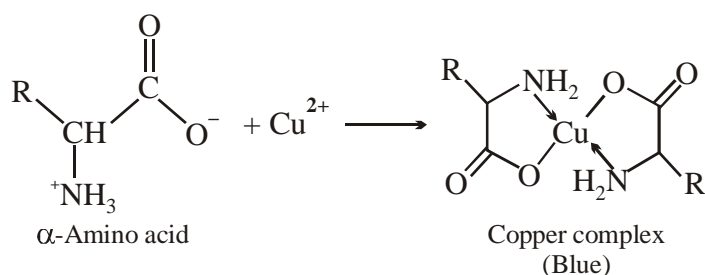
- Amino acids and  $\alpha$ -amino acids react with ninhydrin to give a positive test which is blue or blue-violet color.



- Ammonium salts ( $\text{NH}_4^+ \text{Cl}^-$ ) give a positive test.
- Some amines, such as aniline, yield orange to red colors, which is considered a negative test.
- Proline, hydroxyproline, and 2-, 3-, and 4-aminobenzoic acids fail to give

**Blue colour but produce a yellow color instead.**

### (ii) Copper Complex Formation



- Reaction with copper(II) sulfate solution yields a moderate-to deep-blue liquid or a dark-blue solid.

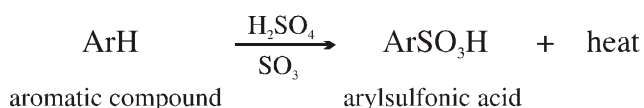


## 8. Tests for Aromatics

- If the molecule already contains reactive chemical substituents (acids, amines, ethers, carbonyl compounds, etc.,) use the corresponding classification test for that particular group.
- New substituents can be added onto the aromatic ring or existing substituents can be modified, such that the new

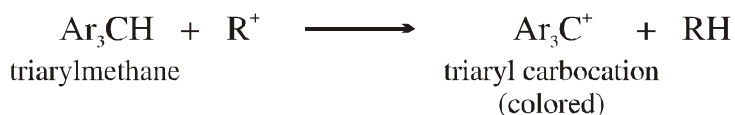
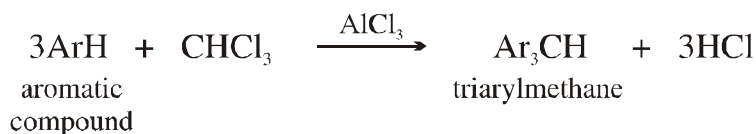
### Compound May be More Readily Characterized.

#### (i) Fuming Sulfuric Acid



- This test is good for aromatics with no other functional groups.
- Positive Test: the aromatic compound dissolves completely in  $\text{H}_2\text{SO}_4$  with the evolution of heat (Fuming)

#### (ii) Chloroform and Aluminum Chloride



- Aromatics give colored solution or powder.
- Positive Test: (Orange, red, blue, purple, green)
- Non aromatics give yellow color (Negative result)

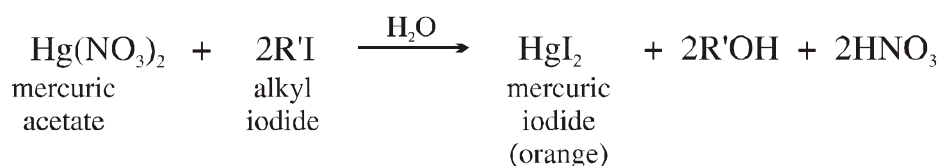
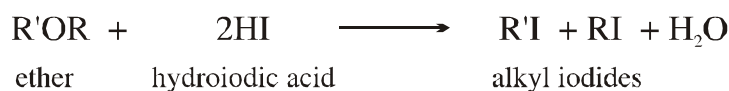
#### (iii) Azoxybenzene and Aluminum Chloride

- The color of the solution or precipitate is dependent on the functional groups present on the aryl group.
- Aromatic hydrocarbons and their halogen derivatives produce a deep-orange to dark-red color in solution or give a precipitate.
- Fused aromatic ring (such as naphthalene, anthracene, and phenanthrene) produce brown color.
- Aliphatic hydrocarbons give no color or, at most, a pale yellow.

## 9. Tests for Ethers

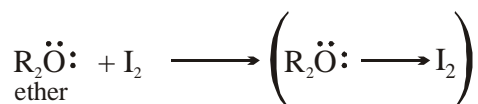
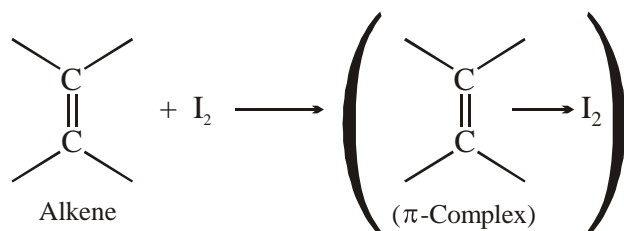
- Ethers are only a little more polar and slightly more reactive than either saturated hydrocarbons or alkyl halides
- Ethers form extremely explosive peroxides upon standing, specially when exposed to air and/or light. Liquid ethers that shows solid precipitates should not be handled.

### (i) Hydroiodic Acid (Zeisel's, Alkoxy method)



- Positive Test: Orange or Orange-red color indicating.
- Note: Ethyl and methyl esters give also positive result.

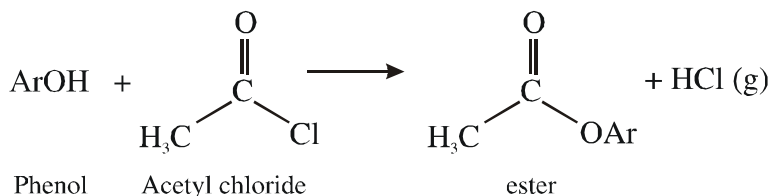
### (ii) Iodine Test for Ethers and Unsaturated Hydrocarbons



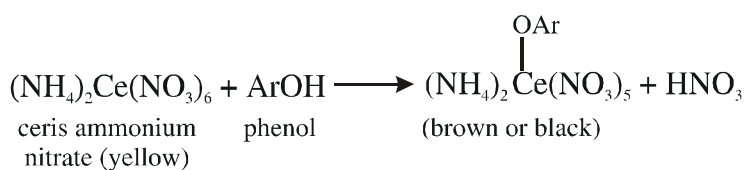
- Positive test: the color of the solution changes from purple to tan.
- Aromatic hydrocarbons, saturated hydrocarbons, fluorinated hydrocarbons and chlorinated hydrocarbons do not react.
- Unsaturated hydrocarbons produce a light-tan solid, while retaining the purple color of the iodine solution.

## 10. Tests for Phenols

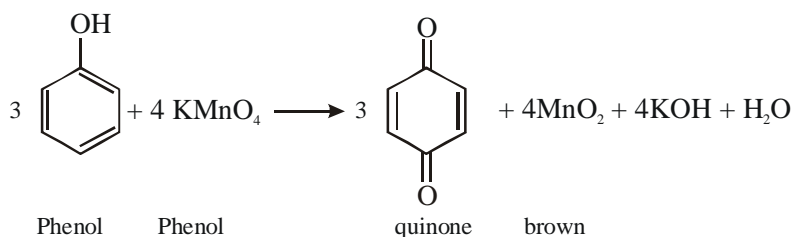
- As with alcohols, the acidic hydrogen in phenol can be detected with sodium (hydrogen gas is evolved) or with acetyl chloride (an ester layer is formed).



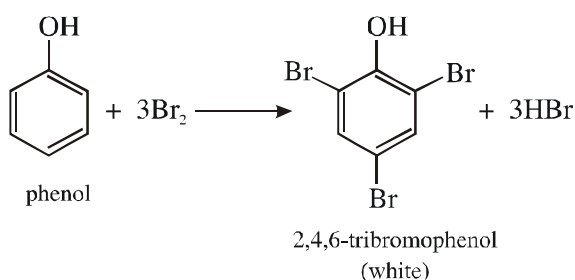
- Phenols undergo reaction with yellow ceric ammonium nitrate to produce brown or black products.



- Phenols reduce potassium permanganate solution and undergo oxidation to quinones.
- The manganese is reduced from +7 which gives a purple solution to +4 which is brown.

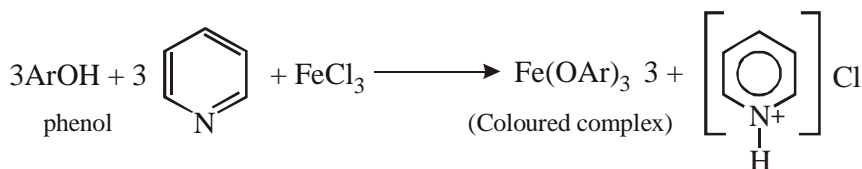


### (i) Bromine water



- Positive Test: decolorization of bromine.
- This is good for water soluble phenols

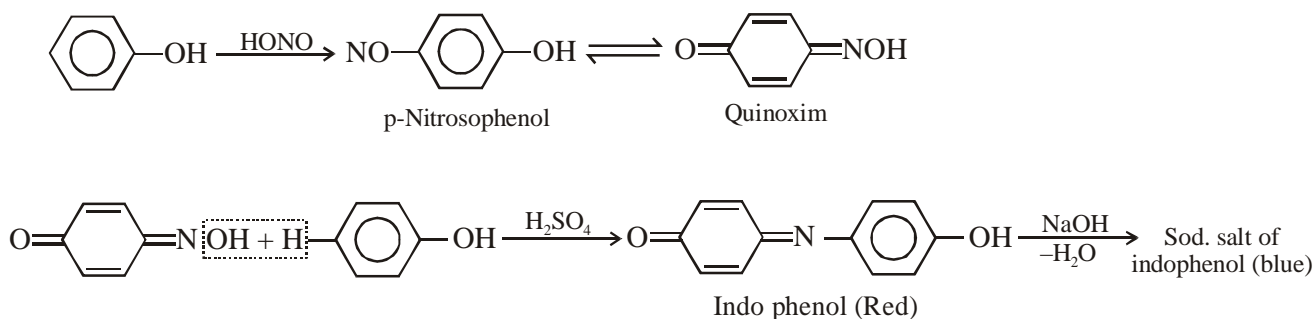
### (ii) Ferric Chloride - Pyridene Reagent



- Positive Test: Production of blue, violet, purple, green, or red-brown colors
- Good for all types of Ar-OH.
- Positive test for enols.  $\left( \begin{array}{c} \text{OH} \\ | \\ \text{C} \\ // \\ \text{C} \\ | \\ \text{O} \end{array} \right)$
- Carboxylic acid with  $\text{FeCl}_3$  gives red colour only when saturating with  $\text{NH}_3$ .

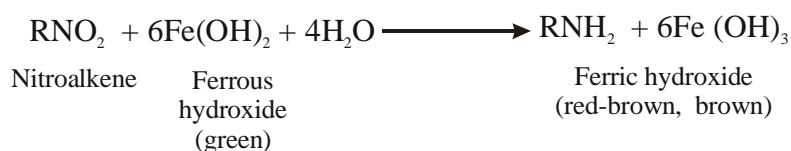
(iii) **Libermann's nitroso test :**

While phenol is reacted with  $\text{NaNO}_2$  and concentrated  $\text{H}_2\text{SO}_4$ , it provides a deep green colour which changes to red on dilution with water. while generated alkaline along with  $\text{NaOH}$ , blue colour is restored. This reaction is termed as Liebermann's nitroso reaction and is employed as a test of phenol.

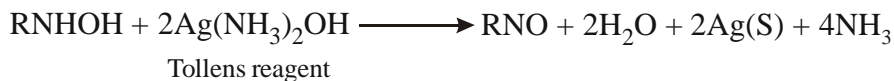
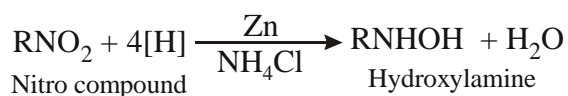


## 11. Test For Nitro Compounds

(i) **Ferrous Hydroxide Reduction**



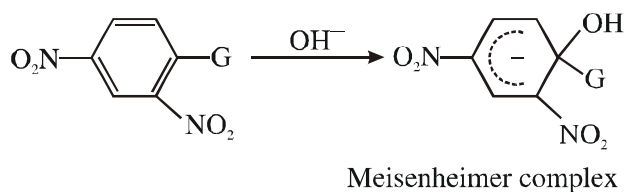
- Positive Test: indicated by the change in color from green to red-brown or brown due to the oxidation of iron from +2 to +3.
- A negative test is indicated by a greenish precipitate.
- Note: Nitroso compounds, quinones, hydroxylamines alkyl nitrates give also positive results

**(ii) Zinc and Ammonium Chloride Reduction**

- Test the solution with Tollens Reagent
- **Positive Test:** formation of metallic silver
- Only 3° aliphatic nitro compounds and aromatic nitro compounds are reduced by Zn/NH<sub>4</sub>Cl to the hydroxylamine.
- The hydroxylamine is then detected by the formation of metallic silver in the Tollens test (or formation of a black or grey precipitate). This is known as Mulliken–baker test:.

**(iii) Treatment of Aromatic Compounds with Sodium Hydroxide**

- The number of nitro groups on an aromatic ring can be determined by the reaction with NaOH
- In the reaction with NaOH:
- Mononitro aromatic compounds yield no color change or a very light yellow
- Dinitro aromatic compounds produce a bluish-purple color
- Trinitro aromatic compounds give a red color
- The color of the solution is due to a Meisenheimer complex



## SEPARATION TECHNIQUES

### METHODS OF PURIFICATION OF ORGANIC COMPOUNDS :

Organic compounds obtained either from natural source (or) synthesized in laboratory are contaminated with impurities. Various methods are used for removal of impurities from an organic compound depends on the nature of compound and type of impurities present in it. The following methods are commonly used for purification

- |                     |  |
|---------------------|--|
| (1) Sublimation     | (2) Crystallisation                              |
| (3) Distillation    | (4) Solvent extraction (differential extraction) |
| (5) Chromatography. |  |

**Note: Most of the pure compounds contain sharp Melting point & Boiling points.**

#### Sublimation :

The process of conversion of sublimable solid to vapour state directly by heating without passing through liquid state is called sublimation.

#### Solid vapour

- This method is used for purification of solids
- Sublimation process is used for separation of sublimable volatile compounds from non sublimable impurities.
- Sublimation is generally used for purification of camphor, naphthalene. Anthracene. Benzoic acid, phthalic anhydride, Anthraquinone, Indigo and Iodine  $HgCl_2$ , solid  $SO_3$

#### Crystallisation :

- It is used for purification of solid organic compounds.
- Crystallisation is based on the difference in solubilities of the compound and impurities in a suitable solvent.
- The principle involved in this method is impure compound dissolved in a solvent is sparingly soluble at low temperature, but appreciably soluble at high temperature. Insoluble impurities are separated by filtration. The filtrate on cooling saturated solution, pure compound crystallises out. If a compound is highly soluble in one solvent and too little soluble in another solvent then crystallisation is carried out by using mixture of these solvents.
- Impurities, which impart colour are removed by adsorbing over activated charcoal.
- Repeated crystallisation is required if organic compound contains impurities of comparable solubilities.
- The process of separation of different components of a mixture by repeated crystallisation is called fractional crystallisation.
- Fractional crystallisation is used for separation of two or more soluble substances which have different solubilities in the same solvent.
- Most commonly used solvents for crystallisation are water, alcohol, ether, chloroform, carbontetrachloride. acetone, benzene, petroleum ether.

- Sugar having an impurity of common salt can be crystallised from hot ethanol. since sugar dissolves in hot ethanol but common salt does not.
- Fractional crystallisation can be used to separate a mixture of  $\text{KClO}_3$  (less soluble) and  $\text{KCl}$  (more soluble).

**DISTILLATION :**

Distillation is an important method used to separate

- i) Volatile liquids from non volatile impurities.
- ii) Liquids having sufficient difference in boiling points.

**Simple Distillation :**

- This process is used for purification of liquids which does not undergo decomposition at their boiling points
- The vapourisation of a liquid by heating and subsequent condensation of vapours by cooling is known as distillation.
- Liquid mixture is taken in a round bottom flask and heated carefully, the vapour component with lower boiling point distills first, the vapour formed is condensed by using condenser and the liquid is collected in a receiver. The vapours of component with higher boiling point distills later.
- The liquids that have boiling point difference greater than  $40^\circ\text{C}$  can be purified by this method,

**e.g:**

- (i) Chloroform (BP. 334 K) & Aniline (B.P. 457 K)
- (ii) Ether (B.P. 308 K) & Toluene (B.P. 384 K)
- (iii) Benzene (B.P. 353 K) & Aniline (B.P. 457 K)

**Fractional Distillation :**

- Fractional distillation is used if the difference in boiling point of two liquids is less than  $40^\circ\text{C}$ .
- Vapours of liquid mixture are passed through fractionating column before condensation, which is fitted over mouth of the round bottom flask.
- Vapours of liquid with higher boiling point condense before the vapours of liquid with lower boiling point the vapours raising up in the fractionating column is richer in more volatile component.
- Fractionating column provides many surfaces for heat exchange between ascending vapours and descending condensed liquid.
- Each successive condensation and vapourisation unit in the fractionating column is called a theoretical plate.
- Liquids forming a constant boiling mixture (azeotropic mixture) can not be separated by this method.
- Fractional distillation is used to separate different fractions of crude oil in petroleum industry.
- This method is used for separation of mixture of acetone (B.P. 330K) and methyl alcohol (B.P. 338K)
- Mixture of benzene and toluene can be separated by fractional distillation.

**Ex.1** How is ethyl alcohol purified from methylated spirit.

**Sol:** Methylated spirit is ethyl alcohol contaminated mainly with methyl alcohol. Ethyl alcohol is purified by fractional distillation since the difference in boiling point is less.

**DISTILLATION UNDER REDUCED PRESSURE (Vacuum Distillation)**

- This method is used to purify liquids having very high boiling points, which decompose at or below their boiling points.
- These liquids are made to boil at a temperature lower than their normal boiling point by reducing pressure on their surface with the help of vacuum pump.
- Glycerine,  $H_2O_2$ , formaldehyde are purified by vacuum distillation.
- Glycerol can be separated from spent-lye in soap industry by using vacuum distillation.
- Sugar cane juice is concentrated in sugar industry by evaporation under reduced pressure which saves lot of fuel.

**Steam Distillation :**

- This method is used for separation and purification of organic compounds (solids or liquids) which
  - i) are steam volatile
  - ii) are insoluble in water.
  - iii) Process high vapour pressure (10-15 mm of Hg at 373 K)
  - iv) Contains non volatile impurities.
- Steam distillation is based on Dalton's law of partial pressure i.e.,  $P = P_1 + P_2$ . where  $P$  = Atmospheric pressure.
  - $P_1$  = Partial pressure of organic liquid
  - $P_2$  = Vapour pressure due to water.
- Compounds which can be purified by steam distillation are aniline, nitrobenzene, bromobenzene, o-nitrophenol, o-hydroxy benzaldehyde (salicylaldehyde), o-hydroxy acetophenone, turpentine oil, essential oils.

**Ex.2** Mention about the purification of (a) aniline and (b) naphthalene

- Sol.** (a) Aniline can be purified by steam distillation because it is immiscible with water and steam volatile.  
 (b) Naphthalene can be purified by sublimation because it changes on heating directly to vapour state and on cooling, it changes back into solid form.

**Solvent Extraction (Differential Extraction) :**

- **Definition:** The process of isolating an organic compound from its aqueous solution by shaking with a suitable solvent is called differential extraction. It is also called solvent extraction
- When an organic compound is present in an aqueous medium, then it is separated by shaking it with an organic solvent in which it is more soluble than in water.
- Solvent should be immiscible with water and organic compound to be separated should be highly soluble in it
- Organic solvent and aqueous solution are immiscible with each other, so they can form two distinct layers (which can be separated by separator funnel).
- Organic solvent is distilled or evaporated to get organic compound.
- If organic compound is less soluble in organic solvent then large quantity of solvent is required to extract small quantity of compound, which is said to be continuous extraction.



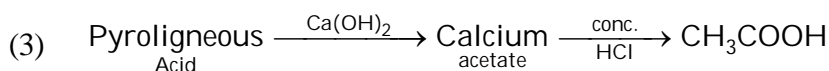
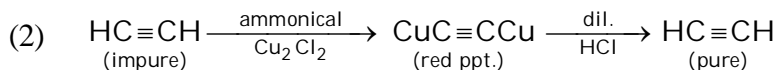
- Benzoic acid can be extracted from its aqueous solution using benzene as solvent.
- Ether is a better solvent in differential extraction due to:
  - its less polarity
  - less reactivity
  - Less Boiling Point
  - higher solubility of organic compounds

### SEPARATION BY CHEMICAL METHODS :

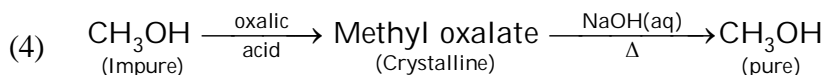
- It is used for mixture of substances which are chemically different.

e.g :

- (1) Separation of acidic and basic compounds of coal-tar.



(from wood distillation industry)  $\rightarrow$   $\text{CH}_3\text{COOH} + \text{MeCoMe} + \text{MeOH}$



### Chromatography :

- This method is used for separation of mixtures into their components, purification of compounds and also to test the purity of compounds.
- Chromatography is obtained from the greek word "Chroma" means colour and "graphy" means writing.
- This method was first used for separation of coloured substances found in plants.
- This method was described by Tswett.
- This Technique consists of two phases one is stationary phase of large surface area while the second is moving phase which is allowed to move slowly over the stationary phase.
- Stationary phase is either liquid or solid, while moving phase may be liquid or gas.
- The technique of chromatography is based on the rates at which the components of the mixture moves through a porous medium (called stationary phase) under the influence of some solvent (or) gas (called mobile phase).
- Mixture of substances is applied on a stationary phase which may be solid or liquid A pure solvent, a mixture of solvents or a gas is allowed to move slowly over the stationary phase, the components of the mixture get gradually separated from one another.
- Recovery of separated substances by using suitable solvent is known as elution. The solvent used is known as eluant.

S.No.	Chromatography process	Stationary Phase	Mobile Phase
1.	Column chromatography (Adsorption)	Solid	Liquid
2.	Liquid-liquid partition chromatography	Liquid	Liquid
3.	Paper chromatography	Liquid	Liquid
4.	Thin layer chromatography (TLC)	Liquid (or) solid	Liquid
5.	Gas-liquid chromatography (GLC)	Liquid	Gas
6.	Gas-solid chromatography (GSC)	Solid	Gas
7.	Ionic exchange chromatography	Solid	Liquid

- Based on the principle involved chromatography is classified in to

- Adsorption chromatography and
- partition chromatography.

(a) **Adsorption Chromatography :**

- Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees.
- Commonly used adsorbents are silica gel, alumina, magnesium oxide, cellulose powder, activated animal charcoal.
- When a mobile phase is allowed to move over stationary phase, the components of the mixture move by varying distances over stationary phase.
- There are two main types of chromatographic techniques based on principle of differential adsorption
  - Column chromatography and
  - Thin layer chromatography (TLC)

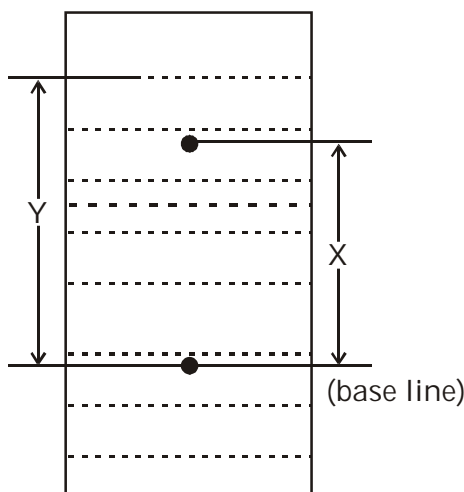
**i) Column Chromatography**

- It involves separation of a mixture over a column of adsorbent packed in a glass tube, which is fitted with stop cock at its lower end.
- The mixture to be separated on the adsorbent is placed at the top of the stationary phase.
- An appropriate eluant, which is a liquid or a mixture of liquids is allowed to flow down the column slowly.
- The strongly adsorbed substances are retained near the top and others come down to various distances in the column,

**(ii) Thin layer chromatography (TLC)**

- It involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate.
- The glass plate is coated with adsorbent (ex: silica gel, alumina) as a thin layer (about 0.2mm thick) is called chromatography plate or chroma plate .
- The solution of mixture to be separated is applied as small spot about 2cm above from one end of the TLC plate.

- The glass plate is placed in a closed jar containing the eluant. As the eluant rises up, the components of the mixture move up along the eluant to different distances depending on their degree of adsorption and separation takes place.
- The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e,  $R_f$  value.



$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

- The spots of coloured compounds are visible on TLC plate due to their original colour.
- The colourless compound which fluoresce are detected with ultraviolet light
- Spots of compounds are even detected by allowing them to adsorb iodine, will show up as brown spots.
- Some times an appropriate reagent is sprayed on the plate.

**eg :** Amino acids are detected by spraying the plate with ninhydrin solution.

### Partition Chromatography :

- Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases.
- Paper chromatography is a type of partition chromatography.
- In paper chromatography a special quality known as chromatography paper is used.
- In Chromatography paper, cellulose helps as support, and water absorbed from air on to hydroxyl groups of cellulose acts as stationary phase.
- The chromatography paper spotted with the solution of mixture at the base is suspended in a suitable solvent or mixture of solvents, this solvent (s) act as mobile phase.
- The solvent rises up the paper by capillary action and flows over the spot.
- The paper selectively retains different component according to their differing partition in the two phases. The paper strip so developed is called chromatogram.
- The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram.

- The spots of the separated colourless compound may be observed either under ultraviolet or by the use of appropriate spraying agent

**Additional Information : Applications of Chromatography:**

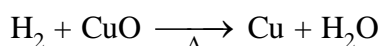
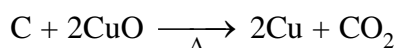
- I. i) In Chemical Industry column chromatography is used for separation of required components obtained after synthesis.  
ii) TLC is useful for monitoring large scale column chromatography.
- II **Pharmaceutical industry** : Chromatography is used for separation of chiral compounds to obtain pharmaceutically active optical isomer.
- III **Food Industry** : Chromatography techniques are used for quality control in food industry. It is used to determine presence and to separate additives, flavours etc. It is also used to detect presence of contaminants like mould, bacteria in food.
- IV **Environment-Testing lab** : Presence and quality of pollutants in air and drinking water can be determined by chromatography technique.
- V) **Diagnostic Technique**: Presence of certain drugs and the marker compounds for medical diagnosis in blood and urine are determined.

**Qualitative Analysis of Organic Compounds ( Detection of Elements):**

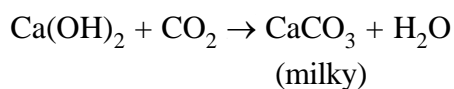
- The qualitative analysis of an organic compound involves detection of all elements present in it

**Detection of Carbon and Hydrogen :**

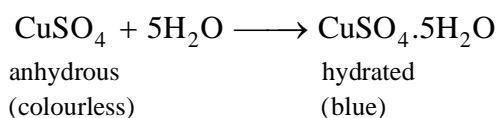
- Carbon and hydrogen are detected by heating the compound with cupric oxide (CuO).
- Carbon present in the compound is oxidised to carbon dioxide, which turns lime water milky.
- Hydrogen present in the compound is converted into water, which turns anhydrous copper sulphate into blue.



- Carbondioxide turns lime water milky.



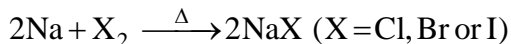
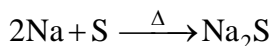
- Water vapours turn anhydrous copper sulphate into blue.



**Detection of Nitrogen, Sulphur Halogens & Phosphorus :**

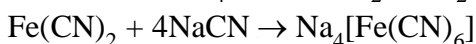
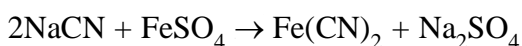
- Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by Lassaigne's test.
- Organic compounds are fused with dry sodium in fusion tube and fused mass after extraction with water is boiled and filtered, the filtrate is called sodium fusion extract
- During preparation of sodium fusion extract covalent compound is converted into ionic compound.

- The following reactions takes place



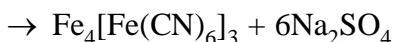
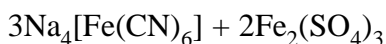
### Test for Nitrogen :

Sodium fusion extract is boiled with freshly prepared ferrous sulphate (  $\text{FeSO}_4$  ) solution and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.



sodium hexacyanoferrate(II)

On heating with concentrated sulphuric acid some Iron(II) ions are oxidised to Iron(III) ion, which reacts with sodium hexacyanoferrate(II) to produce Iron (III) hexacyanoferrate(II) (ferri ferrocyanide) which is Prussian blue in colour.



ferriferrocyanide

(prussianblue)

- This test fails in case of diazo compounds.
- If the amount of nitrogen present is less, then Prussian blue is present in collaidal form and the solution looks green.

**Ex.3** Hydrazine does not give Lassaigne's test, Why?

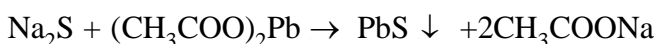
**Sol.** In the Lassaigne's test, nitrogen is converted to cyanide by combining with carbon of the compound Hydrazine does not contain carbon and hence cyanide cannot form.

**Ex.4** Why diazonium salts do not show positive Lassaigne's test for nitrogen ?

**Sol:** Diazonium salts are unstable and lose nitrogen as  $\text{N}_2$  gas on heating. Hence during fusion, no sodium cyanide is formed in Lassaigne's extract due to the loss of nitrogen.

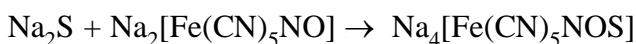
### Test for Sulphur:

- a) Sodium fusion extract is acidified with acetic acid and lead acetate is added to it, a black precipitate of lead sulphide is formed, which indicates presence of sulphur.



black

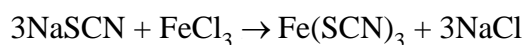
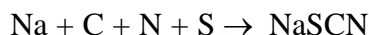
- b) Sodium fusion extract is treated with freshly prepared sodium nitroprusside, appearance of violet colour (purple) indicates presence of sulphur.



(sodium nitro prusside)

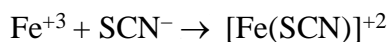
(violet)

- In case both nitrogen and sulphur are present in an organic compound sodium thiocyanate is formed, which gives blood red colour with neutral  $\text{FeCl}_3$  solution.



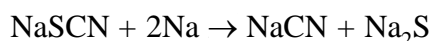
(blood red)

(or)



(blood red)

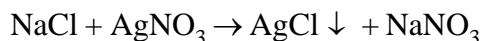
- If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide, these ions give their usual tests.



### Test for Halogens:

- Sodium fusion extract is acidified with nitric acid and then treated with silver nitrate solution.

- White precipitate, soluble in ammonium hydroxide indicates presence of chlorine.

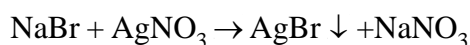


(white ppt)



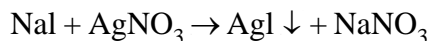
(soluble complex)

- Yellowish precipitate, sparingly soluble in ammonium hydroxide indicates presence of bromine.



(yellowish ppt)

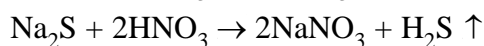
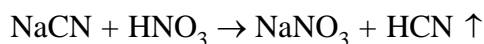
- Yellow precipitate, insoluble in ammonium hydroxide indicates presence of Iodine.



yellow

precipitate

- Nitrogen and sulphur are also present in the compound, the sodium fusion extract is boiled with concentrated nitric acid to decompose sodium cyanide & sodium sulphide formed during Lassaigne's test, otherwise they interfere with silver nitrate test for halogens.



- If  $\text{NaCN}$  and  $\text{Na}_2\text{S}$  are not decomposed, then white and black precipitates of  $\text{AgCN}$  and  $\text{Ag}_2\text{S}$  are formed respectively with silver nitrate solution.

### Beilstein's Test:

A copper wire flattened at one end is heated in an oxidising flame of Bunsen burner. The heating is continued till it does not impart blue colour flame. The hot end of copper wire is now touched with the organic substance and is once again kept in flame, the appearance of green or blue colour indicates the presence of halogens in the organic compound.

**Limitations :**

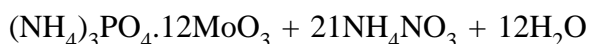
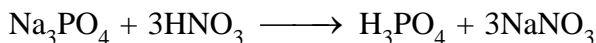
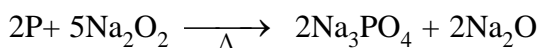
- (a) Substances such as urea, thiourea do not contain halogens but gives this test  
 (b) It does not tell which halogen is present in organic compound.

**Chlorine Water Test for Bromine and Iodine :**

- Both AgBr and AgI are yellow precipitates, it is a little bit difficult to identify given halogen in bromine or iodine, to confirm it chlorine water test is used.
  - Sodium fusion extract is acidified with dilute  $\text{H}_2\text{SO}_4$  (or)  $\text{HNO}_3$ , to this 1(or) 2ml of chloroform (or) Carbon tetrachloride is added and then excess of chlorine water is added with constant shaking.
- (i) If chloroform (or) carbon tetrachloride layer becomes yellow (or) brown indicates presence of bromine.  
 $2\text{NaBr} + \text{Cl}_2 \rightarrow 2\text{NaCl} + \text{Br}_2$   
 $\text{Br}_2$  dissolves in chloroform (or) carbontetrachloride gives yellow (or) brown colour
- (ii) If chloroform (or) carbon tetrachloride layer becomes violet indicates presence of iodine  
 $2\text{NaI} + \text{Cl}_2 \rightarrow 2\text{NaCl} + \text{I}_2$   
 $\text{I}_2$  dissolves in chloroform (or) carbontetrachloride gives violet colour.
- Presence of NaCN (or)  $\text{Na}_2\text{S}$  in sodium fusion extract does not interfere in this test.

**Test for Phosphorus :**

The compound is heated with oxidising agent (sodium peroxide) or with fusion mixture (sodium carbonate and potassium nitrate) phosphorus present in the compound is oxidised to sodium phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate, a canary yellow (ammonium phospho molybdate) precipitate formation (or) yellow colouration indicates presence of phosphorus.



(ammonium phospho molybdate)

**Test for Oxygen :**

- There is no direct test for oxygen.
- If organic compound is heated in a dry test tube in nitrogen atmosphere, if water droplets are formed on the walls of the test tube indicates presence of oxygen.
- Presence of oxygen can be known by testing functional groups containing oxygen.

**eg:**  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CHO}$ ,  $-\text{NO}_2$  etc

**QUANTITATIVE ANALYSIS**

It involves the estimation of percentage composition of various elements by suitable methods.

**Estimation of Carbon and Hydrogen**

- Carbon and hydrogen are estimated by Liebig's combustion method.
- A known mass of an organic compound is burnt in the presence of excess of oxygen (free from  $\text{CO}_2$ ) and Cupric oxide ( $\text{CuO}$ )

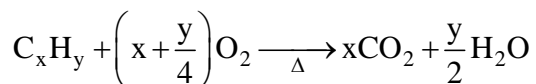
## (A) ELEMENTAL ANALYSIS CHART

### Lassaigne method (Detection of elements)

Element	Sodium Extract (S.E.)	Confirmed Test	Reactions
Nitrogen	$\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$ (S.E.)	S.E. + $\text{FeSO}_4 + \text{NaOH}$ , boil and cool, + $\text{FeCl}_3 + \text{conc. HCl}$ Blue or green colour (i) S.E. + sodium nitro prusside (A) A deep violet colour. (ii) S.E. + $\text{CH}_3\text{COOH}$ + $(\text{CH}_3\text{COO})_2 \text{Pb}$ A black ppt. S.E. + $\text{HNO}_3 + \text{AgNO}_3$ (i) White ppt. soluble in aq $\text{NH}_3$ confirms Cl (ii) Yellow ppt partially soluble in aq. $\text{NH}_3$ confirm Br (iii) Yellow ppt insoluble in aq $\text{NH}_3$ confirms I As in test for nitrogen; instead of green or blue colour, blood red coloration confirms presence of N and S both	$\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe}(\text{OH})_2 + \text{Na}_2\text{SO}_4$ $\text{Fe}(\text{OH})_2 + 6\text{NaCN} \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_6] + 2\text{NaOH}$ $3\text{Na}_4[\text{Fe}(\text{CN})_6] + 4\text{FeCl}_3 \xrightarrow{\text{HCl}} \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{NaCl}$ Prussian blue (i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ (A) deep violet (ii) $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}} \text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$ black ppt.
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$ (S.E.)		
Halogen	$\text{Na} + \text{Cl} \xrightarrow{\Delta} \text{NaCl}$ (S.E.)		
Nitrogen and Sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaCNS}$ (S.E.)		$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$ ppt $\text{AgCl} + 2\text{NH}_3(\text{aq}) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$ white ppt soluble $\text{NaCNS} + \text{FeCl}_3 \longrightarrow [\text{Fe}(\text{CNS})\text{Cl}]_2 + \text{NaCl}$ blood red colour



- Carbon and hydrogen present in the compound are oxidised to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively



- $\text{CO}_2$  and  $\text{H}_2\text{O}$  produced are weighed by absorbing in concentrated solution of potassium hydroxide and anhydrous calcium chloride (or) magnesium perchlorate respectively

$$\% \text{C} = \frac{12}{44} \times \frac{\text{weight of } \text{CO}_2 \text{ formed}}{\text{weight of organic compound}} \times 100$$

$$\% \text{H} = \frac{2}{18} \times \frac{\text{weight of } \text{H}_2\text{O} \text{ formed}}{\text{weight of organic compound}} \times 100$$

**Ex.5** On complete combustion, 0.246g of an organic compound gave 0.198 g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

**Sol.**  $\% \text{ of carbon} = \frac{12 \times 0.198 \times 100}{44 \times 0.246} = 21.95$

$$\% \text{ of hydrogen} = \frac{2 \times 0.1014 \times 100}{18 \times 0.246} = 4.58$$

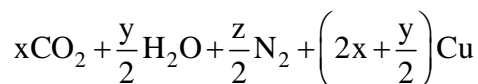
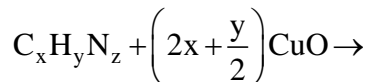
### ESTIMATION OF NITROGEN

Nitrogen present in organic compound is estimated by

- Dumas method
- Kjeldahl's method

#### (a) Dumas method

- In this method nitrogen present in the organic compound is converted in to  $\text{N}_2$  (molecular nitrogen)
- A weighed amount of organic compound is heated with cupric oxide in an atmosphere of carbon dioxide.
- Carbon and hydrogen present in the compound are oxidised to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , while  $\text{N}_2$  is at free.
- Some oxides of nitrogen formed are reduced to free nitrogen by passing over heated copper gauze



- Oxides of nitrogen +  $\text{Cu} \rightarrow \text{N}_2 + \text{CuO}$
- The mixture of gases produced is collected over caustic potash solution (KOH solution) which absorbs  $\text{CO}_2$ .
- Nitrogen is collected in the upper part of nitro meter.

$$\% \text{N} = \frac{28}{22400} \times \frac{\text{Volume of nitrogen in ml at STP}}{\text{Weight of organic compound}} \times 100$$

**Ex.6.** 0.25g of an organic compound gave 30 cm<sup>3</sup> of moist dinitrogen at 288 K and 745 mm pressure. Calculate the percentage of nitrogen. (Aqueous tension at 288 K = 12.7 mm)

**Sol.** Mass of the substance = 0.25 g

Volume of moist dinitrogen = 30 cm<sup>3</sup>

Temperature = 288 K

Pressure = 745 – 12.7 = 732.3 mm

Volume of dinitrogen at STP :

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{732.3 \times 30 \times 273}{288 \times 760} = 27.4 \text{ cm}^3$$

$$\text{Percentage of nitrogen in organic compound} = \frac{28}{22400} \times \frac{\text{vol of N}_2 \text{ at STP}}{\text{wt of organic compound}} \times 100$$

$$\frac{28}{22400} \times \frac{27.4}{0.25} \times 100 = 13.6$$

**Ex.7** 0.3g of an organic compound gave 50 ml nitrogen at 27°C and 715 mm pressure. If the aqueous tension at 27°C is 15 mm, calculate the percentage composition of nitrogen in the compound.

**Sol.** Mass of the substance = 0.3 g

Volume of the moist dinitrogen = 50 ml

Temperature = 27°C = 27 + 273 = 300 K

Pressure = 715 – 15 = 700 mm

Volume of dinitrogen at STP :

$$v_2 = \frac{P_1 V_1}{T_1} = \frac{T_2}{P_2} = \frac{700 \times 50 \times 273}{760 \times 300} = 41.9 \text{ ml}$$

$$\frac{28}{22400} \times \frac{\text{vol of N}_2 \text{ STP}}{\text{wt of organic compound}} \times 100 = \frac{28}{22400} \times \frac{41.9}{0.3} \times 100 = 17.46$$

22400 ml of dinitrogen at STP weight = 28 g

$$41.9 \text{ ml dinitrogen at STP weight} = \frac{28 \times 41.9}{22400} \text{ g}$$

$$0.3 \text{ g of organic compound contains } \frac{28 \times 41.9}{22400} \text{ g of N}_2$$

$$100 \text{ g of organic compound contain } \frac{28 \times 41.9}{22400} \times \frac{100}{0.3} = 17.46$$

percentage of nitrogen = 17.46

**Kjeldahl's Method :**

- In this method nitrogen in the organic compound is converted into ammonia ( $\text{NH}_3$ )
- A known mass of organic compound containing nitrogen is heated with concentrated sulphuric acid in presence of  $\text{K}_2\text{SO}_4$  and  $\text{CuSO}_4$  then nitrogen present in the compound is converted into ammonium sulphate.  $\text{K}_2\text{SO}_4$  increases boiling point of  $\text{H}_2\text{SO}_4$  and  $\text{CuSO}_4$  acts as catalyst.
- Organic compound +  $\text{H}_2\text{SO}_4 \longrightarrow (\text{NH}_4)_2\text{SO}_4$
- The resulting solution is distilled with excess of sodium hydroxide  
 $(\text{NH}_4)_2\text{SO}_4 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{NH}_3 + 2\text{H}_2\text{O}$
- Ammonia evolved is absorbed in a known but excess volume of standard  $\text{HCl}$  (or)  $\text{H}_2\text{SO}_4$  solution.
- The acid left unreacted is estimated by titration against standard solution of sodium hydroxide.


$$\text{Percentage of Nitrogen} = \frac{14}{1000} \times \frac{V \times N}{\text{wt. of organic compound}} \times 100$$

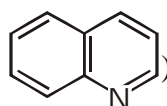
$$\%N = \frac{1.4 \times V \times N}{\text{Weight of organic compound}}$$

Where  $V$  = volume of acid in ml neutralised by ammonia

$N$  = Normality of acid.

- This method is simpler and more convenient
- It is mainly used to find percentage of nitrogen present in food stuffs, soils, fertilizers and various agricultural products.
- This method is not applicable to compounds containing nitro ( $-\text{NO}_2$ ), Nitroso ( $\text{NO}$ ), azo group

( $-\text{N}=\text{N}-$ ), azoxy compounds  $\left[ \begin{array}{c} \text{O} \\ \uparrow \\ -\text{N} = \text{N}- \end{array} \right]$  and nitrogen present in the ring (pyridine , quinoline



) because nitrogen present in these compounds is not quantitatively converted into ammonium sulphate.

**Ex.8** In Kjeldahl's estimation of nitrogen, the ammonia evolved from 0.5 g of an organic compound neutralised 10 ml of 1M  $\text{H}_2\text{SO}_4$ . Calculate the percentage of nitrogen in the compound?

**Sol.** 10 ml of 1M  $\text{H}_2\text{SO}_4 = 20\text{ml}$  of 1M  $\text{NH}_3$   
 1000 ml of 1M ammonia contains 14 g nitrogen

20 ml of 1M ammonia contains  $\frac{14 \times 20}{1000}$  g  $\text{N}_2$

$$\% \text{ of nitrogen} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0$$

**Ex.9** In Kjeldahl's estimation of nitrogen, the ammonia obtained from 0.5 g of an organic substance was passed

into 100 cm<sup>3</sup> of  $\frac{M}{10}$  NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.

**Sol.** m eq. of H<sub>2</sub>SO<sub>4</sub> taken = molarity x basicity x volume (ml)

$$= \frac{1}{10} \times 2 \times 100 = 20$$

$$\text{m.eq of NaOH} = \frac{1}{10} \times 1 \times 154 = 15.4$$

$$\text{m. eq of H}_2\text{SO}_4 \text{ unused} = 20 - 15.4 = 4.6$$

$$\% \text{ of nitrogen} = \frac{1.4 \times \text{meq of H}_2\text{SO}_4 \text{ unused}}{\text{wt of organic compound}} = \frac{1.4 \times 4.6}{0.5} = 12.88\%$$

### ESTIMATION OF HALOGENS CARIUS METHOD

- A weighed amount of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as carius tube.
- Carbon and hydrogen present in the compound is converted into CO<sub>2</sub> and H<sub>2</sub>O.
- Halogen present in the organic compound is converted into silver halide.
- The precipitate is washed, dried and weighed

$$\text{Percentage of halogen} = \frac{\text{Atomic weight of halogen}}{\text{Mwt of silver halide}} \times \frac{\text{Weight of silver halide formed}}{\text{Weight of organic compound}} \times 100$$

$$\% \text{Cl} = \frac{35.5}{143.5} \times \frac{\text{wt of AgCl formed}}{\text{wt of organic compound}} \times 100$$

$$\% \text{Br} = \frac{80}{188} \times \frac{\text{wt. of AgBr formed}}{\text{Wt. of organic compound}} \times 100$$

$$\% \text{I} = \frac{127}{235} \times \frac{\text{Wt. of AgI formed}}{\text{Wt. of organic compound}} \times 100$$

**Ex.10** In Carius method, 0.1890g of an organic compound gave 0.2870g of silver chloride. Calculate the percentage of chlorine in the compound

**Sol:** Weight of substance = 0.1890g

Weight of silver chloride = 0.2870g

$$\% \text{ of chlorine} = \frac{\text{weight of AgCl} \times 35.5 \times 100}{\text{weight of substance} \times 143.5} = \frac{0.2870 \times 35.5 \times 100}{0.1890 \times 143.5} = 37.8$$

**Ex.11** One gram of bromoalkane on heating with excess silver nitrate in Carius tube method gave 0.94g of yellow precipitate. What is the percent weight of halogen ?

**Sol.** Weight of substance = 1g Yellow precipitate is AgBr ; Weight of AgBr = 0.94g

$$\% \text{ of bromine} = \frac{0.94 \times 80 \times 100}{1 \times 188} = 40$$

**Ex.12** In carius method of estimation of halogen 0.15g of an organic compound gave 0.12g of AgBr. Find out the percentage of bromine in the compound

**Sol.**  $\% \text{ of bromine} = \frac{80 \times 0.12 \times 100}{188 \times 0.15} = 34.04$

#### Estimation of Sulphur Carius method:

- A weighed amount of organic compound is heated in a carius tube with sodium peroxide or fuming nitric acid.
- Sulphur present in the compound is oxidised into sulphuric acid, which is treated with  $\text{BaCl}_2$  solution gives precipitate of  $\text{BaSO}_4$ .
- It is filtered, the precipitate is washed, dried and weighed.

$$\% \text{S} = \frac{\text{Atomic wt of sulphur}}{\text{Mol. wt of BaSO}_4} \times \frac{\text{wt of BaSO}_4 \text{ formed}}{\text{wt of organic compound}} \times 100$$

$$\% \text{S} = \frac{32}{233} \times \frac{\text{wt of BaSO}_4 \text{ formed}}{\text{wt. of organic compound}} \times 100$$

**Ex.13** In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

**Sol.** 233 g  $\text{BaSO}_4$  contain 32g sulphur

$$0.4813 \text{g BaSO}_4 \text{ contain } \frac{32 \times 0.4813}{233} \text{ g sulphur}$$

$$\% \text{ of sulphur} = \frac{32 \times 0.4813 \times 100}{233 \times 0.157} = 42.10$$

**Ex.14** On heating 0.2g of an organic compound with a mixture of barium chloride and nitric acid, 0.466g of barium sulphate was obtained. Calculate the percentage of sulphur.

**Sol.** Weight of substance = 0.2 g

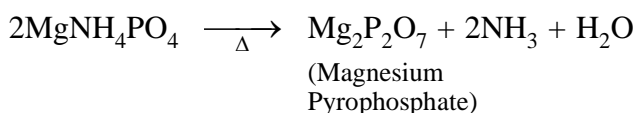
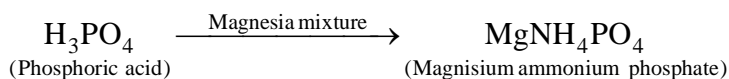
Weight of barium sulphate = 0.466 g

$$\text{Weight percentage of sulphur} = \frac{0.466 \times 32 \times 100}{0.2 \times 233} = 32$$

**Estimation of Phosphorus Carius Method :**

A weighed amount of organic compound is heated with fuming nitric acid, then phosphorus present in the compound is oxidised to phosphoric acid. Phosphoric acid is precipitated as magnesium ammonium phosphate ( $\text{Mg NH}_4 \text{PO}_4$ ), by addition of magnesia mixture ( $\text{MgCl}_2 + \text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ )

- Magnesium ammonium phosphate is washed, dried and it is heated strongly to get magnesium pyrophosphate ( $\text{Mg}_2\text{P}_2\text{O}_7$ ).



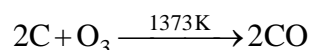
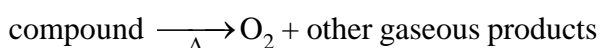
$$\% \text{P} = \frac{62}{222} \times \frac{\text{wt. of } \text{Mg}_2\text{P}_2\text{O}_7 \text{ formed}}{\text{wt. of organic compound}} \times 100$$

- Phosphoric acid is precipitated as ammonium phospho molybdate  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$  by adding ammonia and ammonium molybdate. (Molecular mass of  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 = 1877$ )

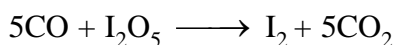
$$\% \text{P} = \frac{31}{1877} \times \frac{\text{wt of } (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \text{ formed}}{\text{wt of organic compound}} \times 100$$

**Estimation of oxygen .**

- Usually percentage of oxygen in organic compound is determined by method of difference % of oxygen = 100 – (sum of the percentages of all other elements)
- Oxygen present in the organic compound is estimated by Aluisse's method.
- A known amount of organic compound is subjected to pyrolysis in a stream of nitrogen.
- The mixture of gaseous products containing oxygen is passed over red-hot coke, then all the oxygen is converted in to carbon monoxide.



- CO formed is quantitatively converted in to  $\text{CO}_2$  by passing over warm Iodine pentoxide ( $\text{I}_2\text{O}_5$ )



The resulting gaseous mixture ( $\text{CO}_2$  and  $\text{I}_2$ ) is passed through potassium iodide solution, which absorbs iodine, and then passed over KOH to absorb  $\text{CO}_2$ .

$$\% \text{ of oxygen} = \frac{16}{44} \times \frac{\text{wt. of } \text{CO}_2 \text{ formed}}{\text{wt. of organic compound}} \times 100$$

**Ex.15** 0.2g of an organic compound on analysis gave 0.147g of carbon dioxide, 0.12g of water and 74.6 c.c of nitrogen at S.T.P. Calculate the weight percentages of constituents.

**Sol.** Weight of compound = W = 0.2g

Weight of  $\text{CO}_2 = W_1 = 0.147\text{g}$

Weight of  $\text{H}_2\text{O} = W_2 = 0.12\text{g}$

Volume of  $N_2$  at STP = 74.6 c.c.

$$\% \text{ of carbon} = \frac{W_1 \times 12 \times 100}{W \times 44} = \frac{0.147 \times 12 \times 100}{0.2 \times 44} = 20.04\%$$

$$\% \text{ of Hydrogen} = \frac{W_2 \times 2 \times 100}{W \times 18} = \frac{0.12 \times 2 \times 100}{0.2 \times 18} = 6.66\%$$

$$\% \text{ of Nitrogen} = \frac{W_2 \times 28 \times 100}{W \times 22400} = \frac{74.6}{8 \times 0.2} = 46.63\%$$

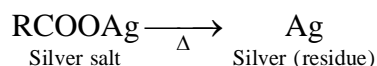
Remaining is oxygen.

$$\% \text{ of Oxygen} = 100 - (\%C + \%H + \%N) = 100 - 73.33 = 26.67\%$$

**Note :** Presently estimation of elements (C,H and N) in organic compound is estimated by using CHN elemental analyser by taking very small amount of substance (1-3 mg), results are displayed on screen with in short time.

#### Chemical Methods used to Find Molecular Mass Silver Salt Method for Acids :

Organic acid form insoluble silver salts, which on heating undergoes decomposition to leave a residue of metallic silver.



$$\frac{\text{Equivalent of silver salt}}{\text{Equivalent wt. of silver}} = \frac{\text{mass of silver salt}}{\text{Mass of silver}}$$

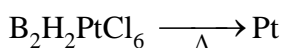
$$\frac{E + 108 - 1}{108} = \frac{\text{Mass of silver salt}}{\text{Mass of silver}}$$

$$E = \left[ \frac{\text{Mass of silver salt}}{\text{Mass of silver}} \times 108 \right] - 107$$

Molecular weight of acid = Equivalent weight of acid (E)  $\times$  basicity.

#### Platinic Chloride Method for Base

- Organic bases combines with chloroplatinic acid ( $H_2PtCl_6$ ) to form insoluble platinichloride, which on ignition gives metallic platinum.
- If 'B' is mono acidic base then formula of salt will be  $B_2H_2PtCl_6$ .



$$\frac{\text{Molecular mass of platinum salt}}{\text{Atomic mass of platinum}} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$$

If E is equivalent weight of base then

$$\frac{2E + 410}{195} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$$

$$E = \frac{1}{2} \left[ \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}} \times 195 - 410 \right]$$

Molecular mass of base = Equivalent mass of base x acidity

### Empirical formula

- The simplest whole number ratio between the atoms of various elements present in one molecule of a substance is called empirical formula.

### Calculation of Empirical Formula

The steps involved are

- Divide mass percentage of each element by its atomic mass, gives relative number of atoms.
- Simplest ratio is obtained when the figures obtained is divided by lowest number.
- If the simplest ratio obtained is not a whole number ratio, then multiply all the figures with suitable integer to get simplest whole number ratio.
- Write symbols of various elements side by side with above numbers at the lower right corner of each, which is empirical formula of compound.

### Molecular formula

The actual number of atoms present in one molecule of a substance is called molecular formula.

Molecular formula = (Empirical formula)<sub>n</sub>

where

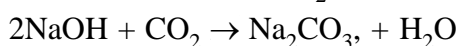
$$n = \frac{\text{Molecular wt of the compound}}{\text{Empirical formula weight of the compound}}$$

- If vapour density is given then molecular weight = 2 × vapour density.

### Determination of molecular formula of Gaseous Hydrocarbons (Eudiometry) :

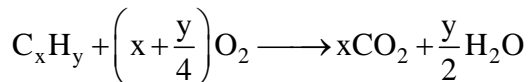
- Eudiometry is a direct method used to find molecular formula of gaseous hydrocarbon without finding percentage composition of elements and its molecular weight.
- A known volume of gaseous hydrocarbon is mixed with excess of pure and dry oxygen in eudiometer tube placed inverted in a trough of mercury.
- The mixture is exploded by passing an electric spark between platinum electrodes. As a result carbon and hydrogen of hydrocarbon are oxidised to CO<sub>2</sub> and H<sub>2</sub>O vapour respectively.
- The tube is allowed to cool to room temperature, then water vapour is condensed in to liquid water, whose volume occupied is almost negligible. Thus the gaseous mixture left in eudiometer tube is CO<sub>2</sub> and O<sub>2</sub>.
- Caustic potash solution is then introduced in to eudiometer tube which absorbs CO<sub>2</sub> completely.

The gas left is unused O<sub>2</sub> -





- Decrease in volume on introducing KOH solution gives volume of CO<sub>2</sub> used.
- Some times volume of O<sub>2</sub> left unused is found by introducing pyrogallol and noting the decrease in volume.
- Let molecular formula of gaseous hydrocarbon is C<sub>x</sub>H<sub>y</sub>. On combustion one volume of it forms x' volumes of CO<sub>2</sub> & 'y/2' volumes of water vapour.



- For 1 volume of hydrocarbon

$$\text{Volume of } O_2 \text{ used} = \left(x + \frac{y}{4}\right) \text{ vol}$$

$$\text{Volume of } CO_2 \text{ produced} = x \text{ vol.}$$

$$\text{Contraction on explosion and cooling} = 1 + \frac{y}{4} \text{ (volume of liquid water is neglected)}$$

#### Determination of Molecular mass by Victor Meyer's Method

- A known mass of the volatile substance is vapourised in victor meyer's method.
- The vapours obtained displaces an equal volume of air in to graduated tube.

- The volume of air displaced is calculated at STP condition by using  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\text{Mol. mass of volatile substance} = \frac{\text{Mass of substance taken}}{\text{Volume of air displaced in ml at STP}} \times 22400$$

## EXERCISE # O-I

1. Which of the following is monomer unit of polystyrene :-  
 (A)  $\text{CH}_2 = \underset{\text{CN}}{\text{CH}}$       (B)  $\text{CF}_2 = \text{CF}_2$       (C)  $\text{CH}_2 = \underset{\text{Cl}}{\text{CH}}$       (D)  $\underset{\text{C}_6\text{H}_5}{\text{CH}} = \text{CH}_2$   
**PL0001**
2. Weakest intermolecular forces are present in :-  
 (A) Neoprene      (B) Terylene      (C) Polystyrene      (D) Bakelite  
**PL0002**
3. Thermosetting polymer, Bakelite is formed by the reaction of phenol with :-  
 (A)  $\text{CH}_3\text{CH}_2\text{CHO}$       (B)  $\text{CH}_3\text{CHO}$       (C)  $\text{HCHO}$       (D)  $\text{HCOOH}$   
**PL0003**
4. Which one is classified as a condensation polymer?  
 (A) Teflon      (B) Acrylonitrile      (C) Dacron      (D) Neoprene  
**PL0004**
5. Novolac is a :  
 (A) linear polymer of urea and formaldehyde  
 (B) crosslink polymer of urea and formaldehyde  
 (C) linear polymer of phenol and formaldehyde  
 (D) crosslink polymer of phenol and formaldehyde  
**PL0005**
6. Which of the following is not a semisynthetic polymer.  
 (A) cis-polyisoprene      (B) cellulose nitrate  
 (C) cellulose acetate      (D) vulcanised rubber  
**PL0006**
7. Which one of the following polymers is prepared by condensation polymerization  
 (A) Styrene      (B) Nylon-6,6      (C) Teflon      (D) Rubber  
**PL0007**
8. Which of the following statement is not true :  
 (A) Natural rubber has the trans-configuration at every double bond.  
 (B) Buna-S is a copolymer of butadiene and styrene.  
 (C) Natural rubber is a 1, 4-polymer of isoprene.  
 (D) In vulcanization, the formation of sulphur bridges between different chains make rubber harder and stronger.  
**PL0008**
9. Structures of some common polymers are given. Which one is not correctly presented ?  
 (A) Nylon 66  $\text{-(NH(CH}_2)_6\text{NHCO(CH}_2)_4\text{-CO)-}_n$       (B) Teflon  $\text{-(CF}_2\text{-CF}_2\text{-)}_n$   
 (C) Neoprene  $\left( \text{-CH}_2\text{-}\underset{\text{Cl}}{\text{C}}\text{=CH-CH}_2\text{-CH}_2\text{-} \right)_n$       (D) Terylene  $\left( \text{OC-}\langle \text{O} \rangle\text{-COOCH}_2\text{-CH}_2\text{-O} \right)_n$   
**PL0009**

10. Of the following which one is classified as polyester polymer ?  
(A) Terylene (B) Bakelite  
(C) Malamine formaldehyde (D) Nylon-66  
PL0010
11. Which one of the following is not a condensation polymer?  
(A) Dacron (B) Neoprene (C) Melamineformaldehyde (D) Glyptal  
PL0011
12. Which of the following statements is false?  
(A) The repeat unit in natural rubber is isoprene  
(B) Both starch and cellulose are polymers of glucose  
(C) Artificial silk is derived from cellulose  
(D) Nylon-66 is an example of elastomer  
PL0012
13. Which one of the following sets forms the biodegradable polymer ?  
(A)  $\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH}$  &  $\text{HOOC} - \text{C}_6\text{H}_4 - \text{COOH}$   
(B)  $\text{C}_6\text{H}_5 - \text{CH} = \text{CH}_2$  and  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$   
(C)  $\text{CH}_2 = \text{CH} - \text{CN}$  and  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$   
(D)  $\text{H}_2\text{N} - \text{CH}_2 - \text{COOH}$  and  $\text{H}_2\text{N} - (\text{CH}_2)_5 - \text{COOH}$   
PL0013
14. Nylon is an example of :-  
(A) Polythene (B) Polyester (C) Polysaccharide (D) Polyamide  
PL0014

## EXERCISE # O-II

1. For the Separation of two immiscible liquids which method (or apparatus) is used?  
(1) Chromatography (2) Fractionating column  
(3) Fractional distillation (4) Separating funnel / Decantation  
**PO0001**
2. A mixture of benzene and chloroform is separated by  
(1) Sublimation (2) Separating funnel (3) Crystallization (4) Distillation  
**PO0002**
3. Which of the following has molecular weight of 92 ?  
(1) Toluene (2) Benzene (3) Methanol (4) Propene  
**PO0003**
4. Aniline is usually purified by  
(1) Chromatographic technique (2) Steam distillation  
(3) By addition of oxalic acid (4) Fractional crystallization  
**PO0004**
5. The most suitable method for separation of 1:1 mixture of ortho- and para- nitrophenols is  
(1) Sublimation (2) Chromatography (3) Crystallization (4) Steam distillation  
**PO0005**
6. Distillation under reduced pressure is employed for  
(1) Benzene (2) Petrol  
(3) Glycerol (4) Organic compounds used in medicine  
**PO0006**
7. Impure glycerine is purified by  
(1) Steam distillation (2) Simple distillation  
(3) Vacuum distillation (4) None of the above  
**PO0007**
8. Absolute alcohol is prepared by  
(1) Fractional distillation (2) Kolbe's method  
(3) Azeotropic distillation (4) Vacuum distillation  
**PO0008**
9. The latest technique used for purification for organic compounds in  
(1) Chromatography (2) Vacuum distillation  
(3) Fractional distillation (4) Crystallisation  
**PO0009**
10. In paper chromatography  
(1) Moving phase is liquid and stationary phase is solid  
(2) Moving phase is liquid and stationary phase is liquid

(3) Moving phase is solid and stationary phase is solid

(4) Moving phase is solid and stationary phase is liquid

**PO0010**

11. A is a lighter phenol and B is an aromatic carboxylic acid. Separation of mixture A and B can be carried out easily by using a solution of

(1) Sodium hydroxide

(2) Sodium sulphate

(3) Calcium chloride

(4) Sodium bicarbonate

**PO0011**

12. In sodium fusion test of organic compounds the nitrogen of the organic compound is converted into

(1) Sodamide

(2) Sodium cyanide

(3) Sodium nitrite

(4) Sodium nitrate

**PO0012**

13. The Lassaigne's extract is boiled with dil.  $\text{HNO}_3$  before testing for halogens because

(1) Silver halides are soluble in  $\text{HNO}_3$

(2)  $\text{Na}_2\text{S}$  and  $\text{NaCN}$  are decomposed by  $\text{HNO}_3$

(3)  $\text{Ag}_2\text{S}$  is soluble in  $\text{HNO}_3$

(4)  $\text{AgCN}$  is soluble in  $\text{HNO}_3$

**PO0013**

14. In a Lassaigne's test for nitrogen, the blue colour is due to the formation of

(1) Potassium ferricyanide

(2) Sodium cyanide

(3) Sodium ferrocyanide

(4) Ferri-ferro cyanide

**PO0014**

15. Which of the following compounds does not show Lassaigne test for nitrogen?

(1) Urea

(2) Hydrazine

(3) Phenyl hydrazine

(4) Azo benzene

**PO0015**

16. When piece of human hair are heated strongly with soda lime smell of ammonia can be detected. which one of the following conclusion can be drawn from this observation.

(1) Ammonia is present in human hair

(2) Ammonium salt is present in hair

(3) Hair contains amino acids

(4) None of the above

**PO0016**

17. The Beilstein test for organic compounds is used to detect

(1) Nitrogen

(2) Sulphur

(3) Carbon

(4) Halogen

**PO0017**

18. Which of the following is the best scientific method to test presence of water in liquid?

(1) Smell

(2) Taste

(3) Use of litmus paper

(4) Use of anhydrous copper sulphate

**PO0018**

19. Liebig's method is used for the estimation of

(1) Nitrogen

(2) Sulphur

(3) Carbon and hydrogen

(4) Halogens

**PO0019**

20. 0.765 gm of an acid gives 0.535 gm of  $\text{CO}_2$  and 0.138 gm of  $\text{H}_2\text{O}$ . Then the ratio of percentage of carbon and hydrogen is  
 (1) 19:2 (2) 18:11 (3) 20:17 (4) 1:7 **PO0020**
21. Nitrogen in an organic compound can be estimated by  
 (1) Kjeldahl's method only (2) Duma's method only  
 (3) Both the methods (4) none of these methods **PO0021**
22. Dumas method involves the determination of nitrogen content in the organic compound in form of  
 (1)  $\text{NH}_3$  (2)  $\text{N}_2$  (3)  $\text{NaCN}$  (4)  $(\text{NH}_4)_2\text{SO}_4$  **PO0022**
23. In Kjeldahl's method, nitrogen present is estimated as  
 (1)  $\text{N}_2$  (2)  $\text{NO}$  (3)  $\text{NH}_3$  (4)  $\text{NO}_2$  **PO0023**
24. The percentage of sulphur in an organic compound whose 0.32g produces 0.233g of  $\text{BaSO}_4$  [At.wt.Ba=137, S=32] is  
 (1) 1.0 (2) 10.0 (3) 23.5 (4) 32.1 **PO0024**
25. If 0.2 gram of an organic compound containing carbon, hydrogen and oxygen on combustion, yielded 0.147 gram carbon dioxide and 0.12 gram water. What will be the content of oxygen in the substance?  
 (1) 73.29% (2) 78.45% (3) 83.23% (4) 89.50% **PO0025**
26. If a compound on analysis was found to contain C=18.5%, H= 1.55 %, Cl=55.04% and Oxygen =24.81%, Then the empirical formula is  
 (1)  $\text{CHClO}$  (2)  $\text{CH}_2\text{ClO}$  (3)  $\text{C}_2\text{H}_2\text{OCl}$  (4)  $\text{ClCH}_2\text{O}$  **PO0026**
27. An organic compound contains C=40 %, H= 13.33% and N=46.6 %. Its empirical formula would be  
 (1)  $\text{CHN}$  (2)  $\text{C}_2\text{H}_2\text{N}$  (3)  $\text{CH}_4\text{N}$  (4)  $\text{C}_3\text{H}_7\text{N}$  **PO0027**
28. Two elements X (atomic weight =75) and Y(atomic weight=16) combine to give a compound having 75.8% X. The formula of the compound is  
 (1)  $\text{XY}$  (2)  $\text{X}_2\text{Y}$  (3)  $\text{X}_2\text{Y}_2$  (4)  $\text{X}_2\text{Y}_3$  **PO0028**
29. On analysis a saturated hydrocarbon is found to contain 83.70% carbon and 16.30% hydrogen. The empirical formula will be (at wt. of C=12, at. wt. of H=1)  
 (1)  $\text{C}_3\text{H}_6$  (2)  $\text{C}_3\text{H}_8$  (3)  $\text{C}_3\text{H}_4$  (4)  $\text{C}_6\text{H}_{12}$  **PO0029**
30. Empirical formula of a hydrocarbon containing 80% carbon and 20% hydrogen is  
 (1)  $\text{CH}$  (2)  $\text{CH}_2$  (3)  $\text{CH}_3$  (4)  $\text{CH}_4$  **PO0030**

31. An organic compound with C= 40% and H= 6.7% will have the empirical formula  
(1)  $\text{CH}_4$  (2)  $\text{CH}_2\text{O}$  (3)  $\text{C}_3\text{H}_6\text{O}_3$  (4)  $\text{C}_2\text{H}_4\text{O}_2$  **PO0031**
32. In a hydrocarbon, mass ratio of hydrogen and carbon 1:3, the empirical formula of hydrocarbon is  
(1)  $\text{CH}_4$  (2)  $\text{CH}_2$  (3)  $\text{C}_2\text{H}$  (4)  $\text{CH}_3$  **PO0032**
33. 8.24 g of a volatile liquid on vaporization gives 45 ml of vapours at NTP. What will be the vapour density of the substance? (Density of  $\text{H}_2=0.089 \text{ g L}^{-1}$ )  
(1) 95.39 (2) 39.95 (3) 99.53 (4) 59.93 **PO0033**
34. 0.1914 g of an organic acid is dissolved in about 20 ml of water. 25 ml of 0.12 N. NaOH is required for the complete neutralization of the acid solution. The equivalent weight of the acid is  
(1) 65.0 (2) 64.0 (3) 63.8 (4) 62.5 **PO0034**
35. The equivalent weight of an acid is equal to  
(1) Molecular weight x acidity (2) Molecular weight x basicity  
(3) Molecular weight /basicity (4) Molecular weight /acidity **PO0035**
36. Simple distillation can be used to separate liquids which differ in their boiling points at least by  
(1)  $5^\circ\text{C}$  (2)  $10^\circ\text{C}$  (3)  $35 - 50^\circ\text{C}$  (4)  $100^\circ\text{C}$  **PO0036**
37. Empirical formula of a compound is  $\text{CH}_2\text{O}$ . If its vapour density is 90, then the molecular formula of the compound is  
(1)  $\text{C}_5\text{H}_{10}\text{O}_5$  (2)  $\text{C}_3\text{H}_6\text{O}_3$  (3)  $\text{C}_6\text{H}_{12}\text{O}_6$  (4)  $\text{C}_4\text{H}_8\text{O}_4$  **PO0037**
38. The empirical formula of an acid is  $\text{CH}_2\text{O}_2$ , the probable molecular formula of the simplest acid may be  
(1)  $\text{CH}_2\text{O}$  (2)  $\text{CH}_2\text{O}_2$  (3)  $\text{C}_2\text{H}_4\text{O}_4$  (4)  $\text{C}_3\text{H}_6\text{O}_6$  **PO0038**
39. A gaseous hydrocarbon has 85% carbon and vapour density of 28. The possible formula of the hydrocarbon will be  
(1)  $\text{C}_3\text{H}_6$  (2)  $\text{C}_2\text{H}_4$  (3)  $\text{C}_2\text{H}_2$  (4)  $\text{C}_4\text{H}_8$  **PO0039**
40. a hydrocarbon has C=85.72% and remaining H. The hydrocarbon is  
(1)  $\text{C}_2\text{H}_4$  (2)  $\text{C}_2\text{H}_6$  (3)  $\text{C}_2\text{H}_2$  (4)  $\text{CH}_4$  **PO0040**

41. An organic compound containing carbon, hydrogen and oxygen contains 52.2 % carbon 13.04% hydrogen. Vapour density of the compound is 23. Its molecular formula will be  
 (1)  $C_2H_6O$  (2)  $C_3H_8O$  (3)  $C_4H_8O$  (4)  $C_5H_{10}O$  **PO0041**
42. percentage of Se(at.wt 78.4) in peroxidase anhydrase enzyme is 0.5% by weight, then minimum molecular weight of peroxidase anhydrase enzyme is  
 (1)  $1.568 \times 10^4$  (2)  $1.568 \times 10^3$   
 (3) 15.68 (4)  $2.136 \times 10^4$  **PO0042**
43. The empirical formula of a compound is  $CH_2$ . One of the compound has a mass of 42 g. its molecular formula is  
 (1)  $CH_2$  (2)  $C_2H_2$  (3)  $C_3H_6$  (4)  $C_3H_8$  **PO0043**
44. In a compound C, H and N atoms are present in 9:1:3.5 by weight. If molecular weight of the compound is 108, then the molecular formula of the compound is  
 (1)  $C_2H_6N_2$  (2)  $C_3H_4N$  (3)  $C_6H_8N_2$  (4)  $C_9H_{12}N_3$  **PO0044**
45. the following is the percentage composition of a compound. Na=16.08%, C=4.19% , O=16.78% , and  $H_2O = 62.95\%$ . Its molecular formula is  
 (1)  $Na_2CO_3$  (2)  $Na_2CO_3 \cdot H_2O$  (3)  $Na_2CO_3 \cdot 10H_2O$  (4)  $Na_2CO_3 \cdot 5H_2O$  **PO0045**
46. An organic compound contains 49.3% carbon, 6.84% hydrogen and its vapour density is 73. Empirical Formula of the compound is  
 (1)  $C_3H_5O_2$  (2)  $CH_{10}O_4$  (3)  $C_3H_{10}O_2$  (4)  $C_4H_{10}O_4$  **PO0046**
47. Molecular mass of a volatile substance may be obtained by  
 (1) Kjeldahl's method (2) Duma's method  
 (3) Victor meyer's method (4) Liebig's method **PO0047**
48. The most suitable method of separation of 1:1 mixture of ortho and para nitro phenol is  
 (1) Distillation (2) Crystallization (3) Sublimation (4) Chromatography **PO0048**
49. Kjeldahl's method can not be used for the estimation of Nitrogen in  
 (1) Pyridine (2) Nitro compounds (3) Azo compounds (4) All **PO0049**
50. In Kjeldahl's method nitrogen present is estimated as  
 (1)  $N_2$  (2)  $NH_3$  (3)  $NO_2$  (4) None **PO0050**



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**ANSWER KEY**

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**EXERCISE # O-I**

- |            |            |            |            |
|------------|------------|------------|------------|
| 1. Ans. D  | 2. Ans. A  | 3. Ans. C  | 4. Ans. C  |
| 5. Ans. C  | 6. Ans. A  | 7. Ans. B  | 8. Ans. A  |
| 9. Ans. C  | 10. Ans. A | 11. Ans. B | 12. Ans. D |
| 13. Ans. D | 14. Ans. D |            |            |

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**EXERCISE # O-II**

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- |            |            |            |            |
|------------|------------|------------|------------|
| 1. Ans. 4  | 2. Ans. 4  | 3. Ans. 1  | 4. Ans. 2  |
| 5. Ans. 4  | 6. Ans. 3  | 7. Ans. 3  | 8. Ans. 3  |
| 9. Ans. 1  | 10. Ans. 2 | 11. Ans. 4 | 12. Ans. 2 |
| 13. Ans. 2 | 14. Ans. 4 | 15. Ans. 2 | 16. Ans. 3 |
| 17. Ans. 4 | 18. Ans. 4 | 19. Ans. 3 | 20. Ans. 1 |
| 21. Ans. 3 | 22. Ans. 2 | 23. Ans. 3 | 24. Ans. 2 |
| 25. Ans. 1 | 26. Ans. 1 | 27. Ans. 3 | 28. Ans. 4 |
| 29. Ans. 2 | 30. Ans. 3 | 31. Ans. 2 | 32. Ans. 1 |
| 33. Ans. 4 | 34. Ans. 3 | 35. Ans. 3 | 36. Ans. 3 |
| 37. Ans. 3 | 38. Ans. 2 | 39. Ans. 4 | 40. Ans. 1 |
| 41. Ans. 1 | 42. Ans. 1 | 43. Ans. 3 | 44. Ans. 3 |
| 45. Ans. 3 | 46. Ans. 1 | 47. Ans. 3 | 48. Ans. 1 |
| 49. Ans. 4 | 50. Ans. 2 |            |            |



## SALT ANALYSIS

Analysis always does not mean breaking of substance into its ultimate constituents. Finding out the nature of substance and identity of its constituents is also analysis and is known as *qualitative analysis*. Qualitative analysis of inorganic salts means the identification of cations and anions present in the salt or a mixture of salts. Inorganic salts may be obtained by complete or partial neutralisation of acid with base or vice-versa. In the formation of a salt, the part contributed by the *acid* is called *anion* and the part contributed by the *base* is called *cation*. For example, in the salts  $\text{CuSO}_4$  and  $\text{NaCl}$ ,  $\text{Cu}^{2+}$  and  $\text{Na}^+$  ions are cations and  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions are anions. Qualitative analysis is carried out on various scales. Amount of substance employed in these is different. In macro analysis, 0.1 to 0.5 g of substance and about 20 mL of solution is used. For semimicro analysis, 0.05 g substance and 1 mL solution is needed while for micro analysis amount required is very small. Qualitative analysis is carried out through the reactions which are easily perceptible to our senses such as sight and smell. Such reactions involve:

- Formation of a precipitate
- Change in colour
- Evolution of gas etc.

Systematic analysis of an inorganic salt involves the following steps:

- Preliminary examination of solid salt and its solution.
- Determination of anions by reactions carried out in solution (wet tests) and confirmatory tests.
- Determination of cations by reactions carried out in solution (wet tests) and confirmatory tests.

Although these tests are not conclusive but sometimes they give quite important clues for the presence of certain anions or cations. These tests can be performed within  $10^{-15}$  minutes. These involve noting the general appearance and physical properties, such as colour, smell, solubility etc. of the salt. These are named as *dry tests*.

***Heating of dry salt, blow pipe test, flame tests, borax bead test, sodium carbonate bead test, charcoal cavity test etc. come under dry tests.***

Solubility of a salt in water and the pH of aqueous solutions give important information about the nature of ions present in the salt. If a solution of the salt is acidic or basic in nature, this means that it is being hydrolysed in water. If the solution is basic in nature then salt may be some carbonate or sulphide etc. If the solution shows acidic nature then it may be an acid salt or salt of weak base and strong acid. In this case it is best to neutralise the solution with sodium carbonate before testing it for anions.

Gases evolved in the preliminary tests with dil.  $\text{H}_2\text{SO}_4$ /dil.  $\text{HCl}$  and conc.  $\text{H}_2\text{SO}_4$  also give good indication about the presence of acid radicals (See Tables 1 and 3). ***Preliminary tests should always be performed before starting the confirmatory tests for the ions.***

**EXPERIMENT 1.1****Aim**

To detect one cation and one anion in the given salt from the following ions:

Cations -  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$

Anions -  $\text{CO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CH}_3\text{COO}^-$ .

(Insoluble salts to be excluded)

**Theory**

Two basic principles of great use in the analysis are:

- (i) the Solubility product
- (ii) the Common ion effect.

When ionic product of a salt exceeds its solubility product, precipitation takes place. Ionic product of salt is controlled by making use of common ion effect.

**Material Required**

- Boiling tube : As per need
- Test tubes : As per requirement
- Measuring cylinder : One
- Test tube stand : One
- Test tube holder : One
- Delivery tube : One
- Corks : As per need
- Filter paper : As per need
- Reagents : As per need

**Step - I :** Preliminary Test with Dilute Sulphuric Acid → In this test the action of dilute sulphuric acid (procedure is given below) on the salt is noted at room temperature and on warming.

Carbonate ( $\text{CO}_3^{2-}$ ), sulphide ( $\text{S}^{2-}$ ), sulphite ( $\text{SO}_3^{2-}$ ), nitrite ( $\text{NO}_2^-$ ) and acetate ( $\text{CH}_3\text{COO}^-$ ) react with dilute sulphuric acid to evolve different gases. Study of the characteristics of the gases evolved gives information about the anions. Summary of characteristic properties of gases is given in Table 1.

**Procedure**

(a) Take 0.1 g of the salt in a test tube and add 1–2 mL of dilute sulphuric acid. Observe the change, if any, at room temperature. If no gas is evolved, warm the content of the test tube. If gas is evolved test it by using the apparatus shown in Fig.1 and identify the gas evolved (See Table 1).

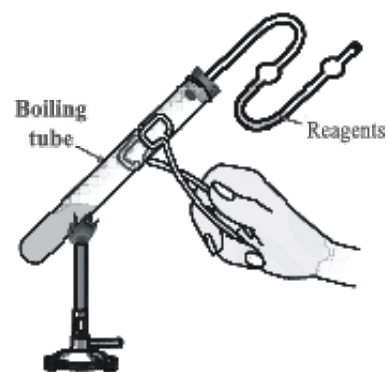


Fig. 1.1 Testing a Gas

Table 1 : Preliminary test with dilute sulphuric acid

Observations	Inference	
	Gas Evolved	Possible Anion
A colourless, odourless gas is evolved with brisk effervescence, which turns lime water milky.	CO <sub>2</sub>	Carbonate (CO <sub>3</sub> <sup>2-</sup> )
Colourless gas with the smell of rotten eggs is evolved which turns lead acetate paper black.	H <sub>2</sub> S	Sulphide (S <sup>2-</sup> )
Colourless gas with a pungent smell, like burning sulphur which turns acidified potassium dichromate solution green.	SO <sub>2</sub>	Sulphite (SO <sub>3</sub> <sup>2-</sup> )
Brown fumes which turn acidified potassium iodide solution containing starch solution blue.	NO <sub>2</sub>	Nitrite (NO <sub>2</sub> <sup>-</sup> )
Colourless vapours with smell of vinegar. Vapours turn blue litmus red.	CH <sub>3</sub> COOH vapours	Acetate, (CH <sub>3</sub> COO <sup>-</sup> )

### Confirmatory tests for CO<sub>3</sub><sup>2-</sup>, S<sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup>

*Confirmatory (wet) tests for anions are performed by using water extract when salt is soluble in water and by using sodium carbonate extract when salt is insoluble in water.* Confirmation of CO<sub>3</sub><sup>2-</sup> is done by using aqueous solution of the salt or by using solid salt as such because sodium carbonate extract contains carbonate ions. Water extract is made by dissolving salt in water. Preparation of sodium carbonate extract is given below.

#### Preparation of sodium carbonate extract

*Take 1 g of salt in a porcelain dish or boiling tube. Mix about 3 g of solid sodium carbonate and add 15 mL of distilled water to it. Stir and boil the content for about 10 minutes. Cool, filter and collect the filtrate in a test tube and label it as sodium carbonate extract.*

Confirmatory tests for acid radicals, which react with dilute sulphuric acid are given in Table 2.

**Table 2 : Confirmatory tests for  $\text{CO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{CH}_3\text{COO}^-$** 

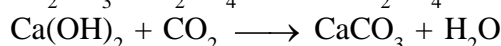
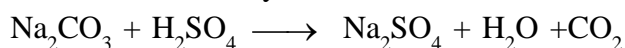
Anion	Confirmatory Test
Carbonate ( $\text{CO}_3^{2-}$ )	Take 0.1 g of salt in a test tube, add dilute sulphuric acid. $\text{CO}_2$ gas is evolved with brisk effervescence which turns lime water milky. On passing the gas for some more time, milkiness disappears.
Sulphide ( $\text{S}^{2-}$ )	Take 1 mL of water extract and make it alkaline by adding ammonium hydroxide or sodium carbonate extract. Add a drop of sodium nitroprusside solution. Purple or violet colouration appears.
Sulphite ( $\text{SO}_3^{2-}$ )	(a) Take 1 mL of water extract or sodium carbonate extract in a test tube and add barium chloride solution. A white precipitate is formed which dissolves in dilute hydrochloric acid and sulphur dioxide gas is also evolved (b) Take the precipitate of step (a) in a test tube and add a few drops of potassium permanganate solution acidified with dil. $\text{H}_2\text{SO}_4$ . Colour of potassium permanganate solution gets discharged.
Nitrite ( $\text{NO}_2^-$ )	(a) Take 1 mL of water extract in a test tube. Add a few drops of potassium iodide solution and a few drops of starch solution, acidify with acetic acid. Blue colour appears. (b) Acidify 1 mL of water extract with acetic acid. Add 2-3 drops of sulphanilic acid solution followed by 2-3 drops of 1-naphthylamine reagent. Appearance of red colour indicates the presence of nitrite ion.
Acetate, ( $\text{CH}_3\text{COO}^-$ )	(a) Take 0.1 g of salt in a china dish. Add 1 mL of ethanol and 0.2 mL conc. $\text{H}_2\text{SO}_4$ and heat. Fruity odour confirms the presence of acetate ion. (b) Take 0.1 g of salt in a test tube, add 1-2 mL distilled water, shake well filter if necessary. Add 1 to 2 mL neutral ferric chloride solution to the filtrate. Deep red colour appears which disappears on boiling and a brown-red precipitate is formed.

### Chemistry of Confirmatory Tests

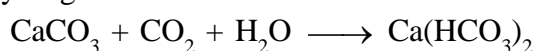
#### 1. Test for Carbonate ion [ $\text{CO}_3^{2-}$ ]

If there is effervescence with the evolution of a colourless and odourless gas on adding dil.  $\text{H}_2\text{SO}_4$  to the solid salt, this indicates the presence of carbonate ion.

The gas turns lime water milky due to the formation of  $\text{CaCO}_3$

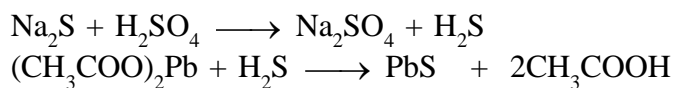


If  $\text{CO}_2$  gas is passed in excess through lime water, the milkiness disappears due to the formation of calcium hydrogen carbonate which is soluble in water.



#### 2. Test for Sulphide ion [ $\text{S}^{2-}$ ]

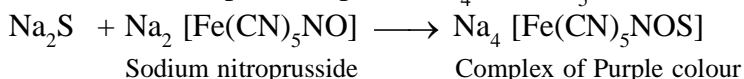
(a) With warm dilute  $\text{H}_2\text{SO}_4$  a sulphide gives hydrogen sulphide gas which smells like rotten eggs. A piece of filter paper dipped in lead acetate solution turns black on exposure to the gas due to the formation of lead sulphide which is black in colour.



Lead sulphide

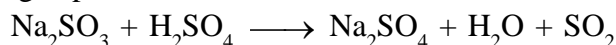
Black precipitate

(b) If the salt is soluble in water, take the solution of salt in water make it alkaline with ammonium hydroxide and add sodium nitroprusside solution. If it is insoluble in water take sodium carbonate extract and add a few drops of sodium nitroprusside solution. Purple or violet colouration due to the formation of complex compound  $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$  confirms the presence of sulphide ion in the salt.

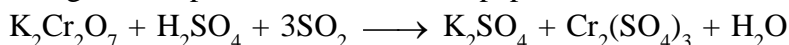


### 3. Test for Sulphite ion [ $\text{SO}_3^{2-}$ ]

(a) On treating sulphite with warm dil.  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_2$  gas is evolved which is suffocating with the smell of burning sulphur.



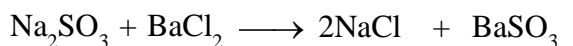
The gas turns potassium dichromate paper acidified with dil.  $\text{H}_2\text{SO}_4$ , green.



Chromium

sulphate (green)

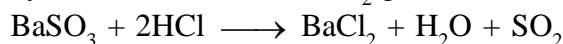
(b) An aqueous solution or sodium carbonate extract of the salt produces a white precipitate of barium sulphite on addition of barium chloride solution.



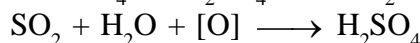
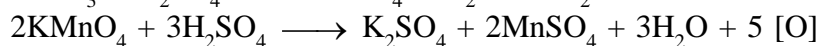
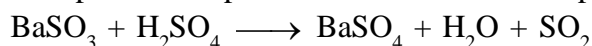
White ppt.

This precipitate gives following tests.

(i) This precipitate on treatment with dilute HCl, dissolves due to decomposition of sulphite by dilute HCl. Evolved  $\text{SO}_2$  gas can be tested.

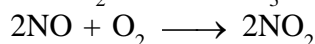
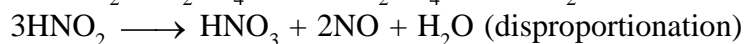
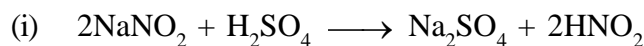


(ii) Precipitate of sulphite decolourises acidified potassium permanganate solution.

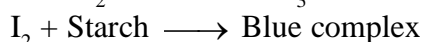
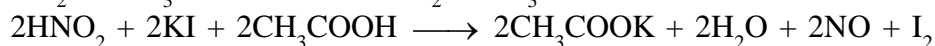
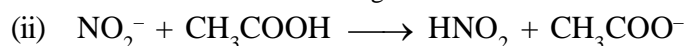


### 4. Test for Nitrite ion [ $\text{NO}_2^-$ ]

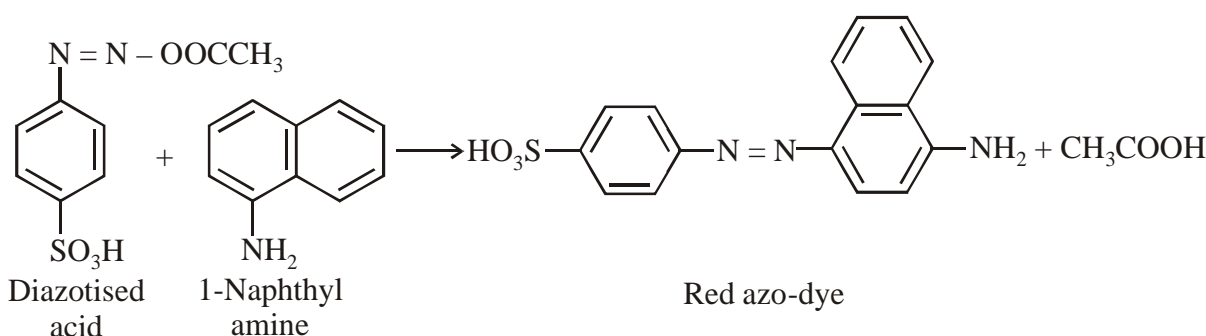
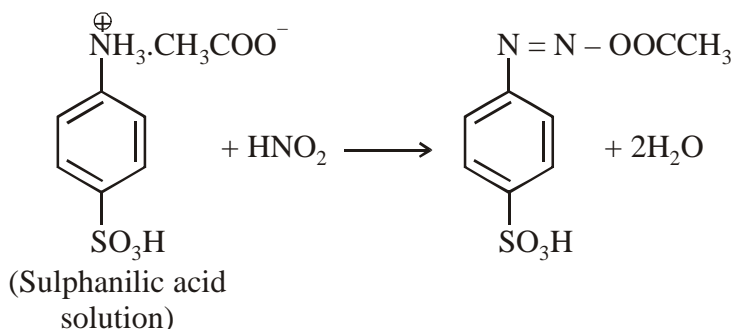
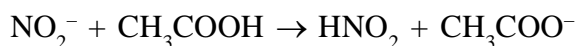
(a) On treating a solid nitrite with dil.  $\text{H}_2\text{SO}_4$  and warming, reddish brown fumes of  $\text{NO}_2$  gas are evolved. Addition of potassium iodide solution to the salt solution followed by freshly prepared starch solution and acidification with acetic acid produces blue colour. Alternatively, a filter paper moistened with potassium iodide and starch solution and a few drops of acetic acid turns blue on exposure to the gas, due to the interaction of liberated iodine with starch.



Brown gas



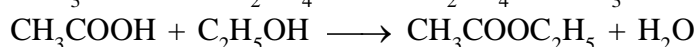
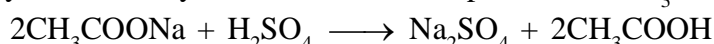
**(b) Sulphanilic acid — 1-naphthylamine reagent test (Griess-Ilosvay test) :** On adding sulphanilic acid and 1-naphthylamine reagent to the water extract or acidified with acetic acid, sulphanilic acid is diazotised in the reaction by nitrous acid formed. Diazotised acid couples with 1-naphthylamine to form a red azo-dye.



*The test solution should be very dilute. In concentrated solutions reaction does not proceed beyond diazotisation.*

### 5. Test for Acetate ion [ $\text{CH}_3\text{COO}^-$ ]

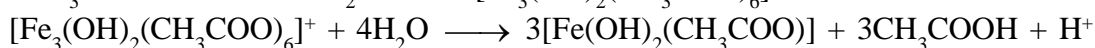
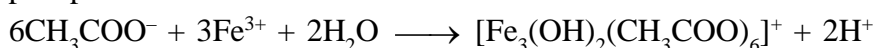
(a) If the salt smells like vinegar on treatment with dil.  $\text{H}_2\text{SO}_4$ , this indicates the presence of acetate ions. Take 0.1 g of salt in a china dish and add 1 mL of ethanol. Then add about 0.2 mL of conc.  $\text{H}_2\text{SO}_4$  and heat. Fruity odour of ethyl acetate indicates the presence of  $\text{CH}_3\text{COO}^-$  ion.



Ethylacetate

(Fruity odour)

(b) Acetate gives deep red colour on reaction with neutral ferric chloride solution due to the formation of complex ion which decomposes on heating to give Iron (III) dihydroxyacetate as brown red precipitate.



Iron(III)dihydroxyacetate

(Brown-red precipitate)

**Step-II :** Preliminary Test with Concentrated Sulphuric Acid If no positive result is obtained from dil.  $\text{H}_2\text{SO}_4$  test, take 0.1 g of salt in a test tube and 3-4 drops of conc.  $\text{H}_2\text{SO}_4$ . Observe the change in the reaction mixture in cold and then warm it. Identify the gas evolved on heating (see Table 3).



**Table 3 : Preliminary examination with concentrated sulphuric acid**

Observations	Inference	
	Gas/Vapours Evolved	Possible Anion
A colourless gas with pungent smell, which gives dense white fumes when a rod dipped in ammonium hydroxide is brought near the mouth of the test tube.	HCl	Chloride, ( $\text{Cl}^-$ )
Reddish brown gas with a pungent odour is evolved. Intensity of reddish gas increases on heating the reaction mixture after addition of solid $\text{MnO}_2$ to the reaction mixture. Solution also acquires red colour.	$\text{Br}_2$ vapours	Bromide, ( $\text{Br}^-$ )
Violet vapours, which turn starch paper blue and a layer of violet sublimate is formed on the sides of the tube. Fumes become dense on adding $\text{MnO}_2$ to the reaction mixture.	$\text{I}_2$ vapours	Iodide, ( $\text{I}^-$ )
Brown fumes evolve which become dense upon heating the reaction mixture after addition of copper turnings and the solution acquires blue colour.	$\text{NO}_2$	Nitrate, ( $\text{NO}_3^-$ )
Colourless, odourless gas is evolved which turns lime water milky and the gas coming out of lime water burns with a blue flame, if ignited.	CO and $\text{CO}_2$	Oxalate, ( $\text{C}_2\text{O}_4^{2-}$ )

Table 4 : Confirmatory tests for  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$  and  $\text{C}_2\text{O}_4^{2-}$ 

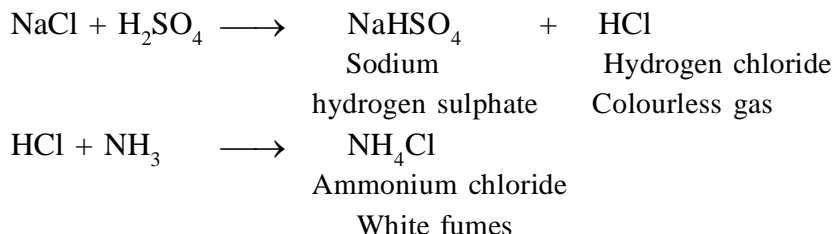
Anion	Confirmatory Test
Chloride ( $\text{Cl}^-$ )	<p>(a) Take 0.1 g of salt in a test tube, add a pinch of manganese dioxide and 3-4 drops of conc. sulphuric acid. Heat the reaction mixture. Greenish yellow chlorine gas is evolved which is detected by its pungent odour and bleaching action.</p> <p>(b) Take 1 mL of sodium carbonate extract in a test tube, acidify it with dil. <math>\text{HNO}_3</math> or take water extract and add silver nitrate solution. A curdy white precipitate is obtained which is soluble in ammonium hydroxide solution.</p> <p>(c) Take 0.1 g salt and a pinch of solid potassium dichromate in a test tube, add conc. <math>\text{H}_2\text{SO}_4</math>, heat and pass the gas evolved through sodium hydroxide solution. It becomes yellow. Divide the solution into two parts. Acidify one part with acetic acid and add lead acetate solution. A yellow precipitate is formed. Acidify the second part with dilute sulphuric acid and add 1 mL of amyl alcohol followed by 1 mL of 10% hydrogen peroxide. After gentle shaking the organic layer turns blue.</p>
Bromide ( $\text{Br}^-$ )	<p>(a) Take 0.1 g of salt and a pinch of <math>\text{MnO}_2</math> in a test tube. Add 3-4 drops conc. sulphuric acid and heat. Intense brown fumes are evolved.</p> <p>(b) Neutralise 1 mL of sodium carbonate extract with hydrochloric acid (or take the water extract). Add 1 mL carbon tetrachloride (<math>\text{CCl}_4</math>)/chloroform (<math>\text{CHCl}_3</math>)/ carbon disulphide. Now add an excess of chlorine water dropwise and shake the test tube. A brown colouration in the organic layer confirms the presence of bromide ion.</p> <p>(c) Acidify 1 mL of sodium carbonate extract with dil. <math>\text{HNO}_3</math> (or take 1 mL water extract) and add silver nitrate solution. A pale yellow precipitate soluble with difficulty in ammonium hydroxide solution is obtained.</p>
Iodide ( $\text{I}^-$ )	<p>(a) Take 1 mL of salt solution neutralised with <math>\text{HCl}</math> and add 1 mL chloroform/carbon tetrachloride/carbon disulphide. Now add an excess of chlorine water drop wise and shake the test tube. A violet colour appears in the organic layer.</p> <p>(b) Take 1 mL of sodium carbonate extract acidify it with dil. <math>\text{HNO}_3</math> (or take water extract). Add, silver nitrate solution. A yellow precipitate insoluble in <math>\text{NH}_4\text{OH}</math> solution is obtained.</p>

Anion	Confirmatory Test
*Nitrate ( $\text{NO}_3^-$ )	Take 1 mL of salt solution in water in a test tube. Add 2 mL of conc. $\text{H}_2\text{SO}_4$ and mix thoroughly. Cool the mixture under the tap. Add freshly prepared ferrous sulphate along the sides of the test tube without shaking. A dark brown ring is formed at the junction of the two solutions.
Oxalate ( $\text{C}_2\text{O}_4^{2-}$ )	<p>(a) Take 1 mL of water extract or sodium carbonate extract acidified with acetic acid and add calcium chloride solution. A white precipitate insoluble in ammonium oxalate and oxalic acid solution but soluble in dilute hydrochloric acid and dilute nitric acid is formed.</p> <p>(b) Take the precipitate from test (a) and dissolve it in dilute <math>\text{H}_2\text{SO}_4</math>. Add very dilute solution of <math>\text{KMnO}_4</math> and warm. Colour of <math>\text{KMnO}_4</math> solution is discharged. Pass the gas coming out through lime water. The lime water turns milky.</p>

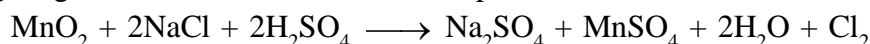
### Chemistry of Confirmatory Tests

#### 1. Test for Chloride ion [Cl<sup>-</sup>]

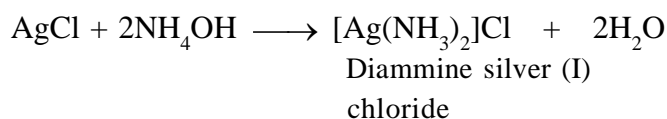
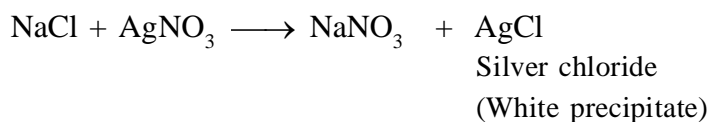
(a) If on treatment with warm conc. H<sub>2</sub>SO<sub>4</sub> the salt gives a colourless gas with pungent smell or if the gas which gives dense white fumes with ammonia solution, then the salt may contain Cl<sup>-</sup> ions and the following reaction occurs.



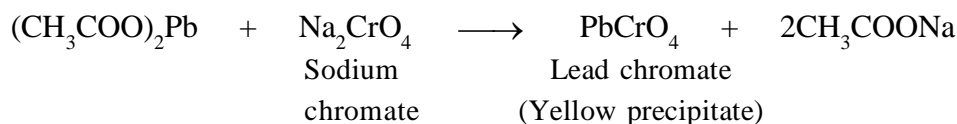
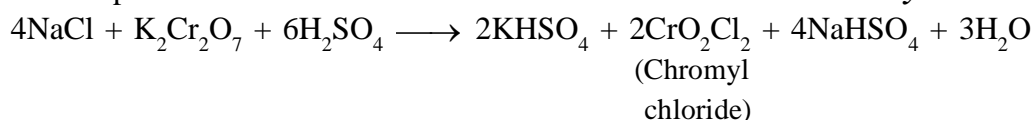
(b) If a salt gives effervescence on heating with conc. H<sub>2</sub>SO<sub>4</sub> and MnO<sub>2</sub> and a light greenish yellow pungent gas is evolved, this indicates the presence of Cl<sup>-</sup> ions.



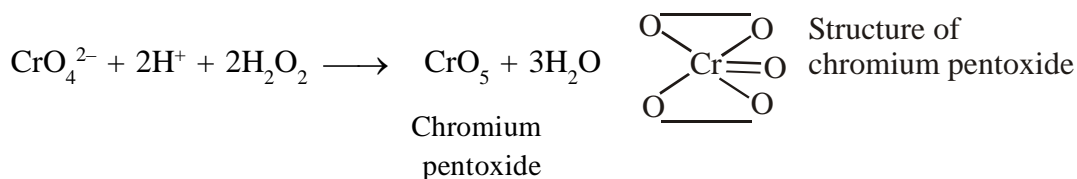
(c) Salt solution acidified with dilute HNO<sub>3</sub> on addition of silver nitrate solution gives a curdy white precipitate soluble in ammonium hydroxide solution. This indicates the presence of Cl<sup>-</sup> ions in the salt.



(d) Mix a little amount of salt and an equal amount of solid potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) in a test tube and add conc. H<sub>2</sub>SO<sub>4</sub> to it. Heat the test tube and pass the evolved gas through sodium hydroxide solution. If a yellow solution is obtained, divide the solution into two parts. Acidify the first part with acetic acid and then add lead acetate solution. Formation of a yellow precipitate of lead chromate confirms the presence of chloride ions in the salt. This test is called **chromyl chloride test**.

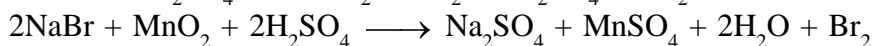
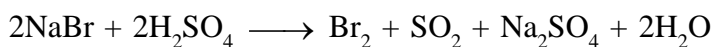


Acidify the second part with dilute sulphuric acid and add small amounts of amyl alcohol and then 1 mL of 10% hydrogen peroxide solution. On gentle shaking organic layer turns blue. CrO<sub>4</sub><sup>2-</sup> ion formed in the reaction of chromyl chloride with sodium hydroxide reacts with hydrogen peroxide to form chromium pentoxide (CrO<sub>5</sub>) (See structure) which dissolves in amyl alcohol to give blue colour.

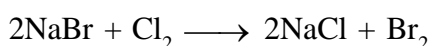


## 2. Test for Bromide ion ( $\text{Br}^-$ )

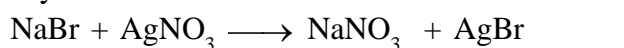
If on heating the salt with conc.  $\text{H}_2\text{SO}_4$  reddish brown fumes of bromine are evolved in excess, this indicates the presence of  $\text{Br}^-$  ions. The fumes get intensified on addition of  $\text{MnO}_2$ . Bromine vapours turn starch paper yellow.



(a) Add 1 mL of carbon tetrachloride ( $\text{CCl}_4$ )/chloroform ( $\text{CHCl}_3$ ) and excess of freshly prepared chlorine water dropwise to the salt solution in water or sodium carbonate extract neutralised with dilute  $\text{HCl}$ . Shake the test tube vigorously. The appearance of an orange brown colouration in the organic layer due to the dissolution of bromine in it, confirms the presence of bromide ions.



(b) Acidify the sodium carbonate extract of the salt with dil.  $\text{HNO}_3$ . Add silver nitrate ( $\text{AgNO}_3$ ) solution and shake the test tube. A pale yellow precipitate is obtained which dissolves in ammonium hydroxide with difficulty.

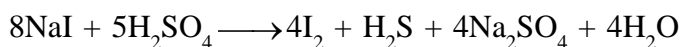
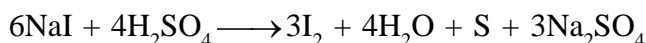
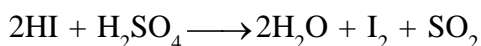
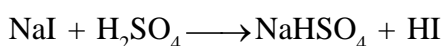
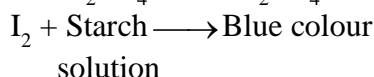
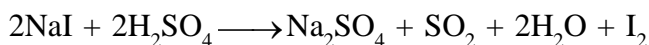


Silver bromide

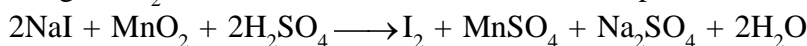
Pale yellow precipitate

## 3. Test for Iodide ion ( $\text{I}^-$ )

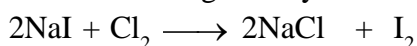
(a) If on heating the salt with conc.  $\text{H}_2\text{SO}_4$ , deep violet vapours with a pungent smell are evolved. These turns starch paper blue and a violet sublimate is formed on the sides of the test tube, it indicates the presence of  $\text{I}^-$  ions. Some  $\text{HI}$ , sulphur dioxide, hydrogen sulphide, and sulphur are also formed due to the following reactions.



On adding  $\text{MnO}_2$  to the reaction mixture, the violet vapours become dense.

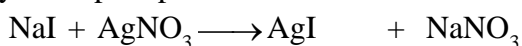


(b) Add 1 mL of  $\text{CHCl}_3$  or  $\text{CCl}_4$  and chlorine water in excess to the salt solution in water or sodium carbonate extract neutralised with dil.  $\text{HCl}$  and shake the test tube vigorously. Presence of violet colouration in the organic layer confirms the presence of iodide ions.



Iodine dissolves in the organic solvent and the solution becomes violet.

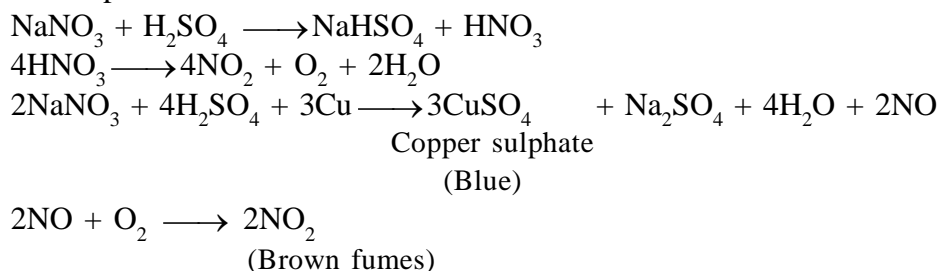
(c) Acidify sodium carbonate extract of the salt with dil.  $\text{HNO}_3$  and add  $\text{AgNO}_3$  solution. Appearance of a yellow precipitate insoluble in excess of  $\text{NH}_4\text{OH}$  confirms the presence of iodide ions.



silver iodide

(Yellow precipitate)

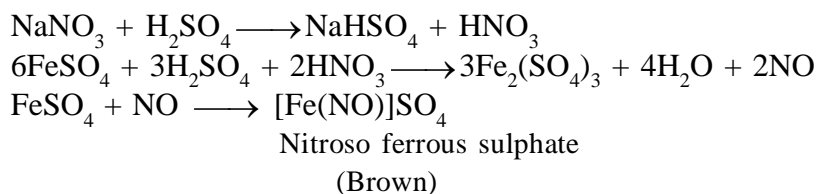
(a) If on heating the salt with conc.  $\text{H}_2\text{SO}_4$  light brown fumes are evolved then heat a small quantity of the given salt with few copper turnings or chips and conc.  $\text{H}_2\text{SO}_4$ . Evolution of excess of brown fumes indicates the presence of nitrate ions. The solution turns blue due to the formation of copper sulphate.



(b) Take 1 mL of an aqueous solution of the salt and add 2 mL conc.  $\text{H}_2\text{SO}_4$  slowly. Mix the solutions thoroughly and cool the test tube under the tap. Now, add freshly prepared ferrous sulphate solution along the sides of the test tube dropwise so that it forms a layer on the top of the liquid already present in the test tube. A dark brown ring is formed at the junction of the two solutions due to the formation of nitroso ferrous sulphate (Fig. 1.2). Alternatively first ferrous sulphate is added and then concentrated sulphuric acid is added.

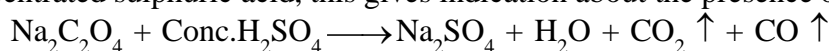


Fig. 1.2 : Formation of brown ring



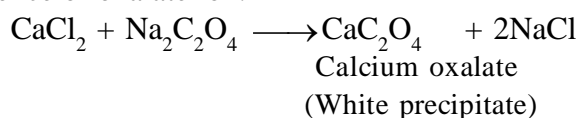
### 5. Test for Oxalate ion $[\text{C}_2\text{O}_4^{2-}]$

If carbon dioxide gas along with carbon monoxide gas is evolved in the preliminary examination with concentrated sulphuric acid, this gives indication about the presence of oxalate ion.



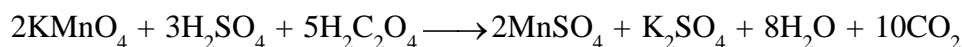
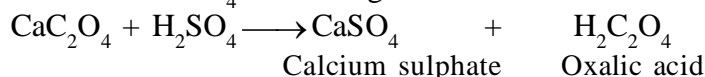
Oxalate is confirmed by the following tests:

(a) Acidify sodium carbonate extract with acetic acid and add calcium chloride solution. A white precipitate of calcium oxalate, insoluble in ammonium oxalate and oxalic acid solution indicates the presence of oxalate ion.



### (b) $\text{KMnO}_4$ test

Filter the precipitate from test (a). Add dil.  $\text{H}_2\text{SO}_4$  to it followed by dilute  $\text{KMnO}_4$  solution and warm. Pink colour of  $\text{KMnO}_4$  is discharged:



Pass the gas evolved through lime water. A white precipitate is formed which dissolves on passing the gas for some more time.

### Step-III : Test for Sulphate and Phosphate

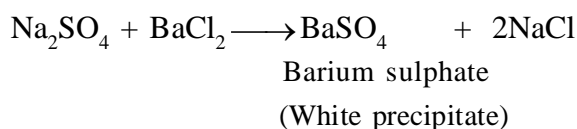
If no positive test is obtained in Steps-I and II, then tests for the presence of sulphate and phosphate ions are performed. These tests are summarised in Table 5.

**Table 5 : Confirmatory tests for Sulphate and Phosphate**

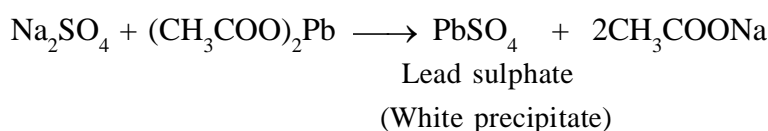
Ion	Confirmatory Test
Sulphate ( $\text{SO}_4^{2-}$ )	(a) Take 1 mL water extract of the salt in water or sodium carbonate and after acidifying with dilute hydrochloric acid add $\text{BaCl}_2$ solution. White precipitate insoluble in conc. $\text{HCl}$ or conc. $\text{HNO}_3$ is obtained. (b) Acidify the aqueous solution or sodium carbonate extract with acetic acid and add lead acetate solution. Appearance of white precipitate confirms the presence of $\text{SO}_4^{2-}$ ion.
Phosphate ( $\text{PO}_4^{3-}$ )	(a) Acidify sodium carbonate extract or the solution of the salt in water with conc. $\text{HNO}_3$ and add ammonium molybdate solution and heat to boiling. A canary yellow precipitate is formed.

#### 1. Test of Sulphate ions [ $\text{SO}_4^{2-}$ ]

(a) Aqueous solution or sodium carbonate extract of the salt acidified with acetic acid on addition of barium chloride gives a white precipitate of barium sulphate insoluble in conc.  $\text{HCl}$  or conc.  $\text{HNO}_3$ .

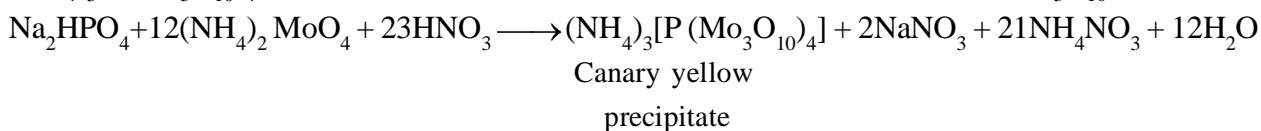


(b) Sulphate ions give white precipitate of lead sulphate when aqueous solution or sodium carbonate extract neutralised with acetic acid is treated with lead acetate solution.



#### 2. Test for Phosphate ion [ $\text{PO}_4^{3-}$ ]

(a) Add conc.  $\text{HNO}_3$  and ammonium molybdate solution to the test solution containing phosphate ions and boil. A yellow colouration in solution or a canary yellow precipitate of ammonium-phosphomolybdate,  $(\text{NH}_4)_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$  is formed. Each oxygen of phosphate has been replaced by  $\text{Mo}_3\text{O}_{10}$  group.



## HEATING DEVICES

Heating during the laboratory work can be done with the help of a gas burner, spirit lamp or a kerosene lamp. The gas burner used in the laboratory is usually Bunsen burner. Various parts of Bunsen burner are shown in Fig. The description of these parts is as follows :

### (A) Parts of Bunsen Burner

#### 1. The Base

Heavy metallic base is connected to a side tube called gas tube. Gas from the source enters the burner through the gas tube and passes through a small hole called Nipple or Nozzle and enters into the burner tube under increased pressure and can be burnt at the upper end of the burner tube.

#### 2. The Burner Tube

It is a long metallic tube having two holes diametrically opposite to each other near the lower end which form the air vent. The tube can be screwed at the base. The gas coming from the nozzle mixes with the air coming through the air vent and burns at its upper end.

#### 3. The Air Regulator

It is a short metallic cylindrical sleeve with two holes diametrically opposite to each other. When it is fitted to the burner tube, it surrounds the air vent of the burner tube. To control the flow of air through the air vent, size of its hole is adjusted by rotating the sleeve.

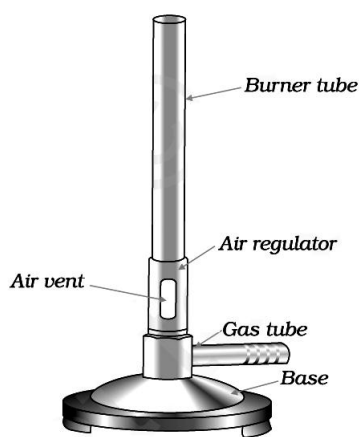


Fig. Bunsen burner

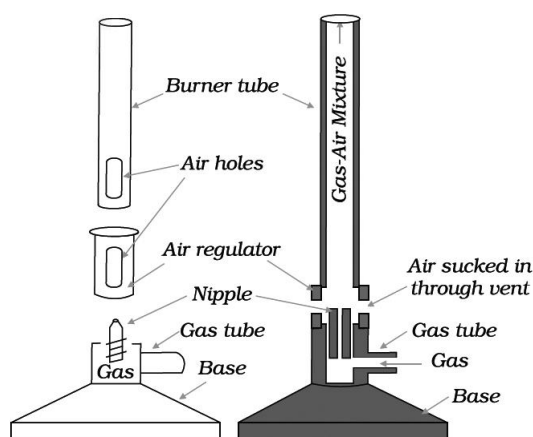
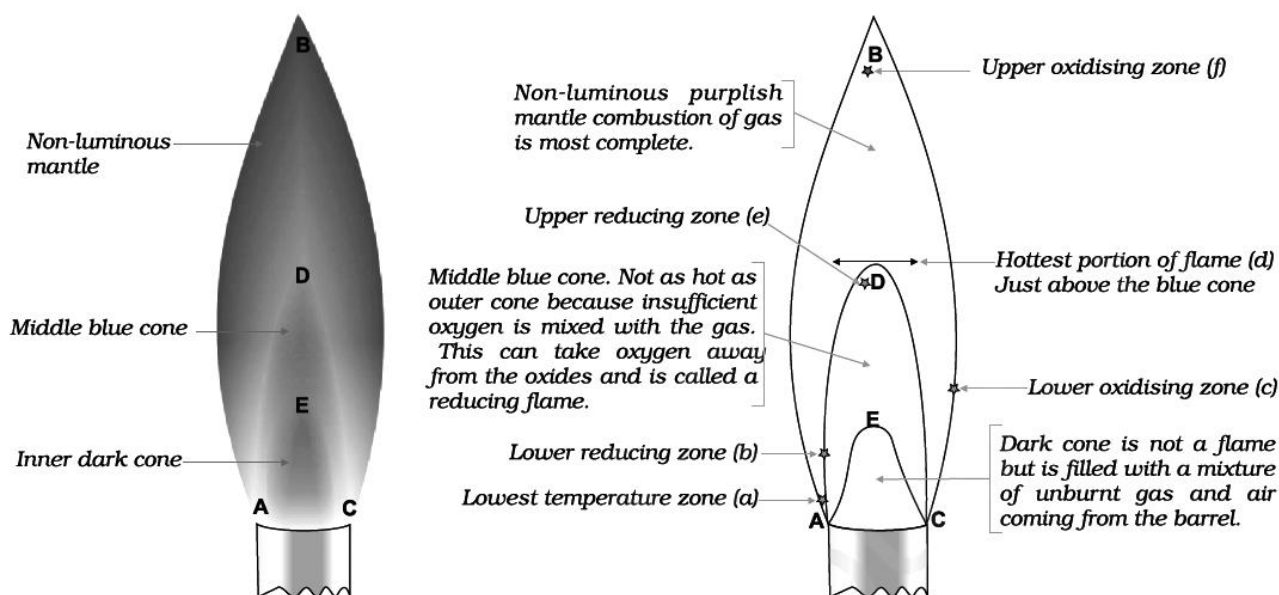


Fig. Parts of Bunsen burner

If the air vent is closed and the gas is ignited, the flame will be large and luminous (smoky and yellow in colour). The light emitted by the flame is due to the radiations given off by the hot carbon particles of partially burnt fuel. The temperature of the flame in this situation is low. If adjustment of sleeve on vent is such that gas mixed with air is fed into the flame, the flame becomes less luminous and finally turns blue. When the flow of air is correctly adjusted, the temperature of the flame becomes quite high. This is called non-luminous flame. Various zones of flame are shown below in Fig.

Three distinctly visible parts of the Bunsen flame are described below :



**Fig. 1.13** : Zones of flame of Bunsen burner

## (B) PRINCIPAL PARTS OF BUNSEN FLAME

### 1. The Inner Dark Cone, A E C

This is innermost dark cone, which is just above the burner tube. It consists of unburnt gases. This zone is the coldest zone of the flame and no combustion takes place here.

### 2. The Middle Blue Cone, A D C E A

This is middle part of the flame. This becomes luminous when the air vent is slightly closed. Luminosity of this part is due to the presence of unburnt carbon particles produced by decomposition of some gas. These particles get heated up to incandescence and glow but do not burn. Since the combustion is not complete in this part, the temperature is not very high.

### 3. The Outer Non-luminous Mantle, A B C D A

This is purplish outer cone. It is the hottest part of the flame. It is in direct contact with the atmosphere and combustion is quite complete in this zone.

**Bunsen identified six different regions in these three principal parts of the flame:**

#### (i) The upper oxidising zone (f)

Its location is in the non-luminous tip of the flame which is in the air. In comparison to inner portions of the flame large excess of oxygen is present here. The temperature is not as high as in region (c) described below. It may be used for all oxidation processes in which highest temperature of the flame is not required.

#### (ii) Upper reducing zone (e)

This zone is at the tip of the inner blue cone and is rich in incandescent carbon. It is especially useful for reducing oxide incrustations to the metals.

#### (iii) Hottest portion of flame (d)

It is the fusion zone. It lies at about one-third of the height of the flame and is approximately equidistant from inside and outside of the mantle i.e. the outermost cone of the flame. Fusibility of the substance can be tested in this region. It can also be employed for testing relative volatility of substances or a mixture of substances.



(iv) **Lower oxidising zone (c)**

It is located on the outer border of the mantle near the lower part of the flame and may be used for the oxidation of substances dissolved in beads of borax or sodium carbonate etc.

(v) **Lower reducing zone (b)**

It is situated in the inner edge of the outer mantle near to the blue cone and here reducing gases mix with the oxygen of the air. It is a less powerful reducing zone than (e) and may be employed for the reduction of fused borax and similar beads.

(vi) **Lowest temperature zone (a)**

Zone (a) of the flame has lowest temperature. It is used for testing volatile substances to determine whether they impart colour to the flame.

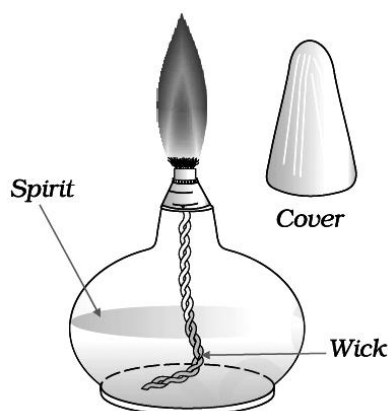
### (C) STRIKING BACK OF THE BUNSEN BURNER

Striking back is the phenomenon in which flame travels down the burner tube and begins to burn at the nozzle near the base. This happens when vents are fully open. The flow of much air and less gas makes the flame become irregular and it strikes back.

The tube becomes very hot and it may produce burns on touching. This may melt attached rubber tube also. If it happens, put off the burner and cool it under the tap and light it again by keeping the air vent partially opened.

### SPIRIT LAMP

If Bunsen burner is not available in the laboratory then spirit lamp can be used for heating. It is a device in which one end of a wick of cotton thread is dipped in a spirit container and the other end of the wick protrudes out of the nozzle at upper end of the container. Spirit rises upto the upper end of the wick due to the capillary action and can be burnt. The flame is non luminous hence can be used for all heating purposes in the laboratory. To put off the lamp, burning wick is covered with the cover. **Never try to put off the lighted burner by blowing at the flame.**



**Fig. 1.14 : The spirit lamp**

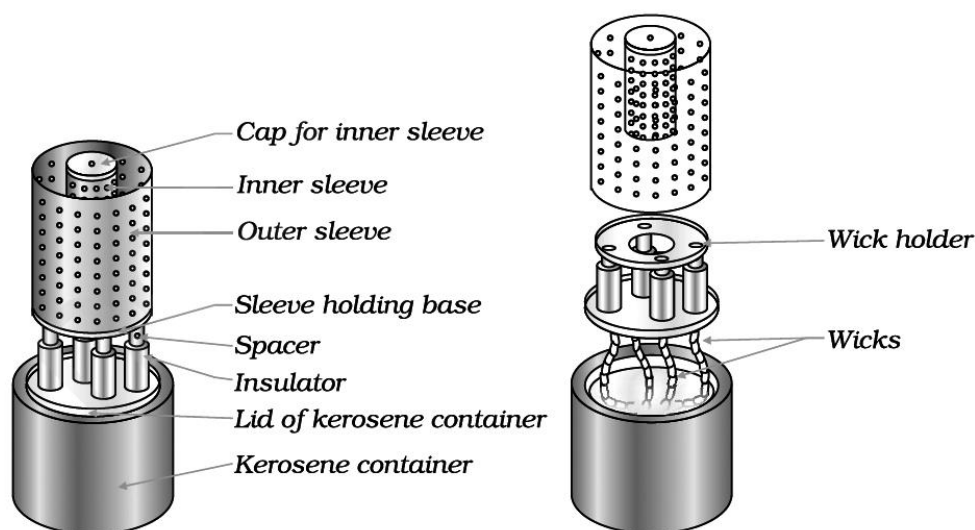
### KEROSENE HEATING LAMP

A kerosene lamp has been developed by National Council of Educational Research and Training (NCERT), which is a versatile and cheaper substitute of spirit lamp. It may be used in laboratories as a source of heat wherever spirit and gas burner are not available. Parts of kerosene lamp are shown in Fig.

### Working of the Kerosene Lamp

More than half of the container is filled with kerosene. Outer sleeve is removed for lighting the wicks. As the outer sleeve is placed back in position, the flames of four wicks combine to form a big soot-free blue flame.

The lighted heating lamp can be put off only by covering the top of the outer sleeve with a metal or asbestos sheet.



**Fig. 1.15** : Parts of Kerosene Heating Lamp

### SYSTEMATIC ANALYSIS OF CATIONS

The tests for cations may be carried out according to the following scheme.

#### Step - I : Preliminary Examination of the Salt for Identification of Cation

##### 1. Colour Test

Observe the colour of the salt carefully, which may provide useful information about the cations. Table 6 gives the characteristic colours of the salts of some cations.

**Table 6** Characteristic colours of the some metal ions

Ion	Confirmatory Test
Light green	$\text{Fe}^{2+}$
Yellowish Brown	$\text{Fe}^{3+}$
Blue	$\text{Cu}^{2+}$
Bright green	$\text{Ni}^{2+}$
Blue, Red Violet, Pink	$\text{Co}^{2+}$
Light pink	$\text{Mn}^{2+}$

##### 2. Dry Heating Test

(i) Take about 0.1 g of the dry salt in a clean and dry test tube.

(ii) Heat the above test tube for about one minute and observe the colour of the residue when it is hot and also when it becomes cold. Observation of changes gives indications about the presence of cations, which may not be taken as conclusive evidence (see Table 7).

Table 7 : Inferences from the colour of the salt in cold and on heating

Colour when cold	Colour when hot	Inference
Blue	White	$\text{Cu}^{2+}$
Green	Dirty white or yellow	$\text{Fe}^{2+}$
White	Yellow	$\text{Zn}^{2+}$
Pink	Blue	$\text{Co}^{2+}$

3. Flame Test

The chlorides of several metals impart characteristic colour to the flame because they are volatile in non-luminous flame. This test is performed with the help of a platinum wire as follows :

- (i) Make a tiny loop at one end of a platinum wire.
- (ii) To clean the loop dip it into concentrated hydrochloric acid and hold it in a non-luminous flame (Fig. 1.3).
- (iii) Repeat step (ii) until the wire imparts no colour to the flame.
- (iv) Put 2-3 drops of concentrated hydrochloric acid on a clean watch glass and make a paste of a small quantity of the salt in it.
- (v) Dip the clean loop of the platinum wire in this paste and introduce the loop in the non-luminous (oxidising) flame (Fig. 1.3).
- (vi) Observe the colour of the flame first with the naked eye and then through a blue glass and identify the metal ion with the help of Table 8.

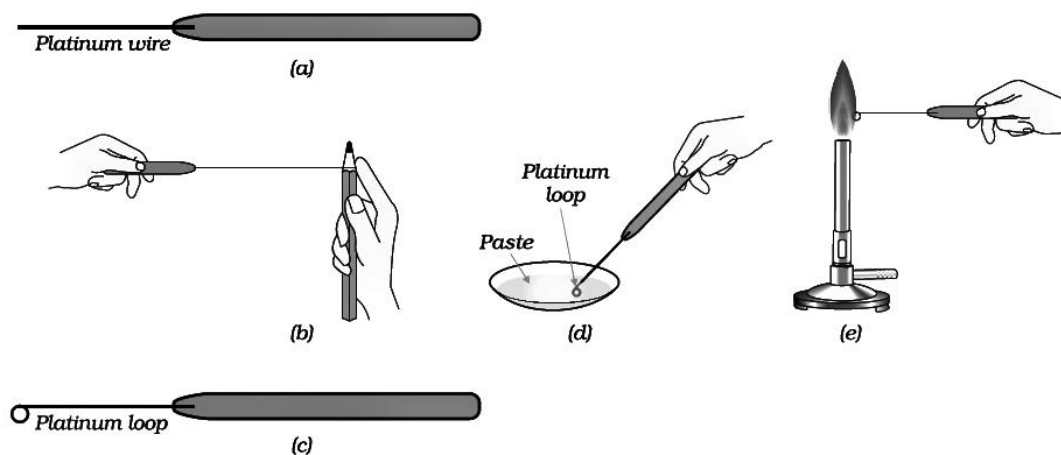


Fig. 1.3 : Performing flame test

Table 8 : Inference from the flame test

Colour fo the flame observed by naked eye	Colour of the flame observed through blue glass	Inference
Green flame with blue centre	Same colour as observed without glass	$\text{Cu}^{2+}$
Crimson red	Purple	$\text{Sr}^{2+}$
Apple green	Bluish green	$\text{Ba}^{2+}$
Brick red	Green	$\text{Ca}^{2+}$

#### 4. Borax Bead Test

This test is employed only for coloured salts because borax reacts with metal salts to form metal borates or metals, which have characteristic colours.

(i) To perform this test make a loop at the end of the platinum wire and heat it in a flame till it is red hot.

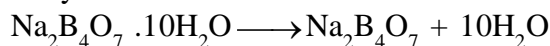
(ii) Dip the hot loop into borax powder and heat it again until borax forms a colourless transparent bead on the loop. Before dipping the borax bead in the test salt or mixture, confirm that the bead is transparent and colourless. If it is coloured this means that, the platinum wire is not clean. Then make a fresh bead after cleaning the wire.

(iii) Dip the bead in a small quantity of the dry salt and again hold it in the flame.

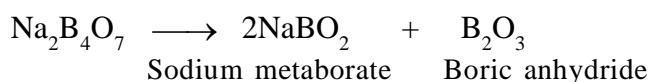
(iv) Observe the colour imparted to the bead in the non-luminous flame as well as in the luminous flame while it is hot and when it is cold (Fig. 1.4).

(v) To remove the bead from the platinum wire, heat it to redness and tap the platinum wire with your finger. (Fig.1.5).

On heating, borax loses its water of crystallisation and decomposes to give sodium metaborate and boric anhydride.

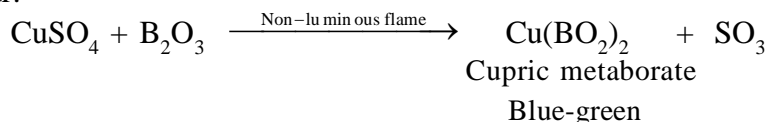


Borax



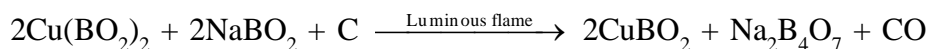
Sodium metaborate      Boric anhydride

On treatment with metal salt, boric anhydride forms metaborate of the metal which gives different colours in oxidising and reducing flame. For example, in the case of copper sulphate, following reactions occur.

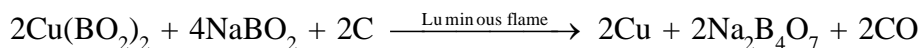


Two reactions may take place in the reducing flame:

(i) The blue  $\text{Cu}(\text{BO}_2)_2$  is reduced to colourless cuprous metaborate as follows:



or (ii) Cupric metaborate may be reduced to metallic copper and the bead appears red and opaque.



The preliminary identification of metal ion can be made from Table 9.

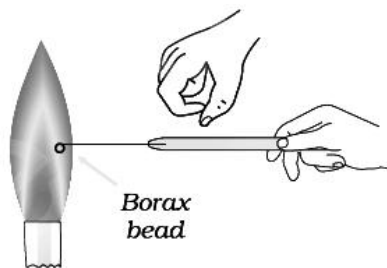


Fig. 1.5 : Removing borax bead

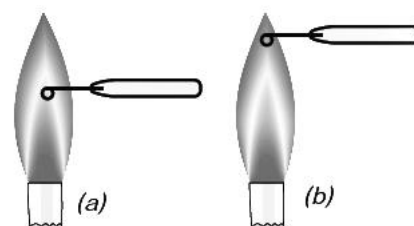


Fig. 1.4 : Borax bead test  
(a) Heating in reducing flame (b) Heating in oxidising flame

Table 9 : Inference from the borax bead test

Heating in oxidising (non-luminous) flame		Heating in reducing (luminous) flame		Inference
Colour of the salt bead		Colour of the salt bead		
In cold	In hot	In cold	In hot	
Blue	Green	Red opaque	Colourless	$\text{Cu}^{2+}$
Reddish brown	Violet	Grey	Grey	$\text{Ni}^{2+}$
Light violet	Light violet	Colourless	Colourless	$\text{Mn}^{2+}$
Yellow	Yellowish brown	Green	Green	$\text{Fe}^{3+}$

### 5. Charcoal Cavity Test

Metallic carbonate when heated in a charcoal cavity decomposes to give corresponding oxide. The oxide appears as a coloured residue in the cavity. Sometimes oxide may be reduced to metal by the carbon of the charcoal cavity.

The test may be performed as follows:

- Make a small cavity in a charcoal block with the help of a charcoal borer [Fig.1.6 (a)].
- Fill the cavity with about 0.2 g of the salt and about 0.5 g of anhydrous sodium carbonate.

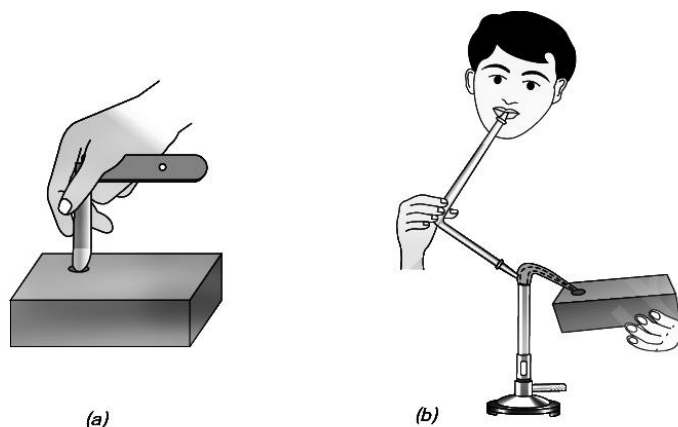


Fig. 1.6 : (a) Making charcoal cavity (b) Heating salt in the cavity

- Moisten the salt in the cavity with one or two drops of water, otherwise salt/mixture will blow away.
- Use a blowpipe to heat the salt in a luminous (reducing) flame and observe the colour of oxide/metallic bead formed in the cavity both when hot and cold [ Fig. (1.6 b)]. Obtain oxidising and reducing flame as shown in Fig. 1.7 a and b.
- Always bore a fresh cavity for testing the new salt.

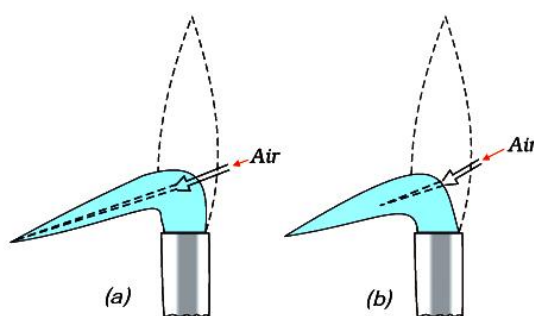
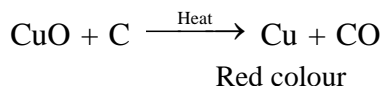
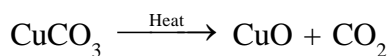
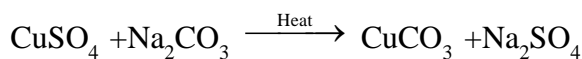
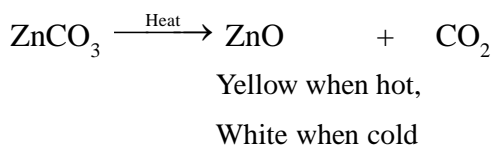
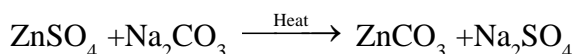


Fig. 1.7 : Obtaining oxidising and reducing flame  
(a) Oxidising flame; and (b) Reducing flame

When test is performed with  $\text{CuSO}_4$ , the following change occurs.



In case of  $\text{ZnSO}_4$  :



The metal ion can be inferred from Table 10.

**Table 10 : Inference from the charcoal cavity test**

Observations	Inference
Yellow residue when hot and grey metal when cold	$\text{Pb}^{2+}$
White residue with the odour of garlic	$\text{As}^{3+}$
Brown residue	$\text{Cd}^{2+}$
Yellow residue when hot and white when cold	$\text{Zn}^{2+}$

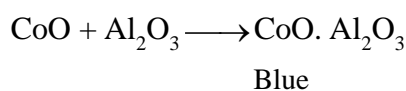
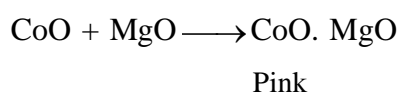
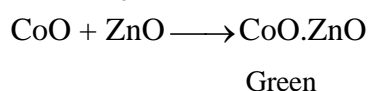
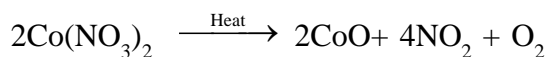
## 6. Cobalt Nitrate Test

If the residue in the charcoal cavity is white, cobalt nitrate test is performed.

- (i) Treat the residue with two or three drops of cobalt nitrate solution.
- (ii) Heat it strongly in non-luminous flame with the help of a blow pipe and observe the colour of the residue.

On heating, cobalt nitrate decomposes into cobalt (II) oxide, which gives a characteristic colour with metal oxide present in the cavity.

Thus, with  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ , the following reactions occur.



**Step-II : Wet Tests for Identification of Cations**

The cations indicated by the preliminary tests given above are confirmed by systematic analysis given below.

The first essential step is to prepare a clear and transparent solution of the salt. This is called original solution. It is prepared as follows:

**Preparation of Original Solution (O.S.)**

To prepare the original solution, following steps are followed one after the other in a systematic order. In case the salt does not dissolve in a particular solvent even on heating, try the next solvent.

The following solvents are tried:

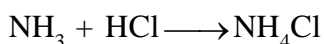
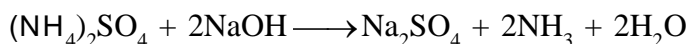
1. Take a little amount of the salt in a clean boiling tube and add a few mL of distilled water and shake it. If the salt does not dissolve, heat the content of the boiling tube till the salt completely dissolves.
2. If the salt is insoluble in water as detailed above, take fresh salt in a clean boiling tube and add a few mL of dil.HCl to it. If the salt is insoluble in cold, heat the boiling tube till the salt is completely dissolved.
3. If the salt does not dissolve either in water or in dilute HCl even on heating, try to dissolve it in a few mL of conc. HCl by heating.
4. If salt does not dissolve in conc. HCl, then dissolve it in dilute nitric acid.
5. If salt does not dissolve even in nitric acid then a mixture of conc. HCl and conc. HNO<sub>3</sub> in the ratio 3 : 1 is tried. This mixture is called aqua regia. A salt not soluble in aqua regia is considered to be an insoluble salt.

**Group Analysis****(I) Analysis of Zero group cation (NH<sub>4</sub><sup>+</sup> ion)**

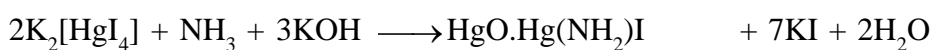
- (a) Take 0.1 g of salt in a test tube and add 1-2 mL of NaOH solution to it and heat. If there is a smell of ammonia, this indicates the presence of ammonium ions. Bring a glass rod dipped in hydrochloric acid near the mouth of the test tube. White fumes are observed.
- (b) Pass the gas through Nessler's reagent. Brown precipitate is obtained.

**Chemistry of Confirmatory Tests for NH<sub>4</sub><sup>+</sup> ion**

(a) Ammonia gas evolved by the action of sodium hydroxide on ammonium salts reacts with hydrochloric acid to give ammonium chloride, which is visible as dense white fume.



On passing the gas through Nessler's reagent, a brown colouration or a precipitate of basic mercury(II) amido-iodine is formed.



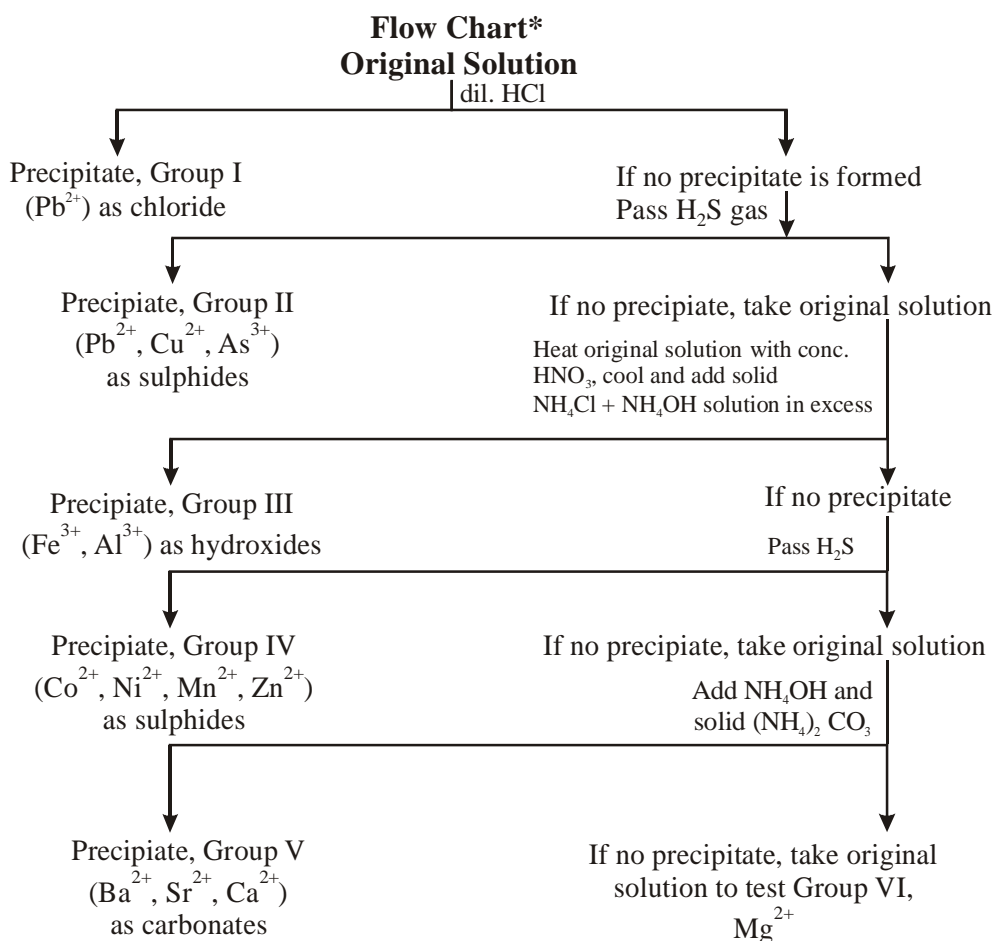
Basic mercury (II)

amido-iodine

(Brown precipitate)

For the analysis of cations belonging to groups I-VI, the cations are precipitated from the original solution by using the group reagents (see Table 1.11) according to the scheme shown in the flow chart given below:

The separation of all the six groups is represented as below :



**Table 11 : Group reagents for precipitating ions**

Group	Cations*	Group Reagent
Group zero	$\text{NH}_4^+$	None
Group - I	$\text{Pb}^{2+}$	Dilute HCl
Group - II	$\text{Pb}^{2+}, \text{Cu}^{2+}, \text{As}^{3+}$	$\text{H}_2\text{S}$ gas in presence of dil. HCl
Group - III	$\text{Al}^{3+}, \text{Fe}^{3+}$	$\text{NH}_4\text{OH}$ in presence of $\text{NH}_4\text{Cl}$
Group - IV	$\text{Co}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}$	$\text{H}_2\text{S}$ in presence of $\text{NH}_4\text{OH}$
Group - V	$\text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}$	$(\text{NH}_4)_2\text{CO}_3$ in presence of $\text{NH}_4\text{OH}$
Group - VI	$\text{Mg}^{2+}$	None



**(II) Analysis of Group-I cations**

Take a small amount of original solution (if prepared in hot conc. HCl) in a test tube and add cold water to it and cool the test tube under tap water. If a white precipitate appears, this indicates the presence of  $\text{Pb}^{2+}$  ions in group -I. On the other hand, if the original solution is prepared in water and on addition of dil. HCl, a white precipitate appears, this may also be  $\text{Pb}^{2+}$ . Confirmatory tests are described below in Table 12.

**Table 12 : Confirmatory tests for Group-I cation ( $\text{Pb}^{2+}$ )**

Experiment	Observation
Dissolve the precipitate in hot water and divide the hot solution into three parts, 1. Add potassium iodide solution to the first part. 2. To the second part add potassium chromate solution. 3. To the third part of the hot solution add few drops of alcohol and dilute sulphuric acid.	A yellow precipitate is obtained. A yellow precipitate is obtained which is soluble, in NaOH and insoluble in ammonium acetate solution. A white precipitate is obtained which is soluble in ammonium acetate solution.

**Chemistry of the Confirmatory Tests of  $\text{Pb}^{2+}$  ions**

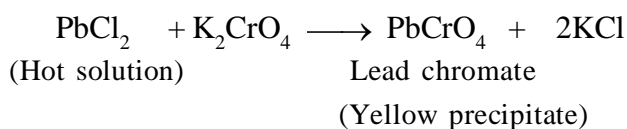
Lead is precipitated as lead chloride in the first group. The precipitate is soluble in hot water.

- On adding potassium iodide (KI) solution, a yellow precipitate of lead iodide is obtained which confirms the presence of  $\text{Pb}^{2+}$  ions.

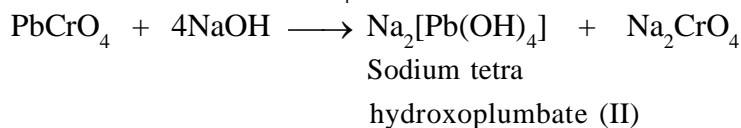


This yellow precipitate ( $\text{PbI}_2$ ) is soluble in boiling water and reappears on cooling as shining crystals.

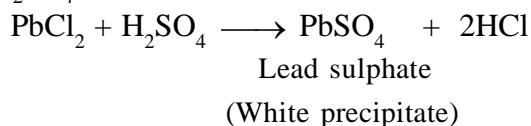
- On addition of potassium chromate ( $\text{K}_2\text{CrO}_4$ ) solution a yellow precipitate of lead chromate is obtained. This confirms the presence of  $\text{Pb}^{2+}$  ions.



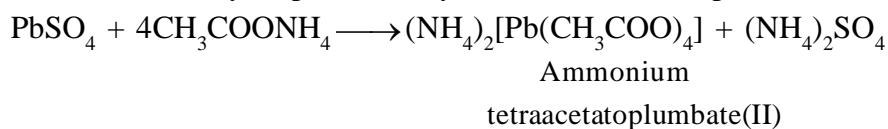
The yellow precipitate ( $\text{PbCrO}_4$ ) is soluble in hot NaOH solution.



- A white precipitate of lead sulphate ( $\text{PbSO}_4$ ) is formed on addition of alcohol followed by dil.  $\text{H}_2\text{SO}_4$ .



Lead sulphate is soluble in ammonium acetate solution due to the formation of tetraacetatoplumbate(II) ions. This reaction may be promoted by addition of few drops of acetic acid.



**(III) Analysis of Group-II cations**

If group-I is absent, add excess of water to the same test tube. Warm the solution and pass  $H_2S$  gas for 1-2 minutes (Fig. 1.6). Shake the test tube. If a precipitate appears, this indicates the presence of group-II cations. Pass more  $H_2S$  gas through the solution to ensure complete precipitation and separate the precipitate. If the colour of the precipitate is black, it indicates the presence of  $Cu^{2+}$  or  $Pb^{2+}$  ions.

If it is yellow in colour, then presence of  $As^{3+}$  ions is indicated.

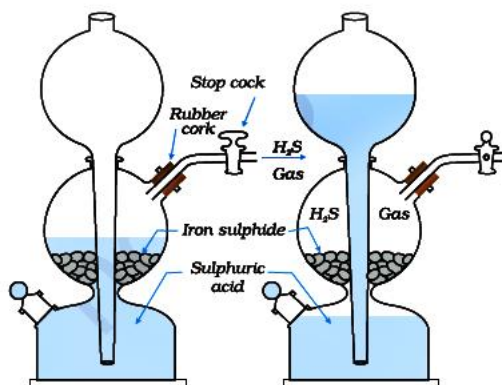


Fig. 1.8 : Kipp's apparatus for preparation of  $H_2S$  gas

Take the precipitate of group-II in a test tube and add excess of yellow ammonium sulphide solution to it. Shake the test tube. If the precipitate is insoluble, group II-A (copper group) is present. If the precipitate is soluble, this indicates the presence of group-II B (arsenic group).

Confirmatory tests for the groups II A and II B are given in Table 13.

**Table 13 : Confirmatory tests for the groups II A and II B cations**

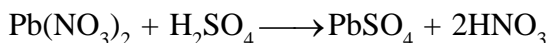
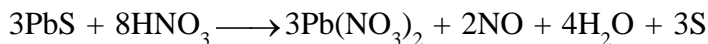
Black precipitate of Group II A ions $Pb^{2+}$ , $Cu^{2+}$ (insoluble in yellow ammonium sulphide) is formed.	If a yellow precipitate soluble in yellow ammonium sulphide is formed then $As^{3+}$ ion is present.
Boil the precipitate of Group II A with dilute nitric acid and add a few drops of alcohol and dil. $H_2SO_4$ .	Acidify this solution with dilute HCl. A yellow precipitate is formed. Heat the precipitate with concentrated nitric acid and add ammonium molybdate solution. A canary yellow precipitate is formed.
<p>White precipitate confirms the presence of <math>Pb^{2+}</math> ions. Dissolve the precipitate in ammonium acetate solution. Acidify with acetic acid and divide the solution into two parts.</p> <p>(i) To the first part add potassium chromate solution, a yellow precipitate is formed.</p> <p>(ii) To the second part, add potassium iodide solution, a yellow precipitate is formed.</p>	If no precipitate is formed, add excess of ammonium hydroxide solution. A blue solution is obtained, acidify it with acetic acid and add potassium ferrocyanide solution. A chocolate brown precipitate is formed.

**Group-II A (Copper Group)**

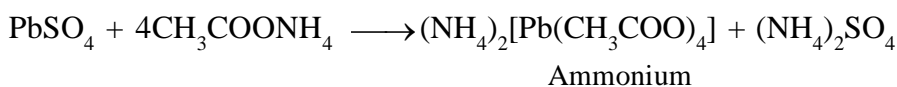
**Chemistry of confirmatory tests of Group-II A cations**

**1. Test for Lead ion (Pb<sup>2+</sup>)**

Lead sulphide precipitate dissolves in dilute HNO<sub>3</sub>. On adding dil. H<sub>2</sub>SO<sub>4</sub> and a few drops of alcohol to this solution a white precipitate of lead sulphate appears. This indicates the presence of lead ions.

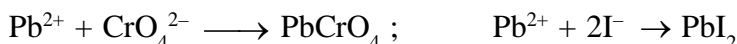


The white precipitate dissolves in ammonium acetate solution on boiling. When this solution is acidified with acetic acid and potassium chromate solution is added, a yellow precipitate of PbCrO<sub>4</sub> is formed. On adding potassium iodide solution, a yellow precipitate of lead iodide is formed.



Ammonium

tetraacetatoplumbate(II)



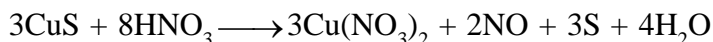
Lead chromate

Lead iodide

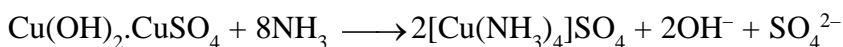
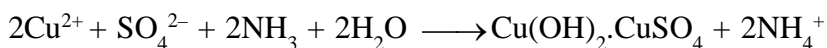
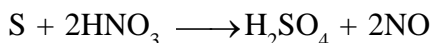
(Yellow precipitate) (Yellow precipitate)

**2. Test for Copper ion (Cu<sup>2+</sup>)**

(a) Copper sulphide dissolves in nitric acid due to the formation of copper nitrate.



On heating the reaction mixture for long time, sulphur is oxidised to sulphate and copper sulphate is formed and the solution turns blue. A small amount of NH<sub>4</sub>OH precipitates basic copper sulphate which is soluble in excess of ammonium hydroxide due to the formation of tetraamminecopper (II) complex.

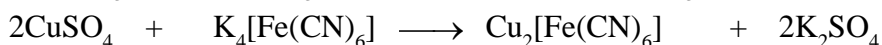
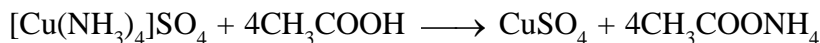


Tetraamminecopper (II)

sulphate (Deep blue)

(b) The blue solution on acidification with acetic acid and then adding potassium ferrocyanide K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution gives a chocolate colouration due to the formation of copper ferrocyanide

i.e. Cu<sub>2</sub>[Fe(CN)<sub>6</sub>].



Potassium

Copper

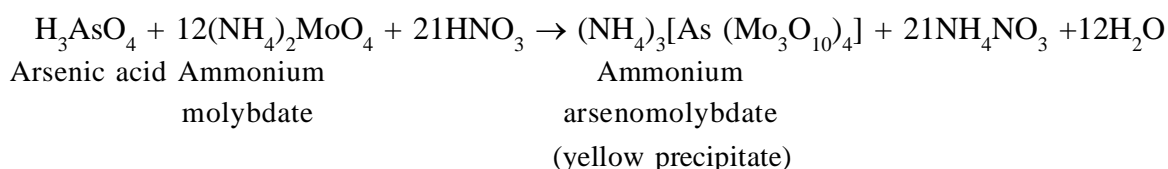
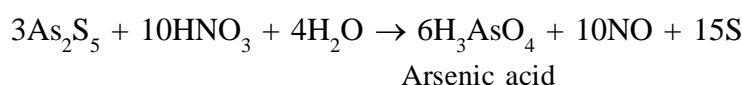
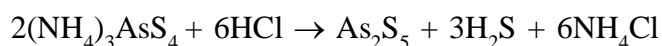
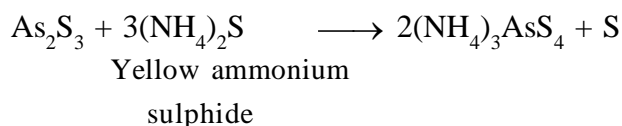
hexacyanoferrate (II)

hexacyanoferrate (II)

(Chocolate brown precipitate)

**Group-II B (Arsenic Group)**

If group-II precipitate dissolves in yellow ammonium sulphide and the colour of the solution is yellow, this indicates the presence of  $As^{3+}$  ions. Ammonium thioarsenide formed on dissolution of  $As_2S_3$  decomposes with dil. HCl, and a yellow precipitate of arsenic (V) sulphide is formed which dissolves in concentrated nitric acid on heating due to the formation of arsenic acid. On adding ammonium molybdate solution to the reaction mixture and heating, a canary yellow precipitate is formed. This confirms the presence of  $As^{3+}$  ions.

**(IV) Analysis of Group-III cations**

If group-II is absent, take original solution and add 2-3 drops of conc.  $HNO_3$  to oxidise  $Fe^{2+}$  ions to  $Fe^{3+}$  ions. Heat the solution for a few minutes. After cooling add a small amount of solid ammonium chloride ( $NH_4Cl$ ) and an excess of ammonium hydroxide ( $NH_4OH$ ) solution till it smells of ammonia. Shake the test tube. If a brown or white precipitate is formed, this indicates the presence of group-III cations. Confirmatory tests of group-III cations are summarised in Table 14.

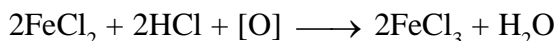
Observe the colour and the nature of the precipitate. A gelatinous white precipitate indicates the presence of aluminium ion ( $Al^{3+}$ ). If the precipitate is brown in colour, this indicates the presence of ferric ions ( $Fe^{3+}$ ).

**Table 14 : Confirmatory test for Group-III cations**

	<b>Brown precipitate <math>Fe^{3+}</math></b>		<b>White precipitate <math>Al^{3+}</math></b>
	Dissolve the precipitate in dilute HCl and divide the solution into two parts.		Dissolve the white precipitate in dilute HCl and divide into two parts.
(a)	To the first part add potassium ferrocyanide solution [Potassium hexacyanoferrate (II)]. A blue precipitate/colouration appears.	(a)	To the first part add sodium hydroxide solution and warm. A white gelatinous precipitate soluble in excess of sodium hydroxide solution is obtained
(b)	To the second part add potassium thiocyanate solution. A blood red colouration appears.	(b)	To the second part first add blue litmus solution and then ammonium hydroxide solution drop by drop along the sides of the test tube. A blue floating mass in the colourless solution is obtained.

### Chemistry of confirmatory tests of Group - III cations

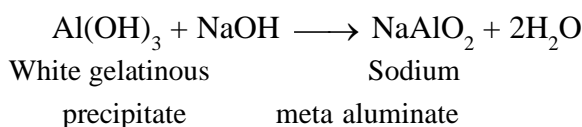
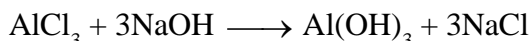
When original solution is heated with concentrated nitric acid, ferrous ion are oxidised to ferric ions.



Their group cations are precipitated as their hydroxides, which dissolve in dilute hydrochloric acid due to the formation of corresponding chlorides.

#### 1. Test for Aluminium ions ( $\text{Al}^{3+}$ )

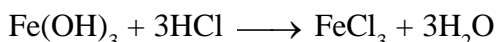
(a) When the solution containing aluminium chloride is treated with sodium hydroxide a white gelatinous precipitate of aluminium hydroxide is formed which is soluble in excess of sodium hydroxide solution due to the formation of sodium meta aluminate.



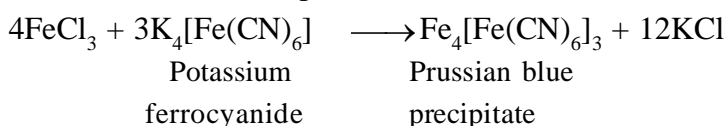
(b) In the second test when blue litmus is added to the solution, a red colouration is obtained due to the acidic nature of the solution. On addition of  $\text{NH}_4\text{OH}$  solution drop by drop, the solution becomes alkaline and aluminium hydroxide is precipitated. Aluminium hydroxide adsorbs blue colour from the solution and forms insoluble adsorption complex named 'lake'. Thus a blue mass floating in the colourless solution is obtained. The test is therefore called **lake test**.

#### 2. Test for ferric ions ( $\text{Fe}^{3+}$ )

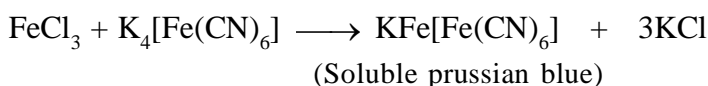
Reddish brown precipitate of ferric hydroxide dissolves in hydrochloric acid and ferric chloride is formed.



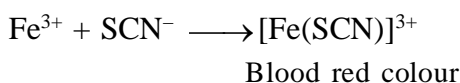
(a) When the solution containing ferric chloride is treated with potassium ferrocyanide solution a blue precipitate/colouration is obtained. The colour of the precipitate is Prussian blue. It is ferric ferrocyanide. The reaction takes place as follows:



If potassium hexacyanoferrate (II) (i.e. potassium ferrocyanide) is added in excess then a product of composition  $\text{KFe}[\text{Fe}(\text{CN})_6]$  is formed. This tends to form a colloidal solution ('soluble Prussian blue') and cannot be filtered.



(b) To the second part of the solution, add potassium thiocyanate (potassium sulphocyanide) solution. The appearance of a blood red colouration confirms the presence of  $\text{Fe}^{3+}$  ions.



#### (V) Analysis of group-IV cations

If group-III is absent, pass  $\text{H}_2\text{S}$  gas in the solution of group-III for a few minutes. If a precipitate appears (white, black or flesh coloured), this indicates the presence of group-IV cations. Table 15 gives a summary of confirmatory tests of group-IV cations.

Table 15 : Confirmatory test for Group - IV cations

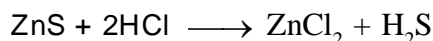
White precipitate (Zn <sup>2+</sup> )	Flesh coloured precipitate (Mn <sup>2+</sup> )	Black precipitate (Ni <sup>2+</sup> , Co <sup>2+</sup> )
Dissolve the precipitate in dilute HCl by boiling. Divide the solution into two parts. (a) To the first part add sodium hydroxide solution. A white precipitate soluble in excess of sodium hydroxide solution confirms the presence of Zn <sup>2+</sup> ions. (b) Neutralise the second part with ammonium hydroxide solution and add potassium ferrocyanide solution. A bluish white precipitate appears	Dissolve the precipitate in dilute HCl by boiling, then add sodium hydroxide solution in excess. A white precipitate is formed which turns brown on keeping.	Dissolve the precipitate in aqua regia. Heat the solution to dryness and cool. Dissolve the residue in water and divide the solution into two parts. (a) To the first part of the solution add ammonium hydroxide solution till it becomes alkaline. Add a few drops of dimethyl glyoxime and shake the test tube. Formation of a bright red precipitate confirms the presence of Ni <sup>2+</sup> ions. (b) Neutralise the second part with ammonium hydroxide solution. Acidify it with dilute acetic acid and add solid potassium nitrite. A yellow precipitate confirms the presence of Co <sup>2+</sup> ions.

### Chemistry of confirmatory tests of Group-IV cations

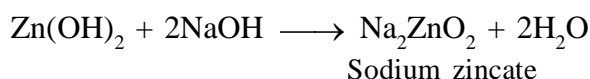
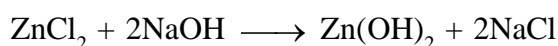
Fourth group cations are precipitated as their sulphides. Observe the colour of the precipitate. A white colour of the precipitate indicates the presence of zinc ions, a flesh colour indicates the presence of manganese ions and a black colour indicates the presence of Ni<sup>2+</sup> or Co<sup>2+</sup> ions.

#### 1. Test for Zinc ion (Zn<sup>2+</sup>)

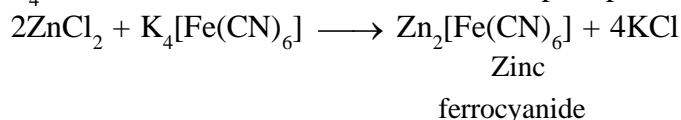
Zinc sulphide dissolves in hydrochloric acid to form zinc chloride.



(a) On addition of sodium hydroxide solution it gives a white precipitate of zinc hydroxide, which is soluble in excess of NaOH solution on heating. This confirms the presence of Zn<sup>2+</sup> ions.

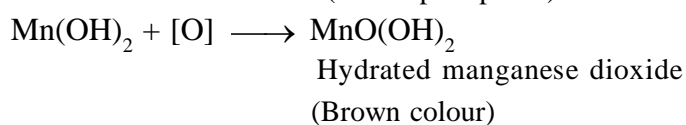
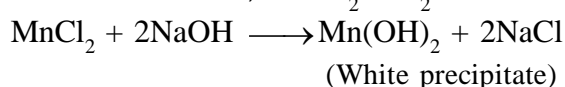
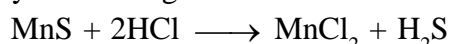


(b) When potassium ferrocyanide K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution is added to the solution after neutralisation by NH<sub>4</sub>OH solution, a white or a bluish white precipitate of zinc ferrocyanide appears.



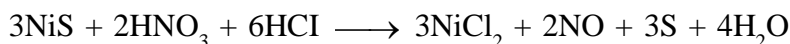
#### 2. Test for Manganese ion (Mn<sup>2+</sup>)

Manganese sulphide precipitate dissolves in dil. HCl on boiling. On addition of NaOH solution in excess, a white precipitate of manganese hydroxide is formed which turns brown due to atmospheric oxidation into hydrated manganese dioxide.

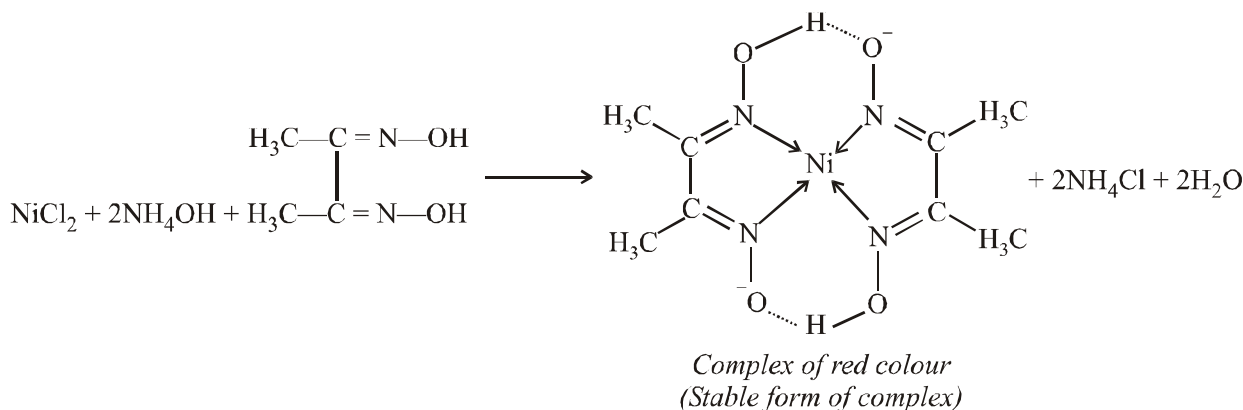


3. Test for Nickel ion (Ni<sup>2+</sup>)

The black precipitate of nickel sulphide dissolves in aqua regia and the reaction takes place as follows:

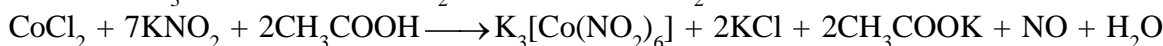
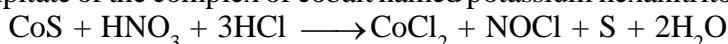


After treatment with aqua regia nickel-chloride is obtained which is soluble in water. When dimethyl glyoxime is added to the aqueous solution of nickel chloride, made alkaline, by adding NH<sub>4</sub>OH solution, a brilliant red precipitate is obtained.



4. Test for Cobalt ion (Co<sup>2+</sup>)

Cobalt sulphide dissolves in aqua regia in the same manner as nickel sulphide. When the aqueous solution of the residue obtained after treatment with aqua regia is treated with a strong solution of potassium nitrite after neutralisation with ammonium hydroxide and the solution is acidified with dil. acetic acid, a yellow precipitate of the complex of cobalt named potassium hexanitritocobaltate (III) is formed.



Potassium  
hexanitritocobaltate(III)  
(Yellow precipitate)

(VI) Analysis of Group-V cations

If group-IV is absent then take original solution and add a small amount of solid NH<sub>4</sub>Cl and an excess of NH<sub>4</sub>OH solution followed by solid ammonium carbonate (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. If a white precipitate appears, this indicates the presence of group-V cations.

Dissolve the white precipitate by boiling with dilute acetic acid and divide the solution into three parts one each for Ba<sup>2+</sup>, Sr<sup>2+</sup> and Ca<sup>2+</sup> ions. Preserve a small amount of the precipitate for flame test. Summary of confirmatory tests is given in Table 16.

16 : Confirmatory test for Group - V cations

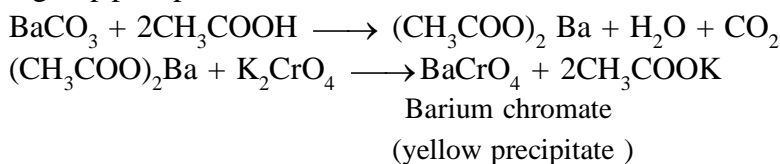
Dissolve the precipitate by boiling with dilute acetic acid and divide the solution into three parts one each for Ba <sup>2+</sup> , Sr <sup>2+</sup> and Ca <sup>2+</sup> ions		
Ba <sup>2+</sup> ions	Sr <sup>2+</sup> ions	Ca <sup>2+</sup> ions
(a) To the first part add potassium chromate solution. A yellow precipitate appears. (b) Perform the flame test with the preserved precipitate. A grassy green flame is obtained.	(a) If barium is absent, take second part of the solution and add ammonium sulphate solution. Heat and scratch the sides of the test tube with a glass rod and cool. A white precipitate is formed. (b) Perform the flame test with the preserved precipitate. A crimson-red flame confirms the presence of Sr <sup>2+</sup> ions.	(a) If both barium and strontium are absent, take the third part of the solution. Add ammonium oxalate solution and shake well. A white precipitate of calcium oxalate is obtained. (b) Perform the flame test with the preserved precipitate. A brick red flame, which looks greenish-yellow through blue glass, confirms the presence of Ca <sup>2+</sup> ions.

### Chemistry of Confirmatory Tests of Group-V cations

The Group-V cations are precipitated as their carbonates which dissolve in acetic acid due to the formation of corresponding acetates.

#### 1. Test for Barium ion ( $\text{Ba}^{2+}$ )

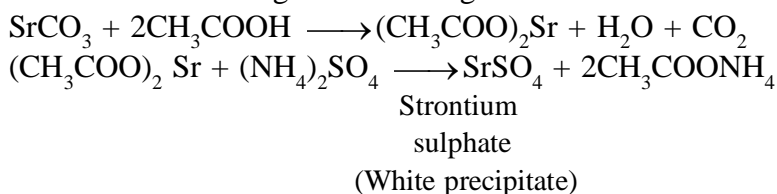
- (a) Potassium chromate ( $\text{K}_2\text{CrO}_4$ ) solution gives a yellow precipitate of barium chromate when the solution of fifth group precipitate in acetic acid is treated with it.



- (b) **Flame test** : Take a platinum wire and dip it in conc. HCl. Heat it strongly until the wire does not impart any colour to the non-luminous flame. Now dip the wire in the paste of the (Group-V) precipitate in conc. HCl. Heat it in the flame. A grassy green colour of the flame confirms the presence of  $\text{Ba}^{2+}$  ions.

#### 2. Test for Strontium ion ( $\text{Sr}^{2+}$ )

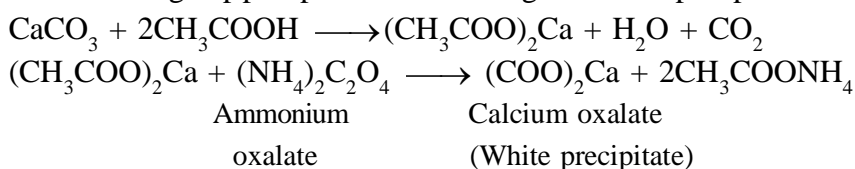
- (a) Solution of V group precipitate in acetic acid gives a white precipitate of strontium sulphate with ammonium sulphate solution on heating and scratching the sides of the test tube with a glass rod.



- (b) **Flame test** : Perform the flame test as given in the case of  $\text{Ba}^{2+}$ . A crimson red flame confirms the presence of  $\text{Sr}^{2+}$  ions.

#### 3. Test for Calcium ion ( $\text{Ca}^{2+}$ )

- (a) Solution of the fifth group precipitate in acetic acid gives a white precipitate with ammonium oxalate solution.



- (b) **Flame test** : Perform the flame test as mentioned above. Calcium imparts brick red colour to the flame which looks greenish-yellow through blue glass.

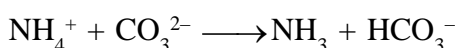
### (VII) Analysis of Group-VI cations

If group-V is absent then perform the test for  $\text{Mg}^{2+}$  ions as given below.

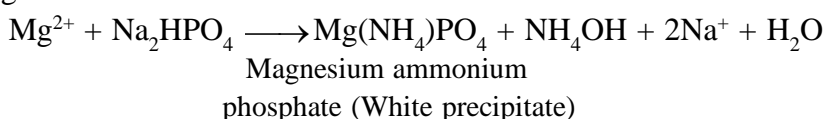
#### Chemistry of Confirmatory Tests of Group-VI cations

Test for Magnesium ion ( $\text{Mg}^{2+}$ )

- (a) If group-V is absent then the solution may contain magnesium carbonate, which is soluble in water in the presence of ammonium salts because the equilibrium is shifted towards the right hand side.



The concentration of carbonate ions required to produce a precipitate is not attained. When disodium hydrogenphosphate solution is added and the inner walls of the test tube are scratched with a glass rod, a white crystalline precipitate of magnesium ammonium phosphate is formed which indicates the presence of  $\text{Mg}^{2+}$  ions.





Note down the observations and the inferences of the qualitative analysis in tabular form as given in the specimen record

### Precautions



**Fig. 1.9 : How to smell a gas**

- (a) Always use an apron, an eye protector and hand gloves while working in the chemistry laboratory.
- (b) Before using any reagent or a chemical, read the label on the bottle carefully. Never use unlabelled reagent.
- (c) Do not mix chemicals and reagents unnecessarily. Never taste any chemical.
- (d) Be careful in smelling chemicals or vapours.

Always fan the vapours gently towards your nose (Fig. 1.9).

- (e) Never add sodium metal to water or throw it in the sink or dustbin.
- (f) Always pour acid into water for dilution. Never add water to acid.
- (g) Be careful while heating the test tube. The test tube should never point towards yourself or towards your neighbours while heating or adding a reagent. Fig. 1.9 : How to smell a gas
- (h) Be careful while dealing with the explosive compounds, inflammable substances, poisonous gases, electric appliances, glass wares, flame and the hot substances.
- (i) Keep your working surroundings clean. Never throw papers and glass in the sink. Always use dustbin for this purpose.
- (j) Always wash your hands after the completion of the laboratory work.
- (k) Always use the reagents in minimum quantity. Use of reagents in excess, not only leads to wastage of chemicals but also causes damage to the environment.

**Discussion Questions**

- (i) What is the difference between a qualitative and a quantitative analysis?
- (ii) Can we use glass rod instead of platinum wire for performing the flame test? Explain your answer.
- (iii) Why is platinum metal preferred to other metals for the flame test?
- (iv) Name the anions detected with the help of dilute  $\text{H}_2\text{SO}_4$ ?
- (v) Why is dilute  $\text{H}_2\text{SO}_4$  preferred over dilute  $\text{HCl}$  while testing anions?
- (vi) Name the anions detected by conc.  $\text{H}_2\text{SO}_4$ .
- (vii) How is sodium carbonate extract prepared ?
- (viii) What is lime water and what happens on passing carbon dioxide gas through it?
- (ix) Carbon dioxide gas and sulphur dioxide gas both turn lime water milky. How will you distinguish these two?
- (x) How will you test the presence of carbonate ion?
- (xi) What is the composition of dark brown ring which is formed at the junction of two layers in the ring test for nitrates?
- (xii) Name the radical confirmed by sodium nitroprusside test.
- (xiii) What is chromyl chloride test ? How do you justify that  $\text{CrO}_2\text{Cl}_2$  is acidic in nature?
- (xiv) Why do bromides and iodides not give tests similar to chromyl chloride test?
- (xv) Describe the layer test for bromide and iodide ions.
- (xvi) Why is silver nitrate solution stored in dark coloured bottles?
- (xvii) How do you test the presence of sulphide ion?
- (xviii) Why does iodine give a blue colour with starch solution?
- (xix) What is Nessler's reagent?
- (xx) Why is original solution for cations not prepared in conc.  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ ?
- (xxi) Why cannot conc.  $\text{HCl}$  be used as a group reagent in place of dil.  $\text{HCl}$  for the precipitation of Ist group cations?
- (xxii) How can one prevent the precipitation of Group-IV radicals, with the second group radicals?
- (xxiii) Why is it essential to boil off  $\text{H}_2\text{S}$  gas before precipitation of radicals of group-III?
- (xxiv) Why is heating with conc. nitric acid done before precipitation of group-III?
- (xxv) Can we use ammonium sulphate instead of ammonium chloride in group-III?
- (xxvi) Why is  $\text{NH}_4\text{OH}$  added before  $(\text{NH}_4)_2\text{CO}_3$  solution while precipitating group-V cations?
- (xxvii) Why do we sometimes get a white precipitate in group-VI even if the salt does not contain  $\text{Mg}^{2+}$  radical?
- (xxviii) What is aqua regia?
- (xxix) Name a cation, which is not obtained from a metal.
- (xxx) How can you test the presence of ammonium ion?
- (xxxii) Why are the group-V radicals tested in the order  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  ?
- (xxxii) Why does conc.  $\text{HNO}_3$  kept in a bottle turn yellow in colour?
- (xxxiii) Why should the solution be concentrated before proceeding to group-V?
- (xxxiv) Why is the reagent bottle containing sodium hydroxide solution never stoppered?
- (xxxv) What do you understand by the term common ion effect?
- (xxxvi) Why is zinc sulphide not precipitated in group-II?

## SPECIMEN RECORD OF SALT ANALYSIS

## Aim

To analyse the given salt for one anion and one cation present in it.

Sl. No.	Experiment	Observation	Inference
1.	Noted the colour of the given salt.	White	$\text{Cu}^{2+}$ , $\text{Fe}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Co}^{2+}$ , $\text{Mn}^{2+}$ are absent.
2.	Noted the smell of the salt.	No specific smell.	$\text{S}^{2-}$ , $\text{SO}_3^{2-}$ , $\text{CH}_3\text{COO}^-$ may be absent.
3.	Heated 0.5 g of the salt in a dry test tube and noted the colour of the gas evolved and change in the colour of the residue on heating and cooling.	(i) No gas was evolved. (ii) No particular change in colour of the residue is observed when heated and when cooled.	(i) $\text{CO}_3^{2-}$ may be present, $\text{NO}_3^-$ , $\text{NO}_2^-$ , $\text{Br}^-$ may be absent. (ii) $\text{Zn}^{2+}$ may be absent.
4.	Prepared a paste of the salt with conc. HCl and performed the flame test.	No distinct colour of the flame seen.	$\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Cu}^{2+}$ may be absent.
5.	Borax bead test was not performed as the salt was white in colour.	—	—
6.	Treated 0.1 g of salt with 1 mL dil. $\text{H}_2\text{SO}_4$ and warmed.	No effervescence and evolution of vapours.	$\text{CO}_3^{2-}$ , $\text{SO}_3^{2-}$ , $\text{S}^{2-}$ , $\text{NO}_2^-$ , $\text{CH}_3\text{COO}^-$ absent.
7.	Heated 0.1 g of salt with 1 mL conc. $\text{H}_2\text{SO}_4$ .	No gas evolved.	$\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{NO}_3^-$ , $\text{C}_2\text{O}_4^{2-}$ are absent.
8.	Acidified 1 mL of aqueous salt solution with conc. $\text{HNO}_3$ . Warmed the contents and then added 4-5 drops of ammonium molybdate solution.	No yellow precipitate	$\text{PO}_4^{3-}$ absent.

Sl. No.	Experiment	Observation	Inference
9.	Acidified water extract of the salt with dil. HCl and then added 2mL of BaCl <sub>2</sub> solution.	A white ppt. is obtained which is insoluble in conc. HNO <sub>3</sub> and conc. HCl.	SO <sub>4</sub> <sup>2-</sup> present.
10.	Heated 0.1 g of salt with 2 mL NaOH solution.	Ammonia gas is not evolved.	NH <sub>4</sub> <sup>+</sup> absent.
11.	Attempted to prepare original solution of the salt by dissolving 1g of it in 20 mL water.	Clear solution formed	Water soluble salt is present.
12.	To a small part of the above salt solution added 2 mL of dil. HCl.	No white precipitate formed.	Group-I absent.
13.	Passed H <sub>2</sub> S gas through one portion of the solution of step 12.	No precipitate formed.	Group-II absent.
14.	Since salt is white, heating with conc. HNO <sub>3</sub> is not required. Added about 0.2 g of solid ammonium chloride and then added excess of ammonium hydroxide to the solution of step 12.	No precipitate formed.	Group-III absent.
15.	Passed H <sub>2</sub> S gas through the above solution.	No precipitate formed.	Group-IV absent.
16.	Added excess of ammonium hydroxide solution to the original solution and then added 0.5 g of ammonium carbonate.	No precipitate formed.	Group-V absent.
17.	To the original solution of salt added ammonium hydroxide solution, followed by disodium hydrogen phosphate solution. Heated and scratched the sides of the test tube.	White precipitate	Mg <sup>2+</sup> confirmed.

**Result**

**the given salt contains**

**Anion : SO<sub>4</sub><sup>2-</sup>**

**Cation : Mg<sup>2+</sup>**

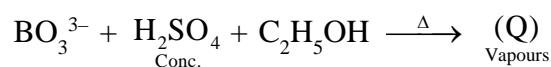
## EXERCISE # I

## ANIONS : Class A (Subgroup - I)

1. The colour developed, when sodium sulphide is added to sodium nitroprusside is:  
 (A) Purple (B) yellow (C) red (D) black SA0001
2. When a neutral or slightly alkaline solution of thiosulphate is treated with the  $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$  complex, then  
 (A) Green precipitate is obtained (B) Brown precipitate is obtained  
 (C) Violet precipitate is obtained (D) Yellow precipitate is obtained SA0002
3. When  $\text{CH}_3\text{COONa}$  heated with solid  $\text{As}_2\text{O}_3$  then compound X is formed. The smell of compound X is -  
 (A) Pungent smell (B) Rotten Fish smell (C) Nauseating smell (D) Rotten egg smell SA0003
4.  $\text{NO}_2^-$  ion can be destroyed by -  
 (A) Sulphamic acid (B) Thiourea (C) Urea (D) All of these SA0004
5. Solutions of sodium azide ( $\text{NaN}_3$ ) and iodine (as  $\text{KI}_3$ ) do not react but on addition of a trace of 'X' ion, which acts as a catalyst there is an immediate vigorous evolution of nitrogen. Then 'X' may be:  
 (A)  $\text{S}_2\text{O}_3^{2-}$  (B)  $\text{S}^{2-}$  (C)  $\overset{\ominus}{\text{S}}\text{CN}$  (D) All are correct. SA0005
6. When  $\text{AgNO}_3$  react with 'X' ion then initially no visible change occurs due to formation of water soluble complex. Then ion 'X' may be:  
 (A)  $\text{SO}_3^{2-}$  (B)  $\text{S}_2\text{O}_3^{2-}$  (C)  $\text{S}^{2-}$  (D)  $\text{CO}_3^{2-}$  SA0006
7. Match the column
- | Column-I                        | Column-II   |
|---------------------------------|---|
| (A) $\text{S}^{2-}$             | (P) Produces white ppt. with excess $\text{AgNO}_3$   |
| (B) $\text{HSO}_3^-$            | (Q) Evolves gas with dil. $\text{HCl}$ which turns lime water milky                             |
| (C) $\text{SO}_3^{2-}$          | (R) Evolves gas with dil. $\text{H}_2\text{SO}_4$ which does <b>not</b> turn Baryta water milky |
| (D) $\text{S}_2\text{O}_3^{2-}$ | (S) Produces ppt. with $\text{Pb}(\text{OAc})_2$ solution.                                      |
|                                 | (T) Produces white ppt with $\text{BaCl}_2$ solution. <span style="float: right;">SA0007</span> |
8. Find the number of acidic radical(s) which can form coloured gas when treated with **dil.**  $\text{H}_2\text{SO}_4$ .  
 $\text{CO}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_3^{2-}$  SA0008

## Class A (Subgroup - II)

9. Chromyl chloride test is given by -  
 (A)  $\text{CH}_3\text{Cl}$  (B)  $\text{AgCl}$  (C)  $\text{Hg}_2\text{Cl}_2$  (D)  $\text{NH}_4\text{Cl}$  SA0009



P & Q are respectively -

- (A)  $\text{H}_3\text{BO}_3$ ,  $\text{H}_3\text{BO}_3$  (B)  $(\text{C}_2\text{H}_5)_3\text{BO}_3$ ,  $\text{H}_3\text{BO}_3$   
 (C)  $(\text{C}_2\text{H}_5)_3\text{BO}_3$ ,  $(\text{C}_2\text{H}_5)_3\text{BO}_3$  (D)  $\text{H}_3\text{BO}_3$ ,  $(\text{C}_2\text{H}_5)_3\text{BO}_3$

SA0010

11. In layer test of  $\text{I}^-$  and  $\text{Br}^-$ . If reddish -brown layer comes first then -

- (A)  $\text{Br}^-$  present (B)  $\text{I}^-$  absent (C) Both (A) and (B) (D) None of these

SA0011

### All Anions Of Class A

12. **Statement-1** : When  $\text{H}_2\text{S}$  gas is passed through Na-nitroprusside solution it gives purple colouration

**Statement-2** :  $\text{H}_2\text{S}$  is an weak acid

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

SA0012

13. When the soda extract containing thiosulphate ion treated with excess of  $\text{AgNO}_3$  solution followed by boiling, then.

- (A) White precipitate is formed (B) Black precipitate is formed  
 (C) brown precipitate is formed (D) No ppt precipitate is formed

SA0013

14. "Cacodyl oxide" is formed in the specific test of -

- (A) Formate (B) Oxalate (C) Acetate (D) Nitrate

SA0014

15. An aqueous solution of gas (X) gives the white turbidity on passing  $\text{H}_2\text{S}$  in the solution. Identify (X)

- (A)  $\text{NH}_3$  (B)  $\text{SO}_2$  (C)  $\text{CO}_2$  (D) None of these

SA0015

16.  $\text{NO}_2^-$  and  $\text{NO}_3^-$  can be distinguished by which of the following reagent.

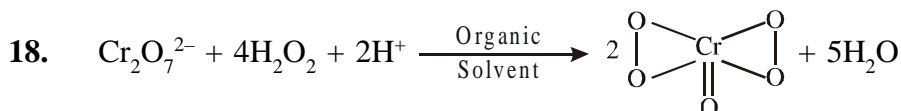
- (A) dil.  $\text{H}_2\text{SO}_4$  (B) conc.  $\text{H}_2\text{SO}_4$   
 (C) Devarda's alloy + conc. NaOH (D) None of these

SA0016

17.  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  is unstable because -  
 (A) It liberates NO gas on warming  
 (B) It liberates NO gas on shaking  
 (C) The charge of central atom is +1 (relatively low enough)  
 (D) None of these

**Class B**

SA0017



In above reaction amyl alcohol is recommended.

Dimethyl ether is not recommended for general use owing to its -

- (A) Highly non-flammable character  
 (B) Highly inflammable character  
 (C) Highly poisonous character  
 (D) None of these
19. If barium sulphate is precipitated in a solution containing potassium permanganate it is coloured pink (violet) by -  
 (A) Absorption of some of the permanganate (B) Adsorption of some of the permanganate  
 (C) Both (A) and (B) (D) None of these

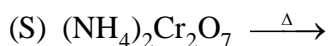
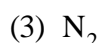
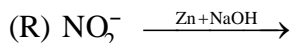
SA0018

SA0019

**All Anions Of Class A & Class B**

**20. List-I (Reaction)**

**List-II (Product)**



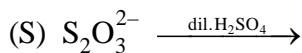
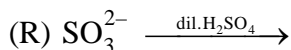
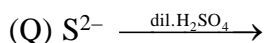
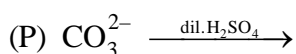
Code :

	P	Q	R	S
(A)	3	4	1	2
(C)	4	2	3	1

	P	Q	R	S
(B)	4	2	1	3
(D)	2	4	1	3

SA0020

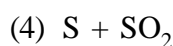
## 21. List-I (Reaction)



Code :

	P	Q	R	S
(A)	3	4	1	2
(C)	3	1	2	4

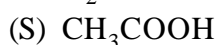
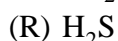
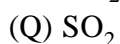
## List-II (Product)



	P	Q	R	S
(B)	2	1	4	3
(D)	2	4	1	3

SA0021

## 22. List-I (Molecule)



Code :

	P	Q	R	S
(A)	4	2	1	3
(C)	3	1	2	4

## List-II (Characteristic Odour)

(1) Rotten egg smell

(2) Suffocating smell of burning sulphur

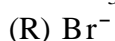
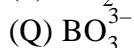
(3) Vinegar like smell

(4) Odour less

	P	Q	R	S
(B)	2	4	1	3
(D)	2	4	1	3

SA0022

## 23. List-I (Acidic radicals)



Code :

	P	Q	R	S
(A)	4	2	1	3
(C)	3	4	2	1

## List-II (Test)

(1) Green flame test

(2) Cacodyl oxide reaction

(3) Griess Ilosvay test

(4) Layer test

	P	Q	R	S
(B)	3	1	4	2
(D)	4	3	2	1

SA0023

## CATIONS : DRY TEST

24. Find the number of water of crystallization in microcosmic salt -

(A) 5

(B) 4

(C) 6

(D) 10

SA0024

25. What is the colour of  $\text{K}^+$  through cobalt/double blue glass -

(A) Lilac,

(B) Violet

(C) Brick red

(D) Crimson red

SA0025





## GROUP - II B

33.  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  can be distinguished by how many of the following methods -
- by passing  $\text{H}_2\text{S}$  in their solution (in acidic medium)
  - by addition of  $\text{NaOH}$  in their solution
  - by addition of excess  $\text{NaOH}$  in their solution
  - by addition of dil.  $\text{HCl}$  in their solution
  - by addition of  $\text{HgCl}_2$  solution in their solution

SA0033

## GROUP - III

34. What is the group-III reagent is generally used for group analysis.
- (A)  $\text{NH}_4\text{OH} + \text{NH}_4\text{NO}_3$  (B)  $\text{NH}_4\text{Cl} + (\text{NH}_4)_2\text{CO}_3$   
 (C)  $\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{SO}_4$  (D)  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$

SA0034

35.  $\text{CrCl}_3$  solution +  $\text{Na}_2\text{S}$  solution  $\longrightarrow$  ppt(A)

The correct formula and colour of A are

- (A)  $\text{Cr}_2\text{S}_3$ , Black (B)  $\text{Cr}(\text{OH})_3$ , Green  
 (C)  $\text{Na}[\text{Cr}(\text{OH})_4]$ , Green (D) None of these

SA0035

## GROUP - IV

36. The auxiliary reagent in group-IV reagent is
- (A)  $\text{H}_2\text{S}$  (B) dil.HCl (C)  $\text{NaOH}$  (D)  $\text{NH}_4\text{OH}$

SA0036

## All Group Cations

37. Which of the following cation gives ppt in two groups during group analysis.
- (A)  $\text{Hg}^{2+}$  (B)  $\text{Hg}_2^{2+}$  (C)  $\text{Pb}^{2+}$  (D)  $\text{Cu}^{2+}$
38. Which of the following cation produces coloured ppt with  $\text{Na}_2\text{SO}_4$  solution -
- (A)  $\text{Pb}^{2+}$  solution (B)  $\text{Ba}^{2+}$  solution (C)  $\text{Hg}^{2+}$  solution (D)  $\text{Ca}^{2+}$  solution
39.  $\text{NH}_4^+$  and  $\text{K}^+$  ions can be distinguished by the use of following reagent
- (A)  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  (B)  $\text{Na}_2[\text{PtCl}_6]$   
 (C)  $\text{HClO}_4$  or  $\text{NaClO}_4$  (D) Boiling with  $\text{NaOH}$
40. Which of the following sulphides is yellow in colour?
- (A)  $\text{CuS}$  (B)  $\text{CdS}$  (C)  $\text{ZnS}$  (D)  $\text{CoS}$

SA0037

SA0038

SA0039

SA0040

## MISCELLANEOUS

## 41. List-I (Compound)

- (P) HgO  
 (Q) BaCO<sub>3</sub>  
 (R) Na<sub>4</sub>[Fe(CN)<sub>5</sub>NOS]  
 (S) KI<sub>3</sub>

<b>Code :</b>	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>
(A)	3	4	1	2
(C)	2	4	3	1

## List-II (Colour)

- (1) Purple solution  
 (2) Yellow ppt  
 (3) Dark brown  
 (4) White ppt

	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>
(B)	2	4	1	3
(D)	2	4	3	1

SA0041

## 42. List-I (Basic Radical)

- (P) Al<sup>+3</sup>  
 (Q) Zn<sup>+2</sup>  
 (R) Ba<sup>+2</sup>  
 (S) Pb<sup>+2</sup>

<b>Code :</b>	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>
(A)	4	2	1	3
(C)	3	1	2	4

## List-II (Group)

- (1) II group  
 (2) V group  
 (3) IV group  
 (4) III group

	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>
(B)	2	4	1	3
(D)	4	3	2	1

SA0042

## 43. List-I (Cations)

- (P) Co<sup>+2</sup>  
 (Q) Fe<sup>+3</sup>  
 (R) Cu<sup>+2</sup>  
 (S) Ca<sup>+2</sup>

<b>Code :</b>	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>
(A)	4	2	1	3
(C)	1	2	3	4

## List-II (Group reagent)

- (1) (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in presence of NH<sub>4</sub>Cl  
 (2) H<sub>2</sub>S gas in acidic medium  
 (3) H<sub>2</sub>S in presence of NH<sub>4</sub>OH  
 (4) NH<sub>4</sub>OH in presence of NH<sub>4</sub>Cl

	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>
(B)	3	1	4	2
(D)	3	4	2	1

SA0043

## EXERCISE # II

## ANIONS : Class A (Subgroup - I)

1. **Statement-1:** On passing  $\text{CO}_2$  gas through lime water, the solution turns milky.  
**because**  
**Statement-2:** Acid-Base (neutralisation) reaction takes place.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

SA0044

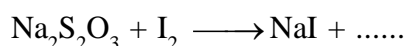
2. A substance on treatment with dil.  $\text{H}_2\text{SO}_4$  liberates a colourless gas which produces (i) turbidity with baryta water and (ii) turns acidified dichromate solution green. The reaction indicates the presence of  
 (A)  $\text{CO}_3^{2-}$  (B)  $\text{S}^{2-}$  (C)  $\text{SO}_3^{2-}$  (D)  $\text{NO}_2^-$

SA0045

3. When  $\text{S}_2\text{O}_3^{2-}$  react with solution of 'X' reagent then reaction is redox followed by precipitation then 'X' is:  
 (A)  $\text{FeCl}_3$  solution (B)  $\text{AgNO}_3$  solution  
 (C)  $\text{CuSO}_4$  solution (D) None of these

SA0046

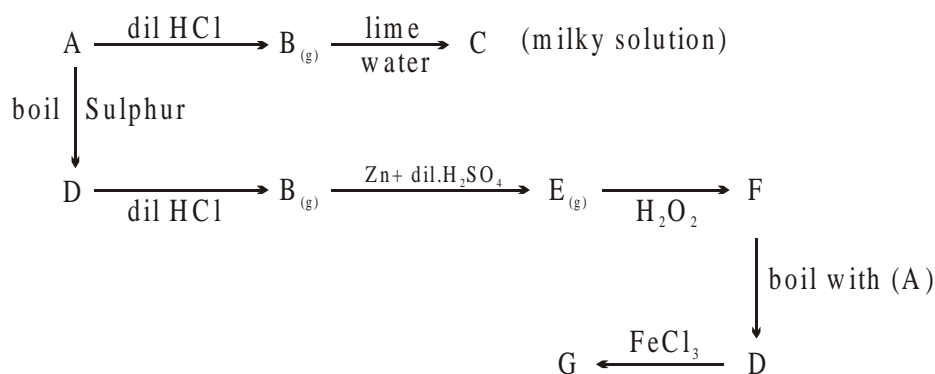
4. In the test for iodine, when  $\text{I}_2$  is treated with sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3$



- (A)  $\text{Na}_2\text{S}_4\text{O}_6$  (B)  $\text{Na}_2\text{SO}_4$  (C)  $\text{Na}_2\text{S}$  (D)  $\text{Na}_3\text{ISO}_4$

SA0047

## Paragraph for Q. 5 to Q. 7



5. Identify A  
 (A)  $\text{CO}_3^{2-}$  (B)  $\text{SO}_3^{2-}$  (C)  $\text{S}_2\text{O}_3^{2-}$  (D) none of these

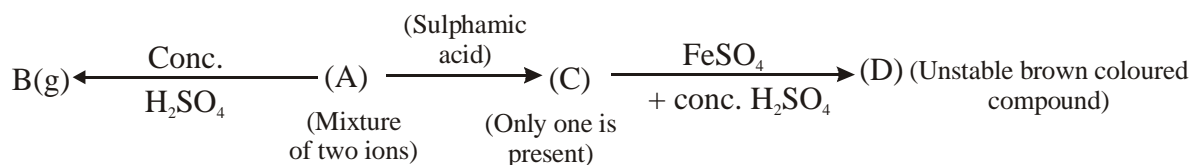
SA0048

6. When A react with  $\text{Pb}(\text{NO}_3)_2$  then compound X is formed. Compound X is oxidized by atmospheric oxygen on boiling, then Y is formed what is the colour of Y  
 (A) yellow (B) White (C) Black (D) Green SA0048
7. When gas E react with sodium nitroprusside in basic medium then compound Z is formed. The colour of compound Z is:  
 (A) Green (B) purple (C) Reddish brown (D) Black SA0048

### Class A (Subgroup - II)

8. When a mixture of solid NaCl, solid  $\text{K}_2\text{Cr}_2\text{O}_7$  is heated with conc.  $\text{H}_2\text{SO}_4$ , orange red vapours are obtained. These are of the compound  
 (A) chromous chloride (B) chromyl chloride  
 (C) chromic chloride (D) chromic sulphate SA0049
9. Which of the following will not give positive chromyl chloride test?  
 (A) Copper chloride,  $\text{CuCl}_2$  (B) Mercuric chloride,  $\text{HgCl}_2$   
 (C) Zinc chloride,  $\text{ZnCl}_2$  (D) Aniline chloride,  $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$  SA0050
10. Sodium borate on reaction with conc.  $\text{H}_2\text{SO}_4$  and  $\text{C}_2\text{H}_5\text{OH}$  gives a compound A which burns with a green edged flame. The compound A is  
 (A)  $\text{H}_2\text{B}_4\text{O}_7$  (B)  $(\text{C}_2\text{H}_5)_2\text{B}_4\text{O}_7$  (C)  $\text{H}_3\text{BO}_3$  (D)  $(\text{C}_2\text{H}_5)_3\text{BO}_3$  SA0051
11. Nitrate is confirmed by ring test. The brown colour of the ring is due to formation of  
 (A) ferrous nitrite (B) nitroso ferrous sulphate  
 (C) ferrous nitrate (D)  $\text{FeSO}_4\text{NO}_2$  SA0052
12. A salt gives violet vapours when treated with conc.  $\text{H}_2\text{SO}_4$ , it contains  
 (A)  $\text{Cl}^-$  (B)  $\text{I}^-$  (C)  $\text{Br}^-$  (D)  $\text{NO}_3^-$  SA0053
13. Unknown salt + Al-powder + NaOH (conc.)  $\rightarrow$  gas comes out which turns Nessler's reagent brown. The salt may be -  
 (A)  $\text{NaNO}_2$  (B)  $\text{NaNO}_3$  (C)  $\text{NH}_4\text{Cl}$  (D)  $\text{NH}_4\text{HCO}_3$  SA0054

## Paragraph for Q. 14 to Q. 17



14. Identify mixture of ions (A) -

- (A)  $\text{NO}_2^-$  and  $\text{Br}^-$       (B)  $\text{NO}_2^-$  and  $\text{I}^-$       (C)  $\text{NO}_2^-$  and  $\text{NO}_3^-$       (D) None of these

SA0055

15. What is oxidation state of central atom of (D)

- (A) +3                      (B) +2                      (C) +1                      (D) Zero

SA0055

16. Identify gas B-

- (A)  $\text{Br}_2$                       (B)  $\text{Br}_2 + \text{NO}_2$                       (C)  $\text{NO}_2$                       (D) None of these

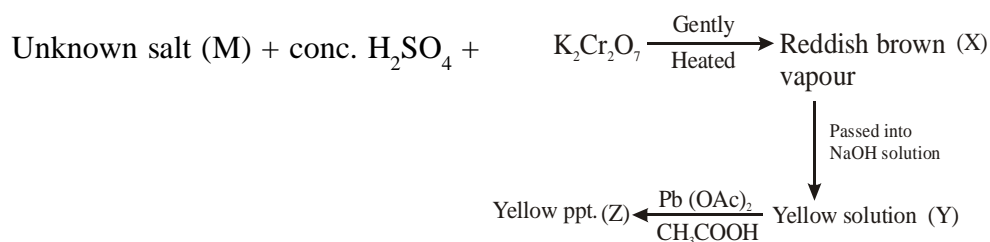
SA0055

17. What is the hybridisation of central atom of D-

- (A)  $d^2sp^3$                       (B)  $sp^3d^2$                       (C)  $sp^3d$                       (D)  $sp^3$

SA0055

## Paragraph for Q. 18 to Q. 20



18. The salt (M) is/are-

- (A)  $\text{AgCl}$                       (B)  $\text{NH}_4\text{Cl} + \text{NaBr}$                       (C)  $\text{NaBr}$                       (D)  $\text{Ca}(\text{ClO}_4)_2$

SA0056

19. How many non axial d-orbitals are involved in hybridisation of central atom of compound (X)-

- (A) 2                      (B) 3                      (C) 4                      (D) None of these

SA0056

20. What is the formula of yellow ppt (Z) -

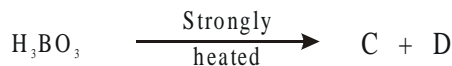
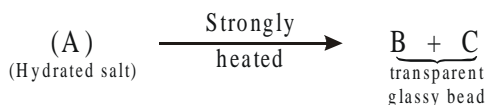
- (A)  $\text{BaCrO}_4$                       (B)  $\text{Na}_2\text{CrO}_4$                       (C)  $\text{Ag}_2\text{CrO}_4$                       (D)  $\text{PbCrO}_4$

SA0056

## CATIONS : DRY TEST

21. In the borax bead test of  $\text{Co}^{2+}$ , the blue colour of bead is due to the formation of:  
 (A)  $\text{B}_2\text{O}_3$  (B)  $\text{Co}_3\text{B}_2$  (C)  $\text{Co}(\text{BO}_2)_2$  (D)  $\text{CoO}$  **SA0057**
22. Which of the following leaves no residue on heating?  
 (A)  $\text{Pb}(\text{NO}_3)_2$  (B)  $\text{NH}_4\text{NO}_3$  (C)  $\text{Cu}(\text{NO}_3)_2$  (D)  $\text{NaNO}_3$  **SA0058**
23. Which of the following cations is detected by the flame test?  
 (A)  $\text{NH}_4^+$  (B)  $\text{K}^+$  (C)  $\text{Mg}^{2+}$  (D)  $\text{Al}^{3+}$  **SA0059**
24. Which metal salt gives a violet coloured bead in the borax bead test (oxidising flame, cold)?  
 (A)  $\text{Fe}^{2+}$  (B)  $\text{Ni}^{2+}$  (C)  $\text{Co}^{2+}$  (D)  $\text{Mn}^{2+}$  **SA0060**
25. The compound formed in the borax bead test of  $\text{Cu}^{2+}$  ion in oxidising flame is:  
 (A)  $\text{Cu}$  (B)  $\text{CuBO}_2$  (C)  $\text{Cu}(\text{BO}_2)_2$  (D) None of these **SA0061**
26. In microcosmic salt bead test  $\text{Co}^{2+}$  produce blue bead due to the formation of -  
 (A)  $\text{Cu}(\text{BO}_2)_2$  (B)  $\text{NaCoPO}_4$  (C)  $\text{Co}_2(\text{PO}_4)(\text{BO}_2)$  (D)  $\text{NaPO}_3$  **SA0062**

## Paragraph for Q. 27 to Q. 30



27. Identify C-  
 (A)  $(\text{BN})_x$  (B)  $\text{NaPO}_3$  (C)  $\text{B}_2\text{O}_3$  (D)  $\text{Mg}(\text{NH}_4)\text{PO}_4$  **SA0063**
28. Find the number of water of crystallizations in (A)-  
 (A) 4 (B) 5 (C) 10 (D) 24 **SA0063**
29. How many X–O–X linkages are present in structure of A (X = central atom)-  
 (A) 4 (B) 3 (C) 5 (D) 2 **SA0063**
30. Find the number of tetrahedral and trigonal planar units in structure of A -  
 (A) 2,1 (B) 2,2 (C) 2,4 (D) 5,2 **SA0063**

## WET TEST : GROUP - I

31. Mercurous ion is represented as:  
 (A)  $\text{Hg}_2^{2+}$  (B)  $\text{Hg}^{2+}$  (C)  $\text{Hg} + \text{Hg}^{2+}$  (D)  $\text{Hg}_2^+$  **SA0064**

32. A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the solution, a white precipitate is obtained which does not dissolve in dil.  $\text{HNO}_3$ . The anion could be:
- (A)  $\text{CO}_3^{2-}$                       (B)  $\text{Cl}^-$                       (C)  $\text{SO}_4^{2-}$                       (D)  $\text{S}^{2-}$
- SA0065**
33. An aqueous solution of a substance gives a white ppt. on treatment with dil.  $\text{HCl}$ , which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black ppt. is obtained. The substance is a
- (A)  $\text{Hg}^{2+}$  salt                      (B)  $\text{Cu}^{2+}$  salt                      (C)  $\text{Ag}^+$  salt                      (D)  $\text{Pb}^{2+}$  salt
- SA0066**
34. A white ppt obtained in a analysis of a mixture becomes black on treatment with  $\text{NH}_4\text{OH}$ . It may be
- (A)  $\text{PbCl}_2$                       (B)  $\text{AgCl}$                       (C)  $\text{HgCl}_2$                       (D)  $\text{Hg}_2\text{Cl}_2$
- SA0067**

### GROUP - II

35. When bismuth chloride is poured into a large volume of water the white precipitate produced is
- (A)  $\text{Bi}(\text{OH})_3$                       (B)  $\text{Bi}_2\text{O}_3$                       (C)  $\text{BiOCl}$                       (D)  $\text{Bi}_2\text{OCl}_3$
- SA0068**
36.  $\text{CuSO}_4$  decolourises on addition of excess  $\text{KCN}$ , the product is
- (A)  $[\text{Cu}(\text{CN})_4]^{2-}$ .  
 (B)  $\text{Cu}^{2+}$  get reduced to form  $[\text{Cu}(\text{CN})_4]^{3-}$   
 (C)  $\text{Cu}(\text{CN})_2$   
 (D)  $\text{CuCN}$
- SA0069**
37. When  $\text{H}_2\text{S}$  gas is passed through the  $\text{HCl}$  containing aqueous solution of  $\text{CuCl}_2$ ,  $\text{HgCl}_2$ ,  $\text{BiCl}_3$  and  $\text{CoCl}_2$ , it does not precipitate out:
- (A)  $\text{CuS}$                       (B)  $\text{HgS}$                       (C)  $\text{Bi}_2\text{S}_3$                       (D)  $\text{CoS}$
- SA0070**
38. Which of the following is soluble in yellow ammonium sulphide?
- (A)  $\text{CuS}$                       (B)  $\text{CdS}$                       (C)  $\text{SnS}$                       (D)  $\text{PbS}$
- SA0071**
39. When excess of  $\text{SnCl}_2$  is added to a solution of  $\text{HgCl}_2$ , a white ppt turning grey is obtained. The grey colour is due to the formation of
- (A)  $\text{Hg}_2\text{Cl}_2$                       (B)  $\text{SnCl}_4$                       (C)  $\text{Sn}$                       (D)  $\text{Hg}$
- SA0072**
40. On passing  $\text{H}_2\text{S}$  gas in II group sometimes the solution turns milky. It indicates the presence of
- (A) oxidising agent                      (B) acidic salt                      (C) s-block cation                      (D) reducing agent.
- SA0073**



41. Which of the following yellow coloured sulphide is insoluble in yellow ammonium sulphide.  
 (A)  $\text{SnS}_2$  (B)  $\text{As}_2\text{S}_5$  (C)  $\text{CdS}$  (D)  $\text{Bi}_2\text{S}_3$  SA0074
42. Type of sulphide ppt may be obtained in the group-II ppt during group analysis.  
 (A)  $\text{M}_2\text{S}_3$  (B)  $\text{M}_2\text{S}$  (C)  $\text{MS}$  (D)  $\text{MS}_2$  SA0075
43. The metal ion which is precipitated when  $\text{H}_2\text{S}$  is passed with  $\text{HCl}$ :  
 (A)  $\text{Zn}^{2+}$  (B)  $\text{Ni}^{2+}$  (C)  $\text{Cd}^{2+}$  (D)  $\text{Mn}^{2+}$  SA0076

### GROUP - III

44. In the precipitation of the iron group in qualitative analysis, ammonium chloride is added before adding ammonium hydroxide to  
 (A) decrease concentration of  $\text{OH}^-$  ions. (B) prevent interference by phosphate ions.  
 (C) increase concentration of  $\text{Cl}^-$  ions. (D) increase concentration of  $\text{NH}_4^+$  ions. SA0077
45. If reddish brown ppt (only) is obtained in group-III during group analysis, then oxidation state of Fe in the original sample may be  
 (A) +2 (B) +3 (C) +2 and +3 both (D) Neither +2 nor +3 SA0078
46. If  $\text{NH}_4\text{Cl}$  is not added to the group-III reagent which of the following ppt could be obtained  
 (A)  $\text{Cr}(\text{OH})_2$  (B)  $\text{Fe}(\text{OH})_3$  (C)  $\text{Mn}(\text{OH})_2$  (D)  $\text{Mg}(\text{OH})_2$  SA0079
47. In which of the following cases blue ppt is obtained  
 (A)  $\text{Fe}^{2+} + [\text{Fe}(\text{CN})_6]^{3-} \longrightarrow$  (B)  $\text{Fe}^{2+} + [\text{Fe}(\text{CN})_6]^{4-} \longrightarrow$   
 (C)  $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{4-} \longrightarrow$  (D)  $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{3-} \xrightarrow{\text{SnCl}_2}$  SA0080
48. What are the following steps are to be done before adding group-III reagent into the group-II filtrate.  
 (A) Group-II filtrate is to be evaporated to dryness  
 (B) Group-II filtrate is to be boiled of first  
 (C) After boiling 2-3 drops of dil.  $\text{H}_2\text{SO}_4$  is added and boiled again.  
 (D) After boiling 2-3 drops of  $\text{HNO}_3$  is added and boiled again. SA0081
49. A pale green crystalline metal salt of M dissolves freely in water. On standing it gives a brown ppt on addition of aqueous  $\text{NaOH}$ . The metal salt solution also gives a black ppt on bubbling  $\text{H}_2\text{S}$  in basic medium. An aqueous solution of the metal salt decolorizes the pink colour of the permanganate solution. The metal in the metal salt solution is  
 (A) copper (B) aluminium (C) lead (D) iron SA0082

50. Which of the following compound on reaction with NaOH and  $\text{Na}_2\text{O}_2$  gives yellow colour?  
 (A)  $\text{Cr}(\text{OH})_3$  (B)  $\text{Zn}(\text{OH})_2$  (C)  $\text{Al}(\text{OH})_3$  (D) None of these

SA0083

## GROUP - IV

51. Colour of nickel chloride solution is  
 (A) pink (B) black (C) colourless (D) green
52. Dimethyl glyoxime in a suitable solvent was refluxed for 10 minutes with pure pieces of nickel sheet, it will result in  
 (A) Red ppt (B) Blue ppt. (C) Yellow ppt. (D) No ppt.

SA0084

SA0085

53. Which one of the following does not produce metallic sulphide with  $\text{H}_2\text{S}$ ?  
 (A)  $\text{ZnCl}_2$  (Neutral sol<sup>n</sup>) (B)  $\text{CdCl}_2$ (aq) (C)  $\text{CoCl}_2$ (aq) (D)  $\text{CuCl}_2$ (aq)

SA0086

54. Which is not dissolved by dil HCl?  
 (A) ZnS (B) MnS (C)  $\text{BaSO}_3$  (D)  $\text{BaSO}_4$

SA0087

## GROUP - V

55. In III group,  $\text{NH}_4\text{Cl}$  is added to decrease concentration of hydroxide ion by  $\text{NH}_4\text{OH}$ . We do not add  $(\text{NH}_4)_2\text{SO}_4$  along with  $\text{NH}_4\text{OH}$  because -  
 (A)  $(\text{NH}_4)_2\text{SO}_4$  is insoluble in water (B) It precipitate other insoluble sulphates  
 (C) It is weak electrolyte (D) None of these

SA0088

## GROUP - VI

56. A metal is burnt in air and the ash on moistening smells of ammonia. The metal is  
 (A) Na (B) Fe (C) Mg (D) Al
57. A metal 'X' on heating in nitrogen gas gives 'Y'. 'Y' on treatment with  $\text{H}_2\text{O}$  gives a colourless gas which when passed through  $\text{CuSO}_4$  solution gives a blue colour Y is:  
 (A)  $\text{Mg}(\text{NO}_3)_2$  (B)  $\text{Mg}_3\text{N}_2$  (C)  $\text{NH}_3$  (D) MgO

SA0089

SA0090

## MISCELLANEOUS

58.  $\text{Na}_2\text{HPO}_4$  + Reagent 'M'  $\rightarrow$  white ppt. The reagent 'M' is -  
 (A)  $\text{BaCl}_2$  solution (B)  $\text{AlCl}_3$  solution (C)  $\text{MnSO}_4$  solution (D)  $\text{FeCl}_3$  solution
59. A white solid is first heated with dil  $\text{H}_2\text{SO}_4$  and then with conc.  $\text{H}_2\text{SO}_4$ . No action was observed in either case. The solid salt contains  
 (A) sulphide (B) sulphite (C) thiosulphate (D) sulphate

SA0091

SA0092

60. A mixture of chlorides of copper, cadmium, chromium, iron and aluminium was dissolved in water acidified with HCl and hydrogen sulphide gas was passed for sufficient time. It was filtered, boiled and a few drops of nitric acid were added while boiling. To this solution ammonium chloride and sodium hydroxide were added in excess and filtered. The filtrate shall give test for  
 (A) sodium and iron ion (B) sodium, chromium and aluminium ion  
 (C) aluminium and iron ion (D) sodium, iron, cadmium and aluminium ion  
**SA0093**
61. In Nessler's reagent, the ion present is:  
 (A)  $\text{HgI}_4^{2-}$  (B)  $\text{HgI}_4^{2-}$  (C)  $\text{Hg}^+$  (D)  $\text{Hg}^{2+}$   
**SA0094**
62. The cations present in slightly acidic solution are  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ . The reagent which when added in excess to this solution would identify and separate  $\text{Fe}^{3+}$  in one step is:  
 (A) 2 M HCl (B) 6 M  $\text{NH}_3$  (C) 6 M NaOH (D)  $\text{H}_2\text{S}$  gas  
**SA0095**
63. In the separation of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  in 2<sup>nd</sup> group qualitative analysis of cation, tetrammine copper (II) sulphate and tetrammine cadmium (II) sulphate react with KCN to form the corresponding cyano complexes. Which one of the following pairs of the complexes and their relative stability enables the separation of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ?  
 (A)  $\text{K}_3[\text{Cu}(\text{CN})_4]$  more stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  less stable.  
 (B)  $\text{K}_2[\text{Cu}(\text{CN})_4]$  less stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  more stable.  
 (C)  $\text{K}_2[\text{Cu}(\text{CN})_4]$  more stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  less stable.  
 (D)  $\text{K}_3[\text{Cu}(\text{CN})_4]$  less stable and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  more stable.  
**SA0096**
64. Which one has the minimum solubility product?  
 (A) AgCl (B)  $\text{AlCl}_3$  (C)  $\text{BaCl}_2$  (D)  $\text{NH}_4\text{Cl}$   
**SA0097**
65. Which of the following sulphate is insoluble in water?  
 (A)  $\text{CuSO}_4$  (B)  $\text{CdSO}_4$  (C)  $\text{PbSO}_4$  (D)  $\text{Bi}_2(\text{SO}_4)_3$   
**SA0098**
66. Which of the following gives blood red colour with KSCN?  
 (A)  $\text{Cu}^{2+}$  (B)  $\text{Fe}^{3+}$  (C)  $\text{Al}^{3+}$  (D)  $\text{Zn}^{2+}$   
**SA0099**
67. Which one of the following metal sulphide has maximum solubility in water?  
 (A)  $\text{HgS}$ ,  $K_{\text{sp}} = 10^{-54}$  (B)  $\text{CdS}$ ,  $K_{\text{sp}} = 10^{-30}$   
 (C)  $\text{FeS}$ ,  $K_{\text{sp}} = 10^{-20}$  (D)  $\text{ZnS}$ ,  $K_{\text{sp}} = 10^{-22}$   
**SA0100**

68. Identify the correct order of solubility of  $\text{Na}_2\text{S}$ ,  $\text{CuS}$  and  $\text{ZnS}$  in aqueous medium is:

- (A)  $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$  (B)  $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$   
 (C)  $\text{Na}_2\text{S} > \text{CuS} > \text{ZnS}$  (D)  $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$

SA0101

69. Match the column -

**Column-I****(Element)**

- (A) Ba  
 (B) Pb  
 (C) Ag  
 (D) Ca

**Column-II****(Correct characteristics)**

- (P) cation in solution produces brick red ppt. with  $\text{CrO}_4^{2-}$   
 (Q) cation in solution produces yellow ppt. with  $\text{CrO}_4^{2-}$   
 (R) corresponding salt produces apple green colour in the flame test  
 (S) corresponding salt produces brick red colour in the flame test  
 (T) cation in solution produces no ppt. with  $\text{CrO}_4^{2-}$  ion

SA0102

70. **Column-I**

**Cation in solution**

- (A)  $\text{Ag}^+$  and  $\text{Pb}^{2+}$   
 (B)  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$   
 (C)  $\text{Pb}^{2+}$  and  $\text{Hg}_2^{2+}$   
 (D)  $\text{Ag}^+$  and  $\text{Fe}^{3+}$

**Column-I****Correct characteristics when no where excess reagent is used**

- (P) can be distinguished by  $\text{Na}_2\text{HPO}_4$  solution  
 (Q) can be distinguished by dil. HCl  
 (R) can be distinguished by KI solution  
 (S) can not be distinguished by  $\text{NH}_4\text{OH}$  solution

SA0103

The following column 1, 2, 3 represent the various tests carried out for identification of various group basic radicals, using various reagents and nature of reaction/properties of products observed.

Answer the questions that follow

**Column-1 - Cations/Basic Radical****Column-2 - Excess Reagent used with cation****Column-3 - Nature of Reaction/Properties of product formed**

Column - 1 Cations	Column - 2 Excess Reagent used with cation	Column - 3 Nature of Reaction/ Properties of product formed
(I) $\text{Cu}^{2+}$	(i) KI (< 6M)	(P) Reduction of cation occurs
(II) $\text{Fe}^{3+}$	(ii) $\text{K}_4[\text{Fe}(\text{CN})_6]$	(Q) Coloured complex formation
(III) $\text{Pb}^{2+}$	(iii) KCN	(R) Precipitation occurs
(IV) $\text{Ni}^{2+}$	(iv) $\text{NH}_4\text{OH}$	(S) Diamagnetic & square planar complex formation

71. For a **group-II** basic radical, which is the only **INCORRECT** combination?  
(A) (I), (i), (P)                      (B) (IV), (iii), (S)                      (C) (III), (iv), (R)                      (D) (III), (iii), (R)  
**SA0104**
72. For a **group-IV** basic radical, which is the only **CORRECT** combination?  
(A) (I), (iv), (S)                      (B) (IV), (iii), (P)                      (C) (II), (iv), (Q)                      (D) (IV), (iv), (Q)  
**SA0104**
73. Which combination has a entirely different colour from others?  
(A) (IV), (iv), (Q)                      (B) (I), (iv), (Q)                      (C) (II), (iii), (Q)                      (D) (II), (ii), (Q)  
**SA0104**
74. How many of the following gives green ppt.  
(i)  $\text{CrCl}_3 + \text{NaOH} \rightarrow$                       (ii)  $\text{CrCl}_3 + \text{excess NaOH} \rightarrow$   
(iii)  $\text{NiCl}_2 + \text{excess NaOH} \rightarrow$                       (iv)  $\text{NiCl}_2 + \text{excess NH}_4\text{OH} \rightarrow$   
(v)  $\text{Hg}_2^{2+} + \text{KI} \rightarrow$   
**SA0104**
75. Find the no. of cation which gives white ppt with  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
 $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$   
**SA0104**

## EXERCISE # JEE MAINS

1. Which products are expected from the disproportionation of hypochlorous acid :[AIEEE-2002]  
 (1)  $\text{HClO}_3$  and  $\text{Cl}_2\text{O}$  (2)  $\text{HClO}_2$  and  $\text{HClO}$  (3)  $\text{HCl}$  and  $\text{Cl}_2\text{O}$  (4)  $\text{HCl}$  and  $\text{HClO}_3$   
**SA0105**
2. A metal M readily forms its sulphate  $\text{MSO}_4$  which is water soluble. It forms oxide  $\text{MO}$  which becomes inert on heating. It forms insoluble hydroxide which is soluble in  $\text{NaOH}$ . The metal M is:-  
 [AIEEE-2002]  
 (1) Mg (2) Ba (3) Ca (4) Be  
**SA0106**
3. Which statement is correct :- [AIEEE-2003]  
 (1)  $\text{Fe}^{3+}$  ions give deep green precipitate with  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
 (2) On heating  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions, we get a precipitate of  $\text{K}_2[\text{Ca}(\text{CO}_3)_2]$   
 (3) Manganese salts give a violet borax bead test in reducing flame  
 (4) From a mixed precipitate of  $\text{AgCl}$  and  $\text{AgI}$  ammonia solution dissolves only  $\text{AgCl}$   
**SA0107**
4. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid - [AIEEE-2003]  
 (1)  $\text{Cr}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are formed (2)  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}_2\text{O}$  are formed  
 (3)  $\text{Cr}_2\text{O}_7^{2-}$  is reduced to +3 state of Cr (4)  $\text{Cr}_2\text{O}_7^{2-}$  is oxidised to +7 state of Cr  
**SA0108**
5. Ammonia forms the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with copper ions in alkaline solutions but not in acidic solution. What is the reason for it :- [AIEEE-2003]  
 (1) In acidic solutions hydration protects copper ions  
 (2) In acidic solutions protons coordinate with ammonia molecules forming  $\text{NH}_4^+$  ions and  $\text{NH}_3$  molecules are not available  
 (3) In alkaline solutions insoluble  $\text{Cu}(\text{OH})_2$  is precipitated which is soluble in excess of any alkali  
 (4) Copper hydroxide is an amphoteric substance  
**SA0109**
6. Excess of  $\text{KI}$  reacts with  $\text{CuSO}_4$  solution and then  $\text{Na}_2\text{S}_2\text{O}_3$  solution is added to it. Which of the statements is incorrect for this reaction : [AIEEE-2004]  
 (1) Evolved  $\text{I}_2$  is reduced (2)  $\text{CuI}_2$  is formed  
 (3)  $\text{Na}_2\text{S}_2\text{O}_3$  is oxidised (4)  $\text{Cu}_2\text{I}_2$  is formed  
**SA0110**

7. Calomel on reaction with  $\text{NH}_4\text{OH}$  gives [AIEEE-2004]  
 (1)  $\text{HgNH}_2\text{Cl}$  (2)  $\text{NH}_2\text{-Hg-Hg-Cl}$  (3)  $\text{Hg}_2\text{O}$  (4)  $\text{HgO}$   
 SA0111
8. One mole of magnesium nitride on reaction with excess of water gives :- [AIEEE-2004]  
 (1) Two mole of  $\text{HNO}_3$  (2) Two mole of  $\text{NH}_3$   
 (3) 1 mole of  $\text{NH}_3$  (4) 1 mole of  $\text{HNO}_3$   
 SA0112
9. The products obtained on heating  $\text{LiNO}_3$  will be :- [AIEEE-2011]  
 (1)  $\text{LiNO}_2 + \text{O}_2$  (2)  $\text{Li}_2\text{O} + \text{NO}_2 + \text{O}_2$   
 (3)  $\text{Li}_3\text{N} + \text{O}_2$  (4)  $\text{Li}_2\text{O} + \text{NO} + \text{O}_2$   
 SA0113
10. What is the best description of the change that occurs when  $\text{Na}_2\text{O}(\text{s})$  is dissolved in water ? [AIEEE-2011]  
 (1) Oxidation number of sodium decreases  
 (2) Oxide ion accepts sharing in a pair of electrons  
 (3) Oxide ion donates a pair of electrons  
 (4) Oxidation number of oxygen increases  
 SA0114
11. Which of the following on thermal-decomposition yields a basic as well as an acidic oxide ? [AIEEE-2012]  
 (1)  $\text{NH}_4\text{NO}_3$  (2)  $\text{NaNO}_3$  (3)  $\text{KClO}_3$  (4)  $\text{CaCO}_3$   
 SA0115
12. The correct statement for the molecule,  $\text{CsI}_3$ , is: [JEE(Main)-2014]  
 (1) it contains  $\text{Cs}^{3+}$  and  $\text{I}^-$  ions (2) it contains  $\text{Cs}^+$ ,  $\text{I}^-$  and lattice  $\text{I}_2$  molecule  
 (3) it is a covalent molecule (4) it contains  $\text{Cs}^+$  and  $\text{I}_3^-$  ions  
 SA0116
13. A metal M on heating in nitrogen gas gives Y. Y on treatment with  $\text{H}_2\text{O}$  gives a colourless gas which when passed through  $\text{CuSO}_4$  solution gives a blue colour, Y is :- [JEE(Main)-2012 online\_P-4]  
 (1)  $\text{NH}_3$  (2)  $\text{MgO}$  (3)  $\text{Mg}_3\text{N}_2$  (4)  $\text{Mg}(\text{NO}_3)_2$   
 SA0117
14. Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown - red vapours of: [JEE(Main)-2013 online\_P-1]  
 (1)  $\text{CrO}_3$  (2)  $\text{Cr}_2\text{O}_3$  (3)  $\text{CrCl}_3$  (4)  $\text{CrO}_2\text{Cl}_2$   
 SA0118
15. Sodium Carbonate cannot be used in place of  $(\text{NH}_4)_2\text{CO}_3$  for the identification of  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  ions (in group V) during mixture analysis because : [JEE(Main)-2013 online\_P-1]  
 (1) Sodium ions will react with acid radicals  
 (2) Concentration of  $\text{CO}_3^{2-}$  ions is very low  
 (3)  $\text{Mg}^{2+}$  ions will also be precipitated  
 (4)  $\text{Na}^+$  ions will interfere with the detection of  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  ions  
 SA0119

16. Which of the following statements is incorrect? [JEE(Main)-2013 online\_P-2]
- (1)  $\text{Fe}^{2+}$  ion also gives blood red colour with  $\text{SCN}^-$  ion
  - (2) Cupric ion reacts with excess of ammonia solution to give deep blue colour of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion.
  - (3)  $\text{Fe}^{3+}$  ion gives blood red colour with  $\text{SCN}^-$  ion.
  - (4) On passing  $\text{H}_2\text{S}$  into  $\text{Na}_2\text{ZnO}_2$  solution, a white ppt of  $\text{ZnS}$  is formed.

SA0120

17. Identify incorrect statement [JEE(Main)-2013 online\_P-3]
- (1) Copper (I) compounds are colourless except where colour results from charge transfer
  - (2) Copper (I) compounds are diamagnetic
  - (3)  $\text{Cu}_2\text{S}$  is black
  - (4)  $\text{Cu}_2\text{O}$  is colourless

SA0121

18. Which one of the following cannot function as an oxidising agent? [JEE(Main)-2013 online\_P-4]
- (1)  $\text{NO}_3^-$  (aq)
  - (2)  $\text{I}^-$
  - (3)  $\text{Cr}_2\text{O}_7^{2-}$
  - (4)  $\text{S}_{(s)}$

SA0122

19. Which of the following statements about  $\text{Na}_2\text{O}_2$  is **not** correct? [JEE(Main)-2014 online\_P-2]
- (1)  $\text{Na}_2\text{O}_2$  oxidises  $\text{Cr}^{3+}$  to  $\text{CrO}_4^{2-}$  in acid medium
  - (2) It is diamagnetic in nature
  - (3) It is the super oxide of sodium
  - (4) It is a derivative of  $\text{H}_2\text{O}_2$

SA0123

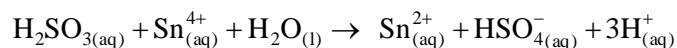
20. Consider the following equilibrium [JEE(Main)-2014 online\_P-2]
- $$\text{AgCl} \downarrow + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^-$$

White precipitate of  $\text{AgCl}$  appears on adding which of the following?

- (1)  $\text{NH}_3$
- (2) Aqueous  $\text{NaCl}$
- (3) Aqueous  $\text{NH}_4\text{Cl}$
- (4) Aqueous  $\text{HNO}_3$

SA0124

21. Consider the reaction [JEE(Main)-2014 online\_P-4]



Which of the following statements is correct?

- (1)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes oxidation
- (2)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes reduction
- (3)  $\text{Sn}^{4+}$  is the reducing agent because it undergoes oxidation
- (4)  $\text{Sn}^{4+}$  is the oxidizing agent because it undergoes oxidation

SA0125



22. Amongst the following, identify the species with an atom in +6 oxidation state :

[JEE(Main)-2014 online\_P-4]

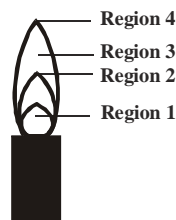
- (1)  $[\text{MnO}_4]^-$                       (2)  $[\text{Cr}(\text{CN})_6]^{3-}$                       (3)  $\text{Cr}_2\text{O}_3$                       (4)  $\text{CrO}_2\text{Cl}_2$

SA0126

23. The hottest region of Bunsen flame shown in the figure below is :

[JEE(Main)-2016]

- (1) region 4  
(2) region 1  
(3) region 2  
(4) region 3



SA0127

24. Sodium extract is heated with concentrated  $\text{HNO}_3$  before testing for halogens because :

- (1)  $\text{S}^{2-}$  and  $\text{CN}^-$ , if present are decomposed by conc.  $\text{HNO}_3$  and hence do not interfere in the test.  
(2) Ag reacts faster with halides in acidic medium  
(3)  $\text{Ag}_2\text{S}$  and  $\text{AgCN}$  are soluble in acidic medium.  
(4) Silver halides are totally insoluble in nitric acid.

[JEE(Main)-2016 online]

SA0128

25. In the following reactions, ZnO is respectively acting as a/an :

- (a)  $\text{ZnO} + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{ZnO}_2$                       (b)  $\text{ZnO} + \text{CO}_2 \rightarrow \text{ZnCO}_3$                       [JEE(Main)-2017 off line]  
(1) base and acid                      (2) base and base                      (3) acid and acid                      (4) acid and base

SA0129

26. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are :-

- (1)  $\text{ClO}^-$  and  $\text{ClO}_3^-$                       (2)  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$                       [JEE(Main)-2017 off line]  
(3)  $\text{Cl}^-$  and  $\text{ClO}^-$                       (4)  $\text{Cl}^-$  and  $\text{ClO}_2^-$

SA0130

27. Sodium salt of an organic acid 'X' produces effervescence with conc.  $\text{H}_2\text{SO}_4$ . 'X' reacts with the acidified aqueous  $\text{CaCl}_2$  solution to give a white precipitate which decolourises acidic solution of  $\text{KMnO}_4$ . 'X' is :-

[JEE(Main)-2017 off line]

- (1)  $\text{C}_6\text{H}_5\text{COONa}$                       (2)  $\text{HCOONa}$                       (3)  $\text{CH}_3\text{COONa}$                       (4)  $\text{Na}_2\text{C}_2\text{O}_4$

SA0131

28. A solution containing a group-IV cation gives a precipitate on passing  $\text{H}_2\text{S}$ . A solution of this precipitate in dil. HCl produces a white precipitate with NaOH solution and bluish-white precipitate with basic potassium ferrocyanide. The cation is :

[JEE(Main)-2017 on line]

- (1)  $\text{Mn}^{2+}$                       (2)  $\text{Zn}^{2+}$                       (3)  $\text{Ni}^{2+}$                       (4)  $\text{Co}^{2+}$

SA0132

29. Which of the following ions does **not** liberate hydrogen gas on reaction with dilute acids?  
(1)  $Ti^{2+}$  (2)  $Cr^{2+}$  [JEE(Main)-2017 on line]  
(3)  $Mn^{2+}$  (4)  $V^{2+}$   
SA0133
30. When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is [JEE(Main)-2018 off line]  
(1) Ca (2) Al (3) Fe (4) Zn  
SA0134
31. A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the aforementioned solution, a white precipitate is obtained which does not dissolve in dil. nitric acid. The anion is : [JEE(Main)-2018 on line]  
(1)  $S^{2-}$  (2)  $SO_4^{2-}$  (3)  $CO_3^{2-}$  (4)  $Cl^-$   
SA0135
32. The incorrect statement is :- [JEE(Main)-2018 on line]  
(1) Ferric ion gives blood red colour with potassium thiocyanate.  
(2)  $Cu^{2+}$  and  $Ni^{2+}$  ions give black precipitate with  $H_2S$  in presence of HCl solution.  
(3)  $Cu^{2+}$  salts give red coloured borax bead test in reducing flame.  
(4)  $Cu^{2+}$  ion gives chocolate coloured precipitate with potassium ferrocyanide solution.  
SA0136
33. When  $XO_2$  is fused with an alkali metal hydroxide in presence of an oxidizing agent such as  $KNO_3$ ; a dark green product is formed which disproportionates in acidic solution to afford a dark purple solution. X is : [JEE(Main)-2018 on line]  
(1) Ti (2) Cr (3) V (4) Mn  
SA0137

## EXERCISE # J-ADVANCED

1. Which of the following statement(s) is (are) correct with reference to the ferrous and ferric ions:  
 (A)  $\text{Fe}^{3+}$  gives brown colour with potassium ferricyanide [JEE 1998]  
 (B)  $\text{Fe}^{2+}$  gives blue precipitate with potassium ferricyanide  
 (C)  $\text{Fe}^{3+}$  give red colour with potassium thiocyanate  
 (D)  $\text{Fe}^{2+}$  gives brown colour with ammonium thiocyanate  
 SA0138
2. Which of the following statement(s) is /are correct. When a mixture of  $\text{NaCl}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  is gently warmed with conc.  $\text{H}_2\text{SO}_4$ ? [JEE 1998]  
 (A) A deep red vapours is evolved.  
 (B) The vapours when passed into  $\text{NaOH}$  solution gives a yellow solution of  $\text{Na}_2\text{CrO}_4$   
 (C) Chlorine gas is evolved  
 (D) Chromyl chloride is formed.  
 SA0139
3. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a : [JEE 2000]  
 (A)  $\text{Hg}_2^+$  salt                      (B)  $\text{Cr}^{2+}$  salt                      (C)  $\text{Ag}^+$  salt                      (D)  $\text{Pb}^{2+}$  salt  
 SA0140
4. A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y': [JEE 2002(Mains)]  
 (A)  $\text{X} = \text{CO}_2$ ,  $\text{Y} = \text{Cl}_2$                       (B)  $\text{X} = \text{Cl}_2$ ,  $\text{Y} = \text{CO}_2$   
 (C)  $\text{X} = \text{Cl}_2$ ,  $\text{Y} = \text{H}_2$                       (D)  $\text{X} = \text{H}_2$ ,  $\text{Y} = \text{Cl}_2$   
 SA0141
5.  $[\text{X}] + \text{H}_2\text{SO}_4 \rightarrow [\text{Y}]$  a colourless gas with irritating smell [JEE 2003]  
 $[\text{Y}] + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \longrightarrow$  green solution  
 $[\text{X}]$  and  $[\text{Y}]$  are:  
 (A)  $\text{SO}_3^{2-}$ ,  $\text{SO}_2$                       (B)  $\text{Cl}^-$ ,  $\text{HCl}$                       (C)  $\text{S}^{2-}$ ,  $\text{H}_2\text{S}$                       (D)  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$   
 SA0142

6. A sodium salt of an unknown anion when treated with  $\text{MgCl}_2$  give white precipitate only on boiling. The anion is: [JEE 2004]
- (A)  $\text{SO}_4^{2-}$  (B)  $\text{HCO}_3^-$  (C)  $\text{CO}_3^{2-}$  (D)  $\text{NO}_3^-$
- SA0143
7.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  on heating gives a gas which is also given by: [JEE 2004]
- (A) heating  $\text{NH}_4\text{NO}_2$  (B) heating  $\text{NH}_4\text{NO}_3$   
(C)  $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O}$  (D)  $\text{NaNO}_2 + \text{H}_2\text{O}_2$
- SA0144
8. A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI convert into orange colour solution. The cation of metal nitrate is: [JEE 2005]
- (A)  $\text{Hg}^{2+}$  (B)  $\text{Bi}^{3+}$  (C)  $\text{Pb}^{2+}$  (D)  $\text{Cu}^+$
- SA0145
9. A solution when diluted with  $\text{H}_2\text{O}$  and boiled, it gives a white precipitate. On addition of excess  $\text{NH}_4\text{Cl} / \text{NH}_4\text{OH}$ , the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in  $\text{NH}_4\text{OH} / \text{NH}_4\text{Cl}$ . [JEE 2006]
- (A)  $\text{Zn}(\text{OH})_2$  (B)  $\text{Al}(\text{OH})_3$  (C)  $\text{Mg}(\text{OH})_2$  (D)  $\text{Ca}(\text{OH})_2$
- SA0146
10.  $\text{CuSO}_4$  decolourises on addition of excess KCN, the product is: [JEE 2006]
- (A)  $[\text{Cu}(\text{CN})_4]^{2-}$  (B)  $\text{Cu}^{2+}$  get reduced to form  $[\text{Cu}(\text{CN})_4]^{3-}$   
(C)  $\text{Cu}(\text{CN})_2$  (D)  $\text{CuCN}$
- SA0147
11. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is: [JEE 2007]
- (A) 3 (B) 4 (C) 5 (D) 6
- SA0148
12. The species present in solution when  $\text{CO}_2$  is dissolved in water are [JEE 2007]
- (A)  $\text{CO}_2, \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-}$  (B)  $\text{H}_2\text{CO}_3, \text{CO}_3^{2-}$   
(C)  $\text{CO}_3^{2-}, \text{HCO}_3^-$  (D)  $\text{CO}_2, \text{H}_2\text{CO}_3$
- SA0149

13. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and  $\text{H}_2\text{SO}_4$  in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of :

[JEE 2007]

- (A)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (B)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$   
 (C)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_2$  (D)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_3$

SA0150

14. **Column I** **Column II** [JEE 2007]

- (A)  $\text{O}_2^- \rightarrow \text{O}_2 + \text{O}_2^{2-}$  (P) Redox reaction  
 (B)  $\text{CrO}_4^{2-} + \text{H}^+ \rightarrow$  (Q) One of the products has trigonal planar structure  
 (C)  $\text{MnO}_4^- + \text{NO}_2^- + \text{H}^+ \rightarrow$  (R) Dimeric bridged tetrahedral metal ion  
 (D)  $\text{NO}_3^- + \text{H}_2\text{SO}_4 + \text{Fe}^{2+} \rightarrow$  (S) Disproportionation

SA0151

15. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt (II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is

[JEE 2007]

- (A)  $\text{Pb}^{2+}$  (B)  $\text{Hg}^{2+}$  (C)  $\text{Cu}^{2+}$  (D)  $\text{Co}^{2+}$

SA0152

16. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are)

[JEE 2008]

- (A)  $\text{NH}_4\text{NO}_3$  (B)  $\text{NH}_4\text{NO}_2$  (C)  $\text{NH}_4\text{Cl}$  (D)  $(\text{NH}_4)_2\text{SO}_4$

SA0153

### Paragraph for Question Nos. 17 to 19

p-Amino-N, N-dimethylaniline is added to a strongly acidic solution of **X**. The resulting solution is treated with a few drops of aqueous solution of **Y** to yield blue coloration due to the formation of methylene blue. Treatment of the aqueous solution of **Y** with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of **Y** with the solution of potassium hexacyanoferrate(III) leads to a brown coloration due to the formation of **Z**.

[JEE 2009]

17. The compound **X** is

- (A)  $\text{NaNO}_3$  (B)  $\text{NaCl}$  (C)  $\text{Na}_2\text{SO}_4$  (D)  $\text{Na}_2\text{S}$

SA0154

18. The compound Y is  
 (A)  $\text{MgCl}_2$  (B)  $\text{FeCl}_2$  (C)  $\text{FeCl}_3$  (D)  $\text{ZnCl}_2$

SA0154

19. The compound Z is  
 (A)  $\text{Mg}_2[\text{Fe}(\text{CN})_6]$  (B)  $\text{Fe}[\text{Fe}(\text{CN})_6]$  (C)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (D)  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$

SA0154

20. Match each of the reactions given in Column I with the corresponding product(s) given in Column II.

**Column I**

- (A)  $\text{Cu} + \text{dil. HNO}_3$   
 (B)  $\text{Cu} + \text{conc. HNO}_3$   
 (C)  $\text{Zn} + \text{dil. HNO}_3$   
 (D)  $\text{Zn} + \text{conc. HNO}_3$

**Column II**

- (P)  $\text{NO}$   
 (Q)  $\text{NO}_2$   
 (R)  $\text{N}_2\text{O}$   
 (S)  $\text{Cu}(\text{NO}_3)_2$   
 (T)  $\text{Zn}(\text{NO}_3)_2$

[JEE 2009]

SA0155

21. Passing  $\text{H}_2\text{S}$  gas into a mixture of  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  ions in an acidified aqueous solution precipitates

[JEE 2011]

- (A)  $\text{CuS}$  and  $\text{HgS}$  (B)  $\text{MnS}$  and  $\text{CuS}$  (C)  $\text{MnS}$  and  $\text{NiS}$  (D)  $\text{NiS}$  and  $\text{HgS}$

SA0156

22. Reduction of the metal centre in aqueous permanganate ion involves -

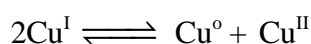
[JEE 2011]

- (A) 3 electrons in neutral medium (B) 5 electrons in neutral medium  
 (C) 3 electrons in weak alkaline medium (D) 5 electrons in acidic medium

SA0157

23. The equilibrium

[JEE 2011]



in aqueous medium at  $25^\circ\text{C}$  shifts towards the left in the presence of

- (A)  $\text{NO}_3^-$  (B)  $\text{Cl}^-$  (C)  $\text{SCN}^-$  (D)  $\text{CN}^-$

SA0158

**Paragraph for Questions Nos. 24 to 26**

When a metal rod M is dipped into an aqueous colourless concentrated solution of compound N, the solution turns light blue. Addition of aqueous  $\text{NaCl}$  to the blue solution gives a white precipitate O. Addition of aqueous  $\text{NH}_3$  dissolves O and gives an intense blue solution. [JEE 2011]

24. The metal rod M is -

- (A)  $\text{Fe}$  (B)  $\text{Cu}$  (C)  $\text{Ni}$  (D)  $\text{Co}$

SA0159

25. The compound N is -

- (A)  $\text{AgNO}_3$  (B)  $\text{Zn}(\text{NO}_3)_2$  (C)  $\text{Al}(\text{NO}_3)_3$  (D)  $\text{Pb}(\text{NO}_3)_2$

SA0159

26. The final solution contains -
- (A)  $[\text{Pb}(\text{NH}_3)_4]^{2+}$  and  $[\text{CoCl}_4]^{2-}$  (B)  $[\text{Al}(\text{NH}_3)_4]^{3+}$  and  $[\text{Cu}(\text{NH}_3)_4]^{2+}$   
 (C)  $[\text{Ag}(\text{NH}_3)_2]^+$  and  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  (D)  $[\text{Ag}(\text{NH}_3)_2]^+$  and  $[\text{Ni}(\text{NH}_3)_6]^{2+}$

SA0159

27. Which of the following hydrogen halides react(s) with  $\text{AgNO}_3(\text{aq})$  to give a precipitate that dissolves in  $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ : [JEE 2012]

- (A) HCl (B) HF (C) HBr (D) HI

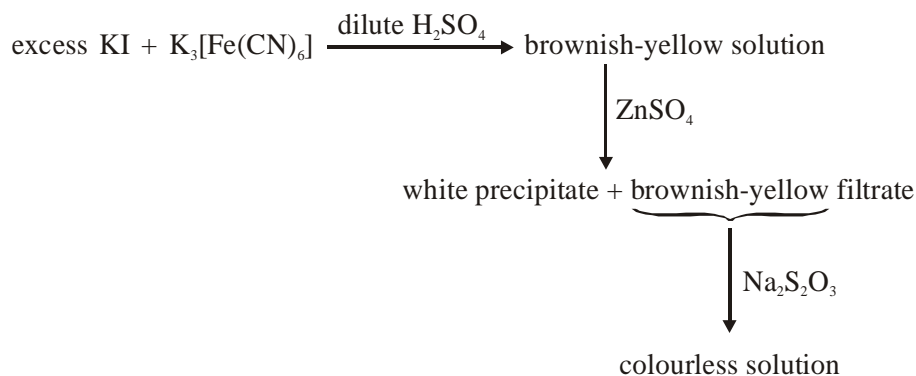
SA0160

28. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type ; the oxidation states of phosphorus in phosphine and the other product are respectively [JEE 2012]

- (A) redox reaction ; -3 and -5 (B) redox reaction ; +3 and +5  
 (C) disproportionation reaction ; -3 and +1 (D) disproportionation reaction ; -3 and +3

SA0161

29. For the given aqueous reactions, which of the statement(s) is (are) true ? [JEE 2012]



- (A) The first reaction is a redox reaction.  
 (B) White precipitate is  $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ .  
 (C) Addition of filtrate to starch solution gives blue colour.  
 (D) White precipitate is soluble in NaOH solution.

SA0162

30. Upon treatment with ammonical  $\text{H}_2\text{S}$ , the metal ion that precipitates as a sulfide is -

- (A) Fe(III) (B) Al(III) (C) Mg(II) (D) Zn (II) [JEE 2013]

SA0163

**Paragraph for Question 31 and 32**

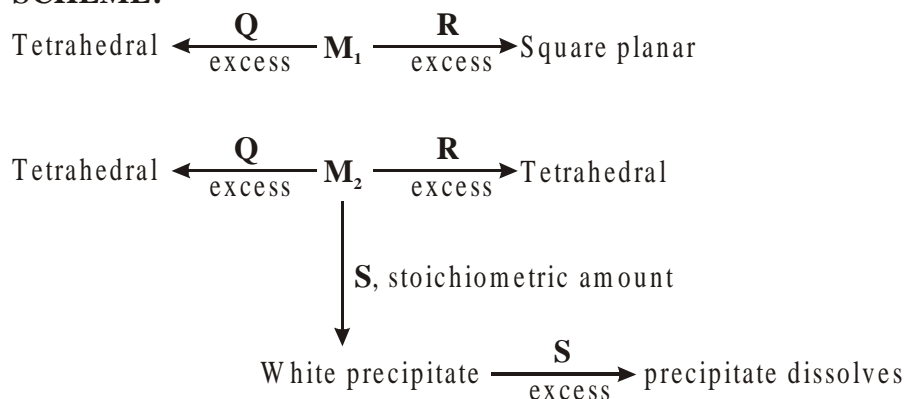
An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (P) and a filtrate (Q). The precipitate (P) was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with H<sub>2</sub>S in a dilute mineral acid medium. However, it gave a precipitate (R) with H<sub>2</sub>S in an ammoniacal medium. The precipitate R gave a coloured solution (S), when treated with H<sub>2</sub>O<sub>2</sub> in an aqueous NaOH medium. [JEE 2013]

31. The coloured solution (S) contains  
 (A) Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>                      (B) CuSO<sub>4</sub>                      (C) ZnSO<sub>4</sub>                      (D) Na<sub>2</sub>CrO<sub>4</sub> SA0164
32. The precipitate (P) contains  
 (A) Pb<sup>2+</sup>                      (B) Hg<sub>2</sub><sup>2+</sup>                      (C) Ag<sup>+</sup>                      (D) Hg<sup>2+</sup> SA0164
33. Consider the following list of reagents : [JEE Adv. 2014]  
 Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, alkaline KMnO<sub>4</sub>, CuSO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, Cl<sub>2</sub>, O<sub>3</sub>, FeCl<sub>3</sub>, HNO<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.  
 The total number of reagents that can oxidise aqueous iodide to iodine is SA0165
34. Among PbS, CuS, HgS, MnS, Ag<sub>2</sub>S, NiS, CoS, Bi<sub>2</sub>S<sub>3</sub>, and SnS<sub>2</sub> the total number of BLACK coloured sulphides is [JEE Adv. 2014]  
SA0166

**Paragraph for Q.No. 35 and 36**

An aqueous solution of metal ion M<sub>1</sub> reacts separately with reagents Q and R in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion M<sub>2</sub> always forms tetrahedral complexes with these reagents. Aqueous solution of M<sub>2</sub> on reaction with reagent S gives white precipitate which dissolves in excess of S. The reactions are summarized in the scheme given below. [JEE Adv. 2014]

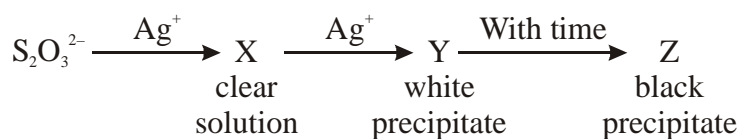
**SCHEME:**



35. M<sub>1</sub>, Q and R, respectively are  
 (A) Zn<sup>2+</sup>, KCN and HCl                      (B) Ni<sup>2+</sup>, HCl and KCN  
 (C) Cd<sup>2+</sup>, KCN and HCl                      (D) Co<sup>2+</sup>, HCl and KCN SA0167



36. Reagent **S** is  
 (A)  $K_4[Fe(CN)_6]$  (B)  $Na_2HPO_4$  (C)  $K_2CrO_4$  (D)  $KOH$  SA0167
37.  $Fe^{3+}$  is reduced to  $Fe^{2+}$  by using - [JEE Adv. 2015]  
 (A)  $H_2O_2$  in presence of  $NaOH$  (B)  $Na_2O_2$  in water  
 (C)  $H_2O_2$  in presence of  $H_2SO_4$  (D)  $Na_2O_2$  in presence of  $H_2SO_4$  SA0168
38. The pair(s) of ions where BOTH the ions are precipitated upon passing  $H_2S$  gas in presence of dilute  $HCl$ , is(are) [JEE Adv. 2015]  
 (A)  $Ba^{2+}$ ,  $Zn^{2+}$  (B)  $Bi^{3+}$ ,  $Fe^{3+}$  (C)  $Cu^{2+}$ ,  $Pb^{2+}$  (D)  $Hg^{2+}$ ,  $Bi^{3+}$  SA0169
39. The reagent(s) that can selectively precipitate  $S^{2-}$  from a mixture of  $S^{2-}$  and  $SO_4^{2-}$  in aqueous solution is(are) : [JEE(Adv.)-2016]  
 (A)  $CuCl_2$  (B)  $BaCl_2$  (C)  $Pb(OOCCH_3)_2$  (D)  $Na_2[Fe(CN)_5NO]$  SA0170
40. In the following reaction sequence in aqueous solution, the species **X**, **Y** and **Z** respectively, are - [JEE(Adv.)-2016]



- (A)  $[Ag(S_2O_3)_2]^{3-}$ ,  $Ag_2S_2O_3$ ,  $Ag_2S$  (B)  $[Ag(S_2O_3)_3]^{5-}$ ,  $Ag_2SO_3$ ,  $Ag_2S$   
 (C)  $[Ag(SO_3)_2]^{3-}$ ,  $Ag_2S_2O_3$ ,  $Ag$  (D)  $[Ag(SO_3)_3]^{3-}$ ,  $Ag_2SO_4$ ,  $Ag$

SA0171

41. Which of the following combination will produce  $H_2$  gas ? [JEE(Adv.)-2017]  
 (A)  $Zn$  metal and  $NaOH(aq)$  (B)  $Au$  metal and  $NaCN(aq)$  in the presence of air  
 (C)  $Cu$  metal and conc.  $HNO_3$  (D)  $Fe$  metal and conc.  $HNO_3$  SA0172

42. Addition of excess aqueous ammonia to a pink coloured aqueous solution of  $MCl_2 \cdot 6H_2O$  (X) and  $NH_4Cl$  gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1 : 3 electrolyte. The reaction of X with excess  $HCl$  at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y. [JEE(Adv.)-2017]

Among the following options, which statements is(are) correct ?

- (A) The hybridization of the central metal ion in Y is  $d^2sp^3$   
 (B) Z is tetrahedral complex  
 (C) Addition of silver nitrate to Y gives only two equivalents of silver chloride  
 (D) When X and Z are in equilibrium at  $0^\circ C$ , the colour of the solution is pink

SA0173

43. The correct option(s) to distinguish nitrate salts of  $\text{Mn}^{2+}$  and  $\text{Cu}^{2+}$  taken separately is (are) :-
- (A)  $\text{Mn}^{2+}$  shows the characteristic green colour in the flame test **JEE(Adv.)-2018]**  
(B) Only  $\text{Cu}^{2+}$  shows the formation of precipitate by passing  $\text{H}_2\text{S}$  in acidic medium  
(C) Only  $\text{Mn}^{2+}$  shows the formation of precipitate by passing  $\text{H}_2\text{S}$  in faintly basic medium  
(D)  $\text{Cu}^{2+}/\text{Cu}$  has higher reduction potential than  $\text{Mn}^{2+}/\text{Mn}$  (measured under similar conditions)

SA0174

44. The green colour produced in the borax bead test of a chromium(III) salt is due to-

[JEE(Adv.)-2019]

- (1)  $\text{Cr}(\text{BO}_2)_3$                       (2)  $\text{CrB}$                       (3)  $\text{Cr}_2(\text{B}_4\text{O}_7)_3$                       (4)  $\text{Cr}_2\text{O}_3$

SA0175

## ANSWER KEY

## EXERCISE # I

1. (A)	2. (C)	3. (C)	4. (D)	5. (D)	6. (A,B)	
7. (A) → R,S; (B) → Q; (C) → P,Q,S,T; (D) → P,Q,S,T	8. (1)					
9. (D)	10. (D)	11. (C)	12. (D)	13. (B)	14. (C)	15. (B)
16. (A)	17. (C)	18. (B)	19. (B)	20. (D)	21. (C)	22. (A)
23. (B)	24. (B)	25. (D)	26. (B)	27. (C)	28. (A,B)	29. (A)
30. (C)	31. (2)	32. (4)	33. (2)	34. (D)	35. (B)	36. (D)
37. (C)	38. (C)	39. (C,D)	40. (B)	41. (B)	42. (D)	43. (D)

## EXERCISE # II

1. (B)	2. (C)	3. (C)	4. (A)	5. (B)	6. (B)	7. (B)
8. (B)	9. (B)	10. (D)	11. (B)	12. (B)	13. (A,B,C,D)	14. (C)
15. (C)	16. (C)	17. (B)	18. (B)	19. (B)	20. (D)	21. (C)
22. (B)	23. (B)	24. (D)	25. (C)	26. (B)	27. (C)	28. (C)
29. (C)	30. (B)	31. (A)	32. (B)	33. (D)	34. (D)	35. (C)
36. (B)	37. (D)	38. (C)	39. (D)	40. (A)	41. (C)	42. (A,C,D)
43. (C)	44. (A)	45. (A,B,C)	46. (B,C,D)	47. (A,C,D)	48. (B,D)	49. (D)
50. (A)	51. (D)	52. (D)	53. (A,C)	54. (D)	55. (B)	56. (C)
57. (B)	58. (A,B)	59. (D)	60. (B)	61. (B)	62. (B)	63. (A)
64. (A)	65. (C)	66. (B)	67. (C)	68. (D)		
69. (A) → Q, R; (B) → Q; (C) → P; (D) → S, T	70. (A) → P; (B) → S; (C) → R; (D) → Q, R					
71. (B)	72. (D)	73. (C)	74. (3)	75. (2)		

## EXERCISE # JEE MAINS

1. (4)	2. (4)	3. (4)	4. (2)	5. (2)	6. (2)	7. (1)
8. (2)	9. (2)	10. (3)	11. (4)	12. (4)	13. (3)	14. (4)
15. (3)	16. (1)	17. (4)	18. (2)	19. (3)	20. (4)	21. (1)
22. (4)	23. (3)	24. (1)	25. (4)	26. (3)	27. (4)	28. (2)
29. (3)	30. (2)	31. (4)	32. (2)	33. (4)		

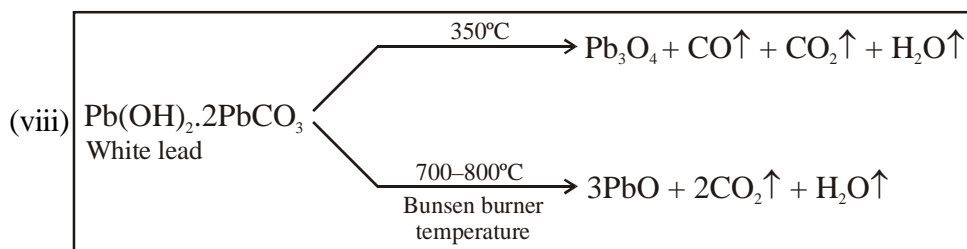
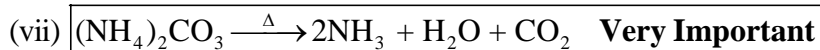
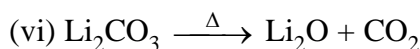
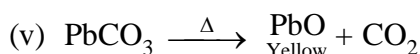
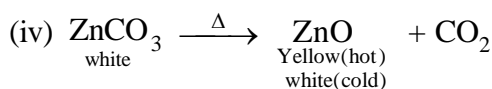
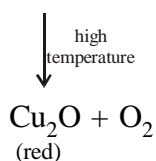
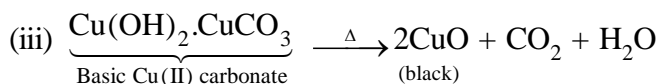
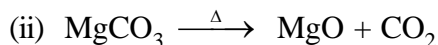
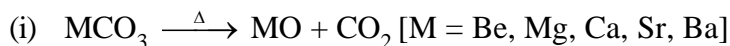
## EXERCISE # J-ADVANCED

1. (A, B, C)	2. (A, B, D)	3. (D)	4. (C)	5. (A)	6. (B)	7. (A)
8. (B)	9. (A)	10. (B)	11. (D)	12. (A)	13. (A)	
14. (A) → P, S; (B) → R; (C) → P, Q; (D) → P	15. (B)	16. (A),(B)	17. (D)			
18. (C)	19. (B)	20. (A) → P,S; (B) → Q,S; (C) → R,T; (D) → Q, T	21. (A)			
22. (A,C,D)	23. (B,C,D)	24. (B)	25. (A)	26. (C)	27. (A,C,D)	28. (C)
29. (A,C,D)	30. (D)	31. (D)	32. (A)	33. (7)	34. (6) / (7)	35. (B)
36. (D)	37. (A, B)	38. (C,D)	39. (A OR A, C)	40. (A)	41. (A)	
42. (A,B,D)	43. (B,D)	44. (1)				

## HEATING EFFECT

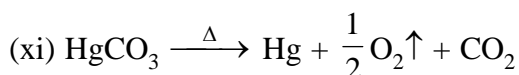
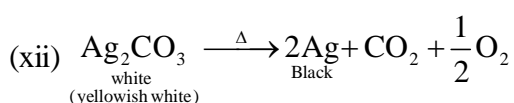
## 1. HEATING EFFECT OF CARBONATE &amp; BICARBONATE SALTS :

(a) Heating effect of carbonate salts :

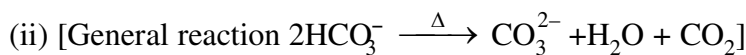
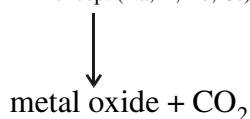
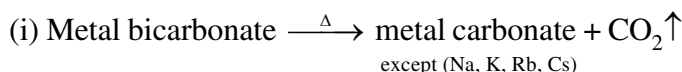
Metal carbonate  $\xrightarrow{\Delta}$  metal oxide +  $\text{CO}_2\uparrow$ (ix) All carbonates **except** (Na, K, Rb, Cs) decompose on heating giving  $\text{CO}_2$ 

(x) Carbonates salts of (Na, K, Rb, Cs) do not decompose on heating, they are melt on high temperature.

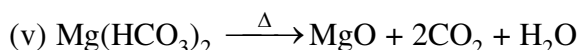
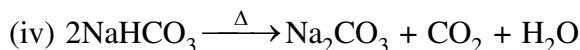
(xi) Oxides of heavier metals are less stable so further decompose into metal &amp; oxygen



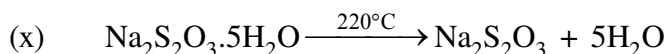
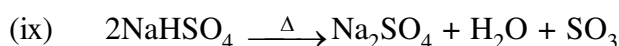
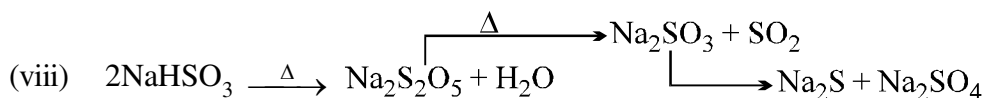
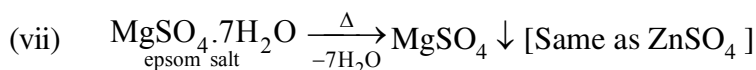
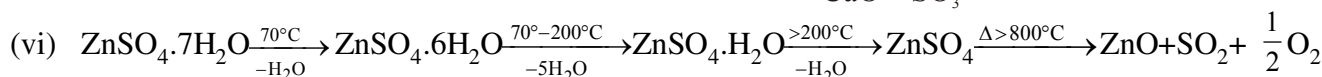
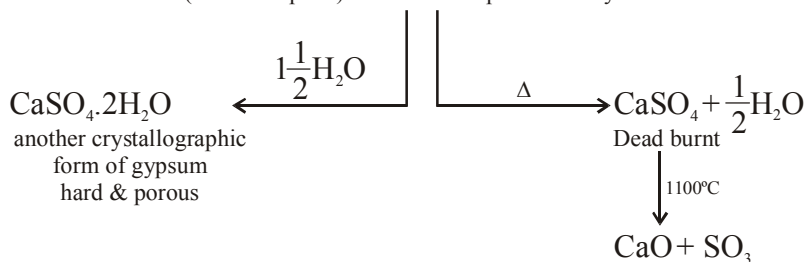
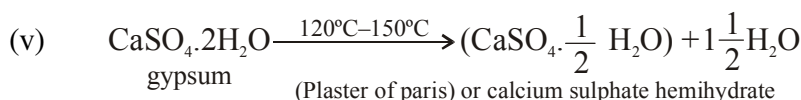
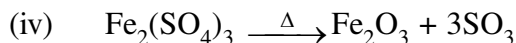
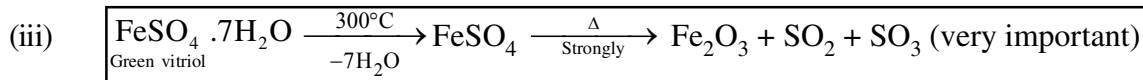
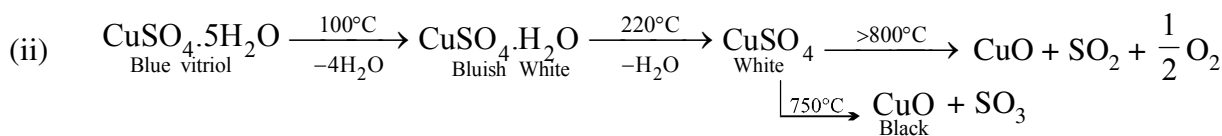
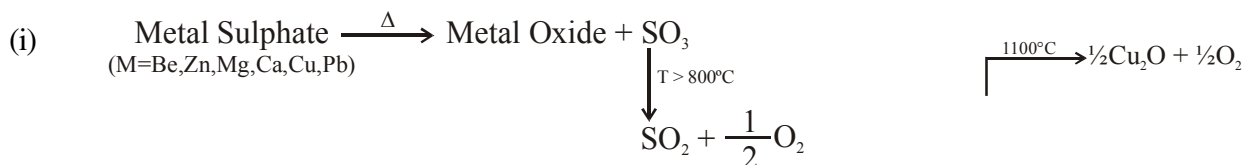
(b) Heating effect of bicarbonate :



(iii) All bicarbonates decompose to give carbonates and CO<sub>2</sub>. eg.



**2. HEATING EFFECT OF HYDRATED SULPHATE SALTS :**

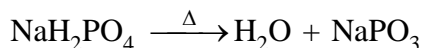




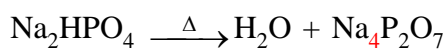
- (i)  $(\text{NH}_4)_2\text{HPO}_4 \xrightarrow{\Delta} \text{HPO}_3 + \text{H}_2\text{O} + 2\text{NH}_3$
- (ii)  $(\text{NH}_4)_2\text{SO}_4 \xrightarrow{\Delta} \text{NH}_3 + \text{H}_2\text{SO}_4$
- (iii)  $2(\text{NH}_4)_3\text{PO}_4 \xrightarrow{\Delta} 2\text{NH}_3 + \text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$
- (iv)  $(\text{NH}_4)_2\text{CO}_3 \xrightarrow{\Delta} 2\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$
- (v)  $\text{NH}_4\text{Cl} \xrightarrow{\Delta} \text{NH}_3\uparrow + \text{HCl}\uparrow$
- (vi)  $(\text{NH}_4)_2\text{S} \xrightarrow{\Delta} \text{NH}_3\uparrow + \text{H}_2\text{S}\uparrow$
- (vii)  $\text{NH}_4\text{F} \xrightarrow{\Delta} \text{NH}_3 + \text{HF}$
- (viii)  $(\text{NH}_4)_2\text{MoO}_4 \xrightarrow{\Delta} \text{NH}_3\uparrow + \text{MoO}_3 + \text{H}_2\text{O}$

## 5. HEATING EFFECT OF PHOSPHATE SALTS :

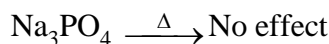
- (i) 1° Phosphate salts gives metaphosphate salt on heating.



- (ii) 2° Phosphate salts gives pyrophosphate



- (iii) 3° Phosphate salt have no heating effect

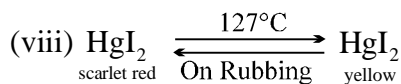


- (iv)  $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O} \xrightarrow[-4\text{H}_2\text{O}]{\Delta} \text{NaNH}_4\text{HPO}_4 \xrightarrow{\text{High temp.}} \text{NaPO}_3 + \text{NH}_3 + \text{H}_2\text{O}$   
microcosmic salt

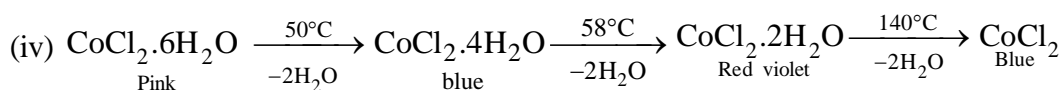
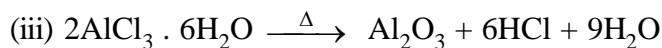
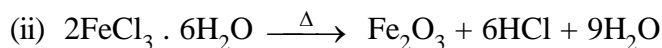
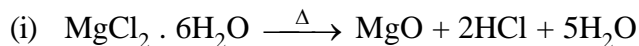
- (v)  $2\text{Mg}(\text{NH}_4)\text{PO}_4 \xrightarrow{\Delta} \text{Mg}_2\text{P}_2\text{O}_7 + 2\text{NH}_3 + \text{H}_2\text{O}$

## 6. HEATING EFFECT OF HALIDES SALTS :

- (i)  $2\text{FeCl}_3 \xrightarrow{\Delta} 2\text{FeCl}_2 + \text{Cl}_2$
- (ii)  $\text{AuCl}_3 \xrightarrow{\Delta} \text{AuCl} + \text{Cl}_2$
- (iii)  $\text{Hg}_2\text{Cl}_2 \xrightarrow{\Delta} \text{HgCl}_2 + \text{Hg}$
- (iv)  $\text{NH}_4\text{Cl} \xrightarrow{\Delta} \text{NH}_3 + \text{HCl}$
- (v)  $\text{Pb}(\text{SCN})_4 \xrightarrow{\Delta} \text{Pb}(\text{SCN})_2 + (\text{SCN})_2$
- (vi)  $\text{PbCl}_4 \xrightarrow{\Delta} \text{PbCl}_2 + \text{Cl}_2$
- (vii)  $\text{PbBr}_4 \xrightarrow{\Delta} \text{PbBr}_2 + \text{Br}_2$  [**PbI<sub>4</sub> does not exists**]



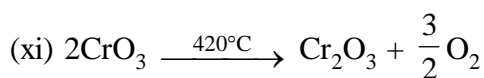
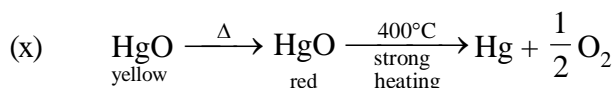
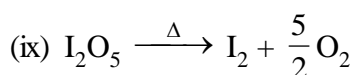
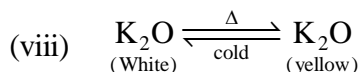
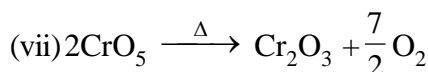
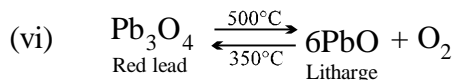
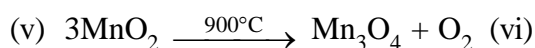
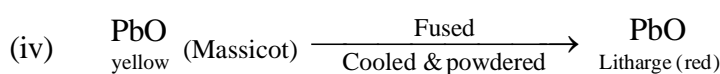
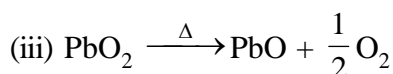
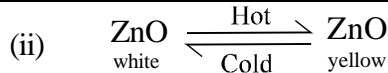
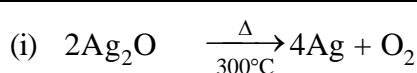
## 7. HEATING EFFECT OF HYDRATED CHLORIDE SALTS



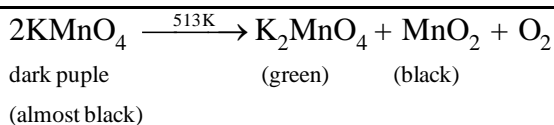
Hydrated  $\text{Co}^{2+}$  salt - Pink

Anhydrous  $\text{Co}^{2+}$  salt - Blue

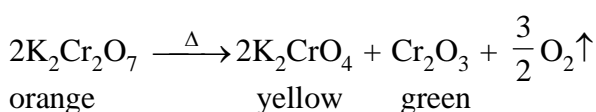
## 8. HEATING EFFECT OF OXIDE :



## 9. HEATING EFFECT OF PERMANGANATE :

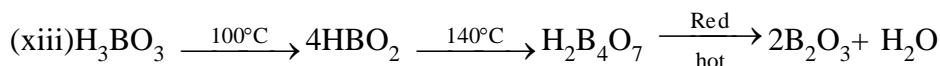
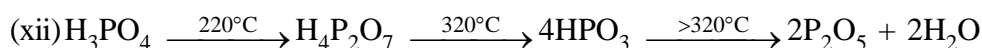
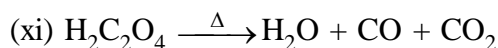
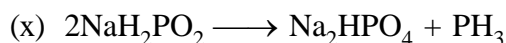
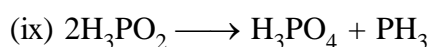
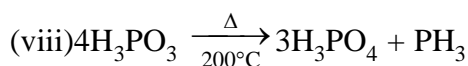
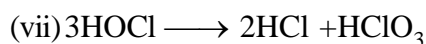
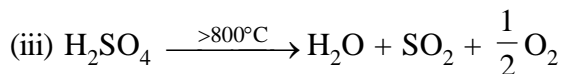
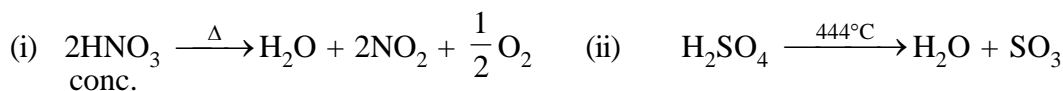


## 10. HEATING EFFECT OF DICHROMATE & CHROMATE SALTS :



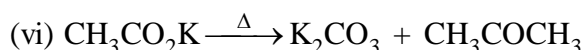
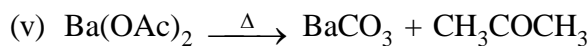
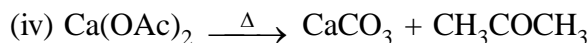
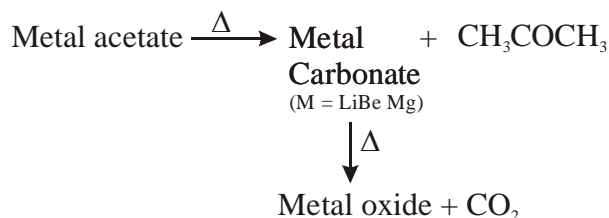
## 11. HEATING EFFECT OF ACIDS :



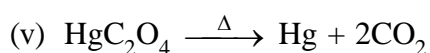
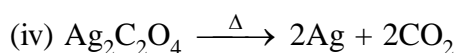
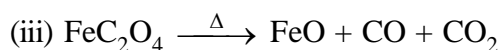
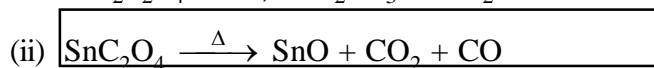
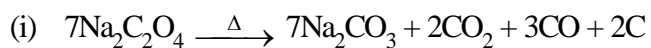
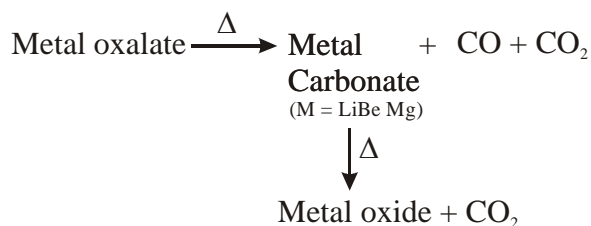


Undergoes  
dispropor-  
-tionation  
reaction

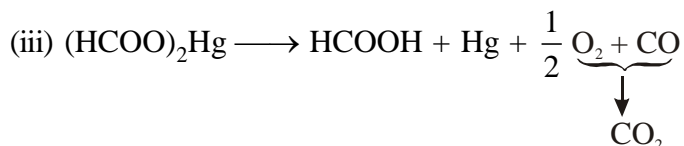
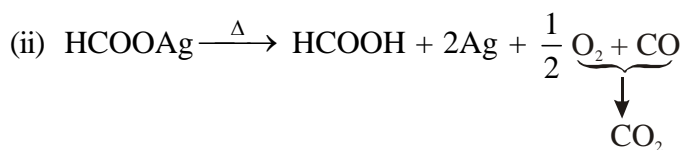
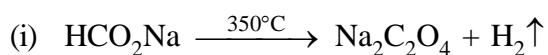
## 12. HEATING EFFECTS OF ACETATE SALTS



## 13. HEATING EFFECTS OF OXALATE SALTS



#### 14. HEATING EFFECTS OF FORMATE SALTS



## EXERCISE

*Single correct*

- Which of the following does not give metal oxide on heating  
(A)  $\text{NaCO}_3$  (B)  $\text{K}_2\text{CO}_3$  (C)  $\text{Rb}_2\text{CO}_3$  (D) All of these  
**HE0001**
- Which of the following metal bicarbonate will give metal oxide and  $\text{CO}_2$  on heating  
(A)  $\text{NaHCO}_3$  (B)  $\text{Mg}(\text{HCO}_3)_2$  (C)  $\text{KHCO}_3$  (D)  $\text{Rb}_2\text{CO}_3$   
**HE0002**
- Which of the following metal nitrate will give metal and oxygen on heating :  
(A)  $\text{KNO}_3$  (B)  $\text{NaNO}_3$  (C)  $\text{AgNO}_3$  (D)  $\text{RbNO}_3$   
**HE0003**
- Which of the following nitrate will give  $\text{N}_2\text{O}$  on heating :  
(A)  $\text{NH}_4\text{NO}_3$  (B)  $\text{NH}_4\text{NO}_2$  (C)  $\text{NaNO}_3$  (D)  $\text{AgNO}_3$   
**HE0004**
- Which of the following ammonium salt will not give acid on heating :  
(A)  $(\text{NH}_4)_2\text{HPO}_4$  (B)  $(\text{NH}_4)_2\text{MoO}_4$  (C)  $(\text{NH}_4)_2\text{SO}_4$  (D)  $\text{NH}_4\text{Cl}$   
**HE0005**
- Which of the following halide will not give halogen gas on heating :  
(A)  $\text{PbCl}_4$  (B)  $\text{PbBr}_4$  (C)  $\text{Hg}_2\text{Cl}_2$  (D) All of these  
**HE0006**
- Select the correct statements  
(A) Hydrated  $\text{Co}^{+2}$  salt is pink (B) Anhydrous  $\text{Co}^{+2}$  salt is of blue colour  
(C) Hybridisation of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  is  $\text{sp}^3\text{d}^2$  (D) All of these  
**HE0007**
- Which of the following metal sulphate will give  $\text{SO}_2$  and  $\text{SO}_3$  both gaseous product on heating :  
(A)  $\text{CuSO}_4$  (B)  $\text{FeSO}_4$  (C)  $\text{Fe}_2(\text{SO}_4)_3$  (D)  $\text{CaSO}_4$   
**HE0008**
- Which of the following compound is called dead burnt plaster :  
(A)  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (B)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (C)  $\text{CaSO}_4$  (anhy.) (D) None of these  
**HE0009**

10. When  $\text{NaH}_2\text{PO}_4$  is heated then which of the following compound is formed :  
 (A)  $\text{Na}_4\text{P}_2\text{O}_7$  (B)  $\text{Na}_3\text{PO}_4$  (C)  $\text{HPO}_3$  (D)  $\text{NaPO}_3$  HE0010
11. When  $\text{KMnO}_4$  is heated then which of the following compound is formed :  
 (A)  $\text{K}_2\text{MnO}_4 + \text{MnO}_2$  (B)  $\text{K}_2\text{MnO}_4 + \text{MnO}$  (C)  $\text{MnO}_2 + \text{MnO}$  (D) No change HE0011
12. When  $\text{CrO}_3$  is heated then ..... + ..... are formed :  
 (A)  $\text{Cr}_2\text{O}_3, \text{O}_2$  (B)  $\text{CrO}_2, \text{O}_2$  (C)  $\text{Cr}_2\text{O}_7^{-2}, \text{O}_2$  (D) None of these HE0012

*More than one may be correct*

13. Which of the following metal carbonate will give of metal and oxygen on heating-  
 (A)  $\text{Ag}_2\text{CO}_3$  (B)  $\text{HgCO}_3$  (C)  $(\text{NH}_4)_2\text{CO}_3$  (D)  $\text{PbCO}_3$  HE0013
14. 
$$\begin{array}{ccc} \text{A} & \xrightarrow{\Delta} & \text{B} + \text{CO}_2 + \text{H}_2\text{O} \\ \text{(Carbonate salt)} & & \text{(Black)} \\ \text{(Green colour)} & & \downarrow \\ & & \begin{array}{c} \text{High} \\ \text{temperature} \\ 920^\circ\text{C} \end{array} \\ & & \text{(C) + (D)} \end{array}$$

Select the correct statements -

- (A) Compound (A) is basic copper carbonate  
 (B) Compound (B)  $\text{CuO}$   
 (C) Compound (C) is  $\text{Cu}_2\text{O}$   
 (D) Compound (D) is paramagnetic in nature HE0014
15. When  $\text{Ag}_2\text{CO}_3$  is heated then product will be -  
 (A)  $\text{Ag}_2\text{O}$  (B)  $\text{Ag}$  (C)  $\text{O}_2$  (D)  $\text{CO}_2$  HE0015
16. When compound A (orange red) is heated then green colour oxide of (B) is formed and inert gas (C) is formed then select the correct statements :  
 (A) Compound (A) is  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$   
 (B) Compound (B) is used in fire works  
 (C) Gas C is  $\text{N}_2$   
 (D) Heating effect of (A) is a type of intra molecular redox reaction HE0016

17. Which of the following hydrated salts will not become anhydrous on heating :

- (A)  $MgCl_2 \cdot 6H_2O$       (B)  $FeCl_3 \cdot 6H_2O$       (C)  $AlCl_3 \cdot 6H_2O$       (D)  $CoCl_2 \cdot 6H_2O$

HE0017

18. Which of the following metal nitrate produce  $NO_2$  on heating

- (A)  $Hg(NO_3)_2$       (B)  $RbNO_3$       (C)  $Pb(NO_3)_2$       (D)  $Cu(NO_3)_2$

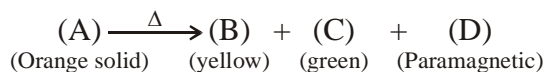
HE0018

19. Which of the following oxides turns yellow on heating and becomes white on cooling :

- (A)  $ZnO$       (B)  $K_2O$       (C)  $PbO$       (D)  $Ag_2O$

HE0019

Paragraph for Q. No. 20 to Q. No. 21



20. Compound (A) is :

- (A)  $K_2Cr_2O_7$       (B)  $K_2CrO_4$       (C)  $Cr_2O_3$       (D)  $O_2$

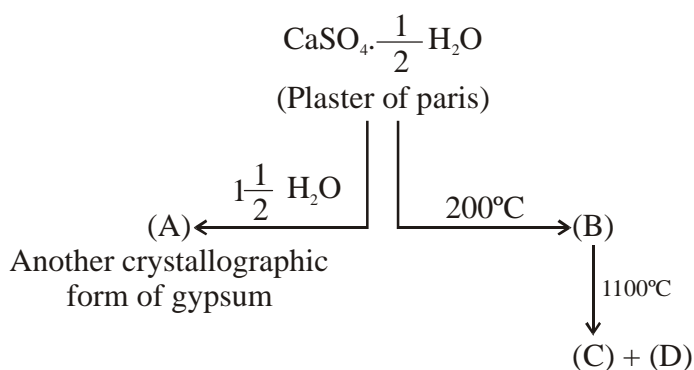
HE0020

21. Compound (C) is also obtained on heating of :

- (A)  $(NH_4)_2Cr_2O_7$       (B)  $NH_4ClO_4$       (C)  $NH_4NO_3$       (D) None of these

HE0020

Paragraph for Q. No. 22 & 23



22. Compound "A" is :

- (A)  $CaSO_4 \cdot 2H_2O$       (B)  $2CaSO_4 \cdot H_2O$       (C)  $CaSO_4 \cdot 3H_2O$       (D)  $CaSO_4 \cdot 5H_2O$

HE0021

23. Compound "C" and "D" are respectively :

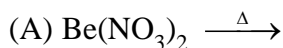
- (A)  $\text{CaO} + \text{CaSO}_4$     (B)  $\text{CaSO}_4 + \text{SO}_2$     (C)  $\text{CaSO}_4 + \text{SO}_3$     (D)  $\text{CaO} + \text{SO}_3$

HE0021

**Matrix match**

24. Match the column

**Column-I**



**Column-II**

(P) Gives  $\text{H}_2\text{O}$

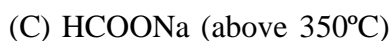
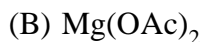
(Q) Oxyacid is obtained

(R) Gives disproportionation reaction

(S) Oxygen gas is evolved

HE0022

25. **Column-I (Compound)**



**Column-II (Products on heating)**

(P)  $\text{CO}_2$  gas is evolved

(Q)  $\text{H}_2$  gas is evolved

(R)  $\text{N}_2$  gas is evolved

(S) Same gas is evolved which is obtained by heating  $(\text{NH}_4)_2\text{SO}_4$

(T) Intra molecular redox reaction

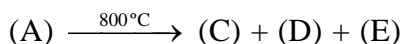
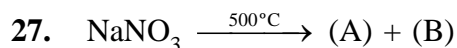
HE0023

**Integer**

26. When calamine is heated then a product (A) is formed then find the total number of following options are correct for compound (A) -

- Compound (A) is white in cold conditions
- Compound (A) is yellow in hot conditions
- Compound (A) is called phillosopher's wool
- Compound (A) when combined with  $\text{CoO}$ , then compound (B) is formed & colour of new compound (B) is green
- Compound (B) is called Rinmann's green

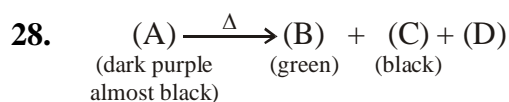
HE0024



Find the number of correct statements

- (1) Compound (B) is paramagnetic in nature
- (2) Compound (B) when undergoes dimerisation then dimer product is diamagnetic in nature
- (3) Bond order of compound (B) is two
- (4) D is  $\text{N}_2$  gas
- (5) Compound B and E are same gas

HE0025



Find the number of correct statements

- (1) Compound B is  $\text{K}_2\text{MnO}_4$
- (2) Compound C is  $\text{MnO}_2$
- (3) Compound D is  $\text{O}_2$
- (4) Compound B is paramagnetic in nature
- (5) Compound D has two unpaired electron in bonding molecular orbital

HE0026

29. Total number of compounds undergoes disproportionation redox reaction on heating  
 $\text{MnO}_2$ ,  $\text{HOCl}$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{HNO}_2$ ,  $\text{CrO}_5$ ,  $\text{HClO}_3$

HE0027

30. On strong heating of  $\text{H}_3\text{PO}_4$  and  $\text{H}_3\text{BO}_3$ , sum of oxidation number of P & B in the final product obtained is

HE0028

## ANSWER-KEY

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	D	B	C	A	B	C	D	B	C	D
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	A	A	A, B	A,B,C,D	B,C,D	A,B,C,D	A, B, C	A,C,D	A, B	A
Que.	21	22	23	24						
Ans.	A	A	D	(A)→(S);(B)→(P,Q,R);(C)→(P);(D)→(Q,R)						
Que.	25					26	27	28	29	30
Ans.	(A)→(R,T);(B)→(P);(C)→(P,Q,T);(D)→(P,S)					5	4	4	4	8



## s-BLOCK ELEMENT

### OBJECTIVES

After studying this unit you will be able to :

- Describe the general characteristics of the alkali metals and their compounds;
- Explain the general characteristics of the alkaline earth metals and their compounds;
- Describe the manufacture, properties and uses of industrially important sodium and calcium compounds including Portland cement :

- Appreciate the biological significance of sodium, potassium, magnesium and calcium.

The *s*-block elements of the Periodic Table are those in which the last electron enters the outermost *s*-orbital. As the *s*-orbital can accommodate only two electrons, two groups (1 & 2) belong to the *s*-block of the Periodic Table. Group 1 of the Periodic Table consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the *alkali metals*. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature. The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the *alkaline earth metals*. These are so called because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust\*.

Among the alkali metals sodium and potassium are abundant and lithium, rubidium and caesium have much lower abundances. Francium is highly radioactive; its longest-lived isotope  $^{223}\text{Fr}$  has a half-life of only 21 minutes. Of the alkaline earth metals calcium and magnesium rank fifth and sixth in abundance respectively in the earth's crust. Strontium and barium have much lower abundances. Beryllium is rare and radium is the rarest of all comprising only 10–10 per cent of igneous rocks .

The general electronic configuration of *s*-block elements is [noble gas] $ns^1$  for alkali metals and [noble gas]  $ns^2$  for alkaline earth metals.

\* *The thin, rocky outer layer of the Earth is crust. † A type of rock formed from magma (molten rock) that has cooled and hardened.*

Lithium and beryllium, the first elements of Group 1 and Group 2 respectively exhibit some properties which are different from those of the other members of the respective group. In these anomalous properties they resemble the second element of the following group. Thus, lithium shows similarities to magnesium and beryllium to aluminium in many of their properties. This type of diagonal similarity is commonly referred to as *diagonal relationship* in the periodic table. The diagonal relationship is due to the similarity in ionic sizes and /or charge/radius ratio of the elements. Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in

biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

## 10.1 GROUP 1 ELEMENTS : ALKALI METALS

The alkali metals show regular trends in their physical and chemical properties with the increasing atomic number. The atomic, physical and chemical properties of alkali metals are discussed below.

### 10.1.1 Electronic Configuration

All the alkali metals have one valence electron,  $ns^1$  outside the noble gas core. The loosely held  $s$ -electron in the outermost valence shell of these elements makes them the most electropositive metals. They readily lose electron to give monovalent  $M^+$  ions. Hence they are never found in free state in nature.

Element	Symbol	Electronic configuration
Lithium	Li	$1s^2s^1$
Sodium	Na	$1s^22s^22p^63s^1$
Potassium	K	$1s^22s^22p^63s^23p^64s^1$
Rubidium	Rb	$1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^1$
Caesium	Cs	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^65p^66s^1$ or [Xe] $6s^1$
Francium	Fr	[Rn] $7s^1$

### 10.1.2 Atomic and Ionic Radii

$Li < Na < K < Rb < Cs$

Increase down the group, because value of  $n$  (principal quantum number) increases.

### 10.1.3 Ionization Enthalpy

$Li > Na > K > Rb > Cs$ .

This is because the effect of increasing size outweighs the increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge.

### 10.1.4 Hydration Enthalpy

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

$Li^+$  has maximum degree of hydration and for this reason lithium salts are mostly hydrated, e.g.,  $LiCl \cdot 2H_2O$

### 10.1.5 Physical Properties

- All the alkali metals are silvery white, soft and light metals.
- Because of the large size, these elements have low density which increases down the group from Li to Cs. However, potassium is lighter than sodium.  
 $Li < K < Na < Rb < Cs$ .
- The melting and boiling points of the alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them.
- The alkali metals and their salts impart characteristic colour to an oxidizing flame. This is because the heat from the flame excites the outermost orbital electron to a higher energy

level. When the excited electron comes back to the ground state, there is emission of radiation in the visible region as given below :

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet	Red violet	Blue
$\lambda/\text{nm}$	670.8	589.2	766.5	780.0	455.5

- (v) Alkali metals can therefore, be detected by the respective flame tests and can be determined by flame photometry or atomic absorption spectroscopy.
- (vi) These elements when irradiated with light, the light energy absorbed may be sufficient to make an atom lose electron.

**Table : Atomic and Physical Properties of the Alkali Metals**

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass ( $\text{g mol}^{-1}$ )	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	$[\text{He}]2s^1$	$[\text{Ne}] 3s^1$	$[\text{Ar}] 4s^1$	$[\text{Kr}] 5s^1$	$[\text{Xe}] 6s^1$	$[\text{Rn}] 7s^1$
Ionization enthalpy/ $\text{kJ mol}^{-1}$	520	496	419	403	376	$\sim 375$
Hydration enthalpy/ $\text{kJ mol}^{-1}$	-506	-406	-330	-310	-276	-
Metallic radius/pm	152	186	227	248	265	-
Ionic radius $M^+$ /pm	76	102	138	152	167	(180)
m.p./K	454	371	336	312	302	-
b.p./K	1615	1156	1032	961	944	-
Density / $\text{g cm}^{-3}$	0.53	0.97	0.86	1.53	1.90	-
Standard Potentials $E^\ominus$ /V for ( $M^+/M$ )	-3.04	-2.714	-2.925	-2.930	-2.927	-
Occurrence in lithosphere	18*	2.27**	1.84**	78-12*	2-6*	$\sim 10^{-18}$ *

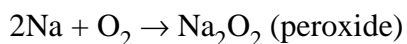
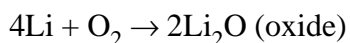
\*ppm (part per million), \*\*percentage by weight; † Lithosphere: The Earth's outer layer: its crust and part of the upper mantle.

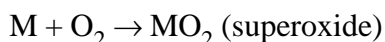
This property makes caesium and potassium useful as electrodes in photoelectric cells.

### 10.1.6 Chemical Properties

The alkali metals are highly reactive due to their large size and low ionization enthalpy. The reactivity of these metals increases down the group.

- (i) **Reactivity towards air :** The alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxides. The superoxide  $\text{O}_2^-$  ion is stable only in the presence of large cations such as K, Rb, Cs.





In all these oxides the oxidation state of the alkali metal is +1. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride,  $Li_3N$  as well. Because of their high reactivity towards air and water, **alkali metals are normally kept in kerosene oil.**

### Problem 10.1

What is the oxidation state of K in  $KO_2$ ?

#### Solution

The superoxide species is represented as  $O_2^-$ ; since the compound is neutral, therefore, the oxidation state of potassium is +1.

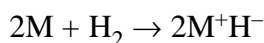
(ii) **Reactivity towards water** : The alkali metals react with water to form hydroxide and dihydrogen.



It may be noted that although lithium has most negative  $E^\ominus$  value, its reaction with water is less vigorous than that of sodium which has the least negative  $E^\ominus$  value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water.

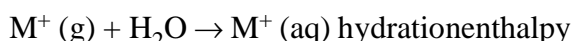
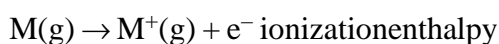
They also react with proton donors such as alcohol, gaseous ammonia and alkynes.

(iii) **Reactivity towards dihydrogen** : The alkali metals react with dihydrogen at about 673K (lithium at 1073K) to form hydrides. All the alkali metal hydrides are ionic solids with high melting points.



(iv) **Reactivity towards halogens** : The alkali metals readily react vigorously with halogens to form ionic halides,  $M^+X^-$ . However, lithium halides are somewhat covalent. It is because of the high polarisation capability of lithium ion (The distortion of electron cloud of the anion by the cation is called polarisation). The  $Li^+$  ion is very small in size and has high tendency to distort electron cloud around the negative halide ion. Since anion with large size can be easily distorted, among halides, lithium iodide is the most covalent in nature.

(v) **Reducing nature** : The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful. The standard electrode potential ( $E^\ominus$ ) which measures the reducing power represents the overall change :



With the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative  $E^\ominus$  value and its high reducing power.

### Problem 10.2

The  $E^\ominus$  for  $\text{Cl}_2/\text{Cl}^-$  is +1.36, for  $\text{I}_2/\text{I}^-$  is +0.53, for  $\text{Ag}^+/\text{Ag}$  is +0.79,  $\text{Na}^+/\text{Na}$  is -2.71 and for  $\text{Li}^+/\text{Li}$  is -3.04. Arrange the following ionic species in decreasing order of reducing strength :

$\text{I}^-$ ,  $\text{Ag}$ ,  $\text{Cl}^-$ ,  $\text{Li}$ ,  $\text{Na}$

### Solution

The order is  $\text{Li} > \text{Na} > \text{I}^- > \text{Ag} > \text{Cl}^-$

(vi) **Solutions in liquid ammonia :** The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.



The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of amide.

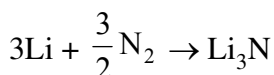
$\text{M}_{(\text{am})}^+ + \text{e}^- + \text{NH}_3(\text{l}) \rightarrow \text{MNH}_{2(\text{am})} + \frac{1}{2}\text{H}_2(\text{g})$  (where 'am' denotes solution in ammonia.) In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

(vii) **Reaction with  $\text{H}_2$**

They react with  $\text{H}_2$  forming metal hydride with formula  $\text{MH}$  which are of ionic nature. Stability of hydride decreases down the group.

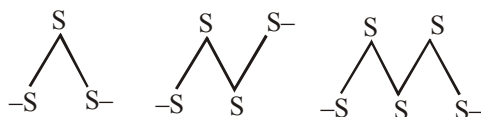
(viii) **Reaction with  $\text{N}_2$**

Only Lithium reacts with  $\text{N}_2$  to form ionic lithium nitride  $\text{Li}_3\text{N}$ .

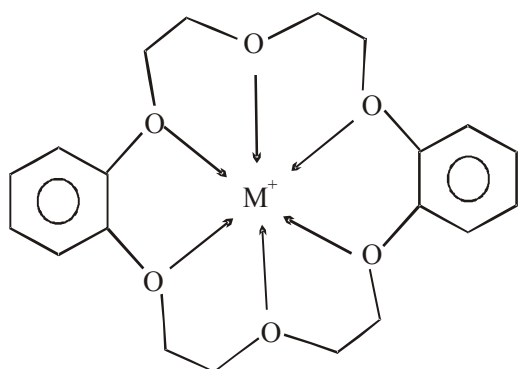


(ix) **Sulphides**

All metals react with S forming sulphides such as  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{S}_n$  ( $n = 2, 3, 4, 5$  or  $6$ ). The polysulphide ions are made from zig-zag chains of sulphur atoms.



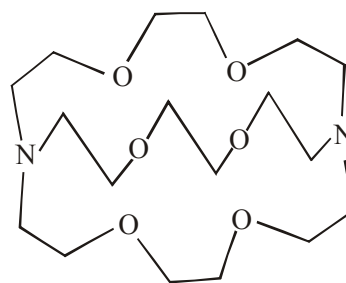
(x) **Crown Ethers and Cryptands :**



Dibenzo-18-Crown-6

$[\text{Na}(\text{Cryptand } 222)]^+ \text{Na}^-$

$[\text{Cs}^+(\text{Cryptand} - 222)]$



Cryptand - 222

$[\text{Contains } \text{Na}^- \text{ (sodide ion)}]$

$[(\text{Cryptand-222})\text{e}^-] \text{ [electride]}$

**10.1.7 Uses :**

Lithium metal is used to make useful alloys, for example with lead to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions.

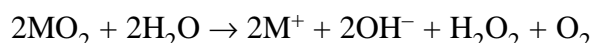
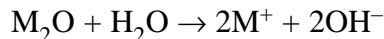
Lithium is also used to make electrochemical cells. Sodium is used to make a Na/Pb alloy needed to make  $\text{PbEt}_4$  and  $\text{PbMe}_4$ . These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors. Potassium has a vital role in biological systems. Potassium chloride is used as a fertilizer. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide. Caesium is used in devising photoelectric cells.

**10.2 GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS**

All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here.

**10.2.1 Oxides and Hydroxides**

On combustion in excess of air, lithium forms mainly the oxide,  $\text{Li}_2\text{O}$  (plus some peroxide  $\text{Li}_2\text{O}_2$ ), sodium forms the peroxide,  $\text{Na}_2\text{O}_2$  (and some oxide  $\text{Na}_2\text{O}$ ) whilst potassium, rubidium and caesium form the superoxides,  $\text{MO}_2$ . Under appropriate conditions pure compounds  $\text{M}_2\text{O}$ ,  $\text{M}_2\text{O}_2$  and  $\text{MO}_2$  may be prepared. The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects. These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions :



The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The superoxides are also paramagnetic. Sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

**Problem 10.3**

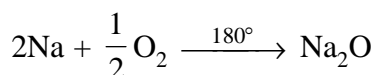
Why is  $\text{KO}_2$  paramagnetic ?

**Solution**

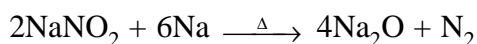
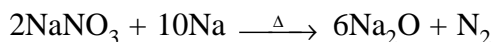
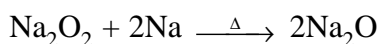
The superoxide  $\text{O}_2^-$  is paramagnetic because of one unpaired electron in  $\pi^*2p$  molecular orbital. The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat on account of intense hydration.

**Sodium Oxide ( $\text{Na}_2\text{O}$ ) :****Preparation :**

- (i) It is obtained by burning sodium at  $180^\circ\text{C}$  in a limited supply of air or oxygen and distilling off the excess of sodium in vacuum.



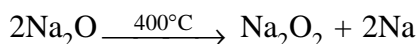
(ii) By heating sodium peroxide, nitrate or nitrite with sodium.



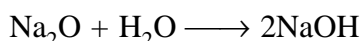
**Properties :**

(i) It is white amorphous mass.

(ii) It decomposes at 400°C into sodium peroxide and sodium

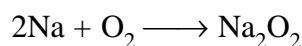


(iii) It dissolve violently in water, yielding caustic soda.



**Sodium Peroxides ( $\text{Na}_2\text{O}_2$ ) :**

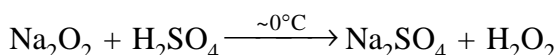
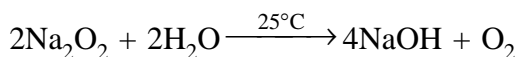
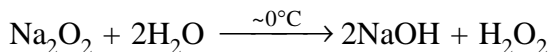
**Preparation:** It is formed by heating the metal in excess of air or oxygen at 300°, which is free from moisture and  $\text{CO}_2$ .



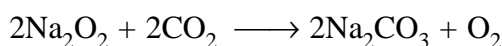
**Properties:**

(i) It is a pale yellow solid, becoming white in air from the formation of a film of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ .

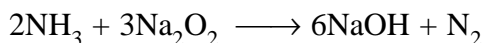
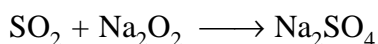
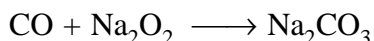
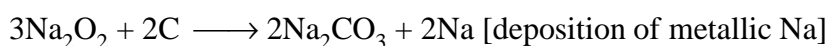
(ii) In cold water ( $\sim 0^\circ\text{C}$ ) produces  $\text{H}_2\text{O}_2$  but at room temperature produces  $\text{O}_2$ . In ice-cold mineral acids also produces  $\text{H}_2\text{O}_2$ .



(iii) It reacts with  $\text{CO}_2$ , giving sodium carbonate and oxygen and hence its use for purifying air in a confined space e.g. submarine, ill-ventilated room,



(iv) It is an oxidising agent and oxidises charcoal,  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ .



(v) It contains peroxide ion  $[-\text{O}-\text{O}-]^{-2}$

**Uses:**

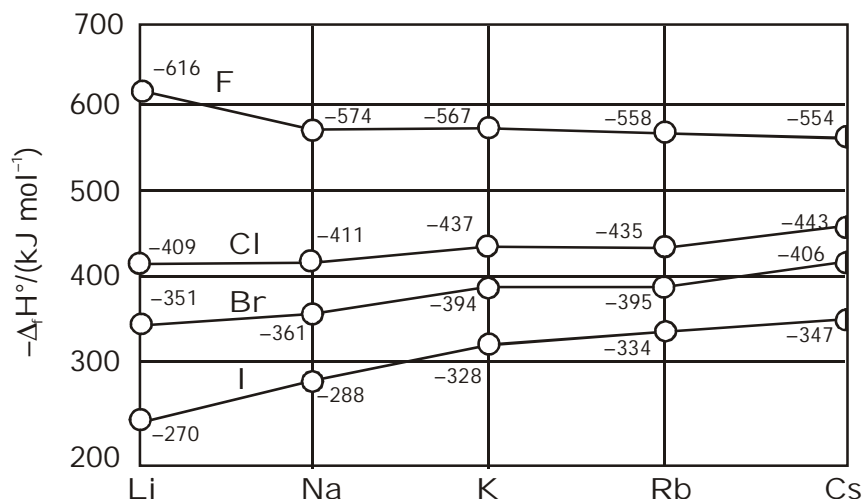
(i) For preparing  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$

(ii) Oxygenating the air in submarines

(iii) Oxidising agent in the laboratory.







The standard enthalpies of formation of the halides of Group 1 elements at 298 K

### 10.2.3 Salts of Oxo-Acids

Oxo-acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom e.g., carbonic acid,  $\text{H}_2\text{CO}_3$  ( $\text{OC}(\text{OH})_2$ ); sulphuric acid,  $\text{H}_2\text{SO}_4$  ( $\text{O}_2\text{S}(\text{OH})_2$ ). The alkali metals form salts with all the oxo-acids. They are generally soluble in water and thermally stable.

Their carbonates ( $\text{M}_2\text{CO}_3$ ) and in most cases the hydrogencarbonates ( $\text{MHCO}_3$ ) also are highly stable to heat. As the electropositive character increases down the group, the stability of the carbonates and hydrogencarbonates increases. Lithium carbonate is not so stable to heat; lithium being very small in size polarises a large  $\text{CO}_3^{2-}$  ion leading to the formation of more stable  $\text{Li}_2\text{O}$  and  $\text{CO}_2$ . Its hydrogencarbonate does not exist as a solid.

## 10.3 ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behaviour of lithium is due to the : (i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/ radius ratio). As a result, there is increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. Further, lithium shows diagonal relationship to magnesium which has been discussed subsequently.

### 10.3.1 Points of Difference between Lithium and other Alkali Metals

- (i) Lithium is much harder. Its m.p. and b.p. are higher than the other alkali metals.
- (ii) Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide,  $\text{Li}_2\text{O}$  and the nitride,  $\text{Li}_3\text{N}$  unlike other alkali metals.
- (iii)  $\text{LiCl}$  is deliquescent and crystallises as a hydrate,  $\text{LiCl} \cdot 2\text{H}_2\text{O}$  whereas other alkali metal chlorides do not form hydrates.
- (iv) Lithium hydrogencarbonate is not obtained in the solid form while all other elements form solid hydrogencarbonates.
- (v) Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.
- (vi) Lithium nitrate when heated gives lithium oxide,  $\text{Li}_2\text{O}$ , whereas other alkali metal nitrates decompose to give the corresponding nitrite.  

$$4\text{LiNO}_3 \rightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$$

$$2\text{NaNO}_3 \rightarrow 2\text{NaNO}_2 + \text{O}_2$$
- (vii)  $\text{LiF}$  and  $\text{Li}_2\text{O}$  are comparatively much less soluble in water than the corresponding

compounds of other alkali metals.

### 10.3.2 Points of Similarities between Lithium and Magnesium

The similarity between lithium and magnesium is particularly striking and arises because of their similar sizes : atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii :  $\text{Li}^+$  = 76 pm,  $\text{Mg}^{2+}$  = 72 pm. The main points of similarity are :

- (i) Both lithium and magnesium are harder and lighter than other elements in the respective groups.
- (ii) Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride,  $\text{Li}_3\text{N}$  and  $\text{Mg}_3\text{N}_2$ , by direct combination with nitrogen.
- (iii) The oxides,  $\text{Li}_2\text{O}$  and  $\text{MgO}$  do not combine with excess oxygen to give any superoxide.
- (iv) The carbonates of lithium and magnesium decompose easily on heating to form the oxides and  $\text{CO}_2$ . Solid hydrogencarbonates are not formed by lithium and magnesium.
- (v) Both  $\text{LiCl}$  and  $\text{MgCl}_2$  are soluble in ethanol.
- (vi) Both  $\text{LiCl}$  and  $\text{MgCl}_2$  are deliquescent and crystallise from aqueous solution as hydrates,  $\text{LiCl}\cdot 2\text{H}_2\text{O}$  and  $\text{MgCl}_2\cdot 8\text{H}_2\text{O}$ .

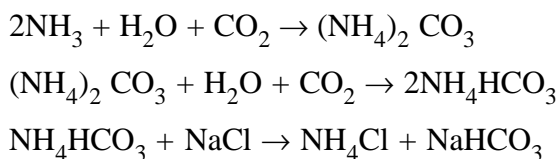
### 10.4 SOME IMPORTANT COMPOUNDS OF SODIUM

Industrially important compounds of sodium include sodium carbonate, sodium hydroxide, sodium chloride and sodium bicarbonate. The large scale production of these compounds and their uses are described below :

#### *Sodium Carbonate (Washing Soda), $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$*

Sodium carbonate is generally prepared by **Solvay Process**. In this process, advantage is taken of the low solubility of sodium hydrogencarbonate whereby it gets precipitated in the reaction of sodium chloride with ammonium hydrogencarbonate. The latter is prepared by passing  $\text{CO}_2$  to a concentrated solution of sodium chloride saturated with ammonia, where ammonium carbonate followed by ammonium hydrogencarbonate are formed.

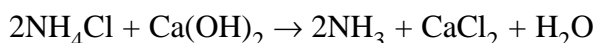
The equations for the complete process may be written as:



Sodium hydrogencarbonate crystal separates. These are heated to give sodium carbonate.



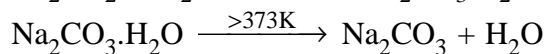
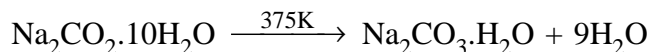
In this process  $\text{NH}_3$  is recovered when the solution containing  $\text{NH}_4\text{Cl}$  is treated with  $\text{Ca}(\text{OH})_2$ . Calcium chloride is obtained as a by-product.



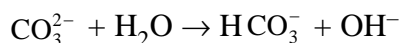
It may be mentioned here that Solvay process cannot be extended to the manufacture of potassium carbonate because potassium hydrogencarbonate is too soluble to be precipitated by the addition of ammonium hydrogencarbonate to a saturated solution of potassium chloride.

**Properties :** Sodium carbonate is a white crystalline solid which exists as a decahydrate,  $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$ . This is also called washing soda. It is readily soluble in water. On heating, the

decahydrate loses its water of crystallisation to form monohydrate. Above 373K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.



Carbonate part of sodium carbonate gets hydrolysed by water to form an alkaline solution.



- Uses:**
- (i) It is used in water softening, laundering and cleaning.
  - (ii) It is used in the manufacture of glass, soap, borax and caustic soda.
  - (iii) It is used in paper, paints and textile industries.
  - (iv) It is an important laboratory reagent both in qualitative and quantitative analysis.

**Note:**  $\text{K}_2\text{CO}_3$  cannot be prepared by **Solvey process** because  $\text{KHCO}_3$  is soluble in water and cannot be separated from  $\text{NH}_4\text{Cl}$ .

### Sodium Chloride, NaCl

The most abundant source of sodium chloride is sea water which contains 2.7 to 2.9% by mass of the salt. In tropical countries like India, common salt is generally obtained by evaporation of sea water. ~~Approximately 50 lakh tons of salt are produced annually in India by solar evaporation.~~

Crude sodium chloride, generally obtained by crystallisation of brine solution, contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride,  $\text{CaCl}_2$ , and magnesium chloride,  $\text{MgCl}_2$ , are impurities because they are deliquescent (absorb moisture easily from the atmosphere).

To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

Sodium chloride melts at 1081K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

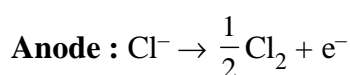
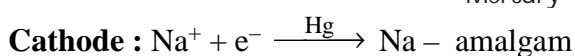
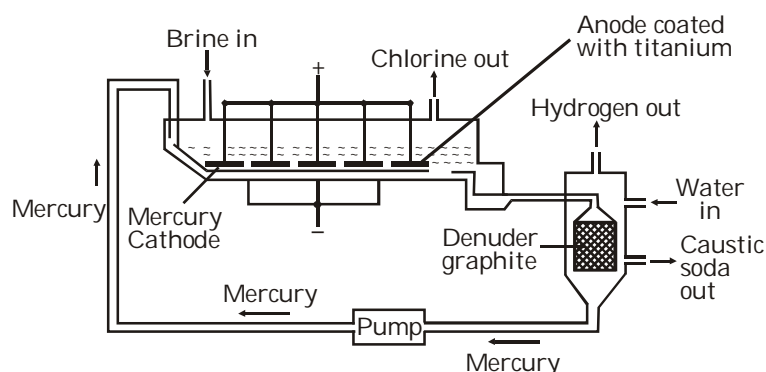
**Uses :**

- (i) It is used as a common salt or table salt for domestic purpose.
- (ii) It is used for the preparation of  $\text{Na}_2\text{O}_2$ ,  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ .
- (iii) It is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to  $-23^\circ\text{C}$ .]
- (iv) For melting ice and snow on road.

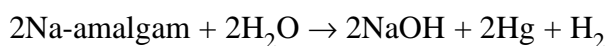
### Sodium Hydroxide (Caustic Soda), NaOH

Sodium hydroxide is generally prepared commercially by the electrolysis of sodium chloride in Castner-Kellner cell. A brine solution is electrolysed using a mercury cathode and a carbon anode.

Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode. (The anodes are now made of steel coated with titanium. Titanium is very resistance to corrosion)



The amalgam is treated with water to give sodium hydroxide and hydrogen gas.



Sodium hydroxide is a white, translucent solid. It melts at 591 K. It is readily soluble in water to give a strong alkaline solution. Crystals of sodium hydroxide are deliquescent. The sodium hydroxide solution at the surface reacts with the  $\text{CO}_2$  in the atmosphere to form  $\text{Na}_2\text{CO}_3$ .

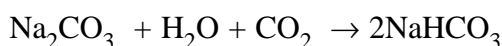
**Uses :** It is used in

- (i) The manufacture of soap, paper, artificial silk and a number of chemicals,
- (ii) In petroleum refining,
- (iii) In the purification of bauxite,
- (iv) In the textile industries for mercerising cotton fabrics, (v) for the preparation of pure fats and oils, and
- (vi) As a laboratory reagent.

### **Sodium Hydrogencarbonate (Baking Soda), $\text{NaHCO}_3$**

Sodium hydrogencarbonate is known as baking soda because it decomposes on heating to generate bubbles of carbon dioxide (leaving holes in cakes or pastries and making them light and fluffy).

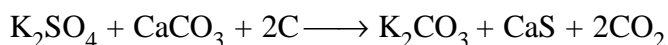
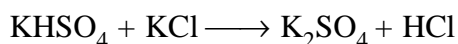
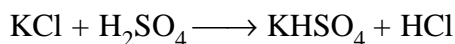
Sodium hydrogencarbonate is made by saturating a solution of sodium carbonate with carbon dioxide. The white crystalline powder of sodium hydrogencarbonate, being less soluble, gets separated out.



Sodium hydrogencarbonate is a mild antiseptic for skin infections. **It is used in fire extinguishers.**

### **Potassium carbonate, $K_2CO_3$**

It is also called potash or pearl ash. It cannot be made by the use of solvay process as potassium bicarbonate is more soluble than sodium bicarbonate. However, it can be prepared by **Le-Blanc process**. KCl is first converted into  $K_2SO_4$ . Potassium sulphate ( $K_2SO_4$ ) is then heated with  $CaCO_3$  and carbon.



It is a white powder, deliquescent in nature. It is highly soluble in water.

**Uses :** It is used in the manufacture of hard glass. The mixture of  $K_2CO_3$  and  $Na_2CO_3$  is used a **fusion mixture** in laboratory.

## 10.5 BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM

A typical 70 kg man contains about 90 g of Na and 170 g of K compared with only 5 g of iron and 0.06 g of copper. Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes.

Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

There is a very considerable variation in the concentration of sodium and potassium ions found on the opposite sides of cell membranes. As a typical example, in blood plasma, sodium is present to the extent of  $143 \text{ mmolL}^{-1}$ , whereas the potassium level is only  $5 \text{ mmolL}^{-1}$  within the red blood cells. These concentrations change to  $10 \text{ mmolL}^{-1}$  ( $Na^+$ ) and  $105 \text{ mmolL}^{-1}$  ( $K^+$ ). These ionic gradients demonstrate that a discriminatory mechanism, called the sodium-potassium pump, operates across the cell membranes which consumes more than one-third of the ATP used by a resting animal and about 15 kg per 24 h in a resting human.

## 10.6 GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The group 2 elements comprise beryllium, magnesium, calcium, strontium, barium and radium. They follow alkali metals in the periodic table. These (except beryllium) are known as alkaline

earth metals. The first element beryllium differs from the rest of the members and shows diagonal relationship to aluminium. The atomic and physical properties of the alkaline earth metals are shown in Table.

### 10.6.1 Electronic Configuration

These elements have two electrons in the  $s$ -orbital of the valence shell. Their general electronic configuration may be represented as [noble gas]  $ns^2$ . Like alkali metals, the compounds of these elements are also predominantly ionic.

Element	Symbol	Electronic configuration
Beryllium	Be	$1s^2 2s^2$
Magnesium	Mg	$1s^2 2s^2 2p^6 3s^2$
Calcium	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Strontium	Sr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Barium	Ba	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or [Xe] $6s^2$
Radium	Ra	[Rn] $7s^2$

### 10.6.2 Atomic and Ionic Radii

The atomic and ionic radii of the alkaline earth metals are smaller than those of the

**Table : Atomic and Physical Properties of the Alkaline Earth Metals**

Property	Beryllium Be	Magnesium mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Atomic mass ( $\text{g mol}^{-1}$ )	9.01	24.31	40.08	87.62	137.33	226.03
Electronic configuration	[He] $2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$
Ionization enthalpy (I)/ $\text{kJ mol}^{-1}$	899	737	590	549	503	509
Ionization enthalpy (II) $\text{kJ mol}^{-1}$	1757	1450	1145	1064	965	979
Hydration enthalpy/ $\text{kJ mol}^{-1}$	-2494	-1921	-1577	-1443	-1305	-
Metallic radius/pm	111	160	197	215	222	-
Ionic radius $M^+$ /pm	31	72	100	118	135	148
m.p./K	1560	924	1124	1062	1002	973
b.p./K	2745	1363	1767	1655	2078	(1973)
Density / $\text{g cm}^{-3}$	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard Potentials $E^-$ /V for ( $M^{+2}/M$ )	-1.97	-2.36	-2.84	-2.89	-2.92	-2.92
Occurrence in lithosphere	2*	2.76**	4.6**	384*	390*	$10^{-6}$ *

\*ppm (part per million); \*\* percentage by weight :

Corresponding alkali metals in the same periods. This is due to the increased nuclear charge in these elements. Within the group, the atomic and ionic radii increase with increase in atomic number.

### 10.6.3 Ionization Enthalpies

#### *Ionization Enthalpy*

$\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$

Down the group IE decreases due to increase in size

Q.  $\text{IE}_1$  of AM  $<$   $\text{IE}_1$  of AEM

$\text{IE}_2$  of AM  $>$   $\text{IE}_2$  of AEM

[where AM = Alkali metal, AEM = Alkaline earth metal]

**Reason :**  $\text{IE}_1$  of AEM is large due to increased nuclear charge in AEM as compared to AM but  $\text{IE}_2$  of AM is large because second electron in AM is to be removed from cation which has already acquired noble gas configuration.

### 10.6.4 Hydration Enthalpies

Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions decrease with increase in ionic size down the group.

$\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, e.g.,  $\text{MgCl}_2$  and  $\text{CaCl}_2$  exist as  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  while NaCl and KCl do not form such hydrates.

### 10.6.5 Physical Properties

- (i) The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish.
- (ii) The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes. The trend is, however, not systematic.
- (iii) Because of the low ionisation enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba.
- (iv) Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours respectively to the flame. In flame the electrons are excited to higher energy levels and when they drop back to the ground state, energy is emitted in the form of visible light. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence, these elements do not impart any colour to the flame. The flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis and estimation by flame photometry.
- (v) The alkaline earth metals like those of alkali metals have high electrical and thermal conductivities which are typical characteristics of metals.

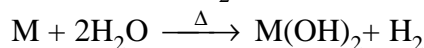
### 10.6.6 Chemical Properties

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

(i) **Reactivity towards air** : Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and Be<sub>3</sub>N<sub>2</sub>. Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and Mg<sub>3</sub>N<sub>2</sub>. Calcium, strontium and barium are readily attacked by air to form the oxide and nitride.

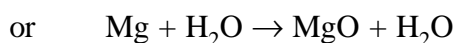
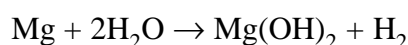
(ii) **Reactivity towards water.**

**Reaction with H<sub>2</sub>O** : AEM have lesser tendency to react with water as compared to AM. They form hydroxides and liberate H<sub>2</sub> on reaction with H<sub>2</sub>O



\* Be is inert towards water.

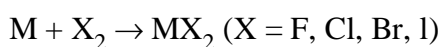
\* Magnesium react as



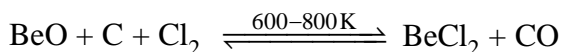
MgO forms protective layer, that is why it does not react readily unless layer is removed amalgamating with Hg. Other metals react quite readily (Ca, Sr, Ba).

**Note:** Be(OH)<sub>2</sub> is amphoteric but other hydroxides are basic in nature.

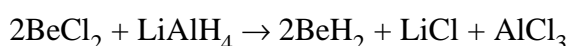
(iii) **Reactivity towards the halogens** : All the alkaline earth metals combine with halogen at elevated temperatures forming their halides.



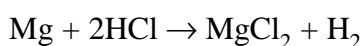
Thermal decomposition of (NH<sub>4</sub>)<sub>2</sub>BeF<sub>4</sub> is the best route for the preparation of BeF<sub>2</sub>, and BeCl<sub>2</sub> is conveniently made from the oxide.



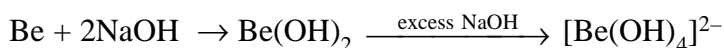
(iv) **Reactivity towards hydrogen** : All the elements except beryllium combine with hydrogen upon heating to form their hydrides, MH<sub>2</sub>. BeH<sub>2</sub>, however, can be prepared by the reaction of BeCl<sub>2</sub> with LiAlH<sub>4</sub>.



(v) **Reactivity towards acids** : AEM react with acids & liberate H<sub>2</sub>



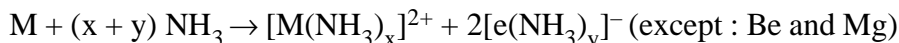
Be is amphoteric as it also react with NaOH, other metals do not react as they are purely basic.



(vi) **Reducing nature** : Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by large negative values of their reduction potentials. However their reducing power is less than those of their corresponding alkali metals. Beryllium has less negative value compared to other alkaline earth metals. However, its reducing nature is due to large hydration energy associated with the small size of Be<sup>2+</sup> ion and relatively large value of the atomization enthalpy of the metal.



(vii) **Solutions in liquid ammonia** : Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.



From these solutions, the ammoniates,  $[\text{M}(\text{NH}_3)_6]^{2+}$  can be recovered.

### 10.6.7 Uses :

**Be** : Beryllium is used in the manufacture of alloys. Copper-beryllium alloys are used in the preparation of high strength springs. Metallic beryllium is used for making windows of X-ray tubes.

**Mg** : Magnesium forms alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys being light in mass are used in air-craft construction. Magnesium (powder and ribbon) is used in flash powders and bulbs, incendiary bombs and signals. A suspension of magnesium hydroxide in water (called *milk of magnesia*) is used as antacid in medicine. Magnesium carbonate is an ingredient of toothpaste.

**Ca** : Calcium is used in the extraction of metals from oxides which are difficult to reduce with carbon. Calcium and barium metals, owing to their reactivity with oxygen and nitrogen at elevated temperatures, have often been used to remove air from vacuum tubes.

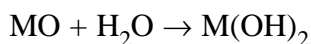
**Ra** : Radium salts are used in radiotherapy, for example, in the treatment of cancer.

## 10.7 GENERAL CHARACTERISTICS OF COMPOUNDS OF THE ALKALINE EARTH METALS

The dipositive oxidation state ( $M^{2+}$ ) is the predominant valence of Group 2 elements. The alkaline earth metals form compounds which are predominantly ionic but less ionic than the corresponding compounds of alkali metals. This is due to increased nuclear charge and smaller size. The oxides and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and large sized members (Ca, Sr, Ba). The general characteristics of some of the compounds of alkali earth metals are described below.

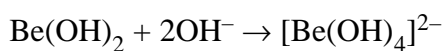
### (i) **Oxides and Hydroxides** :

The alkaline earth metals burn in oxygen to form the monoxide, MO which, except for BeO, have rock-salt structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. BeO is amphoteric while oxides of other elements are ionic in nature. All these oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides.

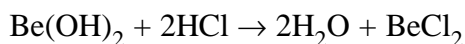


The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from  $\text{Mg}(\text{OH})_2$  to  $\text{Ba}(\text{OH})_2$ . The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it

reacts with acid and alkali both.

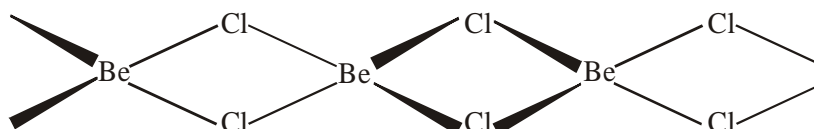


Beryllate ion



(ii) **Halides :**

Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride has a chain structure in the solid state as shown below:



In the vapour phase  $\text{BeCl}_2$  tends to form a chloro-bridged dimer which dissociates into the linear monomer at high temperatures of the order of 1200 K. The tendency to form halide hydrates gradually decreases (for example,  $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) down the group. The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be achieved on heating; however, the corresponding hydrated halides of Be and Mg on heating suffer hydrolysis. The fluorides are relatively less soluble than the chlorides owing to their high lattice energies.

(iii) **Salts of Oxoacids :** The alkaline earth metals also form salts of oxoacids. Some of these are :

**Carbonates :** Carbonates of alkaline earth metals are insoluble in water and can be precipitated by addition of a sodium or ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases as the atomic number of the metal ion increases. All the carbonates decompose on heating to give carbon dioxide and the oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of  $\text{CO}_2$ . The thermal stability increases with increasing cationic size.

**Sulphates :** The sulphates of the alkaline earth metals are all white solids and stable to heat.  $\text{BeSO}_4$ , and  $\text{MgSO}_4$  are readily soluble in water; the solubility decreases from  $\text{CaSO}_4$  to  $\text{BaSO}_4$ . The greater hydration enthalpies of  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$  ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water.

**Nitrates :** The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy. All of them decompose on heating to give the oxide like lithium nitrate.



(M + Be, Mg, Ca, Sr, Ba)

**Problem 10.4**

Why does the solubility of alkaline earth metal hydroxides in water increase down the group?

### Solution

Among alkaline earth metal hydroxides, the anion being common the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases as we go down the group.

### Problem 10.5

Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

### Solution

The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

## 10.8 ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium which is discussed subsequently.

- (i) Beryllium has exceptionally small atomic and ionic sizes and thus does not compare well with other members of the group. Because of high ionisation enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.
- (ii) Beryllium does not exhibit coordination number more than four as in its valence shell there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of *d*-orbitals.
- (iii) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

### 10.8.1 Diagonal Relationship between Beryllium and Aluminium

The ionic radius of  $\text{Be}^{2+}$  is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the  $\text{Al}^{3+}$  ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are:

- (i) Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.
- (ii) Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion,  $[\text{Be}(\text{OH})_4]^{2-}$  just as aluminium hydroxide gives aluminate ion,  $[\text{Al}(\text{OH})_4]^-$ .
- (iii) The chlorides of both beryllium and aluminium have  $\text{Cl}^-$  bridged chloride structure in vapour phase. Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.

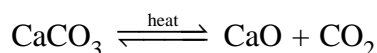
(iv) Beryllium and aluminium ions have strong tendency to form complexes,  $\text{BeF}_4^{2-}$ ,  $\text{AlF}_6^{3-}$

### 10.9 SOME IMPORTANT COMPOUNDS OF CALCIUM

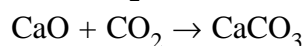
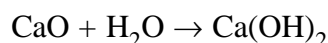
Important compounds of calcium are calcium oxide, calcium hydroxide, calcium sulphate, calcium carbonate and cement. These are industrially important compounds. The large scale preparation of these compounds and their uses are described below.

#### Calcium Oxide or Quick Lime, CaO

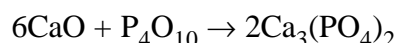
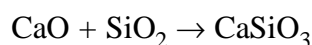
It is prepared on a commercial scale by heating limestone ( $\text{CaCO}_3$ ) in a rotary kiln at 1070-1270 K.



The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion. Calcium oxide is a white amorphous solid. It has a melting point of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide.



The addition of limited amount of water breaks the lump of lime. This process is called *slaking of lime*. Quick lime slaked with soda gives solid sodalime. Being a basic oxide, it combines with acidic oxides at high temperature.



**Uses :** (i) It is an important primary material for manufacturing cement and is the cheapest form of alkali.

(ii) It is used in the manufacture of sodium carbonate from caustic soda.

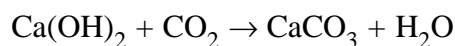
(iii) It is employed in the purification of sugar and in the manufacture of dye stuffs.

#### Calcium Hydroxide (Slaked lime), Ca(OH)<sub>2</sub>

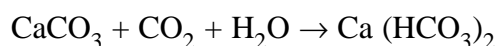
Calcium hydroxide is prepared by adding water to quick lime, CaO.

It is a white amorphous powder. It is sparingly soluble in water. The aqueous solution is known as *lime water* and a suspension of slaked lime in water is known as *milk of lime*.

When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.



On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogencarbonate.



Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.



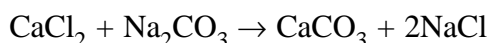
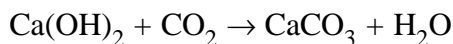
**Uses:** (i) It is used in the preparation of mortar, a building material.

(ii) It is used in white wash due to its disinfectant nature.

- (iii) It is used in glass making, in tanning industry, for the preparation of bleaching powder and for purification of sugar.

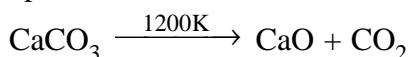
### Calcium Carbonate, $\text{CaCO}_3$

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.

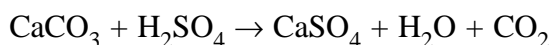
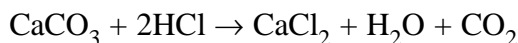


Excess of carbon dioxide should be avoided since this leads to the formation of water soluble calcium hydrogencarbonate.

Calcium carbonate is a white fluffy powder. It is almost insoluble in water. When heated to 1200 K, it decomposes to evolve carbon dioxide.



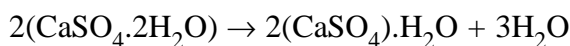
It reacts with dilute acid to liberate carbon dioxide.



**Uses:** It is used as a building material in the form of marble and in the manufacture of quick lime. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron. Specially precipitated  $\text{CaCO}_3$  is extensively used in the manufacture of high quality paper. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and a filler in cosmetics.

### Calcium Sulphate (Plaster of Paris), $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$

It is a hemihydrate of calcium sulphate. It is obtained when gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , is heated to 393 K.



Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate,  $\text{CaSO}_4$  is formed. This is known as 'dead burnt plaster'.

It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes.

**Uses:** The largest use of Plaster of Paris is in the building industry as well as plasters. It is used for immobilising the affected part of organ where there is a bone fracture or sprain. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

**Cement:** Cement is an important building material. It was first introduced in England in 1824 by Joseph Aspdin. It is also called '**Portland cement**' because it resembles with the natural limestone quarried in the Isle of Portland, England.

Cement is a product obtained by combining a material rich in lime, CaO with other material such as clay which contains silica, SiO<sub>2</sub> along with the oxides of aluminium, iron and magnesium. The average composition of Portland cement is :

CaO, 50-60%; SiO<sub>2</sub>, 20-25%; Al<sub>2</sub>O<sub>3</sub>, 5-10%; MgO, 2-3%; Fe<sub>2</sub>O<sub>3</sub>, 1-2% and SO<sub>3</sub>, 1-2%. For a good quality cement, the ratio of silica (SiO<sub>2</sub>) to alumina (Al<sub>2</sub>O<sub>3</sub>) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of the oxides of silicon (SiO<sub>2</sub>) aluminium (Al<sub>2</sub>O<sub>3</sub>) and iron (Fe<sub>2</sub>O<sub>3</sub>) should be as close as possible to 2.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) to form cement. Thus important ingredients present in Portland cement are dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>) 26%, tricalcium silicate (Ca<sub>3</sub>SiO<sub>5</sub>) 51% and tricalcium aluminate (Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>) 11%.

**Setting of Cement :** When mixed with water, the setting of cement takes place to give a hard mass. This is due to the hydration of the molecules of the constituents and their rearrangement. The purpose of adding gypsum is only to slow down the process of setting of the cement so that it gets sufficiently hardened.

**Uses:** Cement has become a commodity of national necessity for any country next to iron and steel. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

### 10.10 BIOLOGICAL IMPORTANCE OF MAGNESIUM AND CALCIUM

An adult body contains about 25 g of Mg and 1200 g of Ca compared with only 5 g of iron and 0.06 g of copper. The daily requirement in the human body has been estimated to be 200 – 300 mg. All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. About 99 % of body calcium is present in bones and teeth. It also plays important roles in neuromuscular function, interneuronal transmission, cell membrane integrity and blood coagulation. The calcium concentration in plasma is regulated at about 100 mgL<sup>-1</sup>. It is maintained by two hormones: calcitonin and parathyroid hormone. Do you know that bone is not an inert and unchanging substance but is continuously being solubilised and redeposited to the extent of 400 mg per day in man? All this calcium passes through the plasma.

**Summary :** The **s-Block** of the periodic table constitutes **Group 1** (alkali metals) and **Group 2** (alkaline earth metals). They are so called because their oxides and hydroxides are alkaline in nature. The alkali metals are characterised by one s-electron and the alkaline earth metals by two s-electrons in the valence shell of their atoms. These are highly reactive metals forming monopositive (M<sup>+</sup>) and dipositive (M<sup>2+</sup>) ions respectively.

There is a regular trend in the physical and chemical properties of the alkali metal with increasing atomic numbers. The **atomic** and **ionic** sizes increase and the **ionization enthalpies** decrease systematically down the group.

Somewhat similar trends are observed among the properties of the alkaline earth metals. The first element in each of these groups, lithium in Group 1 and beryllium in Group 2 shows similarities in properties to the second member of the next group. Such similarities are termed as the '**diagonal relationship**' in the periodic table.

As such these elements are anomalous as far as their group characteristics are concerned.

The alkali metals are silvery white, soft and low melting. They are highly reactive. The compounds of alkali metals are predominantly ionic. Their oxides and hydroxides are soluble in water forming strong alkalis. Important compounds of sodium includes sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogencarbonate. Sodium hydroxide is manufactured by **Castner-Kellner** process and sodium carbonate by **Solvay** process.

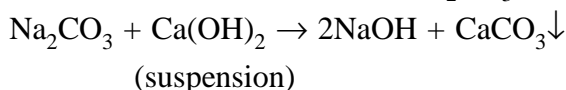
The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. Industrially important compounds of calcium include calcium oxide (lime), calcium hydroxide (slaked lime), calcium sulphate (**Plaster of Paris**), calcium carbonate (limestone) and cement. **Portland cement** is an important constructional material.

It is manufactured by heating a pulverised mixture of limestone and clay in a rotary kiln. The clinker thus obtained is mixed with some gypsum (2-3%) to give a fine powder of cement. All these substances find variety of uses in different areas.

Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in **biological fluids**. These ions perform important **biological functions** such as maintenance of ion balance and nerve impulse conduction.

#### FEW IMPORTANT POINTS

- (i) Magnesium Peroxide ( $\text{MgO}_2$ ) and Calcium Peroxide ( $\text{CaO}_2$ ) are obtained by passing  $\text{H}_2\text{O}_2$  in a suspension of  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ .
- (ii)  $\text{MgO}_2$  is used as an antiseptic in tooth paste and as a bleaching agent.
- (iii) Preparation of  $\text{NaOH}$  : Caustication of  $\text{Na}_2\text{CO}_3$  (Gossage's method):



Since the  $K_{\text{sp}}(\text{CaCO}_3) < K_{\text{sp}}(\text{Ca}(\text{OH})_2)$ , the reaction shifts towards right.

- (iv) As a reagent  $\text{KOH}$  is less frequently used but in absorption of  $\text{CO}_2$ ,  $\text{KOH}$  is preferably used compared to  $\text{NaOH}$ . Because  $\text{KHCO}_3$  formed is soluble whereas  $\text{NaHCO}_3$  is sparingly soluble and may therefore choke the tubes of apparatus used.
- (v) Calcium hydroxide is used as a mortar.  
[Mortar is a mixture of slaked lime (1 Part) and sand (3 Parts) made into paste with water.]
- (vi)  $\text{NaCl}$  is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to  $-23^\circ\text{C}$ .]
- (vii) On heating  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  undergoes hydrolysis as follows:

## EXERCISE # O-1

SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)

*Alkali metals*

1.  $\text{Cs}^+$  ions impart violet colour to Bunsen flame. This is due to the fact that the emitted radiations are of -  
 (A) high energy (B) lower frequencies  
 (C) longer wave-lengths (D) zero wave number
- SB0001**
2. The reaction of an element A with water produces combustible gas B and an aqueous solution of C. When another substance D reacts with this solution C also produces the same gas B. D also produces the same gas even on reaction with dilute  $\text{H}_2\text{SO}_4$  at room temperature. Element A imparts golden yellow colour to Bunsen flame. Then, A, B, C and D may be identified as  
 (A) Na,  $\text{H}_2$ , NaOH and Zn (B) K,  $\text{H}_2$ , KOH and Zn  
 (C) K,  $\text{H}_2$ , NaOH and Zn (D) Ca,  $\text{H}_2$ ,  $\text{CaCO}_3$  and Zn
- SB0002**
3. Which of the following carbonate of alkali metals has the least thermal stability?  
 (A)  $\text{Li}_2\text{CO}_3$  (B)  $\text{K}_2\text{CO}_3$  (C)  $\text{Cs}_2\text{CO}_3$  (D)  $\text{Na}_2\text{CO}_3$
- SB0003**
4. The alkali metals which form normal oxide, peroxide as well as super oxides are  
 (A) Na, Li (B) K, Li (C) Li, Cs (D) K, Rb
- SB0004**
5. The pair of compounds, which cannot exist together in a solution is  
 (A)  $\text{NaHCO}_3$  and NaOH (B)  $\text{Na}_2\text{CO}_3$  and NaOH  
 (C)  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  (D)  $\text{NaHCO}_3$  and  $\text{H}_2\text{O}$
- SB0005**
6. Solution of sodium metal in liquid ammonia is a strong reducing agent due to presence of  
 (A) solvated sodium ions (B) solvated hydrogen ions  
 (C) sodium atoms or sodium hydroxide (D) solvated electrons
- SB0006**
7. The order of solubility of lithium halides in non-polar solvents follows the order  
 (A)  $\text{LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$  (B)  $\text{LiF} > \text{LiI} > \text{LiBr} > \text{LiCl}$   
 (C)  $\text{LiCl} > \text{LiF} > \text{LiI} > \text{LiBr}$  (D)  $\text{LiBr} > \text{LiCl} > \text{LiF} > \text{LiI}$
- SB0007**
8. The salt which finds uses in qualitative inorganic analysis is  
 (A)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  or  $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$  (B)  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (C)  $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$  (D)  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
- SB0008**



9. Fire extinguishers contain  
 (A) conc.  $\text{H}_2\text{SO}_4$  solution (B)  $\text{H}_2\text{SO}_4$  and  $\text{NaHCO}_3$  solutions  
 (C)  $\text{NaHCO}_3$  solution (D)  $\text{CaCO}_3$  solution **SB0009**
10.  $\text{CsBr}_3$  contains  
 (A) Cs–Br covalent bonds (B)  $\text{Cs}^{3+}$  and  $\text{Br}^-$  ions  
 (C)  $\text{Cs}^+$  and  $\text{Br}_3^-$  ions (D)  $\text{Cs}^{3+}$  and  $\text{Br}_3^{3-}$  ions **SB0010**
11.  $\text{Na} + \text{Al}_2\text{O}_3 \xrightarrow{\text{High temperature}} \text{X} \xrightarrow[\text{water}]{\text{CO}_2 \text{ in}} \text{Y}$ ; compound Y is  
 (A)  $\text{NaAlO}_2$  (B)  $\text{NaHCO}_3$  (C)  $\text{Na}_2\text{CO}_3$  (D)  $\text{Na}_2\text{O}_2$  **SB0011**
12. aq.  $\text{NaOH} + \text{P}_4$  (white)  $\longrightarrow \text{PH}_3 + \text{X}$ ; compound X is  
 (A)  $\text{NaH}_2\text{PO}_2$  (B)  $\text{NaHPO}_4$  (C)  $\text{Na}_2\text{CO}_3$  (D)  $\text{NaHCO}_3$  **SB0012**
13. When  $\text{K}_2\text{O}$  is added to water, the solution becomes basic in nature because it contains a significant concentration of  
 (A)  $\text{K}^+$  (B)  $\text{O}^{2-}$  (C)  $\text{OH}^-$  (D)  $\text{O}_2^{2-}$  **SB0013**
14. The order of melting point of chlorides of alkali metals is  
 (A)  $\text{LiCl} > \text{NaCl} > \text{KCl} < \text{CsCl}$  (B)  $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{CsCl}$   
 (C)  $\text{NaCl} > \text{KCl} > \text{CsCl} > \text{LiCl}$  (D)  $\text{LiCl} > \text{NaCl} > \text{CsCl} > \text{KCl}$  **SB0014**
15.  $\text{NaOH}(\text{Solid}) + \text{CO} \xrightarrow{200^\circ\text{C}} \text{X}$ ; product X is  
 (A)  $\text{NaHCO}_3$  (B)  $\text{Na}_2\text{CO}_3$  (C)  $\text{HCOONa}$  (D)  $\text{H}_2\text{CO}_3$  **SB0015**
16. The aqueous solutions of lithium salts are poor conductor of electricity rather than other alkali metals because of  
 (A) high ionisation energy  
 (B) high electronegativity  
 (C) lower ability of  $\text{Li}^+$  ions to polarize water molecules  
 (D) higher degree of hydration of  $\text{Li}^+$  ions **SB0016**
17. In  $\text{LiAlH}_4$ , metal Al is present in  
 (A) anionic part (B) cationic part  
 (C) in both anionic and cationic part (D) neither in cationic nor in anionic part **SB0017**
18. Which one of the following fluoride of alkali metals has the highest lattice energy?  
 (A)  $\text{LiF}$  (B)  $\text{CsF}$  (C)  $\text{NaF}$  (D)  $\text{KF}$  **SB0018**

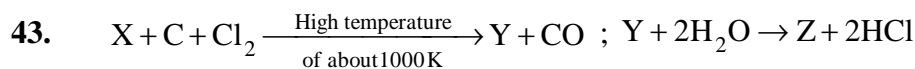
19. Crown ethers and cryptands form  
 (A) complexes with alkali metals  
 (B) salts of alkali metals  
 (C) hydroxides of alkali metals used for inorganic quantitative analysis  
 (D) organic salts of alkali metals
- SB0019**
20. The correct order of degree of hydration of  $M^+$  ions of alkali metals is  
 (A)  $Li^+ < K^+ < Na^+ < Rb^+ < Cs^+$                       (B)  $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$   
 (C)  $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$                       (D)  $Cs^+ < Rb^+ < Na^+ < K^+ < Li^+$
- SB0020**
21. The commercial method of preparation of potassium by reduction of molten KCl with metallic sodium at  $850^\circ\text{C}$  is based on the fact that  
 (A) potassium is solid and sodium distils off at  $850^\circ\text{C}$   
 (B) potassium being more volatile and distils off thus shifting the reaction forward  
 (C) sodium is less reactive than potassium at  $850^\circ\text{C}$  with respect to  $\text{Cl}_2$   
 (D) sodium has less affinity to chloride ions in the presence of potassium ion

**SB0021***Alkaline earth metals*

22. The 'milk of magnesia' used as an antacid is chemically  
 (A)  $\text{Mg}(\text{OH})_2$                       (B)  $\text{MgO}$                       (C)  $\text{MgCl}_2$                       (D)  $\text{MgO} + \text{MgCl}_2$
- SB0022**
23. An alkaline earth metal (M) gives a salt with chlorine, which is soluble in water at room temperature. It also forms an insoluble sulphate whose mixture with a sulphide of a transition metal is called 'lithopone' - a white pigment. Metal M is  
 (A) Ca                      (B) Mg                      (C) Ba                      (D) Sr
- SB0023**
24. The hydroxide of II<sup>nd</sup> A metal, which has the lowest value of solubility product ( $K_{sp}$ ) at normal temperature ( $25^\circ\text{C}$ ) is  
 (A)  $\text{Ca}(\text{OH})_2$                       (B)  $\text{Mg}(\text{OH})_2$                       (C)  $\text{Sr}(\text{OH})_2$                       (D)  $\text{Be}(\text{OH})_2$
- SB0024**
25. Which of the following metal is inert towards reaction with  $\text{H}_2\text{O}$ .  
 (A) Be                      (B) Na                      (C) Ca                      (D) K
- SB0025**
26.  $\text{Mg}_2\text{C}_3 + \text{H}_2\text{O} \longrightarrow \text{X}$  (organic compound). Compound X is  
 (A)  $\text{C}_2\text{H}_2$                       (B)  $\text{CH}_4$                       (C) propyne                      (D) ethene
- SB0026**

27. The hydration energy of  $\text{Mg}^{2+}$  is  
(A) more than that of  $\text{Mg}^{3+}$  ion (B) more than that of  $\text{Na}^+$  ion  
(C) more than that of  $\text{Al}^{3+}$  ion (D) more than that of  $\text{Be}^{2+}$  ion
- SB0027**
28. The correct order of second ionisation potentials (IP) of Ca, Ba and K is  
(A)  $\text{K} > \text{Ca} > \text{Ba}$  (B)  $\text{Ba} > \text{Ca} > \text{K}$  (C)  $\text{K} > \text{Ba} > \text{Ca}$  (D)  $\text{K} = \text{Ba} = \text{Ca}$
- SB0028**
29. EDTA is used in the estimation of  
(A)  $\text{Mg}^{2+}$  ions (B)  $\text{Ca}^{2+}$  ions  
(C) both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions (D)  $\text{Mg}^{2+}$  ions but not  $\text{Ca}^{2+}$  ions
- SB0029**
30. The correct order of solubility is  
(A)  $\text{CaCO}_3 < \text{KHCO}_3 < \text{NaHCO}_3$  (B)  $\text{KHCO}_3 < \text{CaCO}_3 < \text{NaHCO}_3$   
(C)  $\text{NaHCO}_3 < \text{CaCO}_3 < \text{KHCO}_3$  (D)  $\text{CaCO}_3 < \text{NaHCO}_3 < \text{KHCO}_3$
- SB0030**
31. The complex formation tendency of alkaline earth metals decreases down the group because  
(A) atomic size increases  
(B) availability of empty d and f-orbitals increases  
(C) nuclear charge to volume ratio increases  
(D) all the above
- SB0031**
32. The alkaline earth metals, which do not impart any colour to Bunsen flame are  
(A) Be and Mg (B) Mg and Ca (C) Be and Ca (D) Be and Ba
- SB0032**
33.  $\text{Y} \xleftarrow{\Delta, 205^\circ\text{C}} \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta, 120^\circ\text{C}} \text{X}$ . X and Y are respectively  
(A) plaster of paris, dead burnt plaster  
(B) dead burnt plaster, plaster of paris  
(C) CaO and plaster of paris  
(D) plaster of paris, mixture of gases
- SB0033**
34. A metal M readily forms water soluble sulphate, and water insoluble hydroxide  $\text{M}(\text{OH})_2$ . Its oxide MO is amphoteric, hard and having high melting point. The alkaline earth metal M must be  
(A) Mg (B) Be (C) Ca (D) Sr
- SB0034**

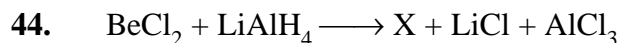
35. The purpose of addition of gypsum in the cement is -  
 (A) To slow down the process of setting of the cement  
 (B) To fasten the process of setting of the cement  
 (C) Not to affect the process of setting of the cement by any means  
 (D) None of these
- SB0035**
36. (Milky Cloud)  $C \xleftarrow{\text{CO}_2} A + \text{Na}_2\text{CO}_3 \longrightarrow B + C$   
 The chemical formulae of A and B are  
 (A) NaOH and  $\text{Ca}(\text{OH})_2$  (B)  $\text{Ca}(\text{OH})_2$  and NaOH  
 (C) NaOH and CaO (D) CaO and  $\text{Ca}(\text{OH})_2$
- SB0036**
37. The correct order of basic-strength of oxides of alkaline earth metals is  
 (A)  $\text{BeO} > \text{MgO} > \text{CaO} > \text{SrO}$  (B)  $\text{SrO} > \text{CaO} > \text{MgO} > \text{BeO}$   
 (C)  $\text{BeO} > \text{CaO} > \text{MgO} > \text{SrO}$  (D)  $\text{SrO} > \text{MgO} > \text{CaO} > \text{BeO}$
- SB0037**
38.  $X \xrightarrow{\text{N}_2, \Delta} Y \xrightarrow{\text{H}_2\text{O}} Z(\text{colourless gas}) \xrightarrow{\text{CuSO}_4} T(\text{blue colour})$   
 Then, substances Y and T are  
 (A)  $Y = \text{Mg}_3\text{N}_2$  and  $T = \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (B)  $Y = \text{Mg}_3\text{N}_2$  and  $T = \text{CuSO}_4 \cdot 4\text{NH}_3$   
 (C)  $Y = \text{Mg}(\text{NO}_3)_2$  and  $T = \text{CuO}$  (D)  $Y = \text{MgO}$  and  $T = \text{CuSO}_4 \cdot 4\text{NH}_3$
- SB0038**
39. Weakest base among KOH, NaOH,  $\text{Ca}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$  is  
 (A)  $\text{Ca}(\text{OH})_2$  (B) KOH  
 (C) NaOH (D)  $\text{Zn}(\text{OH})_2$
- SB0039**
40. If X and Y are the second ionisation potentials of alkali and alkaline earth metals of same period, then -  
 (A)  $X > Y$  (B)  $X < Y$  (C)  $X = Y$  (D)  $X \ll Y$
- SB0040**
41. In castner-kellner cell if cathode is made up of graphite instead of mercury, then product that will be obtained first at cathode will be -  
 (A) Na-amalgam (B) Na only (C)  $\text{H}_2$  gas (D) NaOH
- SB0041**
42.  $\text{Na}^+$  ion can form complex with which of the following ligand.  
 (A) Cryptands (B) Crown ether (C) Both (A) and (B) (D) None
- SB0042**



Compound Y is found in polymeric chain structure and is an electron deficient molecule. Y must be

- (A) BeO                      (B) BeCl<sub>2</sub>                      (C) BeH<sub>2</sub>                      (D) AlCl<sub>3</sub>

SB0043



- (A) X is LiH    (B) X is BeH<sub>2</sub>  
(C) X is BeCl<sub>2</sub>·2H<sub>2</sub>O    (D) None

SB0044

45. The order of thermal stability of carbonates of IIA group is

- (A) BaCO<sub>3</sub> > SrCO<sub>3</sub> > CaCO<sub>3</sub> > MgCO<sub>3</sub>  
(B) MgCO<sub>3</sub> > CaCO<sub>3</sub> > SrCO<sub>3</sub> > BaCO<sub>3</sub>  
(C) CaCO<sub>3</sub> > SrCO<sub>3</sub> > BaCO<sub>3</sub> > MgCO<sub>3</sub>  
(D) MgCO<sub>3</sub> = CaCO<sub>3</sub> > SrCO<sub>3</sub> = BaCO<sub>3</sub>

SB0045

46. A pair of substances which gives all the same products on reaction with water is

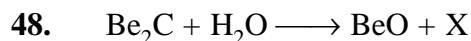
- (A) Mg and MgO      (B) Sr and SrO      (C) Ca and CaH<sub>2</sub>      (D) Be and BeO

SB0046

47. A metal which is soluble in both water and liquid NH<sub>3</sub> separately -

- (A) Cr                      (B) Mn                      (C) Ba                      (D) Al

SB0047



$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + Y$ ; then X and Y are respectively

- (A) CH<sub>4</sub>, CH<sub>4</sub>      (B) CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>      (C) CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>      (D) C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>

SB0048

49. Which of the following groups of elements have chemical properties that are most similar

- (A) Na, K, Ca      (B) Mg, Sr, Ba      (C) Be, Al, Ca      (D) Be, Ra, Cs

SB0049

50. MgBr<sub>2</sub> and MgI<sub>2</sub> are soluble in acetone because of

- (A) Their ionic nature    (B) Their coordinate nature  
(C) Their metallic nature    (D) Their covalent nature

SB0050

## EXERCISE # O-2

SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)

*Alkali metals*

1. Nitrogen dioxide can be prepared by heating-  
 (A)  $\text{KNO}_3$  (B)  $\text{AgNO}_3$  (C)  $\text{Pb}(\text{NO}_3)_2$  (D)  $\text{Cu}(\text{NO}_3)_2$

SB0051

2. Which of the following compounds are not paramagnetic in nature?  
 (A)  $\text{KO}_2$  (B)  $\text{K}_2\text{O}_2$  (C)  $\text{Na}_2\text{O}_2$  (D)  $\text{RbO}_2$

SB0052

3. The golden yellow colour associated with NaCl to Bunsen flame can be explained on the basis of  
 (A) low ionisation potential of sodium  
 (B) emission spectrum  
 (C) photosensitivity of sodium  
 (D) sublimation of metallic sodium of yellow vapours

SB0053

4.  $\text{KO}_2$  finds use in oxygen cylinders used for space and submarines. The fact(s) related to such use of  $\text{KO}_2$  is/are  
 (A) it produces  $\text{O}_2$  (B) it produces  $\text{O}_3$   
 (C) it absorbs  $\text{CO}_2$  (D) it absorbs both CO and  $\text{CO}_2$

SB0054

5. The compound(s) which have  $-\text{O}-\text{O}-$  bond(s) is/are  
 (A)  $\text{BaO}_2$  (B)  $\text{Na}_2\text{O}_2$  (C)  $\text{CrO}_5$  (D)  $\text{Fe}_2\text{O}_3$

SB0055

6. Highly pure dilute solution of sodium in ammonia  
 (A) shows blue colouration due to solvated electrons  
 (B) shows electrical conductivity due to both solvated electrons as well as solvated sodium ions  
 (C) shows red colouration due to solvated electrons but a bad conductor of electricity  
 (D) produces hydrogen gas or carbonate

SB0056

7. Sodium metal is highly reactive and can be stored under  
 (A) toluene (B) kerosene oil (C) alcohol (D) benzene

SB0057

*Alkaline earth metals*

8. The compound(s) of II<sup>nd</sup> A metals, which are amphoteric in nature is/are  
 (A) BeO (B) MgO (C)  $\text{Be}(\text{OH})_2$  (D)  $\text{Mg}(\text{OH})_2$

SB0058



15. Which of the following statements are **CORRECT** :

- (A) Mg is present in chlorophyll
- (B) Alkaline earth metals does not form super oxide
- (C)  $\text{NaHCO}_3$  is known as baking soda
- (D) Permanent hardness of water is removed by boiling

SB0065

16. Which of the following carbides on hydrolysis does not form methane :

- (A)  $\text{Be}_2\text{C}$
- (B)  $\text{CaC}_2$
- (C)  $\text{SrC}_2$
- (D)  $\text{Mg}_2\text{C}_3$

SB0066

17. Select the incorrect order for given properties :

- (A) Thermal stability :  $\text{BaSO}_4 > \text{SrSO}_4 > \text{CaSO}_4$
- (B) Solubility :  $\text{BaSO}_4 > \text{SrSO}_4 > \text{CaSO}_4$
- (C) Thermal stability :  $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3$
- (D) Solubility :  $\text{Li}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{K}_2\text{CO}_3$

SB0067

18. The correct statement(s) is/are

- (A) Mg cannot form complexes
- (B) Be can form complexes due to a very small atomic size
- (C) the first ionisation potential of Be is higher than that of Mg
- (D) Mg forms an alkaline hydroxide while Be forms amphoteric oxides

SB0068

19. Which of the following is are the characteristic of barium?

- (A) It produce water soluble sulphide, sulphite and sulphate
- (B) It is a silvery white metal
- (C) It forms  $\text{Ba}(\text{NO}_3)_2$  which is used in preparation of green fire
- (D) It produce blue-black solution in liquid ammonia

SB0069



## EXERCISE # S-1

## NUMERIC GRID TYPE QUESTIONS :

1. Find the number of compounds from the following in which the element in the anionic part is in the minimum oxidation state of it



SB0070

2. How many nitrate groups are present in 1 molecule of Basic beryllium nitrate?

SB0071

3. Consider the following order :

(1)  $\text{CH}_4 < \text{CCl}_4 < \text{CF}_4$  : E.N. of central atom C

(2)  $\text{Mg}^{+2} < \text{K}^+ < \text{S}^{-2} < \text{Se}^{-2}$  : Ionic radius

(3)  $\text{Be}_{(\text{aq})}^{+2} > \text{Mg}_{(\text{aq})}^{+2} > \text{Ca}_{(\text{aq})}^{+2}$  : Ionic mobility

(4)  $\text{Be}^{+2} > \text{Li}^+ > \text{Al}^{+3}$  : Hydrated size

(5)  $\text{Be} > \text{Li} > \text{Cs}$  : Reducing power

(6)  $\text{F}_{(\text{aq})}^{\ominus} > \text{Cl}_{(\text{aq})}^{\ominus} > \text{Br}_{(\text{aq})}^{\ominus}$  : Electrical conductance in infinite dilute solution

Then calculate value of  $|x - y|^2$ , where x and y are correct and incorrect orders respectively.

SB0072

4. Consider the following elements :

Li, Cs, Mg, Pb, Al, N

- $x$  = number of elements which can form MO type of oxides.
- $y$  = the highest oxidation state shown by any one of them.
- $z$  = the number of elements which can form amphoteric oxide(s).

Find the sum of  $x$ ,  $y$  and  $z$ .

SB0073

*Fill your answer as sum of digits till you get the single digit answer.*

5. Find the number of s-block elements which can produce ammoniated cation and ammoniated electron with liquid ammonia.

Li, Na, K, Rb, Cs, Ca, Sr, Ba

SB0074

6. How many of the following metal chlorides impart characteristic colour to the oxidising flame.

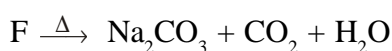
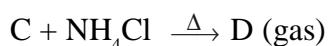
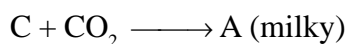
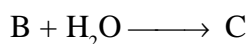
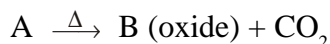
LiCl, NaCl, KCl,  $\text{BeCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{BaCl}_2$

SB0075

## EXERCISE # S-2

## COMPREHENSION BASED QUESTIONS

## Comprehension # 1



1. A is :

- (A)  $\text{Ca}(\text{HCO}_3)_2$       (B)  $\text{CaCO}_3$       (C)  $\text{CaO}$       (D)  $\text{Na}_2\text{CO}_3$

SB0076

2. B and C are :

- (A)  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$       (B)  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$   
 (C)  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$       (D)  $\text{Ca}(\text{OH})_2$ ,  $\text{CaO}$

SB0076

3. D, E and F are :

- (A)  $\text{NH}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{HCO}_3$       (B)  $\text{NH}_3$ ,  $\text{NH}_4\text{HCO}_3$ ,  $\text{NaHCO}_3$   
 (C)  $\text{NH}_4\text{HCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$       (D) None

SB0076

## Comprehension # 2

Alkali metals readily react with oxyacids forming corresponding salts like  $\text{M}_2\text{CO}_3$ ,  $\text{MHCO}_3$ ,  $\text{MNO}_3$ ,  $\text{M}_2\text{SO}_4$  etc. with evolution of hydrogen. They also dissolve in liquid  $\text{NH}_3$  but without the evolution of hydrogen. The colour of its dilute solution is blue but when it is heated and concentrated then its colour becomes bronze.

4. Among the nitrate of alkali metals which one can be decomposed to its oxide easily?

- (A)  $\text{NaNO}_3$       (B)  $\text{KNO}_3$       (C)  $\text{LiNO}_3$       (D)  $\text{RbNO}_3$

SB0077

5. Among the carbonates of alkali metals which one has highest stability?

- (A)  $\text{Cs}_2\text{CO}_3$       (B)  $\text{Rb}_2\text{CO}_3$       (C)  $\text{K}_2\text{CO}_3$       (D)  $\text{Na}_2\text{CO}_3$

SB0078



**MATCH THE CODE :****11. List-I**

- (P)  $\text{CaH}_2$   
 (Q)  $\text{K}_2\text{O}_2$   
 (R)  $\text{KO}_2$   
 (S)  $\text{NaCl}$

**List-II**

- (1) Paramagnetic anion  
 (2) Homodiatomic, diamagnetic anion  
 (3) Neutral aqueous solution  
 (4) Gives hydrogen on hydrolysis

**Codes :**

	P	Q	R	S
(A)	3	2	1	4
(B)	4	2	3	1
(C)	4	3	2	1
(D)	4	2	1	3

**SB0084****12. Column-I**

- (P) Solvay process used for  
 (Q) Evolve  $\text{CO}_2 \uparrow$  on heating  
 (R) aq. soln. is neutral towards litmus  
 (S) Oxone

**Column-II**

- (1)  $\text{NaCl}$   
 (2)  $\text{Na}_2\text{O}_2$   
 (3)  $\text{NaHCO}_3$   
 (4)  $\text{Na}_2\text{CO}_3$

**Codes :**

	P	Q	R	S
(A)	3,4	3	1	2
(B)	4,1	1	3	2
(C)	2,3	4	1	3
(D)	2,4	1	3	4

**SB0085****ASSERTION & REASONING :**

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

- (A) if both (A) and (R) are true and (R) is the correct explanation of (A)  
 (B) if both (A) and (R) are true but (R) is not correct explanation of (A)  
 (C) if (A) is true but (R) is false  
 (D) if (A) is false and (R) is true

**13. Assertion :** Beryllium does not impart any characteristic colour to the bunsen flame.

**Reason :** Due to its very high ionization energy, beryllium requires a large amount of energy for excitation of the electrons.

**SB0086**

14. **Assertion** : In fused state, calcium chloride cannot be used to dry alcohol or  $\text{NH}_3$ .  
**Reason** : Anhy.  $\text{CaCl}_2$  is not a good desiccant. SB0087
15. **Assertion** : Diagonal relationship is shown between Be and Al.  
**Reason** : Ionic potential of Be is almost the same as that of Al. SB0088
16. **Assertion** : Beryllium halides dissolve in organic solvents.  
**Reason** : Beryllium halides are ionic in character. SB0089
17. **Assertion** :  $\text{BeCl}_2$  fumes in moist air.  
**Reason** :  $\text{BeCl}_2$  reacts with moisture to form HCl gas. SB0090
18. **Assertion** : Calcium carbide on hydrolysis gives methane.  
**Reason** : Calcium carbide contains  $\text{C}_2^{2-}$  anion. SB0091
19. **Assertion** : When  $\text{CO}_2$  is passed through lime water, it first turns milky and then the solution becomes clear when the passage of  $\text{CO}_2$  is continued.  
**Reason** : The milkiness is due to the formation of insoluble  $\text{CaCO}_3$  which then changes to soluble  $\text{Ca}(\text{HCO}_3)_2$  when excess of  $\text{CO}_2$  is present. SB0092
20. **Assertion** :  $\text{MgCO}_3$  is soluble in water when a current of  $\text{CO}_2$  is passed.  
**Reason** : The solubility of  $\text{MgCO}_3$  is due to the formation of  $\text{Mg}(\text{HCO}_3)_2$ . SB0093

**MATCHING LIST TYPE 1 × 3 Q. (THREE LIST TYPE Q.)**

The following column 1, 2, 3 represent elements of s block and their different oxide formation abilities. Answer the questions that follow

**Column-1 - Elements of s-Block**

**Column-2 - Product formed on reaction with excess oxygen**

**Column-3 - Characteristics of species form on reaction with excess oxygen**

Column - 1 Elements	Column - 2 Product formed on reaction with excess oxygen	Column - 3 Characteristics of species form on reaction with excess oxygen
(I) Na	(A) Superoxide	(P) Paramagnetic
(II) Ba	(B) Peroxide	(Q) Diamagnetic
(III) K	(C) Monoxide	(R) Bond order = 1.5
(IV) Ca	(D) Dioxide	(S) Bond order = 1

21. Which of the following is an **INCORRECT** match.

- (A) (I), (B), (QS)      (B) (II), (B), (QS)      (C) (II), (A), (PR)      (D) (IV), (C), (Q)

**SB0094**

22. Which of the following matches will result in species having magnetic moment equal to that of  $\text{Mn}^{+6}$

- (A) I, (B), QS      (B) IV, B, (QS)      (C) IV, (A), (PR)      (D) III, (A), (PR)

**SB0094**

23. On reaction with oxygen, which of the following combination is possible

- (A) I, (A, C), (P, Q)      (B) I, (B), (Q)  
(C) II, (A, B), (P, Q, S)      (D) IV, (B, C), Q

**SB0094**

## EXERCISE # JEE-MAIN

1. A metal M readily forms its sulphate  $MSO_4$  which is water soluble. It forms oxide MO which becomes inert on heating. It forms insoluble hydroxide which is soluble in NaOH. The metal M is:- [AIEEE-2002]  
(1) Mg (2) Ba (3) Ca (4) Be **SB0095**
2.  $KO_2$  is used in space and submarines because it [AIEEE-2002]  
(1) Absorbs  $CO_2$  and increase  $O_2$  concentration  
(2) Absorbs moisture  
(3) Absorbs  $CO_2$   
(4) Produces ozone **SB0096**
3. In curing cement plasters, water is sprinkled from time to time. This helps in :- [AIEEE-2003]  
(1) Hydrating sand and gravel mixed with cement  
(2) Converting sand into silicate  
(3) Developing interlocking needle like crystals of hydrated silicates  
(4) Keeping it cool **SB0097**
4. The solubilities of carbonates decreases down the magnesium group due to decrease in-[AIEEE-2003]  
(1) Inter-ionic attraction  
(2) Entropy of solution formation  
(3) Lattice energy of solids  
(4) Hydration energy of cations **SB0098**
5. The substance not likely to contain  $CaCO_3$  is :- [AIEEE-2003]  
(1) Sea shells (2) Dolomite  
(3) A marble statue (4) Calcined gypsum **SB0099**
6. One mole of magnesium nitride on reaction with excess of water gives :- [AIEEE-2004]  
(1) Two mole of  $HNO_3$  (2) Two mole of  $NH_3$   
(3) 1 mole of  $NH_3$  (4) 1 mole of  $HNO_3$  **SB0100**
7. Beryllium and aluminium exhibit many properties which are similar. But the two elements differ in - [AIEEE-2004]  
(1) Exhibiting maximum covalency in compounds  
(2) Forming polymeric hydrides  
(3) Forming covalent halides  
(4) Exhibiting amphoteric nature in their oxides. **SB0101**

8. The ionic mobility of alkali metal ions in aqueous solution is maximum for :- [AIEEE-2006]  
(1)  $\text{Rb}^+$                       (2)  $\text{Li}^+$                       (3)  $\text{Na}^+$                       (4)  $\text{K}^+$   
**SB0102**
9. The products obtained on heating  $\text{LiNO}_3$  will be :- [AIEEE-2011]  
(1)  $\text{LiNO}_2 + \text{O}_2$                       (2)  $\text{Li}_2\text{O} + \text{NO}_2 + \text{O}_2$   
(3)  $\text{Li}_3\text{N} + \text{O}_2$                       (4)  $\text{Li}_2\text{O} + \text{NO} + \text{O}_2$   
**SB0103**
10. What is the best description of the change that occurs when  $\text{Na}_2\text{O}(\text{s})$  is dissolved in water ? [AIEEE-2011]  
(1) Oxidation number of sodium decreases  
(2) Oxide ion accepts sharing in a pair of electrons  
(3) Oxide ion donates a pair of electrons  
(4) Oxidation number of oxygen increases  
**SB0104**
11. Which of the following on thermal-decomposition yields a basic as well as an acidic oxide ? [AIEEE-2012]  
(1)  $\text{NH}_4\text{NO}_3$                       (2)  $\text{NaNO}_3$                       (3)  $\text{KClO}_3$                       (4)  $\text{CaCO}_3$   
**SB0105**
12. Fire extinguishers contain  $\text{H}_2\text{SO}_4$  and which one of the following :-[JEE MAIN-2012, Online]  
(1)  $\text{CaCO}_3$                       (2)  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$   
(3)  $\text{Na}_2\text{CO}_3$                       (4)  $\text{NaHCO}_3$   
**SB0106**
13. Based on lattice energy and other considerations, which one of the following alkali metal chloride is expected to have the highest melting point ? [JEE MAIN-2012, Online]  
(1)  $\text{RbCl}$                       (2)  $\text{LiCl}$                       (3)  $\text{KCl}$                       (4)  $\text{NaCl}$   
**SB0107**
14. Which one of the following will react most vigorously with water ? [JEE MAIN-2012, Online]  
(1)  $\text{Li}$                       (2)  $\text{K}$                       (3)  $\text{Rb}$                       (4)  $\text{Na}$   
**SB0108**
15. A metal M on heating in nitrogen gas gives Y. Y on treatment with  $\text{H}_2\text{O}$  gives a colourless gas which when passed through  $\text{CuSO}_4$  solution gives a blue colour, Y is :- [JEE MAIN-2012, Online]  
(1)  $\text{NH}_3$                       (2)  $\text{MgO}$                       (3)  $\text{Mg}_3\text{N}_2$                       (4)  $\text{Mg}(\text{NO}_3)_2$   
**SB0109**



16. The correct statement for the molecule,  $\text{CsI}_3$ , is : [JEE(Main)-2014]  
 (1) it contains  $\text{Cs}^{3+}$  and  $\text{I}^-$  ions  
 (2) it contains  $\text{Cs}^+$ ,  $\text{I}^-$  and lattice  $\text{I}_2$  molecule  
 (3) it is a covalent molecule  
 (4) it contains  $\text{Cs}^+$  and  $\text{I}_3^-$  ions  
SB0110
17. Which of the following statements about  $\text{Na}_2\text{O}_2$  is **not** correct ? [JEE MAIN-2014, Online]  
 (1)  $\text{Na}_2\text{O}_2$  oxidises  $\text{Cr}^{3+}$  to  $\text{CrO}_4^{2-}$  in acid medium  
 (2) It is diamagnetic in nature  
 (3) It is the super oxide of sodium  
 (4) It is a derivative of  $\text{H}_2\text{O}_2$   
SB0111
18. Amongst  $\text{LiCl}$ ,  $\text{RbCl}$ ,  $\text{BeCl}_2$  and  $\text{MgCl}_2$  the compounds with the greatest and the least ionic character, respectively are : [JEE MAIN-2014, Online]  
 (1)  $\text{RbCl}$  and  $\text{MgCl}_2$  (2)  $\text{LiCl}$  and  $\text{RbCl}$   
 (3)  $\text{MgCl}_2$  and  $\text{BeCl}_2$  (4)  $\text{RbCl}$  and  $\text{BeCl}_2$   
SB0112
19. The correct order of thermal stability of hydroxides is : JEE(Main)Online-2015]  
 (1)  $\text{Ba}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Mg}(\text{OH})_2$  (2)  $\text{Mg}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Ba}(\text{OH})_2$   
 (3)  $\text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ba}(\text{OH})_2$  (4)  $\text{Ba}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Mg}(\text{OH})_2$   
SB0113
20. Which of the alkaline earth metal halides given below is essentially covalent in nature :-  
 (1)  $\text{SrCl}_2$  (2)  $\text{CaCl}_2$  (3)  $\text{BeCl}_2$  (4)  $\text{MgCl}_2$   
JEE(Main)Online-2015]  
SB0114
21. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy ? [JEE(Main)-2015]  
 (1)  $\text{BaSO}_4$  (2)  $\text{SrSO}_4$  (3)  $\text{CaSO}_4$  (4)  $\text{BeSO}_4$   
SB0115
22. The commercial name for calcium oxide is : [JEE(Main)-2016]  
 (1) Quick lime (2) Milk of lime (3) Limestone (4) Slaked lime  
SB0116
23. The correct order of the solubility of alkaline-earth metal sulphates in water is : [JEE(Main)-2016]  
 (1)  $\text{Mg} < \text{Sr} < \text{Ca} < \text{Ba}$  (2)  $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$   
 (3)  $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$  (4)  $\text{Mg} > \text{Sr} > \text{Ca} > \text{Ba}$   
SB0117

24. The main oxides formed on combustion of Li, Na and K in excess of air are respectively :
- (1)  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}_2$  and  $\text{KO}_2$  (2)  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{KO}_2$  [JEE(Main)-2016]  
(3)  $\text{LiO}_2$ ,  $\text{Na}_2\text{O}_2$  and  $\text{K}_2\text{O}$  (4)  $\text{Li}_2\text{O}_2$ ,  $\text{Na}_2\text{O}_2$  and  $\text{KO}_2$
- SB0118
25. Both lithium and magnesium display several similar properties due to the diagonal relationship ; however, the one which is incorrect is : [JEE(Main)-2017]
- (1) Both form basic carbonates  
(2) Both form soluble bicarbonates  
(3) Both form nitrides  
(4) Nitrates of both Li and Mg yield  $\text{NO}_2$  and  $\text{O}_2$  on heating
- SB0119
26. Which of the following ions does **not** liberate hydrogen gas on reaction with dilute acids?
- (1)  $\text{Ti}^{2+}$  (2)  $\text{Cr}^{2+}$  [JEE(Main)-2017 on line]  
(3)  $\text{Mn}^{2+}$  (4)  $\text{V}^{2+}$
- SB0120
27. In  $\text{KO}_2$ , the nature of oxygen species and the oxidation state of oxygen atom are, respectively [JEE(Main)ONLINE-2018]
- (1) Superoxide and  $-1/2$   
(2) Oxide and  $-2$   
(3) Peroxide and  $-1/2$   
(4) Superoxide and  $-1$

SB0121

## EXERCISE # JEE-ADVANCED

1. The species that do not contain peroxide linkage are - [JEE 1992]  
 (A)  $\text{PbO}_2$                       7(B)  $\text{H}_2\text{O}_2$                       (C)  $\text{SrO}_2$                       (D)  $\text{BaO}_2$  SB0122
2. Read the following statement and explanation and answer as per the options given below :  
**Statement-1** : The alkali metals can form ionic hydrides which contain the hydride ion  $\text{H}^-$ .  
**Statement-2** : The alkali metals have low electronegativity ; their hydrides conduct electricity when fused and liberate hydrogen at the anode. [JEE 1994]  
 (A) Both 1 and 2 are true and 2 is the correct explanation of 1.  
 (B) Both 1 and 2 are true but 2 is not the correct explanation of 1.  
 (C) 1 is true but 2 is false.  
 (D) 1 is false but 2 is true. SB0123
3. The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order. [JEE 1996]  
 $\text{K}_2\text{CO}_3$ (I)  $\text{MgCO}_3$ (II)  $\text{CaCO}_3$ (III)  $\text{BeCO}_3$ (IV)  
 (A) I < II < III < IV                      (B) IV < II < III < I  
 (C) IV < II < I < III                      (D) II < IV < III < I SB0124
4. Property of all the alkaline earth metals that increase with their atomic number is - [JEE 1997]  
 (A) ionisation energy                      (B) solubility of their hydroxides  
 (C) solubility of their sulphate                      (D) electronegativity SB0125
5. Highly pure dilute solution of sodium in liquid ammonia - [JEE 1998]  
 (A) shows blue colour                      (B) exhibits electrical conductivity  
 (C) produces sodium amide                      (D) produces hydrogen gas SB0126
6. The set representing the correct order of first ionization potential is - [JEE 2001S]  
 (A)  $\text{K} > \text{Na} > \text{Li}$                       (B)  $\text{Be} > \text{Mg} > \text{Ca}$                       (C)  $\text{B} > \text{C} > \text{N}$                       (D)  $\text{Ge} > \text{Si} > \text{C}$  SB0127
- Assertion and Reason**
7. This questions contains statement-1 (assertion) and statement-2 (reason) and has 4 choices (a), (b), (c) and (d) out of which only one is correct.  
**Statement-1** : Alkali metals dissolve in liquid ammonia to give blue solutions. because.  
**Statement-2** : Alkali metals in liquid ammonia give solvated species of the type  $[\text{M}(\text{NH}_3)_n]^+$  (M = alkali metals). [JEE 2007]  
 (A) Both 1 and 2 are true and 2 is the correct explanation of 1.  
 (B) Both 1 and 2 are true but 2 is not the correct explanation of 1.  
 (C) 1 is true but 2 is false.  
 (D) 1 is false but 2 is true. SB0128
8. The compound(s) formed upon combustion of sodium metal in excess air is (are) [JEE 2009]  
 (A)  $\text{Na}_2\text{O}_2$                       (B)  $\text{Na}_2\text{O}$                       (C)  $\text{NaO}_2$                       (D)  $\text{NaOH}$  SB0129

## ANSWER KEY

## EXERCISE # O-1

- |         |         |         |         |
|---------|---------|---------|---------|
| 1. (A)  | 2. (A)  | 3. (A)  | 4. (D)  |
| 5. (A)  | 6. (D)  | 7. (A)  | 8. (C)  |
| 9. (B)  | 10. (C) | 11. (C) | 12. (A) |
| 13. (C) | 14. (C) | 15. (C) | 16. (D) |
| 17. (A) | 18. (A) | 19. (A) | 20. (C) |
| 21. (B) | 22. (A) | 23. (C) | 24. (D) |
| 25. (A) | 26. (C) | 27. (B) | 28. (A) |
| 29. (C) | 30. (D) | 31. (A) | 32. (A) |
| 33. (A) | 34. (B) | 35. (A) | 36. (B) |
| 37. (B) | 38. (B) | 39. (D) | 40. (A) |
| 41. (C) | 42. (C) | 43. (B) | 44. (B) |
| 45. (A) | 46. (C) | 47. (C) | 48. (C) |
| 49. (B) | 50. (D) |         |         |

## EXERCISE # O-2

- |                 |                     |                 |                 |
|-----------------|---------------------|-----------------|-----------------|
| 1. (B),(C), (D) | 2. (B),(C)          | 3. (A),(B)      | 4. (A),(C)      |
| 5. (A),(B),(C)  | 6. (A), (B)         | 7. (A), (B),(D) | 8. (A),(C)      |
| 9. (A),(B),(C)  | 10. (A),(C)         | 11. (A), (C)    | 12. (C),(D)     |
| 13. (A),(B),(D) | 14. (A),(B),(C),(D) | 15. (A),(B),(C) | 16. (B),(C),(D) |
| 17. (B), (D)    | 18. (B),(C),(D)     | 19. (B),(C),(D) |                 |

## EXERCISE # S-1

- |        |        |        |                    |
|--------|--------|--------|--------------------|
| 1. (4) | 2. (6) | 3. (4) | 4. (10), OMR - (1) |
| 5. (8) |        |        |                    |
| 6. (6) |        |        |                    |

Except Be & Mg other s-block metals impart characteristic colour to oxidising flame.

## EXERCISE # S-2

- Comprehension Based Questions

## Comprehension # 1

1. (B)                      2. (A)                      3. (B)

## Comprehension # 2

4. (C)                      5. (A)                      6. (D)                      7. (D)                      8. (A)

- Match the column

9. (A)  $\rightarrow$  P,R ; (B)  $\rightarrow$  P,Q ; (C)  $\rightarrow$  P ; (D)  $\rightarrow$  S10. (A)  $\rightarrow$  P,Q,S ; (B)  $\rightarrow$  P,Q ; (C)  $\rightarrow$  P,Q,R ; (D)  $\rightarrow$  P,Q

- Match the code

11. (D)                      12. (A)

- Assertion & Reasoning

13. A                      14. C                      15. A                      16. C

17. A                      18. D                      19. A                      20. A

21. C                      22. D                      23. B

## EXERCISE # JEE-MAIN

1. (4)	2. (1)	3. (3)	4. (4)
5. (4)	6. (2)	7. (1)	8. (1)
9. (2)	10. (3)	11. (4)	12. (4)
13. (4)	14. (3)	15. (3)	16. (4)
17. (3)	18. (4)	19. (3)	20. (3)
21. (4)	22. (1)	23. (3)	24. (1)
25. (1)	26. (3)	27. (1)	

## EXERCISE # JEE-ADVANCED

1. A	2. A	3. B	4. B
5. A,B	6. B	7. B	8. A,B

## d-BLOCK COMPOUND

### TRANSITION ELEMENTS

**Definition :** They are often called 'transition elements' because their position in the periodic table is between s-block and p-block elements

Typically, the transition elements have incompletely filled d-level. Since Zn group has  $d^{10}$  configuration in their ground state as well as in stable oxidation state, they are not considered as transition elements but they are d-block elements.

1st Series										
Z	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

2nd Series										
Z	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	1	1	2	1	1	0	1	2
4d	1	2	4	5	5	7	8	10	10	10

3rd Series										
Z	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

4th Series										
Z	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

#### General Characteristics :

(i) **Metallic character :** They are all metal and good conductor of heat & electricity

(ii) **Electronic configuration :**  $(n-1)d^{1-10}ns^{1-2}$

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
others are	}			$4s^1$					$4s^1$	
as usual				$3d^5$					$3d^{10}$	

(iii) <b>M.P.</b>	<table style="display: inline-table; vertical-align: middle;"> <tr> <td style="text-align: right;">Cr</td> <td rowspan="3" style="font-size: 3em; vertical-align: middle;">}</td> <td style="text-align: left;">→ Maximum</td> <td style="text-align: right;">Zn</td> <td rowspan="3" style="font-size: 3em; vertical-align: middle;">}</td> <td style="text-align: left;">lowest m.p.</td> </tr> <tr> <td style="text-align: right;">Mo</td> <td style="text-align: left;">6 no. of unpaired <math>e^-</math>s</td> <td style="text-align: right;">Cd</td> <td style="text-align: left;">due to no unpaired <math>e^-</math></td> </tr> <tr> <td style="text-align: right;">W</td> <td style="text-align: left;">are involved in metallic bonding</td> <td style="text-align: right;">Hg</td> <td style="text-align: left;">for metallic bonding</td> </tr> </table>	Cr	}	→ Maximum	Zn	}	lowest m.p.	Mo	6 no. of unpaired $e^-$ s	Cd	due to no unpaired $e^-$	W	are involved in metallic bonding	Hg	for metallic bonding
Cr	}	→ Maximum		Zn	}		lowest m.p.								
Mo		6 no. of unpaired $e^-$ s		Cd			due to no unpaired $e^-$								
W		are involved in metallic bonding	Hg	for metallic bonding											

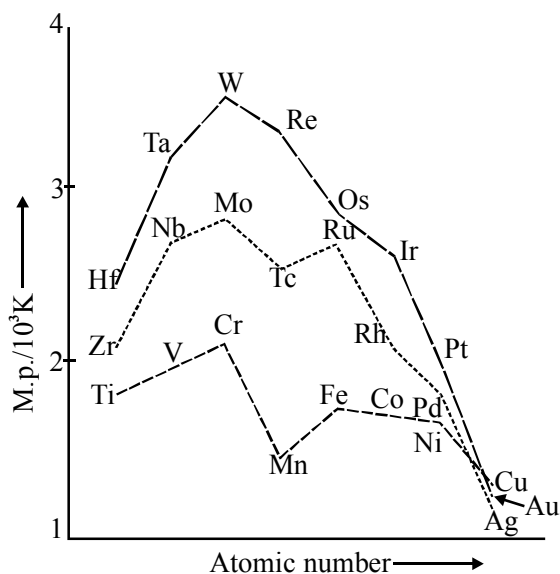


Fig. : Trends in melting points of transition elements

(iv) Variation in atomic radius :

Sc → Mn Fe Co Ni Cu Zn

decreases      remains same      increases again

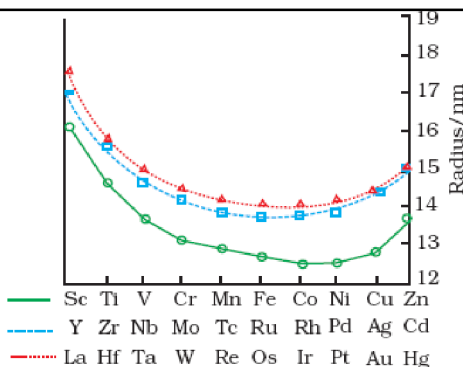


Fig. 8.3: Trends in atomic radii of transition elements

(v) Ionisation energy :

1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> IE's are increasing from left to right for 1<sup>st</sup> Transition series, but not regularly.  
 For 2<sup>nd</sup> IE Cr > Fe > Mn and Cu > Zn  
 For 3<sup>rd</sup> IE Mn > Cr > Fe and Zn has highest.

(vi) DENSITY

- (a) The atomic volume of the transition elements are low, compared with s-block, so their density is comparatively high ( $D = M/V$ )
- (b) Os ( $22.57 \text{ gm cm}^{-3}$ ) and Ir ( $22.61 \text{ gm cm}^{-3}$ ) have highest density.
- (c) In all the groups (except IIIB) there is normal increase in density from 3d to 4d series, and from 4d to 5d, it increases just double. Due to lanthanide contraction Ex. : Ti < Zr << Hf

## (d) In 3d series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Density/g cm <sup>-3</sup>	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

(e) In 3d series highest density – Cu lowest density – Sc

(f) Some important orders of density

**Electronic configurations and some other properties of the first series of transition elements**

Element	Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Electronic configuration										
M	3d <sup>1</sup> 4s <sup>2</sup>	3d <sup>2</sup> 4s <sup>2</sup>	3d <sup>3</sup> 4s <sup>2</sup>	3d <sup>5</sup> 4s <sup>2</sup>	3d <sup>5</sup> 4s <sup>2</sup>	3d <sup>6</sup> 4s <sup>2</sup>	3d <sup>7</sup> 4s <sup>2</sup>	3d <sup>8</sup> 4s <sup>2</sup>	3d <sup>10</sup> 4s <sup>1</sup>	3d <sup>10</sup> 4s <sup>2</sup>
M <sup>+</sup>	3d <sup>1</sup> 4s <sup>1</sup>	3d <sup>2</sup> 4s <sup>1</sup>	3d <sup>3</sup> 4s <sup>1</sup>	3d <sup>5</sup>	3d <sup>5</sup> 4s <sup>1</sup>	3d <sup>6</sup> 4s <sup>1</sup>	3d <sup>7</sup> 4s <sup>1</sup>	3d <sup>8</sup> 4s <sup>1</sup>	3d <sup>10</sup>	3d <sup>10</sup> 4s <sup>1</sup>
M <sup>2+</sup>	3d <sup>1</sup>	3d <sup>2</sup>	3d <sup>3</sup>	3d <sup>4</sup>	3d <sup>5</sup>	3d <sup>6</sup>	3d <sup>7</sup>	3d <sup>8</sup>	3d <sup>9</sup>	3d <sup>10</sup>
M <sup>3+</sup>	[Ar]	3d <sup>1</sup>	3d <sup>2</sup>	3d <sup>3</sup>	3d <sup>4</sup>	3d <sup>5</sup>	3d <sup>6</sup>	3d <sup>7</sup>	–	–
Enthalpy of atomisation, Δ <sub>a</sub> H <sup>⊖</sup> /kJ mol <sup>-1</sup>	326	473	515	397	281	416	425	430	339	126
Ionisation Enthalpy, Δ <sub>1</sub> H <sup>⊖</sup> /kJ mol <sup>-1</sup>										
Δ <sub>1</sub> H <sup>⊖</sup>	I	631	656	650	653	717	762	758	736	906
	II	1235	1309	1414	1592	1509	1561	1644	1752	1958
	III	2393	2657	2833	2990	3260	2962	3243	3402	3556
Metallic/Ionic radii/pm										
M	164	147	135	129	137	126	125	125	128	137
M <sup>2+</sup>	–	–	79	82	82	77	74	70	73	75
M <sup>3+</sup>	73	67	64	62	65	65	61	60	–	–
Standard electrode potential E <sup>⊖</sup> /V										
M <sup>2+</sup> /M	–	-1.63	-1.18	-0.90	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76
M <sup>3+</sup> /M <sup>2+</sup>	–	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	–	–	–
Density/g cm <sup>-3</sup>	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

**VARIABLE OXIDATION STATES POSSIBLE :**

- (1) The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7.
- (2) The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn).
- (3) Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II).
- (4) At the other end, the only oxidation state of zinc is +2 (no d electrons are involved).
- (5) The maximum oxidation states of reasonable stability correspond in value to the sum of the s and d electrons upto manganese (Ti<sup>IV</sup>O<sub>2</sub>, V<sup>V</sup>O<sub>2</sub><sup>+</sup>, Cr<sup>VI</sup>O<sub>4</sub><sup>2-</sup>, Mn<sup>VII</sup>O<sub>4</sub><sup>-</sup>) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are Fe<sup>II,III</sup>, Co<sup>II,III</sup>, Ni<sup>II</sup>, Cu<sup>I,II</sup>, Zn<sup>II</sup>.



- (6) The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of d orbitals in such a way that their oxidation states differ from each other by unity, e.g.,  $V^{II}$ ,  $V^{III}$ ,  $V^{IV}$ ,  $V^V$ .
- (7) This is in contrast with the variability of oxidation states of non transition elements where oxidation states normally differ by a unit of two.
- (8) An interesting feature in the variability of oxidation states of the d-block elements is noticed among the groups (groups 4 through 10).
- (9) In group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas  $MoO_3$  and  $WO_3$  are not.
- (10) Low oxidation states are found when a complex compound has ligands capable of  $\pi$ -acceptor character in addition to the  $\sigma$ -bonding. For example, in  $Ni(CO)_4$  and  $Fe(CO)_5$ , the oxidation state of nickel and iron is zero.
- (11) As the oxidation number of a metal increases, ionic character decreases. In the case of Mn,  $Mn_2O_7$  is a covalent green oil. Even  $CrO_3$  and  $V_2O_5$  have low melting points. In these higher oxides, the acidic character is predominant. Thus,  $Mn_2O_7$  gives  $HMnO_4$  and  $CrO_3$  gives  $H_2CrO_4$  and  $H_2Cr_2O_7$ .  $V_2O_5$  is, however, amphoteric though mainly acidic and it gives  $VO_4^{3-}$  as well as  $VO_2^+$  salts. In vanadium there is gradual change from the basic  $V_2O_3$  to less basic  $V_2O_4$  and to amphoteric  $V_2O_5$ .  $V_2O_4$  dissolves in acids to give  $VO^{2+}$  salts. Similarly,  $V_2O_5$  reacts with alkalies as well as acids to give  $VO_4^{3-}$  and  $VO_2^+$  respectively. The well characterised CrO is basic but  $Cr_2O_3$  is amphoteric.

**Oxidation states of the 1<sup>st</sup> transition series**  
most common ones are in bold types :

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1					+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3		
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

**Trends in stability of higher oxidation state :**

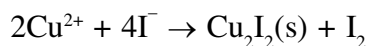
- Table shows the stable halides of the 3d series of transition metals. The highest oxidation numbers are achieved in  $TiX_4$  (tetrahalides),  $VF_5$  and  $CrF_6$ . The +7 state for Mn is not represented in simple halides but  $MnO_3F$  is known, and beyond Mn no metal has a trihalide except  $FeX_3$  and  $CoF_3$ .
- The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of  $CoF_3$ , or higher bond enthalpy terms for the higher covalent compounds, e.g.,  $VF_5$  and  $CrF_6$ .
- Although  $V^V$  is represented only by  $VF_5$ , the other halides, however, undergo hydrolysis to give oxohalides,  $VOX_3$ .
- Another feature of fluorides is their instability in the low oxidation states e.g.,  $VX_2$  (X = Cl, Br or I)

## Formulas of halides of 3d-metals

Oxidation Number									
+ 6			CrF <sub>6</sub>						
+ 5		VF <sub>5</sub>	CrF <sub>5</sub>						
+ 4	TiX <sub>4</sub>	VX <sub>4</sub> <sup>I</sup>	CrX <sub>4</sub>	MnF <sub>4</sub>					
+ 3	TiX <sub>3</sub>	VX <sub>3</sub>	CrX <sub>3</sub>	MnF <sub>3</sub>	FeX <sub>3</sub> <sup>I</sup>	CoF <sub>3</sub>			
+ 2	TiX <sub>2</sub> <sup>III</sup>	VX <sub>2</sub>	CrX <sub>2</sub>	MnX <sub>2</sub>	FeX <sub>2</sub>	CoX <sub>2</sub>	NiX <sub>2</sub>	CuX <sub>2</sub> <sup>II</sup>	ZnX <sub>2</sub>
+ 1								CuX <sup>III</sup>	

Key : X = F → I ; X<sup>I</sup> = F → Br ; X<sup>II</sup> = F → Cl ; X<sup>III</sup> = Cl → I

and the same applies to CuX. On the other hand, all Cu(II) halides are known except the iodide. In this case, Cu<sup>2+</sup> oxidises I<sup>-</sup> to I<sub>2</sub>:



(5) However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.



(6) The stability of Cu<sup>2+</sup>(aq) rather than Cu<sup>+</sup>(aq) is due to the much more negative  $\Delta_{\text{Hyd}}H^{\circ}$  of Cu<sup>2+</sup>(aq) than Cu<sup>+</sup>, which more than compensates for the second ionisation enthalpy of Cu.

(7) The ability of oxygen to stabilise the highest oxidation state is demonstrated in the oxides.

(8) The highest oxidation number in the oxides coincides with the group number and is attained in Sc<sub>2</sub>O<sub>3</sub> to Mn<sub>2</sub>O<sub>7</sub>.

(9) Beyond Group 7, no higher oxides of Fe above Fe<sub>2</sub>O<sub>3</sub>, are known, although ferrates (VI)(FeO<sub>4</sub>)<sup>2-</sup>, are formed in alkaline media but they readily decompose to Fe<sub>2</sub>O<sub>3</sub> and O<sub>2</sub>.

(10) Besides the oxides, oxocations stabilise V<sup>v</sup> as VO<sub>2</sub><sup>+</sup>, V<sup>IV</sup> as VO<sup>2+</sup> and Ti<sup>IV</sup> as TiO<sup>2+</sup>

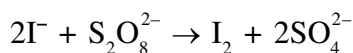
(11) The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is MnF<sub>4</sub> whereas the highest oxide is Mn<sub>2</sub>O<sub>7</sub>. The ability of oxygen to form multiple bonds to metals explains its superiority.

(12) In the covalent oxide Mn<sub>2</sub>O<sub>7</sub>, each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge.

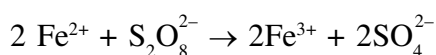
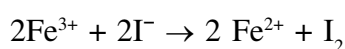
(13) The tetrahedral [MO<sub>4</sub>]<sup>n</sup> ions are known for V<sup>v</sup>, Cr<sup>VI</sup>, Mn<sup>v</sup>, Mn<sup>VI</sup> and Mn<sup>VII</sup>.

**FORMATION OF COLOURED ION :****Colour : (aquated)** $\text{Ti}^{4+} \longrightarrow$  colourless $\text{V}^{4+} \longrightarrow$  blue $\text{V}^{2+} \longrightarrow$  violet $\text{Cr}^{3+} \longrightarrow$  violet $\text{Mn}^{2+} \longrightarrow$  light pink $\text{Fe}^{3+} \longrightarrow$  yellow $\text{Ni}^{2+} \longrightarrow$  green $\text{Zn}^{2+} \longrightarrow$  colourless $\text{Sc}^{3+} \longrightarrow$  colourless $\text{Ti}^{3+} \longrightarrow$  purple $\text{V}^{3+} \longrightarrow$  green $\text{Cr}^{2+} \longrightarrow$  blue $\text{Mn}^{3+} \longrightarrow$  violet $\text{Fe}^{2+} \longrightarrow$  light green $\text{Co}^{2+} \longrightarrow$  pink $\text{Cu}^{2+} \longrightarrow$  blue**CATALYTIC PROPERTIES**

- (1) The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples.
- (2) Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3d and 4s electrons for bonding).
- (3) This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering).
- (4) Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.



An explanation of this catalytic action can be given as:



Catalyst	Used
TiCl <sub>3</sub>	→ Used as the Ziegler-Natta catalyst in the production of polythene.
V <sub>2</sub> O <sub>5</sub>	→ Convert SO <sub>2</sub> to SO <sub>3</sub> in the contact process for making H <sub>2</sub> SO <sub>4</sub>
MnO <sub>2</sub>	→ Used as a catalyst to decompose KClO <sub>3</sub> to give O <sub>2</sub>
Fe	→ Promoted iron is used in the Haber-Bosch process for making NH <sub>3</sub>
FeCl <sub>3</sub>	→ Used in the production of CCl <sub>4</sub> from CS <sub>2</sub> and Cl <sub>2</sub>
PdCl <sub>2</sub>	→ Wacker process for converting C <sub>2</sub> H <sub>4</sub> + H <sub>2</sub> O + PdCl <sub>2</sub> to CH <sub>3</sub> CHO + 2HCl + Pd.
Pd	→ Used for hydrogenation (e.g. phenol to cyclohexanone).
Pt/PtO	→ Adams catalyst, used for reductions.
Pt	→ Formerly used for SO <sub>2</sub> → SO <sub>3</sub> in the contact process for making H <sub>2</sub> SO <sub>4</sub>
Pt/Rh	→ Formerly used in the Ostwald process for making HNO <sub>3</sub> to oxidize NH <sub>3</sub> to NO
Cu	→ Is used in the direct process for manufacture of (CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub> used to make silicones.
Cu/V	→ Oxidation of cyclohexanol/cyclohexanone mixture to adipic acid which is used to make nylon-66
CuCl <sub>2</sub>	→ Deacon process of making Cl <sub>2</sub> from HCl
Ni	→ Raney nickel, numerous reduction processes (e.g. manufacture of hexamethylenediamine, production of H <sub>2</sub> from NH <sub>3</sub> , reducing anthraquinone to anthraquinol in the production of H <sub>2</sub> O <sub>2</sub> )
FeSO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub>	→ Used as Fenton's reagent for oxidizing alcohols to aldehydes.

### Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. The principal physical and chemical characteristics of these compounds are as follows:

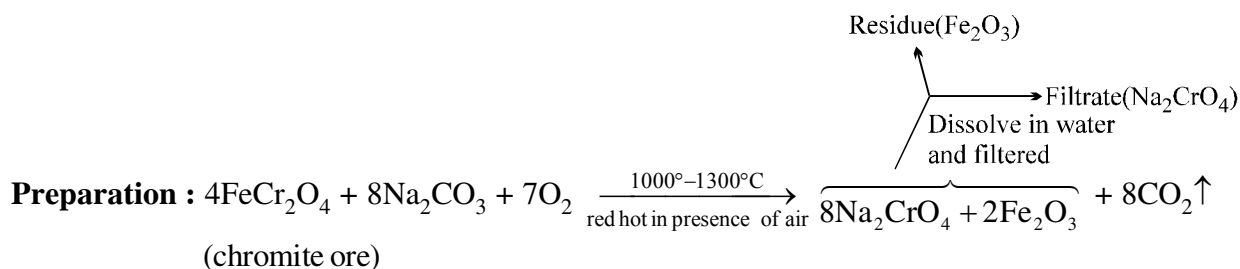
- They have high melting points, higher than those of pure metals.
- They are very hard, some borides approach diamond in hardness.
- They retain metallic conductivity.
- They are chemically inert.

### Alloy Formation

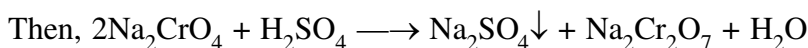
An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points.

The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

**CHROMATE -DICHROMATE**



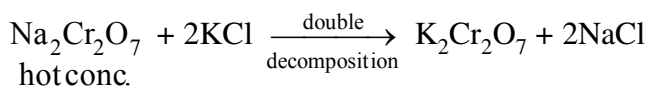
[Lime (CaO) added with  $\text{Na}_2\text{CO}_3$  which keeps the mass porous so that air has access to all parts and prevents fusion]



conc.      It's solubility      Hence, suitable temp. is to be  
 upto  $32^\circ\text{C}$  increases      employed to crystallise out  
 and then decreases      }  
 $\text{Na}_2\text{SO}_4$  first.

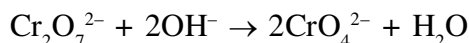
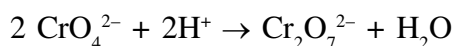
Then  $\text{Na}_2\text{Cr}_2\text{O}_7$  is crystallised out as  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  on evaporation.  
 (red crystal)

**How to get  $\text{K}_2\text{Cr}_2\text{O}_7$  :**



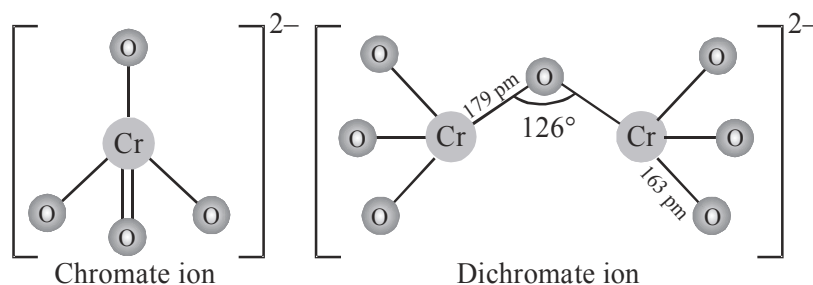
$\text{NaCl}$  crystallises out first and filtered off. Then  $\text{K}_2\text{Cr}_2\text{O}_7$  crystallised out on cooling

**The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.**

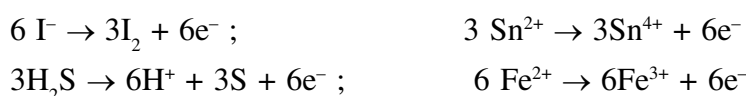


The structures of chromate ion,  $\text{CrO}_4^{2-}$  and the dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}$  are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of  $126^\circ$ . Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:

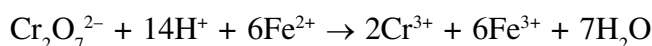




Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:



The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,



\* Similarities between hexavalent Cr & S-compounds :

- (i)  $\text{SO}_3$  &  $\text{CrO}_3 \longrightarrow$  both acidic.
- (ii)  $\text{S} \longrightarrow \text{SO}_4^{2-}, \text{S}_2\text{O}_7^{2-}, \text{Cr} \longrightarrow \text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-}$
- (iii)  $\text{CrO}_4^{2-}$  &  $\text{SO}_4^{2-}$  are isomorphous
- (iv)  $\text{SO}_2\text{Cl}_2$  &  $\text{CrO}_2\text{Cl}_2 \xrightarrow{\text{OH}^-} \text{SO}_4^{2-}$  &  $\text{CrO}_4^{2-}$  respectively.
- (v)  $\text{SO}_3\text{Cl}^-$  &  $\text{CrO}_3\text{Cl}^- \xrightarrow{\text{OH}^-} \text{SO}_4^{2-}$  &  $\text{CrO}_4^{2-}$
- (vi)  $\text{CrO}_3$  &  $\beta(\text{SO}_3)$  has same structure  $-\overset{\text{O}}{\parallel}{\text{Cr}}-\text{O}-\overset{\text{O}}{\parallel}{\text{Cr}}-\text{O}-\overset{\text{O}}{\parallel}{\text{Cr}}-$

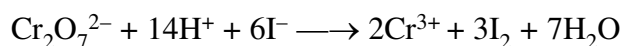
**Q.** In laboratory  $\text{K}_2\text{Cr}_2\text{O}_7$  is used mainly not  $\text{Na}_2\text{Cr}_2\text{O}_7$ . Why?

**Sol.**  $\text{Na}_2\text{Cr}_2\text{O}_7$  is deliquescent enough and changes its concentration and can not be taken as primary standard solution whereas  $\text{K}_2\text{Cr}_2\text{O}_7$  has no water of crystallisation and not deliquescent.

**Q.** How to standardise  $\text{Na}_2\text{S}_2\text{O}_3$  solution in iodometry?

**Sol.**  $\text{K}_2\text{Cr}_2\text{O}_7$  is primary standard  $\Rightarrow$  strength is known by weighing the salt in chemical balance and dissolving in measured amount of water.

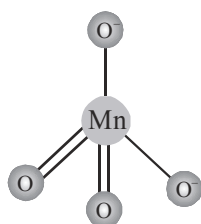
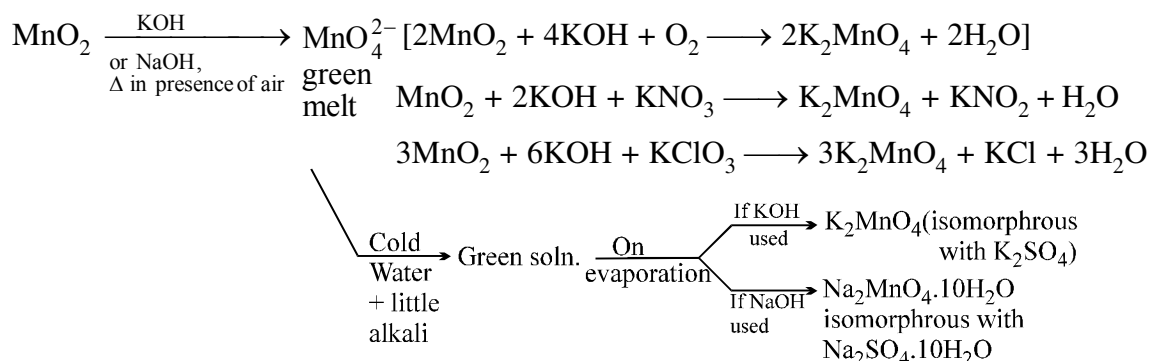
Then in acidic solution add. KI



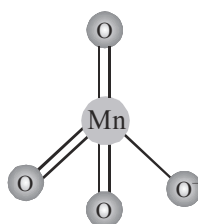
This  $\text{I}_2$  is liberated can be estimated with  $\text{S}_2\text{O}_3^{2-}$ .

### MANGANATE & PERMANGANATE

#### PREPARATION OF MANGANATE ( $\text{MnO}_4^{2-}$ ) :-



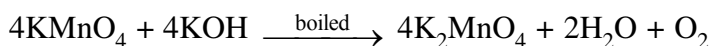
Tetrahedral  
manganate  
(green) ion



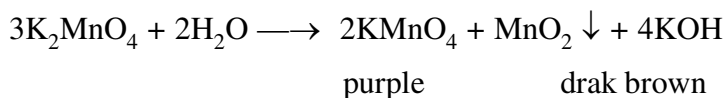
Tetrahedral  
permanganate  
(purple) ion

In presence of  $\text{KClO}_3$  &  $\text{KNO}_3$  the above reaction is more faster because these two on decomposition provides  $\text{O}_2$  easily.

\* Manganate is also obtained when  $\text{KMnO}_4$  is boiled with  $\text{KOH}$ .



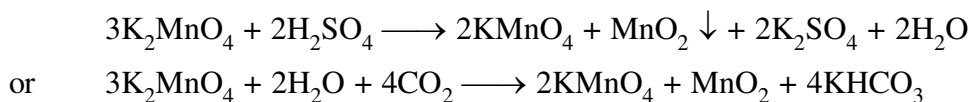
**Properties :** The above green solution is quite stable in alkali, but in pure water and in presence of acids, depositing  $\text{MnO}_2$  and giving a purple solution of permanganate.



$$\text{Prob. : } E_{\text{MnO}_4^{2-}/\text{MnO}_2}^0 = 2.26 \text{ V} \quad ; \quad E_{\text{MnO}_4^-/\text{MnO}_4^{2-}}^0 = -0.56 \text{ V}$$

Prove that  $\text{MnO}_4^{2-}$  will disproportionate in acidic medium.

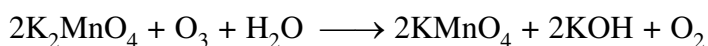
#### Conversion of $\text{MnO}_4^{2-}$ to $\text{MnO}_4^-$



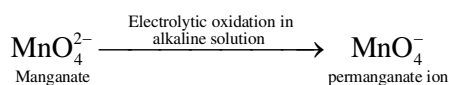
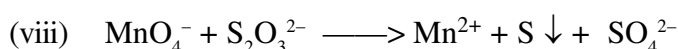
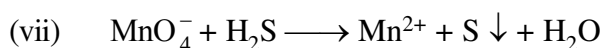
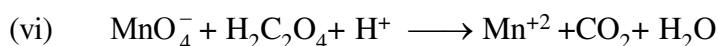
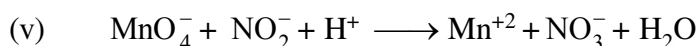
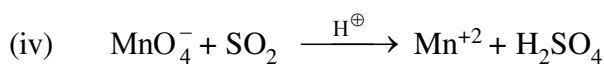
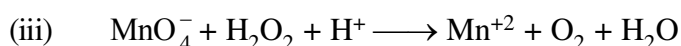
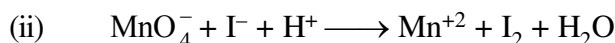
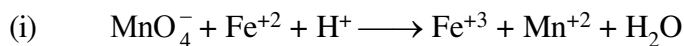
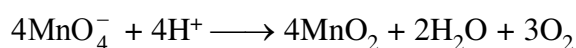
But in the above method  $\frac{1}{3}$  of Mn is lost as  $\text{MnO}_2$  but when oxidised either by  $\text{Cl}_2$  or by  $\text{O}_3$



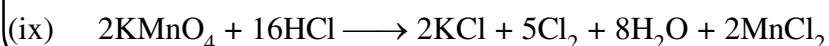
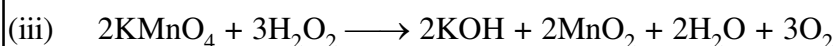
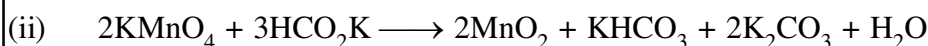
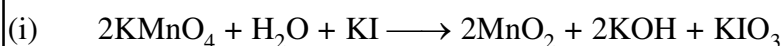
OR



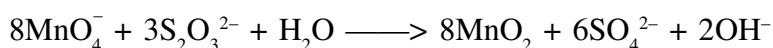
OR

**Oxidising Prop. of  $\text{KMnO}_4$  : (in acidic medium)**(1)\* It is not a primary standard since it is difficult to get it in a high degree of purity and free from traces of  $\text{MnO}_2$ .(2)\* It is slowly reduced to  $\text{MnO}_2$  especially in presence of light or acid

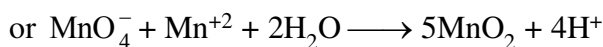
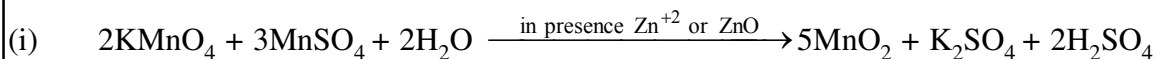
Hence it should be kept in dark bottles and standardise just before use.

**Note:** Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.**Oxidising Prop. of  $\text{KMnO}_4$  in neutral or faintly alkaline solution.**

(iv) Thiosulphate is oxidised almost quantitatively to sulphate:





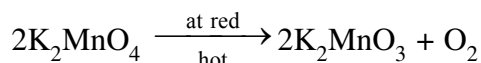
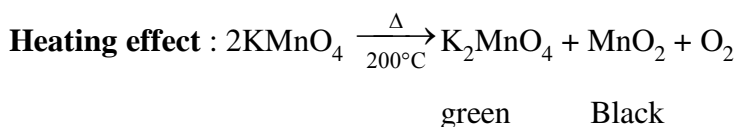
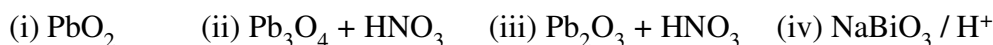
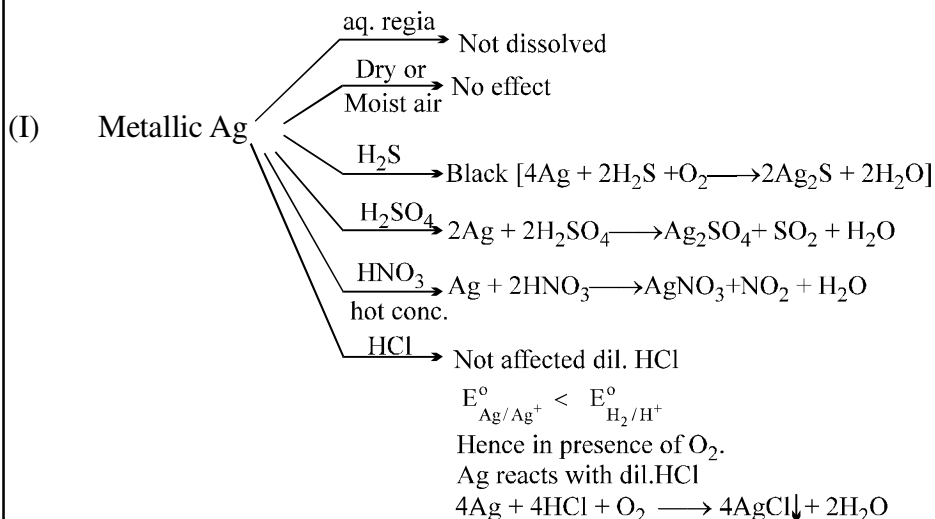
**Oxidising Prop. in neutral or weakly acidic solution:**

In absence of  $\text{Zn}^{+2}$  ions, some of the  $\text{Mn}^{+2}$  ion may escape, oxidation through the formation of insoluble  $\text{Mn}^{\text{II}}[\text{Mn}^{\text{IV}}\text{O}_3]$  manganous permanganite.

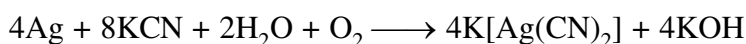
**Uses of  $\text{KMnO}_4$  :**

Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

\*\* In laboratory conversion of  $\text{Mn}^{+2}$  to  $\text{MnO}_4^-$  is done by :

**SILVER AND ITS COMPOUND**

In the same way in presence of  $\text{O}_2$ , Ag complexes with  $\text{NaCN}$  /  $\text{KCN}$ .

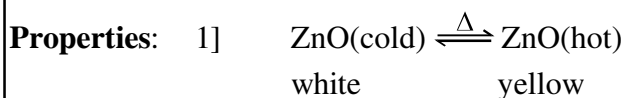
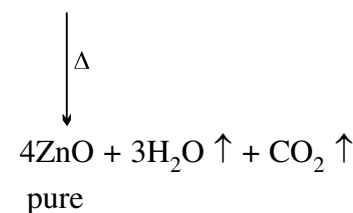
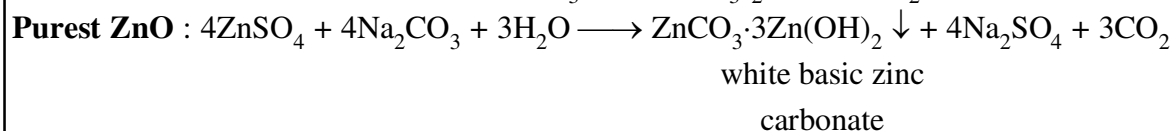
 **$\text{AgNO}_3$** 

**Preparation :** Reaction of Ag with dilute  $\text{HNO}_3$  or conc.  $\text{HNO}_3$ .



ZINC COMPOUNDS**ZnO**

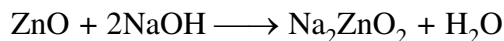
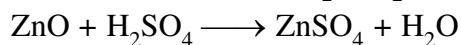
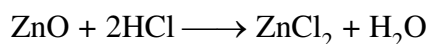
It is called as phillospher's wool due to its wooly flock type appearance



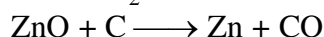
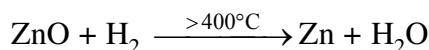
2] It is insoluble in water

3] It sublimes at  $400^\circ\text{C}$

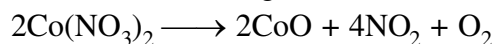
4] It is amphoteric oxide, react with acid & base both.



5]  $\text{ZnO} \longrightarrow \text{Zn}$  by  $\text{H}_2$  & C



6] It forms Rinmann's green with  $\text{Co(NO}_3)_2$

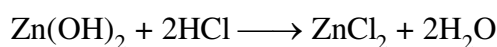
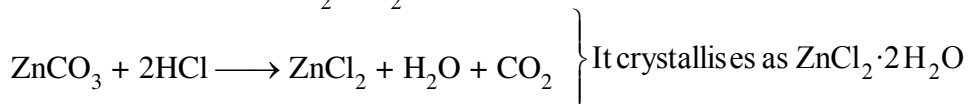


Rinmann's green

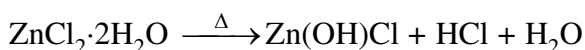
**Uses:** (1) As white pigment, it is superior than white lead because it does not turn into black

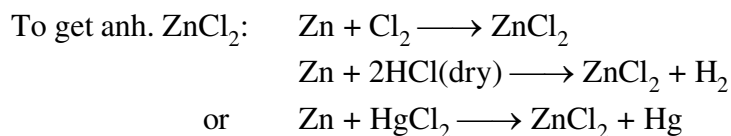
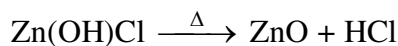
(2) Rinmann's green is used as green pigment

(3) It is used as zinc ointment in medicine

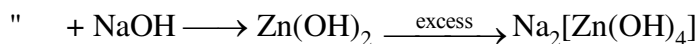
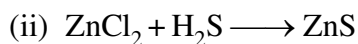
**ZnCl<sub>2</sub>**

Anh.  $\text{ZnCl}_2$  cannot be made by heating  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  because





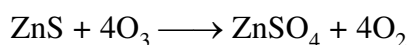
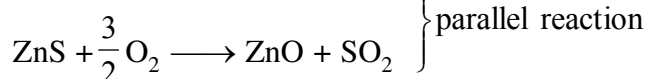
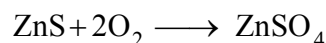
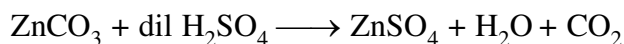
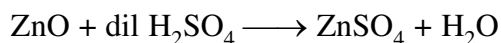
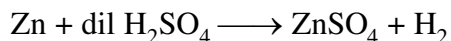
**Properties:** (i) It is deliquescent white solid (when anhydrous)



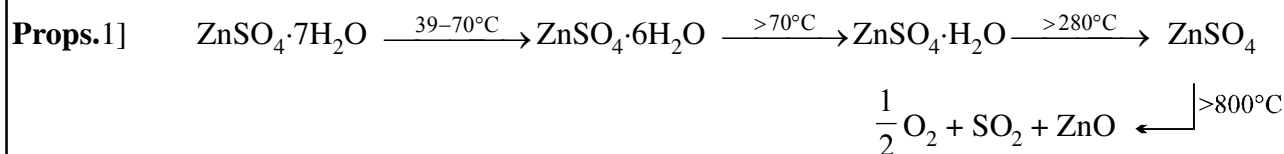
- Uses:** 1] Used for impregnating timber to prevent destruction by insects  
 2] As dehydrating agent when anhydrous  
 3]  $\text{ZnO} \cdot \text{ZnCl}_2$  used in dental filling

### **ZnSO<sub>4</sub>**

Preparation: →



} parallel reaction

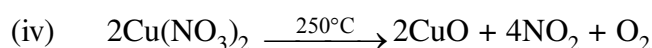
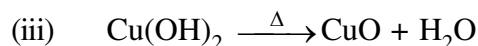


- Uses:** 1] in eye lotion  
 2] Lithophone ( $\text{ZnS} + \text{BaSO}_4$ ) is used as white pigment

### **COPPER COMPOUNDS**

#### **CuO**

**Preparation :** (i)  $\text{CuCO}_3 \cdot \text{Cu(OH)}_2 \xrightarrow{\Delta} 2\text{CuO} + \text{H}_2\text{O} + \text{CO}_2$  (Commercial process)  
 Malachite Green  
 (native Cu-carbonate)



- Properties :**
- (i) CuO is insoluble in water
  - (ii) Readily dissolves in dil. acids
 
$$\text{CuO} + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{H}_2\text{O}$$

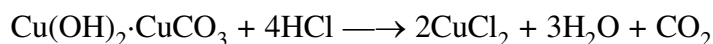
$$\text{HCl} \longrightarrow \text{CuCl}_2$$

$$\text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2$$
  - (iii) It decomposes when, heated above  $1100^\circ\text{C}$ 

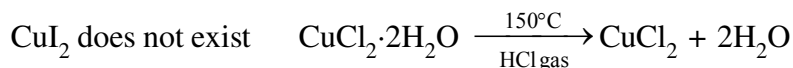
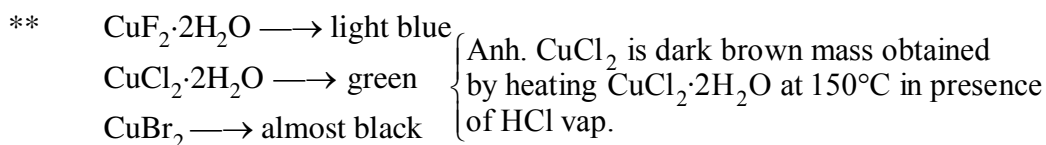
$$4\text{CuO} \longrightarrow 2\text{Cu}_2\text{O} + \text{O}_2$$
  - (iv) CuO is reduced to Cu by  $\text{H}_2$  or C under hot condition
 
$$\text{CuO} + \text{C} \longrightarrow \text{Cu} + \text{CO} \uparrow$$

$$\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O} \uparrow$$

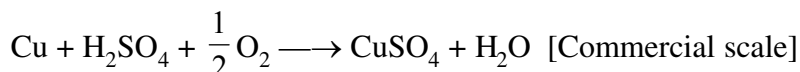
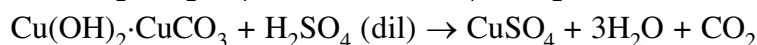
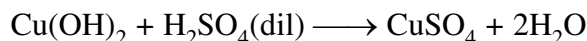
### CuCl<sub>2</sub>



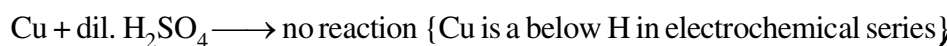
- Properties :**
- (i) It is crystallised as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  of Emerald green colour
  - (ii) dil. solution in water is blue in colour due to formation of  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  complex.
  - (iii) When conc. HCl or KCl added to dil. solution of  $\text{CuCl}_2$  the colour changes into yellow, owing to the formation of  $[\text{CuCl}_4]^{2-}$
  - (iv) The conc. aq. solution is green in colour having the two complex ions in equilibrium  $2[\text{Cu}(\text{H}_2\text{O})_4]\text{Cl}_2 \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_4]^{2+} + [\text{CuCl}_4]^{2-} + 4\text{H}_2\text{O}$
  - (v)  $\text{CuCl}_2 \longrightarrow \text{CuCl}$  by no. of reagents
    - (a)  $\text{CuCl}_2 + \text{Cu-turnings} \xrightarrow{\Delta} 2\text{CuCl}$
    - (b)  $2\text{CuCl}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \longrightarrow 2\text{CuCl} + 2\text{HCl} + 2\text{H}_2\text{SO}_4$
    - (c)  $2\text{CuCl}_2 + \text{Zn}/\text{HCl} \longrightarrow 2\text{CuCl} + \text{ZnCl}_2$
    - (d)  $\text{CuCl}_2 + \text{SnCl}_2 \longrightarrow \text{CuCl} + \text{SnCl}_4$



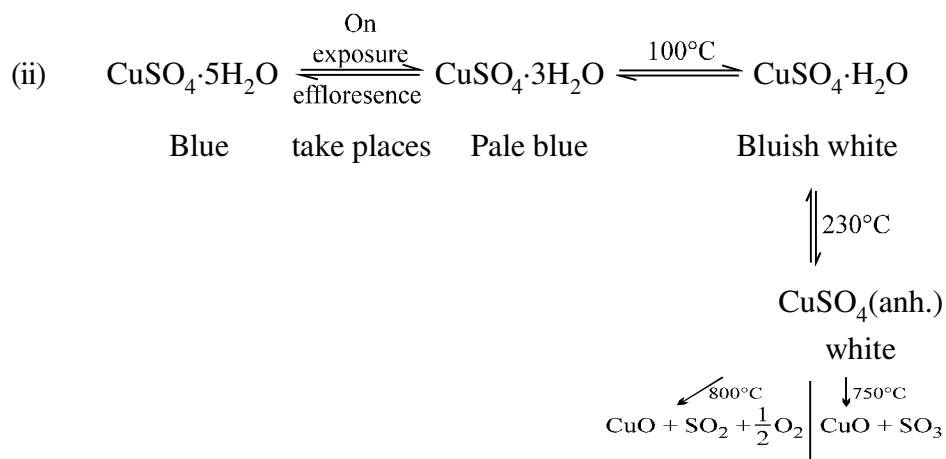
### CuSO<sub>4</sub>



(Scrap)



**Properties:** → (i) It is crystallised as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$



(iii) Revision with all others reagent

### IRON COMPOUNDS

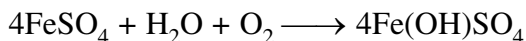
#### $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

**Preparation:** → (i) Scrap Fe +  $\text{H}_2\text{SO}_4$  (dil.)  $\longrightarrow$   $\text{FeSO}_4 + \text{H}_2\uparrow$

(ii) From Kipp's waste  
 $\text{FeS} + \text{H}_2\text{SO}_4(\text{dil}) \longrightarrow \text{FeSO}_4 + \text{H}_2\text{S}\uparrow$

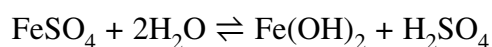
(iii)  $\text{FeS}_2 + 2\text{H}_2\text{O} + \frac{7}{2}\text{O}_2 \longrightarrow \text{FeSO}_4 + \text{H}_2\text{SO}_4$

**Properties:** → (i) It undergoes aerial oxidation forming basic ferric sulphate



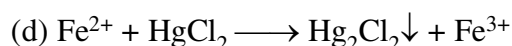
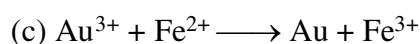
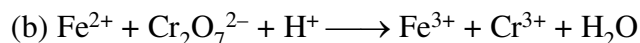
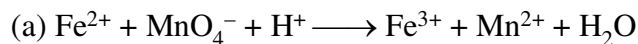
(ii)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{300^\circ\text{C}} \text{anh. white } \text{FeSO}_4 \xrightarrow[\text{temp.}]{\text{high}} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$

(iii) Aq. solution is acidic due to hydrolysis



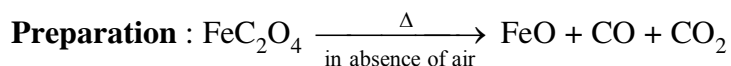
weak base

(iv) It is a reducing agent

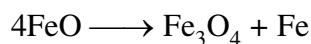
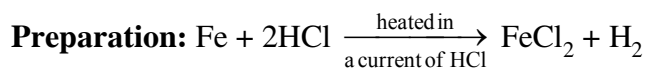


white ppt.

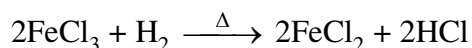
(v) It forms double salt. Example  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

**FeO(Black)**

**Properties :** It is stable at high temperature and on cooling slowly disproportionates into  $\text{Fe}_3\text{O}_4$  and iron

**FeCl<sub>2</sub>**

OR



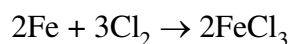
- Properties:** → (i) It is deliquescent in air like  $\text{FeCl}_3$
- (ii) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature
- (iii) It volatilises at about  $1000^\circ\text{C}$  and vapour density indicates the presence of  $\text{Fe}_2\text{Cl}_4$ . Above  $1300^\circ\text{C}$  density becomes normal
- (iv) It oxidises on heating in air
- $$12\text{FeCl}_2 + 3\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{FeCl}_3$$
- (v)  $\text{H}_2$  evolves on heating in steam
- $$3\text{FeCl}_2 + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$$
- (vi) It can exist as different hydrated form
- $$\text{FeCl}_2 \cdot 2\text{H}_2\text{O} \longrightarrow \text{colourless}$$
- $$\text{FeCl}_2 \cdot 4\text{H}_2\text{O} \longrightarrow \text{pale green}$$
- $$\text{FeCl}_2 \cdot 6\text{H}_2\text{O} \longrightarrow \text{green}$$

**Ferric Chloride (FeCl<sub>3</sub>)**

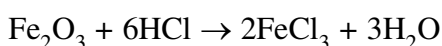
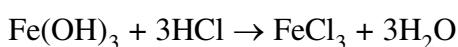
This is the most important ferric salt. It is known in anhydrous and hydrated forms. The hydrated form consists of six water molecules,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ .

**Preparation :**

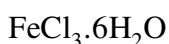
- (i) Anhydrous ferric chloride is obtained by passing dry chlorine gas over heated iron fillings. The vapours are condensed in a bottle attached to the outlet of the tube.

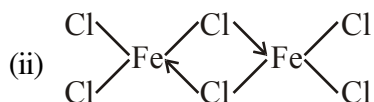
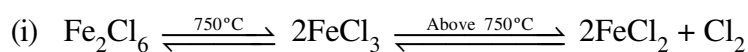


- (ii)  $\text{Fe}_2(\text{CO}_3)_3 + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} + 3\text{CO}_2$

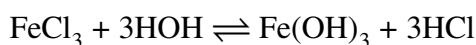


The solution on evaporation and cooling deposits yellow crystals of hydrated ferric chloride.



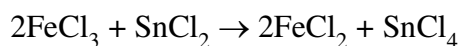
**Properties**

(iii) It dissolves in water. The solution is acidic in nature due to its hydrolysis as shown below :

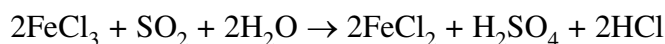


(v) Ferric chloride acts as an oxidising agent.

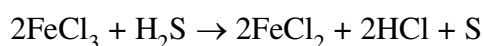
(a) It oxidises stannous chloride to stannic chloride.



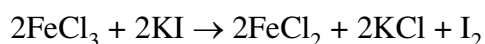
(b) It oxidises  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$



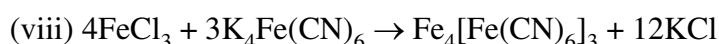
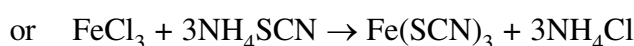
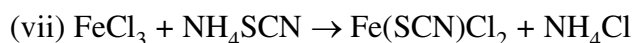
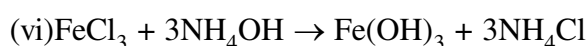
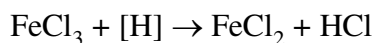
(c) It oxidises  $\text{H}_2\text{S}$  to S



(d) It liberates iodine from KI.



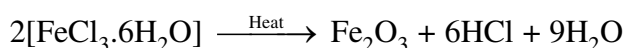
(e) Nascent hydrogen reduces  $\text{FeCl}_3$  into  $\text{FeCl}_2$



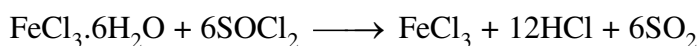
Prussian blue

(Ferri ferrocyanide)

(ix) On heating hydrated ferric chloride  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , anhydrous ferric chloride is not obtained. It is changed to  $\text{Fe}_2\text{O}_3$  with evolution of  $\text{H}_2\text{O}$  and  $\text{HCl}$ .



Hydrated ferric chloride may be dehydrated by heating with thionyl chloride.





## EXERCISE # O-1

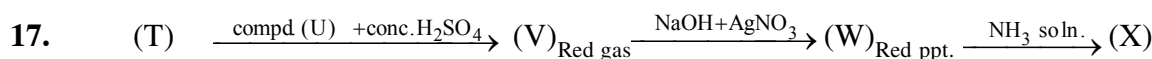
SELECT ONLY ONE IS CORRECT OPTIONS :

## General Properties of d-block

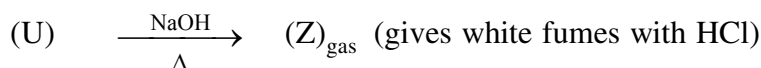
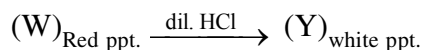
1.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightleftharpoons{\text{Fe + Mo}} 2\text{NH}_3(\text{g})$  ; Haber's process, Mo is used as  
 (A) a catalyst (B) a catalytic promoter  
 (C) an oxidising agent (D) as a catalytic poison  
**DB0001**
2. An ornamental of gold having 75% of gold, it is of ..... carat.  
 (A) 18 (B) 16 (C) 24 (D) 20  
**DB0002**
3. Transition elements having more tendency to form complex than representative elements (s and p-block elements) due to -  
 (A) availability of d-orbitals for bonding  
 (B) variable oxidation states are not shown by transition elements  
 (C) all electrons are paired in d-orbitals  
 (D) f-orbitals are available for bonding  
**DB0003**
4. A compound of mercury used in cosmetics, in Ayurvedic and Yunani medicines and known as Vermilion is -  
 (A)  $\text{HgCl}_2$  (B)  $\text{HgS}$  (C)  $\text{Hg}_2\text{Cl}_2$  (D)  $\text{HgI}$   
**DB0004**
5. Transition elements are usually characterised by variable oxidation states but Zn does not show this property because of  
 (A) completion of np-orbitals (B) completion of (n-1)d orbitals  
 (C) completion of ns-orbitals (D) inert pair effect  
**DB0005**
6. The d-block element which is a liquid at room temperature, having high specific heat, less reactivity than hydrogen and its chloride ( $\text{MX}_2$ ) is volatile on heating is  
 (A) Cu (B) Hg (C) Ce (D) Pm  
**DB0006**
7. Coinage metals show the properties of  
 (A) typical elements (B) normal elements  
 (C) inner-transition elements (D) transition element  
**DB0007**
8. The transition metal used in X-rays tube is  
 (A) Mo (B) Ta (C) Tc (D) Pm  
**DB0008**
9. The higher oxidation states of transition elements are found to be in the combination with A and B, which are  
 (A) F, O (B) O, N (C) O, Cl (D) F, Cl  
**DB0009**

10. The metals present in insulin and haemoglobin are respectively  
(A) Zn, Hg (B) Zn, Fe (C) Co, Fe (D) Mg, Fe  
**DB0010**
11. A metal M which is not affected by strong acids like conc.  $\text{HNO}_3$ , conc.  $\text{H}_2\text{SO}_4$  and conc. solution of alkalies like NaOH, KOH forms  $\text{MCl}_3$  which finds use for toning in photography. The metal M is  
(A) Ag (B) Hg (C) Au (D) Cu  
**DB0011**
12. Manganese steel is used for making railway tracks because  
(A) it is hard with high percentage of Mn  
(B) it is soft with high percentage of Mn  
(C) it is hard with small concentration of manganese with impurities  
(D) it is soft with small concentration of manganese with impurities  
**DB0012**
13. Transition elements in lower oxidation states act as Lewis acid because  
(A) they form complexes  
(B) they are oxidising agents  
(C) they donate electrons  
(D) they do not show catalytic properties  
**DB0013**
14. The electrons which take part in order to exhibit variable oxidation states by transition metals are  
(A) ns only  
(B)  $(n-1)d$  only  
(C) ns and  $(n-1)d$  only but not np  
(D)  $(n-1)d$  and np only but not ns  
**DB0014**
15. Solution of  $\text{MnO}_4^-$  is purple-coloured due to  
(A) d-d-transition  
(B) charge transfer from O to Mn  
(C) due to both d-d-transition and charge transfer  
(D) none of these  
**DB0015**
16. An element of 3d-transition series shows two oxidation states x and y, differ by two units then  
(A) compounds in oxidation state x are ionic if  $x > y$   
(B) compounds in oxidation state x are ionic if  $x < y$   
(C) compounds in oxidation state y are covalent if  $x < y$   
(D) compounds in oxidation state y are covalent if  $y < x$   
**DB0016**

## Compounds of d-block



imparts violet  
colour in the  
flame test



sublimes on  
heating

Identify (T) to (Z).

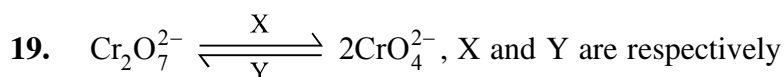
- (A) T =  $\text{KMnO}_4$ , U = HCl, V =  $\text{Cl}_2$ , W =  $\text{HgI}_2$ , X =  $\text{Hg}(\text{NH}_2)\text{NO}_3$ , Y =  $\text{Hg}_2\text{Cl}_2$ , Z =  $\text{N}_2$   
 (B) T =  $\text{K}_2\text{Cr}_2\text{O}_7$ , U =  $\text{NH}_4\text{Cl}$ , V =  $\text{CrO}_2\text{Cl}_2$ , W =  $\text{Ag}_2\text{CrO}_4$ , X =  $[\text{Ag}(\text{NH}_3)_2]^+$ , Y = AgCl, Z =  $\text{NH}_3$   
 (C) T =  $\text{K}_2\text{CrO}_4$ , U = KCl, V =  $\text{CrO}_2\text{Cl}_2$ , W =  $\text{HgI}_2$ , X =  $\text{Na}_2\text{CrO}_4$ , Y =  $\text{BaCO}_3$ , Z =  $\text{NH}_4\text{Cl}$   
 (D) T =  $\text{K}_2\text{MnO}_4$ , U = NaCl, V =  $\text{CrO}_3$ , W =  $\text{AgNO}_2$ , X =  $(\text{NH}_4)_2\text{CrO}_4$ , Y =  $\text{CaCO}_3$ , Z =  $\text{SO}_2$

DB0017

18. The number of moles of acidified  $\text{KMnO}_4$  required to convert one mole of sulphite ion into sulphate ion is

- (A) 2/5 (B) 3/5 (C) 4/5 (D) 1

DB0018



- (A) X =  $\text{OH}^-$ , Y =  $\text{H}^+$  (B) X =  $\text{H}^+$ , Y =  $\text{OH}^-$   
 (C) X =  $\text{OH}^-$ , Y =  $\text{H}_2\text{O}_2$  (D) X =  $\text{H}_2\text{O}_2$ , Y =  $\text{OH}^-$

DB0019

20.  $\text{CrO}_3$  dissolves in aqueous NaOH to give

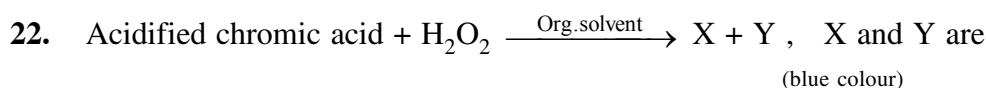
- (A)  $\text{Cr}_2\text{O}_7^{2-}$  (B)  $\text{CrO}_4^{2-}$  (C)  $\text{Cr}(\text{OH})_3$  (D)  $\text{Cr}(\text{OH})_2$

DB0020

21. During estimation of oxalic acid Vs  $\text{KMnO}_4$ , self indicator is

- (A)  $\text{KMnO}_4$  (B) oxalic acid (C)  $\text{K}_2\text{SO}_4$  (D)  $\text{MnSO}_4$

DB0021



- (A)  $\text{CrO}_5$  and  $\text{H}_2\text{O}$  (B)  $\text{Cr}_2\text{O}_3$  and  $\text{H}_2\text{O}$  (C)  $\text{CrO}_2$  and  $\text{H}_2\text{O}$  (D) CrO and  $\text{H}_2\text{O}$

DB0022

23. 
$$Y \xleftarrow{KI} CuSO_4 \xrightarrow{dil\ H_2SO_4} X(\text{Blue colour}), X \text{ and } Y \text{ are}$$
  
 (diatomic covalent molecule)

- (A)  $X = I_2, Y = [Cu(H_2O)_4]^{2+}$  (B)  $X = [Cu(H_2O)_4]^{2+}, Y = I_2$   
 (C)  $X = [Cu(H_2O)_4]^+, Y = I_2$  (D)  $X = [Cu(H_2O)_5]^{2+}, Y = I_2$

DB0023

24.  $(NH_4)_2Cr_2O_7$  (Ammonium dichromate) is used in fire works. The green coloured powder blown in air is

- (A)  $Cr_2O_3$  (B)  $CrO_2$  (C)  $Cr_2O_4$  (D)  $CrO_3$

DB0024

25. Iron becomes passive by ..... due to formation of .....

- (A) dil. HCl,  $Fe_2O_3$  (B) 80% conc.  $HNO_3$ ,  $Fe_3O_4$   
 (C) conc.  $H_2SO_4$ ,  $Fe_3O_4$  (D) conc. HCl,  $Fe_3O_4$

DB0025

26. Bayer's reagent used to detect olifinic double bond is

- (A) acidified  $KMnO_4$  (B) aqueous  $KMnO_4$   
 (C) 1% alkaline  $KMnO_4$  solution (D)  $KMnO_4$  in benzene

DB0026

27. 
$$MnO_4^- + xe^- \xrightarrow{\text{(Alkaline medium)}} MnO_4^{2-}$$
  

$$\quad \quad \quad + ye^- \xrightarrow{\text{(Acidic medium)}} Mn^{2+}$$
  

$$\quad \quad \quad + ze^- \xrightarrow{\text{(Neutral medium)}} MnO_2$$

x, y and z are respectively

- (A) 1, 2, 3 (B) 1, 5, 3 (C) 1, 3, 5 (D) 5, 3, 1

DB0027

28.  $Cu + conc. HNO_3 \xrightarrow{\text{(hot)}} Cu(NO_3)_2 + X$  (oxide of nitrogen); then X is

- (A)  $N_2O$  (B)  $NO_2$  (C) NO (D)  $N_2O_3$

DB0028

29.  $CuSO_4$  solution reacts with excess KCN to give

- (A)  $Cu(CN)_2$  (B)  $CuCN$  (C)  $K_2[Cu(CN)_2]$  (D)  $K_3[Cu(CN)_4]$

DB0029

30. Pick out the incorrect statement:

- (A)  $MnO_2$  dissolves in conc. HCl, but does not form  $Mn^{4+}$  ions  
 (B)  $MnO_2$  react with hot concentrated  $H_2SO_4$  liberating oxygen  
 (C)  $K_2MnO_4$  is formed when  $MnO_2$  in fused KOH is oxidised by air,  $KNO_3$ ,  $PbO_2$  or  $NaBiO_3$   
 (D) Decomposition of acidic  $KMnO_4$  is not catalysed by sunlight.

DB0030

31. 1 mole of  $\text{Fe}^{2+}$  ions are oxidised to  $\text{Fe}^{3+}$  ions with the help of (in acidic medium)  
 (A)  $1/5$  moles of  $\text{KMnO}_4$  (B)  $5/3$  moles of  $\text{KMnO}_4$   
 (C)  $2/5$  moles of  $\text{KMnO}_4$  (D)  $5/2$  moles of  $\text{KMnO}_4$  **DB0031**
32. To an acidified dichromate solution, a pinch of  $\text{Na}_2\text{O}_2$  is added and shaken. What is observed:  
 (A) blue colour (B) Orange colour changing to green  
 (C) Copious evolution of oxygen (D) Bluish - green precipitate **DB0032**
33. The rusting of iron is formulated as  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  which involves the formation of  
 (A)  $\text{Fe}_2\text{O}_3$  (B)  $\text{Fe}(\text{OH})_3$  (C)  $\text{Fe}(\text{OH})_2$  (D)  $\text{Fe}_2\text{O}_3 + \text{Fe}(\text{OH})_3$  **DB0033**
34. Solid  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  having covalent, ionic as well as co-ordinate bonds. Copper atom/ion forms ..... co-ordinate bonds with water.  
 (A) 1 (B) 2 (C) 3 (D) 4 **DB0034**
35.  $\text{KMnO}_4 + \text{HCl} \longrightarrow \text{H}_2\text{O} + \text{X}(\text{g})$ , X is a (acidified)  
 (A) red liquid (B) violet gas  
 (C) greenish yellow gas (D) yellow-brown gas **DB0035**
36. Purple of cassius is:  
 (A) Pure gold (B) Colloidal solution of gold  
 (C) Gold (I) hydroxide (D) Gold (III) chloride **DB0036**
37. Amongst the following species, maximum covalent character is exhibited by  
 (A)  $\text{FeCl}_2$  (B)  $\text{ZnCl}_2$  (C)  $\text{HgCl}_2$  (D)  $\text{CdCl}_2$  **DB0037**
38. Number of moles of  $\text{SnCl}_2$  required for the reduction of 1 mole of  $\text{K}_2\text{Cr}_2\text{O}_7$  into  $\text{Cr}_2\text{O}_3$  is (in acidic medium)  
 (A) 3 (B) 2 (C) 1 (D)  $1/3$  **DB0038**
39. Pick out the incorrect statement:  
 (A)  $\text{MnO}_4^{2-}$  is quite strongly oxidizing and stable only in very strong alkalies. In dilute alkali, neutral solutions, it disproportionates.  
 (B) In acidic solutions,  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$  and thus,  $\text{KMnO}_4$  is widely used as oxidising agent  
 (C)  $\text{KMnO}_4$  does not acts as oxidising agent in alkaline medium  
 (D)  $\text{KMnO}_4$  is manufactured by the fusion of pyrolusite ore with  $\text{KOH}$  in presence of air or  $\text{KNO}_3$ , followed by electrolytic oxidation in strongly alkaline solution. **DB0039**
40. The aqueous solution of  $\text{CuCrO}_4$  is green because it contains  
 (A) green  $\text{Cu}^{2+}$  ions (B) green  $\text{CrO}_4^{2-}$  ions  
 (C) blue  $\text{Cu}^{2+}$  ions and green  $\text{CrO}_4^{2-}$  ions (D) blue  $\text{Cu}^{2+}$  ions and yellow  $\text{CrO}_4^{2-}$  ions **DB0040**

41. In nitroprusside ion, the iron exists as  $\text{Fe}^{2+}$  and  $\text{NO}$  as  $\text{NO}^+$  rather than  $\text{Fe}^{3+}$  and  $\text{NO}$  respectively. These forms of ions are established with the help of  
 (A) magnetic moment in solid state (B) thermal decomposition method  
 (C) by reaction with KCN (D) by action with  $\text{K}_2\text{SO}_4$
- DB0041**
42. Which of the following reaction is possible at anode?  
 (A)  $2\text{Cr}^{3+} + 7\text{H}_2\text{O} \longrightarrow \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+$  (B)  $\text{F}_2 \longrightarrow 2 \text{F}^-$   
 (C)  $\frac{1}{2}\text{O}_2 + 2\text{H}^+ \longrightarrow \text{H}_2\text{O}$  (D) None of these
- DB0042**
43. Colourless solutions of the following four salts are placed separately in four different test tubes and a strip of copper is dipped in each one of these. Which solution will turn blue?  
 (A)  $\text{KNO}_3$  (B)  $\text{AgNO}_3$  (C)  $\text{Zn}(\text{NO}_3)_2$  (D)  $\text{ZnSO}_4$
- DB0043**
44. When acidified  $\text{KMnO}_4$  is added to hot oxalic acid solution, the decolourization is slow in the beginning, but becomes very rapid after some time. This is because:  
 (A)  $\text{Mn}^{2+}$  acts as autocatalyst (B)  $\text{CO}_2$  is formed as the product  
 (C) Reaction is exothermic (D)  $\text{MnO}_4^-$  catalyses the reaction
- DB0044**
45. Metre scales are made-up of alloy  
 (A) invar (B) stainless steel (C) elektron (D) magnalium
- DB0045**
46. The Ziegler-Natta catalyst used for polymerisation of ethene and styrene is  $\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}$ , the catalysing species (active species) involved in the polymerisation is  
 (A)  $\text{TiCl}_4$  (B)  $\text{TiCl}_3$  (C)  $\text{TiCl}_2$  (D)  $\text{TiCl}$
- DB0046**
47. 'Bordeaux mixture' is used as a fungicide. It is a mixture of  
 (A)  $\text{CaSO}_4 + \text{Cu}(\text{OH})_2$  (B)  $\text{CuSO}_4 + \text{Ca}(\text{OH})_2$   
 (C)  $\text{CuSO}_4 + \text{CaO}$  (D)  $\text{CuO} + \text{CaO}$
- DB0047**
48. Peacock ore is:  
 (A)  $\text{FeS}_2$  (B)  $\text{CuFeS}_2$  (C)  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (D)  $\text{Cu}_5\text{FeS}_4$
- DB0048**

## EXERCISE # O-2

## SELECT MORE THAN ONE IS CORRECT OPTIONS

## General Properties of d-block

1. Potash alum is a double salt, its aqueous solution shows the characteristics of  
(A)  $\text{Al}^{3+}$  ions (B)  $\text{K}^+$  ions (C)  $\text{SO}_4^{2-}$  ions (D)  $\text{Al}^{3+}$  ions but not  $\text{K}^+$  ions  
DB0049
2. Addition of non-metals like B and C to the interstitial sites of a transition metal results the metal  
(A) of more ductability (B) of less ductability  
(C) less malleable (D) of more hardness  
DB0050
3. Mercury is a liquid at  $0^\circ\text{C}$  because of  
(A) very high ionisation energy (B) weak metallic bonds  
(C) high heat of hydration (D) high heat of sublimation  
DB0051
4. The correct statement(s) about transition elements is/are  
(A) the most stable oxidation state is +3 and its stability decreases across the period  
(B) transition elements of 3d-series have almost same atomic sizes from Cr to Cu  
(C) the stability of +2 oxidation state increases across the period  
(D) some transition elements like Ni, Fe, Cr may show zero oxidation state in some of their compounds  
DB0052
5. The ionisation energies of transition elements are  
(A) less than p-block elements (B) more than s-block elements  
(C) less than s-block elements (D) more than p-block elements  
DB0053
6. The metal(s) which does/do not form amalgam is/are  
(A) Fe (B) Pt (C) Zn (D) Ag  
DB0054
7. Which of the following statements concern with d-block metals?  
(A) compounds containing ions of transition elements are usually coloured  
(B) Zinc has lowest melting point among 3d-series elements  
(C) they show variable oxidation states, which differ by two units only  
(D) they easily form complexes  
DB0055
8. The highest oxidation state among transition elements is  
(A) + 7 by Mn (B) + 8 by Os (C) + 8 by Ru (D) + 7 by Fe  
DB0056
9. Amphoteric oxide(s) is/are  
(A)  $\text{Al}_2\text{O}_3$  (B) SnO (C) ZnO (D)  $\text{Fe}_2\text{O}_3$   
DB0057

10. The catalytic activity of transition elements is related to their  
 (A) variable oxidation states (B) free surface valencies  
 (C) complex formation ability (D) magnetic moment  
**DB0058**
11. In the equation:  $M + 8CN^- + 2H_2O + O_2 \longrightarrow 4[M(CN)_2]^- + 4OH^-$ , metal M is  
 (A) Ag (B) Au (C) Cu (D) Hg  
**DB0059**
12.  $CuSO_4(aq) + 4NH_3 \longrightarrow X$ , then X is  
 (A)  $[Cu(NH_3)_4]^{2+}$  (B) paramagnetic  
 (C) coloured (D) of a magnetic moment of 1.73 BM  
**DB0060**
13. Amphoteric oxide(s) of Mn is/are  
 (A)  $MnO_2$  (B)  $Mn_3O_4$  (C)  $Mn_2O_7$  (D) MnO  
**DB0061**
14. The lanthanide contraction is responsible for the fact that  
 (A) Zr and Hf have same atomic sizes (B) Zr and Hf have same properties  
 (C) Zr and Hf have different atomic sizes (D) Zr and Hf have different properties  
**DB0062**
15. Ion(s) having non zero magnetic moment (spin only) is/are  
 (A)  $Sc^{3+}$  (B)  $Ti^{3+}$  (C)  $Cu^{2+}$  (D)  $Zn^{2+}$   
**DB0063**

### Compounds of d-block

16. Correct statement(s) is/are  
 (A) an acidified solution of  $K_2Cr_2O_7$  liberates iodine from KI  
 (B)  $K_2Cr_2O_7$  is used as a standard solution for estimation of  $Fe^{2+}$  ions  
 (C) in acidic medium,  $M = N/6$  for  $K_2Cr_2O_7$   
 (D)  $(NH_4)_2Cr_2O_7$  on heating decomposes to yield  $Cr_2O_3$  through an endothermic reaction  
**DB0064**
17. Interstitial compounds are formed by  
 (A) Co (B) Ni (C) Fe (D) Ca  
**DB0065**
18. Acidified  $KMnO_4$  can be decolourised by  
 (A)  $SO_2$  (B)  $H_2O_2$  (C)  $FeSO_4$  (D)  $Fe_2(SO_4)_3$   
**DB0066**



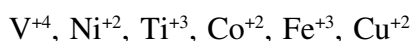
## EXERCISE # S-1

## NUMERICAL GRID TYPE QUESTIONS :

1. When mixture of NaCl and  $K_2Cr_2O_7$  is gently warmed with conc.  $H_2SO_4$  then compound X is formed. What is the oxidation state of central atom of X.

DB0067

2. Number of ions which gives blue colour in aqueous state :



DB0068

3. Define the oxidation states of Mn in product of the given reaction



If the oxidation state of Mn in product X and Y are  $n_1$  and  $n_2$  respectively. Then find out the value of  $(n_1 + n_2)$  -

DB0069

4. Find number of metal ion which can produce high spin and low spin octahedral complex :

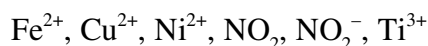


DB0070

5. How many non-axial d-orbitals are involved in hybridisation of  $CrO_2Cl_2$ .

DB0071

6. Find the number of species from the following which has magnetic moment value of 1.73 B.M.

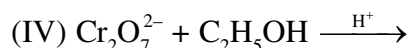
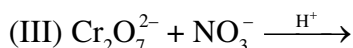
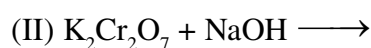


DB0072

7. Total no. of moles of Mohr's salt are required for per mole of dichromate ions during volumetric analysis.

DB0073

8. Find number of reaction(s) in which no redox change takes place -



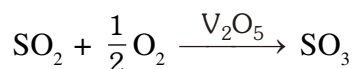
DB0074

## EXERCISE # S-2

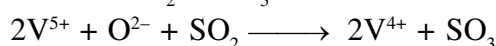
## COMPREHENSION TYPE QUESTIONS :

## Comprehension # 01 to 04

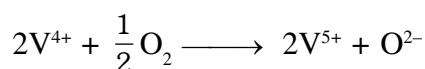
Transition metal and their compounds are used as catalysts in industry and in biological system. For example, in the Contact process, vanadium compounds in the +5 state ( $V_2O_5$  or  $VO_3^-$ ) are used to oxidise  $SO_2$  to  $SO_3$ :



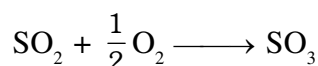
It is thought that the actual oxidation process takes place in two stages. In the first step,  $V^{5+}$  in the presence of oxide ions converts  $SO_2$  to  $SO_3$ . At the same time,  $V^{5+}$  is reduced to  $V^{4+}$ .



In the second step,  $V^{5+}$  is regenerated from  $V^{4+}$  by oxygen :



The overall process is, of course, the sum of these two steps:



- Transition metals and their compounds catalyse reactions because :  
(A) They have completely filled s-subshell  
(B) They have a comparable size due to poor shielding of d-subshell  
(C) They introduce an entirely new reaction mechanism with a lower activation energy  
(D) They have variable oxidation states differ by two units
- During the course of the reaction :  
(A) Catalyst undergoes changes in oxidation state  
(B) Catalyst increases the rate constant  
(C) Catalyst is regenerated in its original form when the reactants form the products  
(D) All are correct.
- Catalytic activity of transition metals depends on :  
(A) Their ability to exist in different oxidation states  
(B) The size of the metal atoms  
(C) The number of empty atomic orbitals available  
(D) None of these
- Which of the following ion involved in the above process will show paramagnetism?  
(A)  $V^{5+}$                       (B)  $V^{4+}$                       (C)  $O^{2-}$                       (D)  $VO_3^-$

DB0075

DB0075

DB0075

DB0075



**MATCH THE COLUMN : (Matrix Match)****10. Column-I (Metals)**

- (A) Zn  
(B) Cu  
(C) Ag  
(D) Au

**Column-II**

- (P) Cyanide process involve in the comerial extration  
(Q) Extracted by hydrometallurgical process  
(R) Roasting involve in the comerial extration  
(S) Present in Brass

DB0078

**11. Column-I (catalyst)**

- (A)  $TiCl_4$   
(B)  $PdCl_2$   
(C) Pt/PtO  
(D) Cu

**Column-II (Used)**

- (P) Adams catalyst in reduction  
(Q) In preparation of  $(CH_3)_2SiCl_2$   
(R) Used as the ziegler-natta catalyst in polythene production  
(S) Wacker process for converting  $C_2H_4$  to  $CH_3CHO$

DB0079

**SELECT CORRECT CODE :****12. Column-I**

- (P)  $Cr_2O_3$   
(Q)  $CrO_3$   
(R)  $Fe_3O_4$   
(S)  $N_2O$

**Column-II**

- (1) Neutral oxide  
(2) Amphoteric oxide  
(3) Mix oxide  
(4) Acidic oxide

Select correct code for matching -

**Code :**

	P	Q	R	S
(A)	2	4	3	1
(B)	2	3	4	1
(C)	4	2	3	1
(D)	4	3	1	2

DB0080

**13. Column-I****(Metal ion of 3d-series)**

- (P)  $Ni^{2+}$   
(Q)  $Cr^{2+}$   
(R)  $V^{2+}$   
(S)  $Ti^{4+}$

**Column-II****(Characteristic)**

- (1) produce blue aq. solution  
(2) half filled  $t_{2g}$  orbitals in octahedral complex  
(3) diamagnetic ion  
(4) calculated  $\mu = 2.84$  B.M. (spin only)

Select correct code for matching -

**Code :**

	P	Q	R	S
(A)	4	2	1	3
(B)	3	1	2	4
(C)	4	1	2	3
(D)	1	2	4	3

DB0081

**ASSERTION & REASONING :**

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

(A) if both (A) and (R) are true and (R) is the correct explanation of (A)

(B) if both (A) and (R) are true but (R) is not correct explanation of (A)

(C) if (A) is true but (R) is false

(D) if (A) is false and (R) is true

14. **Assertion** :  $\text{KMnO}_4$  is purple in colour due to charge transfer.

**Reason** : In  $\text{MnO}_4^-$ , there is no electron present in d-orbitals of manganese.

DB0082

15. **Assertion** :  $\text{K}_2\text{CrO}_4$  has yellow colour due to charge transfer.

**Reason** :  $\text{CrO}_4^{2-}$  ion is tetrahedral in shape.

DB0083

16. **Assertion** : The highest oxidation state of chromium in its compounds is +6.

**Reason** : Chromium atom has only six electrons in ns and (n-1) d orbitals.

DB0084

17. **Assertion** :  $\text{CrO}_3$  reacts with HCl to form chromyl chloride gas.

**Reason** : Chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) has tetrahedral shape.

DB0085

18. **Assertion** : Zinc does not show characteristic properties of transition metals.

**Reason** : In zinc outermost shell is completely filled.

DB0086

19. **Assertion** : Tungsten has a very high melting point.

**Reason** : Tungsten is a covalent compound.

DB0087

20. **Assertion** : Equivalent mass of  $\text{KMnO}_4$  is equal to one-third of its molecular mass when it acts as an oxidising agent in an alkaline medium.

**Reason** : Oxidation number of Mn is +7 in  $\text{KMnO}_4$ .

DB0088

21. **Assertion** :  $\text{Cu}^+$  ion is colourless.

**Reason** : Four water molecules are coordinated to  $\text{Cu}^+$  ion in water.

DB0089

**MATCHING LIST TYPE 1 × 3 Q. (THREE LIST TYPE Q.)**

The following column 1, 2, 3 represent the different metals of 3d series and their properties

Answer the questions that follow

**Column-1 - Hexa aqua complex of dipositive ion of given metal**

**Column-2 - Magnetic moment (spin only)**

**Column-3 - Colour**

Column - 1 Hexa aqua complex of dipositive ion of given metal	Column - 2 Magnetic moment (spin only)	Column - 3 Colour
(I) Co	(i) $\sqrt{8}$ B.M.	(P) Green
(II) Ni	(ii) $\sqrt{3}$ B.M.	(Q) Pink
(III) V	(iii) $\sqrt{15}$ B.M.	(R) Colourless
(IV) Zn	(iv) Zero	(S) Violet
		(T) Blue

22. Select **CORRECT** combination for metal which have same magnetism as in  $[\text{Ti}(\text{H}_2\text{O})_6]^{4+}$   
 (A) (II), (iv), (R)      (B) (I), (iv), (R)      (C) (IV), (iv), (R)      (D) (IV), (iv), (T)  
**DB0090**
23. Which is **CORRECT** magnetic moment and colour combination of the product when  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$  is react with conc. HCl solution  
 (A) (ii), (Q)      (B) (ii), (T)      (C) (iii), (Q)      (D) (iii), (T)  
**DB0090**
24. Select **CORRECT** combination for hexaaqua complex of metal ion  $M^{+2}$  which have half filled  $t_{2g}$  configuration (i.e.  $t_{2g}^3$ )  
 (A) (III), (iii), (S)      (B) (III), (iii), (P)      (C) (III), (ii), (S)      (D) (III), (iv), (P)  
**DB0090**
25.  $[\text{M}(\text{H}_2\text{O})_6]^{+2}$  of a metal in **column-1** have combination (i), (P) in **column-2, 3**. Select **CORRECT** combination for hexaammine complex of same metal ion.  
 (A) (i), (T)      (B) (i), (S)      (C) (iv), (R)      (D) (iv) (T)  
**DB0090**

## EXERCISE # JEE-MAIN

1. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid - [AIIEE-2003]

(1)  $\text{Cr}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are formed      (2)  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}_2\text{O}$  are formed  
 (3)  $\text{Cr}_2\text{O}_7^{2-}$  is reduced to +3 state of Cr      (4)  $\text{Cr}_2\text{O}_7^{2-}$  is oxidised to +7 state of Cr

DB0091

2. Excess of KI reacts with  $\text{CuSO}_4$  solution and then  $\text{Na}_2\text{S}_2\text{O}_3$  solution is added to it. Which of the statements is incorrect for this reaction : [AIIEE-2004]

(1) Evolved  $\text{I}_2$  is reduced      (2)  $\text{CuI}_2$  is formed  
 (3)  $\text{Na}_2\text{S}_2\text{O}_3$  is oxidised      (4)  $\text{Cu}_2\text{I}_2$  is formed

DB0092

3. In context with the transition elements, which of the following statements is incorrect? [AIIEE-2009]

(1) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.  
 (2) Once the  $d^5$  configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.  
 (3) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.  
 (4) In the highest oxidation states, the transition metal show basic character and form cationic complexes.

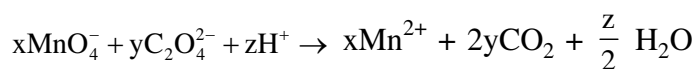
DB0093

4. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is **incorrect** ? [AIIEE-2012]

(1) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.  
 (2) Ferrous oxide is more basic in nature than the ferric oxide.  
 (3) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.  
 (4) Ferrous compounds are less volatile than the corresponding ferric compounds.

DB0094

5. Consider the following reaction : [JEE MAIN-2013]



The values of x, y and z in the reaction are respectively :-

(1) 5,2 and 16      (2) 2,5 and 8      (3) 2, 5 and 16      (4) 5,2 and 8

DB0095

6. Which of the following arrangements does not represent the correct order of the property stated against it ? [JEE MAIN-2013]

(1)  $\text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$  : paramagnetic behaviour  
 (2)  $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$  : ionic size  
 (3)  $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$  : stability in aqueous solution  
 (4)  $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$  : number of oxidation states

DB0096

7. Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown - red vapours of: [JEE MAIN-2013, Online]

- (1)  $\text{CrO}_3$             (2)  $\text{Cr}_2\text{O}_3$             (3)  $\text{CrCl}_3$             (4)  $\text{CrO}_2\text{Cl}_2$

DB0097

8. The element with which of the following outer electron configuration may exhibit the largest number of oxidation states in its compounds : [JEE MAIN-2013, Online]

- (1)  $3d^74s^2$             (2)  $3d^84s^2$             (3)  $3d^54s^2$             (4)  $3d^64s^2$

DB0098

9. When a small amount of  $\text{KMnO}_4$  is added to concentrated  $\text{H}_2\text{SO}_4$ , a green oily compound is obtained which is highly explosive in nature. Compound may be : [JEE MAIN-2013, Online]

- (1)  $\text{Mn}_2\text{O}_3$             (2)  $\text{MnSO}_4$             (3)  $\text{Mn}_2\text{O}_7$             (4)  $\text{MnO}_2$

DB0099

10. Which series of reactions correctly represents chemical relations related to iron and its compound?

- (1)  $\text{Fe} \xrightarrow{\text{Cl}_2, \text{heat}} \text{FeCl}_3 \xrightarrow{\text{heat, air}} \text{FeCl}_2 \xrightarrow{\text{Zn}} \text{Fe}$   
 (2)  $\text{Fe} \xrightarrow{\text{O}_2, \text{heat}} \text{Fe}_3\text{O}_4 \xrightarrow{\text{CO, } 600^\circ\text{C}} \text{FeO} \xrightarrow{\text{CO, } 700^\circ\text{C}} \text{Fe}$   
 (3)  $\text{Fe} \xrightarrow{\text{dil H}_2\text{SO}_4} \text{FeSO}_4 \xrightarrow{\text{H}_2\text{SO}_4, \text{O}_2} \text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\text{Heat}} \text{Fe}$   
 (4)  $\text{Fe} \xrightarrow{\text{O}_2, \text{heat}} \text{FeO} \xrightarrow{\text{dil H}_2\text{SO}_4} \text{FeSO}_4 \xrightarrow{\text{Heat}} \text{Fe}$

[JEE MAIN-2014]

DB0100

11. The equation which is balanced and represents the correct product (s) is : [JEE MAIN-2014]

- (1)  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} + (\text{EDTA})^{4-} \xrightarrow{\text{excess NaOH}} [\text{Mg}(\text{EDTA})]^{2-} + 6\text{H}_2\text{O}$   
 (2)  $\text{CuSO}_4 + 4\text{KCN} \rightarrow \text{K}_2[\text{Cu}(\text{CN})_4] + \text{K}_2\text{SO}_4$   
 (3)  $\text{Li}_2\text{O} + 2\text{KCl} \rightarrow 2\text{LiCl} + \text{K}_2\text{O}$   
 (4)  $[\text{CoCl}(\text{NH}_3)_5]^+ + 5\text{H}^+ \rightarrow \text{Co}^{2+} + 5\text{NH}_4^+ + \text{Cl}^-$

DB0101

12. Which of the following is **not** formed when  $\text{H}_2\text{S}$  reacts with acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  solution ?

- (1)  $\text{K}_2\text{SO}_4$             (2)  $\text{Cr}_2(\text{SO}_4)_3$   
 (3) S            (4)  $\text{CrSO}_4$

[JEE MAIN-2014, Online]

DB0102



13. Copper becomes green when exposed to moist air for a long period. This is due to :-

[JEE MAIN-2014, Online]

- (1) the formation of a layer of cupric oxide on the surface of copper.
- (2) the formation of basic copper sulphate layer on the surface of the metal
- (3) the formation of a layer of cupric hydroxide on the surface of copper.
- (4) the formation of a layer of basic carbonate of copper on the surface of copper.

DB0103

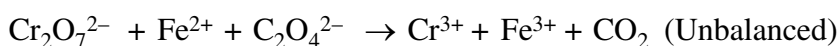
14. Which one of the following exhibits the largest number of oxidation states ?

[JEE MAIN-2014, Online]

- (1) Mn(25)      (2) V(23)      (3) Cr (24)      (4) Ti (22)

DB0104

15. How many electrons are involved in the following redox reaction ? [JEE MAINS-2014,Online]



- (1) 3      (2) 4      (3) 5      (4) 6

DB0105

16. Amongst the following, identify the species with an atom in +6 oxidation state:

[JEE MAIN-2014, Online]

- (1)  $[\text{MnO}_4]^-$       (2)  $[\text{Cr}(\text{CN})_6]^{3-}$       (3)  $\text{Cr}_2\text{O}_3$       (4)  $\text{CrO}_2\text{Cl}_2$

DB0106

17. Match the catalysts to the correct processes :-

[JEE MAIN-2015]

	Catalyst		Process
(A)	$\text{TiCl}_3$	(i)	Wacker process
(B)	$\text{PdCl}_2$	(ii)	Ziegler-Natta polymerization
(C)	$\text{CuCl}_2$	(iii)	Contact process
(D)	$\text{V}_2\text{O}_5$	(iv)	Deacon's process

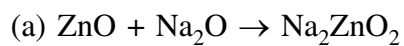
- (1) A-ii, B-iii, C-iv, D-i
- (2) A-iii, B-i, C-ii, D-iv
- (3) A-iii, B-ii, C-iv, D-i
- (4) A-ii, B-i, C-iv, D-iii

DB0107

18. Which of the following statements is false :- [JEE MAIN-2015, Online]
- (1)  $\text{Cr}_2\text{O}_7^{2-}$  has a Cr – O – Cr bond  
 (2)  $\text{CrO}_4^{2-}$  is tetrahedral in shape  
 (3)  $\text{Na}_2\text{Cr}_2\text{O}_7$  is a primary standard in volumetry  
 (4)  $\text{K}_2\text{Cr}_2\text{O}_7$  is less soluble than  $\text{Na}_2\text{Cr}_2\text{O}_7$
- DB0108
19. The transition metal ions responsible for colour in ruby and emerald are, respectively : [Jee Main 2016]
- (1)  $\text{Cr}^{3+}$  and  $\text{Cr}^{3+}$       (2)  $\text{Cr}^{3+}$  and  $\text{Co}^{3+}$       (3)  $\text{Co}^{3+}$  and  $\text{Cr}^{3+}$       (4)  $\text{Co}^{3+}$  and  $\text{Co}^{3+}$
- DB0109
20. Galvanization is applying a coating of :- [Jee Main 2016]
- (1) Zn      (2) Pb      (3) Cr      (4) Cu
- DB0110
21. Which of the following compounds is metallic and ferromagnetic ? [Jee Main 2016]
- (1)  $\text{MnO}_2$       (2)  $\text{TiO}_2$       (3)  $\text{CrO}_2$       (4)  $\text{VO}_2$
- DB0111
22. Which one of the following species is stable in aqueous solution? [Jee Main 2016]
- (1)  $\text{MnO}_4^{3-}$       (2)  $\text{MnO}_4^{2-}$       (3)  $\text{Cu}^+$       (4)  $\text{Cr}^{2+}$
- DB0112
23. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1M  $\text{ZnSO}_4$  ? [Jee Main 2016]
- (1) The copper metal will dissolve and zinc metal will be deposited  
 (2) No reaction will occur  
 (3) The copper metal will dissolve with evolution of oxygen gas  
 (4) The copper metal will dissolve with evolution of hydrogen gas
- DB0113
24. Which of the following ions does **not** liberate hydrogen gas on reaction with dilute acids? [JEE MAIN-2017, Online]
- (1)  $\text{Ti}^{2+}$       (2)  $\text{Cr}^{2+}$       (3)  $\text{Mn}^{2+}$       (4)  $\text{V}^{2+}$
- DB0114

25. In the following reactions, ZnO is respectively acting as a/an :

[JEE MAIN-2017]



(1) base and acid

(2) base and base

(3) acid and acid

(4) acid and base

DB0115



8. Anhydrous ferric chloride is prepared by: [JEE 2002]  
(A) heating hydrated ferric chloride at a high temperature in a stream of air  
(B) heating metallic iron in a stream of dry chlorine gas  
(C) reaction of ferric oxide with HCl  
(D) reaction of metallic iron with HCl  
DB0123
9. When  $\text{MnO}_2$  is fused with KOH, a coloured compound is formed, the product and its colour is: [JEE 2003]  
(A)  $\text{K}_2\text{MnO}_4$ , green (B)  $\text{KMnO}_4$ , purple  
(C)  $\text{Mn}_2\text{O}_3$ , brown (D)  $\text{Mn}_3\text{O}_4$ , black  
DB0124
10. The product of oxidation of  $\text{I}^-$  with  $\text{MnO}_4^-$  in alkaline medium is - [JEE 2004]  
(A)  $\text{IO}_3^-$  (B)  $\text{I}_2$  (C)  $\text{IO}^-$  (D)  $\text{IO}_4^-$   
DB0125
11.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  on heating liberates a gas. The same gas will be obtained by - [JEE 2004]  
(A) heating  $\text{NH}_4\text{NO}_2$  (B) heating  $\text{NH}_4\text{NO}_3$   
(C) treating  $\text{H}_2\text{O}_2$  with  $\text{NaNO}_2$  (D) treating  $\text{Mg}_3\text{N}_2$  with  $\text{H}_2\text{O}$   
DB0126
12. Which of the following combination will produce  $\text{H}_2$  gas ? [JEE Advance 2017]  
(A) Zn metal and  $\text{NaOH}(\text{aq})$  (B) Au metal and  $\text{NaCN}(\text{aq})$  in the presence of air  
(C) Cu metal and conc.  $\text{HNO}_3$  (D) Fe metal and conc.  $\text{HNO}_3$   
DB0127

**MULTIPLE CHOICE QUESTIONS WITH ONE OR MORE THAN ONE CORRECT ANSWER :**

13. Which of the following alloys contains (s) Cu and Zn ? [JEE 1993]  
(A) Bronze (B) Brass (C) Gun metal (D) Type metal  
DB0128
14. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese. [JEE 1998]  
(A) gives hardness to steel  
(B) helps the formation of oxides of iron  
(C) can remove oxygen and sulphur  
(D) can show highest oxidation state of +7.  
DB0129

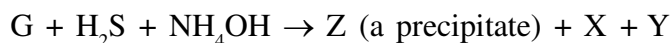
15. The correct statement(s) about  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  is (are) [JEE Advance 2015]  
[Atomic numbers of Cr = 24 and Mn = 25]
- (A)  $\text{Cr}^{2+}$  is a reducing agent  
(B)  $\text{Mn}^{3+}$  is an oxidizing agent  
(C) Both  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  exhibit  $d^4$  electronic configuration  
(D) When  $\text{Cr}^{2+}$  is used as a reducing agent, the chromium ion attains  $d^5$  electronic configuration

DB0130

16. Fusion of  $\text{MnO}_2$  with  $\text{KOH}$  in presence of  $\text{O}_2$  produces a salt **W**. Alkaline solution of **W** upon electrolytic oxidation yields another salt **X**. The manganese containing ions present in **W** and **X**, respectively, are **Y** and **Z**. Correct statement(s) is (are) [JEE Advance 2019]
- (1) **Y** is diamagnetic in nature while **Z** is paramagnetic  
(2) Both **Y** and **Z** are coloured and have tetrahedral shape  
(3) In both **Y** and **Z**,  $\pi$ -bonding occurs between p-orbitals of oxygen and d-orbitals of manganese.  
(4) In aqueous acidic solution, **Y** undergoes disproportionation reaction to give **Z** and  $\text{MnO}_2$ .

DB0131

17. Consider the following reactions (unbalanced) [JEE Advance 2019]



Choose the correct option(s).

- (1) The oxidation state of Zn in T is +1  
(2) Bond order of Q is 1 in its ground state  
(3) Z is dirty white in colour  
(4) R is a V-shaped molecule

DB0132

## ANSWER KEY

## EXERCISE # O-1

- |         |         |         |           |
|---------|---------|---------|-----------|
| 1. (B)  | 2. (A)  | 3. (A)  | 4. (B)    |
| 5. (B)  | 6. (B)  | 7. (D)  | 8. (A)    |
| 9. (A)  | 10. (B) | 11. (C) | 12. (A)   |
| 13. (A) | 14. (C) | 15. (B) | 16. (B,C) |
| 17. (B) | 18. (A) | 19. (A) | 20. (B)   |
| 21. (A) | 22. (A) | 23. (B) | 24. (A)   |
| 25. (B) | 26. (C) | 27. (B) | 28. (B)   |
| 29. (D) | 30. (D) | 31. (A) | 32. (A,C) |
| 33. (D) | 34. (D) | 35. (C) | 36. (B)   |
| 37. (C) | 38. (A) | 39. (C) | 40. (D)   |
| 41. (A) | 42. (A) | 43. (B) | 44. (A)   |
| 45. (A) | 46. (B) | 47. (B) | 48. (D)   |

## EXERCISE # O-2

- |               |               |              |                  |
|---------------|---------------|--------------|------------------|
| 1. (A, B, C)  | 2. (B, C, D)  | 3. (A, B)    | 4. (A, C, D)     |
| 5. (A, B)     | 6. (A, B)     | 7. (A, B, D) | 8. (B, C)        |
| 9. (A, B, C)  | 10. (A, B, C) | 11. (A, B)   | 12. (A, B, C, D) |
| 13. (A, B)    | 14. (A, B)    | 15. (B, C)   | 16. (A, B, C)    |
| 17. (A, B, C) | 18. (A, B, C) |              |                  |

## EXERCISE # S-1

- (6), In this reaction  $\text{CrO}_2\text{Cl}_2$  is formed in which Cr is +6.
- (2),  $\text{V}^{+4}$ ,  $\text{Cu}^{+2}$
- (11), +7, +4
- (3),  $\text{Mn}^{+3}$ ,  $\text{Fe}^{+3}$ ,  $\text{Co}^{+3}$
- $\text{CrO}_2\text{Cl}_2$  has  $d^3s$  hybridisation and all 3d-orbitals are non-axial which are  $d_{xy}$ ;  $d_{yz}$  and  $d_{zx}$ .
- (003)
- (6), Mohr's salt  

$$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$$

$$6 \text{Fe}^{+2} + \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ \rightarrow 2\text{Cr}^{+3} + 7\text{H}_2\text{O} + 6\text{Fe}^{+3}$$
- 3  
 (I)  $\text{BaCl}_2 + \text{Na}_2\text{CrO}_4 \xrightarrow{\text{CH}_3\text{COOH}} \text{BaCrO}_4 \downarrow + 2\text{NaCl}$   
 (II)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{NaOH} \longrightarrow \text{K}_2\text{CrO}_4$   

$$\text{CrO}_4^{2-} \xrightleftharpoons[\text{OH}^-]{\text{H}^+} \text{Cr}_2\text{O}_7^{2-}$$
  
 (III)  $\text{Cr}_2\text{O}_7^{2-} + \text{NO}_3^- \xrightarrow{\text{H}^+} \text{no reaction.}$   
 (IV)  $\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}^+} \text{CH}_3 - \text{COOH} + \text{Cr}^{+3}$

**EXERCISE # S-2**

- |   |   |         |         |
|---|---|---------|---------|
| 1. (C)                                    | 2. (D)  | 3. (A)  | 4. (B)  |
| 5. (B)                                    | 6. (D)  | 7. (C)  | 8. (A)  |
| 9. (D)                                    | 10. (A)-(R,S) ; (B)-(R,S) ; (C)-(P,Q) ; (D)-(P,Q) |         |         |
| 11. (A)-(R) ; (B)-(S) ; (C)-(P) ; (D)-(Q) | 12. (A)   | 13. (C) |         |
| 14. (B)                                   | 15. (B)   | 16. (A) | 17. (B) |
| 18. (C)                                   | 19. (C)   | 20. (B) | 21. (C) |
| 22. (C)                                   | 23. (D)   | 24. (A) | 25. (A) |

**EXERCISE # JEE-MAIN**

- |         |         |         |                      |
|---------|---------|---------|----------------------|
| 1. (2)  | 2. (2)  | 3. (4)  | 4. (1)               |
| 5. (3)  | 6. (1)  | 7. (4)  | 8. (3)               |
| 9. (3)  | 10. (2) | 11. (4) | 12. (4)              |
| 13. (4) | 14. (1) | 15. (4) | 16. (4)              |
| 17. (4) | 18. (3) | 19. (1) | 20. (1)              |
| 21. (3) | 22. (2) | 23. (2) | 24. (3)      25. (4) |

**EXERCISE # JEE-ADVANCED**

TRUE/FALSE :

1. True

FILL IN THE BLANKS :

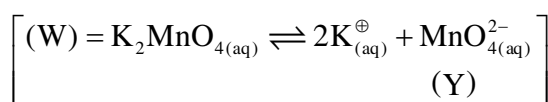
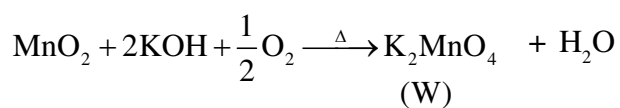
2. H
- <sub>2</sub>
- S

MULTIPLE CHOICE QUESTIONS WITH ONE CORRECT ANSWER :

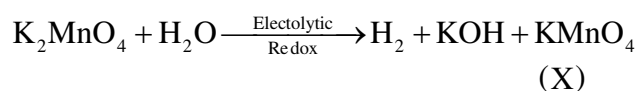
- |         |         |        |         |
|---------|---------|--------|---------|
| 3. (C)  | 4. (B)  | 5. (A) | 6. (B)  |
| 7. (B)  | 8. (B)  | 9. (A) | 10. (A) |
| 11. (A) | 12. (A) |        |         |

MULTIPLE CHOICE QUESTIONS WITH ONE OR MORE THAN ONE CORRECT ANSWER :

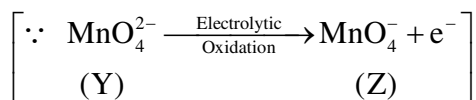
- |                 |         |                   |
|-----------------|---------|-------------------|
| 13. (B, C)      | 14. (A) | 15. (A), (B), (C) |
| 16. Ans.(2,3,4) |         |                   |



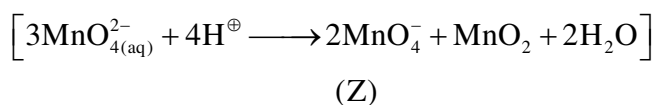




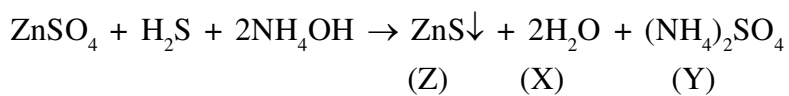
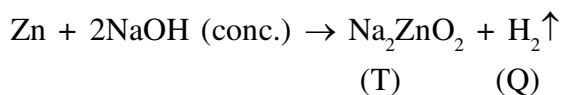
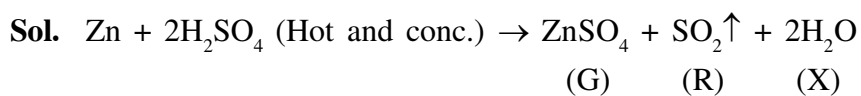
[anion of X =  $\text{MnO}_4^-$ ]  
(Z)



$\therefore$  In acidic solution; Y undergoes disproportionation reaction



### 17. Ans.(2,3,4)



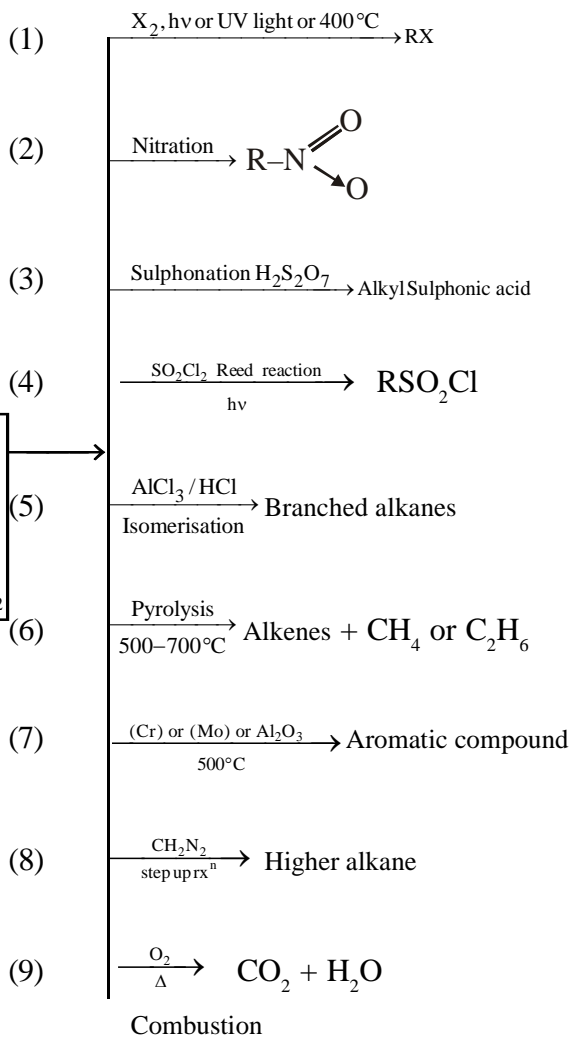
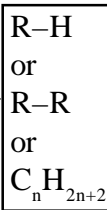
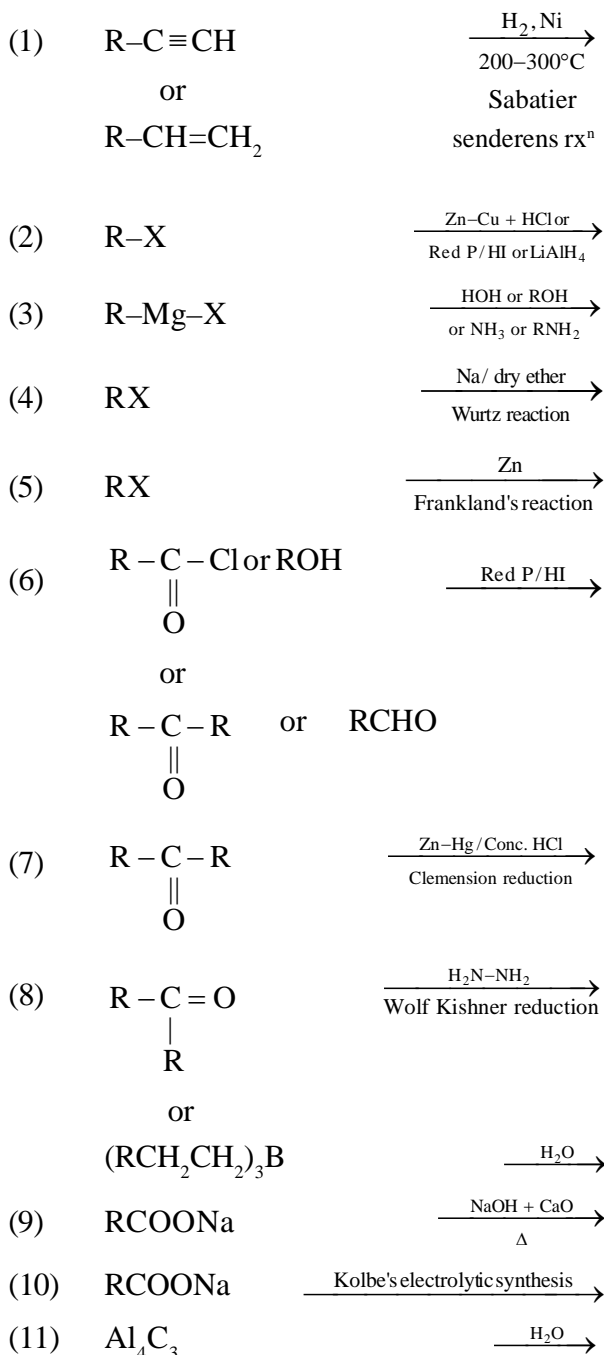


HYDROCARBON

REACTION CHART FOR ALKANES

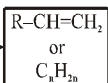
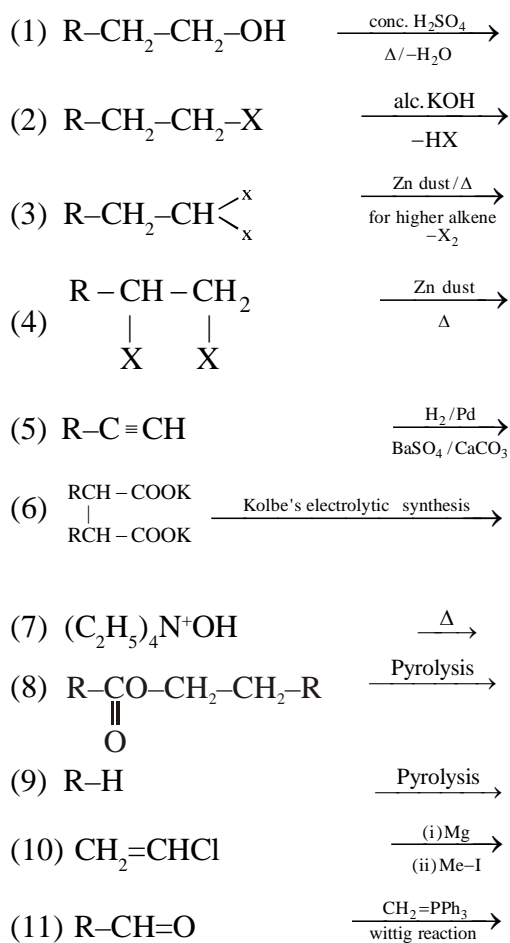
GMP

GR

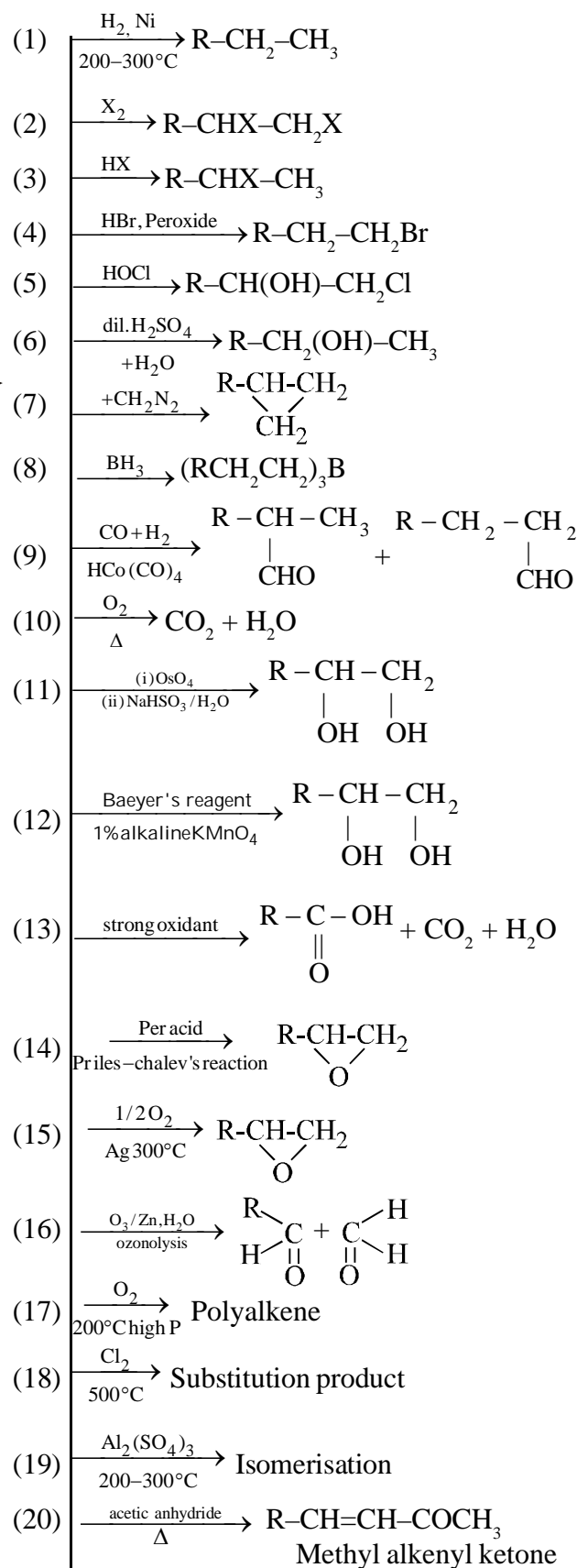


## REACTION CHART FOR ALKENES

GMP



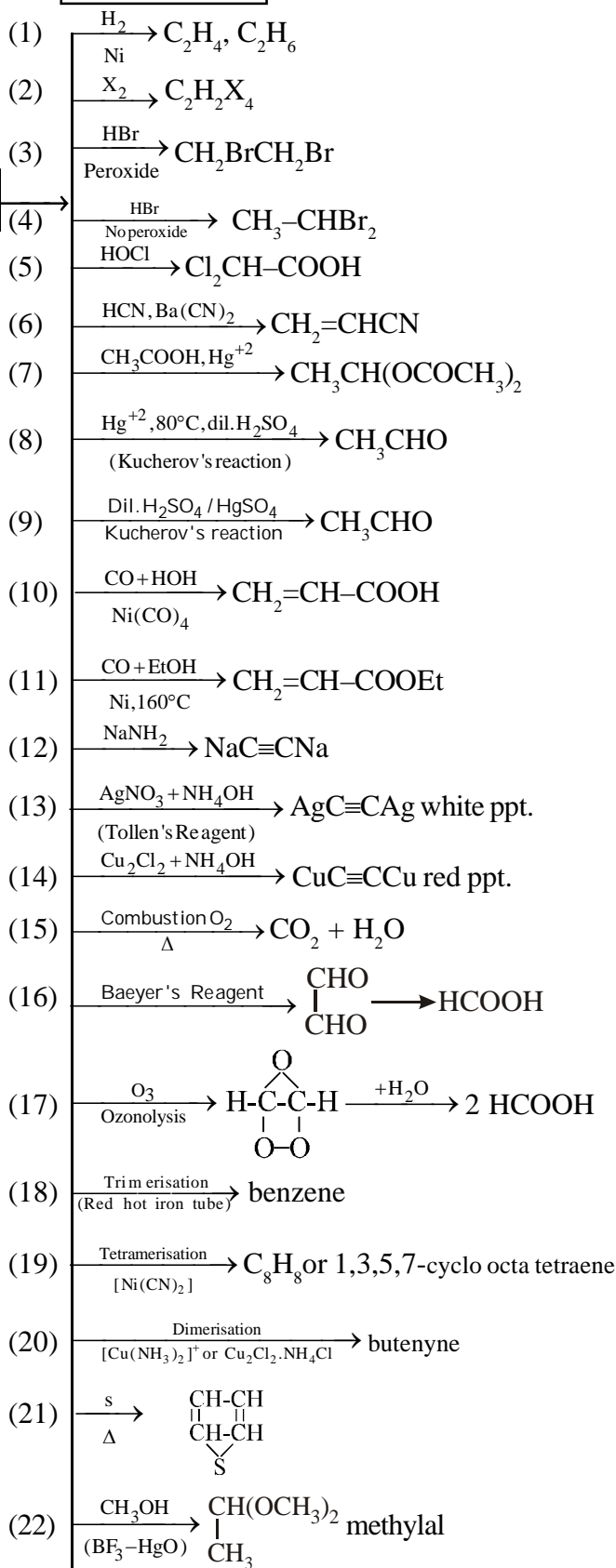
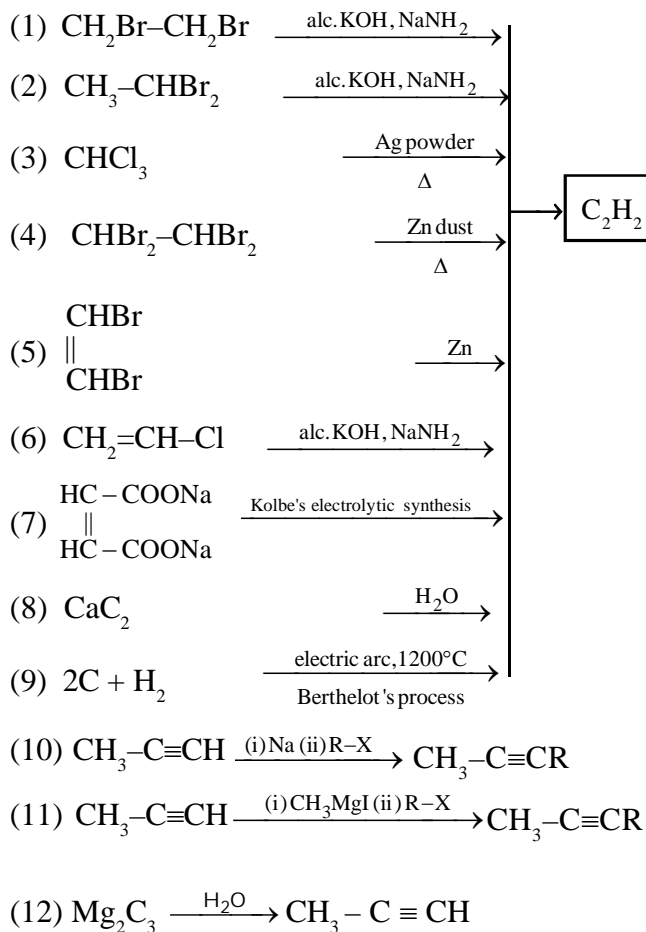
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REACTION CHART FOR ALKYNES

GMP

GR

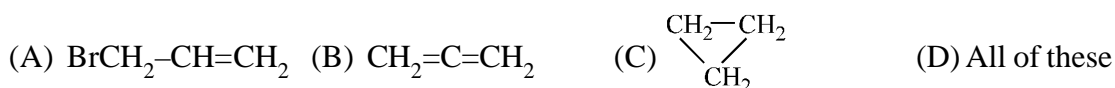


## EXERCISE # O-1

1. During the preparation of ethane by Kolbe's electrolytic method using inert electrodes the pH of the electrolyte –
- (A) Increases progressively as the reaction proceeds  
 (B) Decreases progressively as the reaction proceeds  
 (C) Remains constant throughout the reaction  
 (D) May decrease if the concentration of the electrolyte is not very high

HC0001

2.  $\text{BrCH}_2\text{-CH}_2\text{-CH}_2\text{Br}$  reacts with Na in the presence of ether at  $100^\circ\text{C}$  to produce –



HC0002

3. How many products will be formed excluding stereo when cis-1,3,5-trimethyl cyclohexene reacts with NBS?

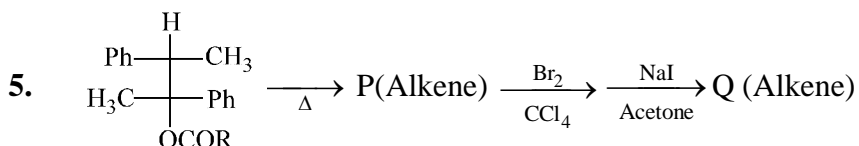


HC0003

4. How many dibromo derivatives are formed when bromine is added to 3-Methyl Cyclohexene in 1,2-dichloroethane.



HC0004



Alkene (P) & (Q) respectively are

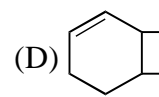
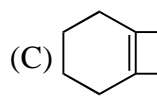
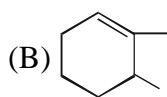
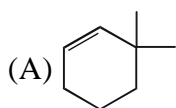
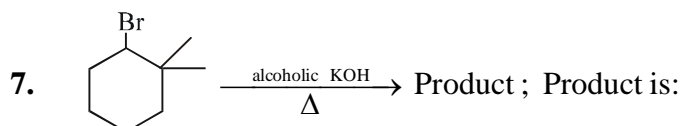


HC0005

6. Anti-Markownikoff's addition of HBr is not observed in –

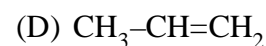
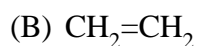
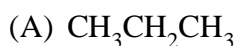


HC0006



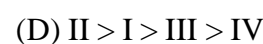
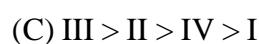
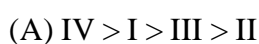
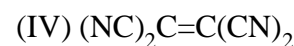
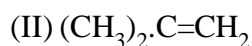
HC0007

8. Which is expected to react most readily with bromine –



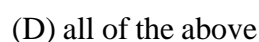
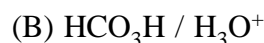
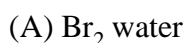
HC0008

9. For the ionic reaction of hydrochloric acid with the following alkenes, predict the correct sequence of reactivity as measured by reaction rates:



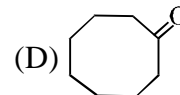
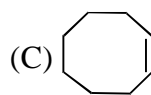
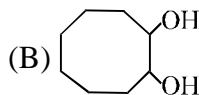
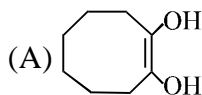
HC0009

10.  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 \xrightarrow{x}$  Product is Y (non-resolvable) then X can be –  
cis

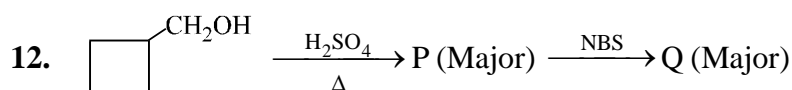


HC0010

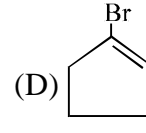
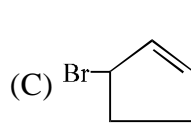
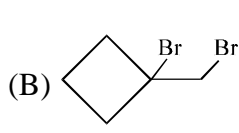
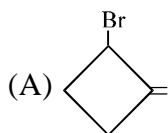
11. The reaction of cyclooctyne with  $\text{HgSO}_4$  in the presence of a  $\text{H}_2\text{SO}_4$  gives



HC0011

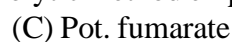
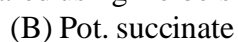
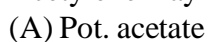


The structure of Q is

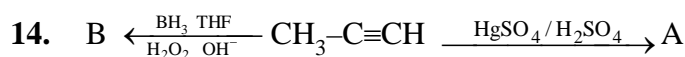


HC0012

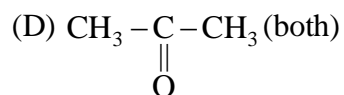
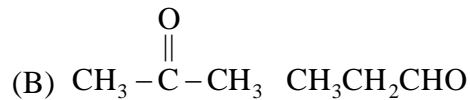
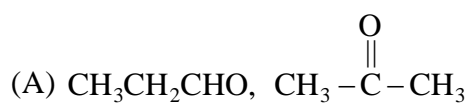
13. Acetylene may be prepared using Kolbe's electrolytic method employing –



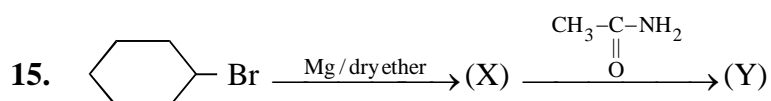
HC0013



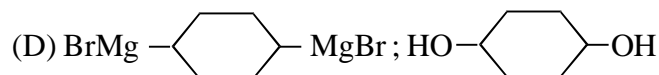
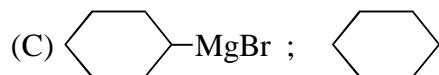
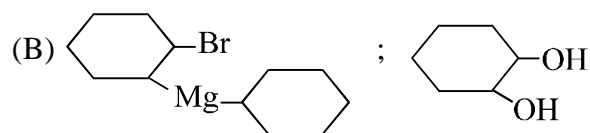
A and B are –



HC0014



The structures of (X) and (Y) respectively are



HC0015



EXERCISE # O-2

1.  $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow[\text{H}_2\text{O}_2/\text{OH}^-]{\text{B}_2\text{D}_6}$  product X ; X is –
- (A)  $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2\text{D}$  (B)  $\text{CH}_3-\underset{\text{D}}{\text{CH}}-\text{CH}_2\text{OH}$
- (C)  $\text{CH}_3-\underset{\text{OD}}{\text{CH}}-\text{CH}_3$  (D) none is correct

HC0016

2. Aqueous solution of potassium propanoate is electrolysed. Possible organic products are:
- (A) n-Butane (B)  $\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5$
- (C)  $\text{CH}_3-\text{CH}_3$  (D)  $\text{CH}_2=\text{CH}_2$

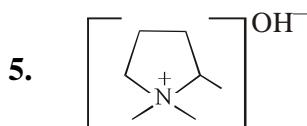
HC0017

3.  $\text{CH}_2 = \text{CHCH}_2\text{CH} = \text{CH}_2 \xrightarrow{\text{NBS}}$  A, A can be
- (A)  $\text{CH}_2 = \underset{\text{Br}}{\text{CH}}\text{CHCH} = \text{CH}_2$  (B)  $\text{CH}_2 = \text{CHCH} = \text{CH}-\text{CH}_2\text{Br}$
- (C)  $\text{CH}_2 = \text{CHCH}_2\text{CH} = \text{CHBr}$  (D)  $\text{CH}_2 = \text{CHCH}_2\underset{\text{Br}}{\text{C}} = \text{CH}_2$

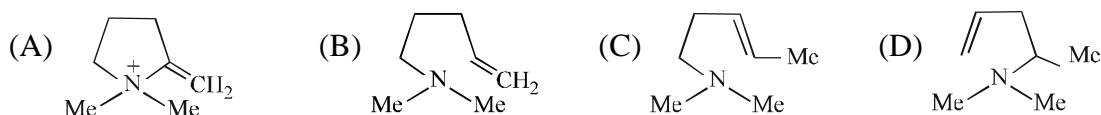
HC0018

4. Which of the following elimination reactions will occur to give but-1-ene as the major product?
- (A)  $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{CH}_3 + \text{KOH} \xrightarrow{\text{EtOH}}$  (B)  $\text{CH}_3\cdot\underset{\text{NMe}_3^+}{\text{CH}}\cdot\text{CH}_2\cdot\text{CH}_3 + \text{NaOEt} \xrightarrow[\Delta]{\text{EtOH}}$
- (C)  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_3 + \text{Me}_3\text{COK}^+ \xrightarrow{\Delta}$  (D)  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH(OH)}\cdot\text{CH}_3 + \text{conc. H}_2\text{SO}_4 \xrightarrow{\Delta}$

HC0019



The above compound undergoes elimination on heating can yield which of the following products?



HC0020

6. Which of the following will give same product with HBr in presence or absence of peroxide.
- (A) Cyclohexene (B) 1-methylcyclohexene  
(C) 1,2-dimethylcyclohexene (D) 1-butene

HC0021

7. The ionic addition of HCl to which of the following compounds will produce a compound having Cl on carbon next to terminal.
- (A)  $\text{CF}_3 \cdot (\text{CH}_2)_3 \cdot \text{CH}=\text{CH}_2$  (B)  $\text{CH}_3 \cdot \text{CH}=\text{CH}_2$   
(C)  $\text{CF}_3 \cdot \text{CH}=\text{CH}_2$  (D)  $\text{CH}_3 \cdot \text{CH}_2 \text{CH}=\text{CH} \cdot \text{CH}_3$

HC0022

8.  $\text{C} \xleftarrow[\text{H}_2\text{O}_2/\text{OH}^-]{\text{BH}_3/\text{THF}} \text{A} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} \text{B}$

B & C are identical when A is –

- (A)  $\text{HC}\equiv\text{CH}$  (B)  $\text{CH}_3-\text{C}\equiv\text{CH}$  (C)  $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$  (D)  $\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{CH}$

HC0023

9. Match List-I with List-II and select the correct answer using the codes given below the lists:

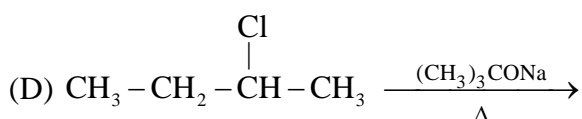
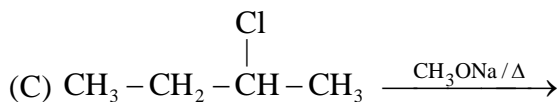
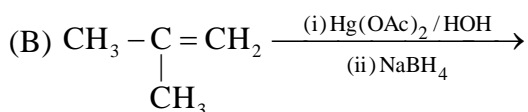
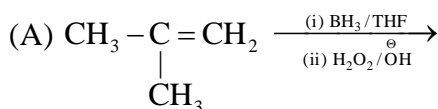
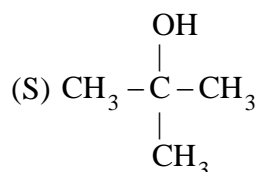
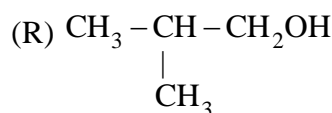
**List-I (Reaction)**

- (A)  $\text{CH}_3-\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3-\text{CHBr}-\text{CH}_3$   
(B)  $\text{CH}_3-\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3-\text{CH}_2-\text{CH}_2\text{Br}$   
(C)  $\text{CH}_3-\text{CH}=\text{CH}_2 \rightarrow \text{BrCH}_2-\text{CH}=\text{CH}_2$   
(D)  $\text{CH}_3-\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3-\text{CHBr}-\text{CH}_2\text{Br}$

**List-II (Reagents)**

- (P) HBr  
(Q)  $\text{Br}_2 / \text{CCl}_4$   
(R) HBr / Peroxide  
(S) NBS

HC0024

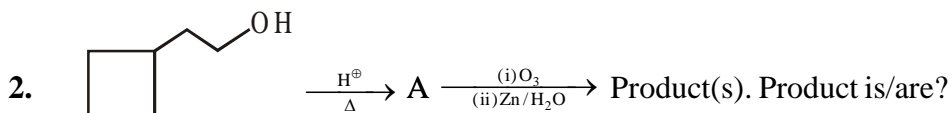
**10. Column I (Reaction)****Column II (Major product)**

HC0025

EXERCISE # S-1

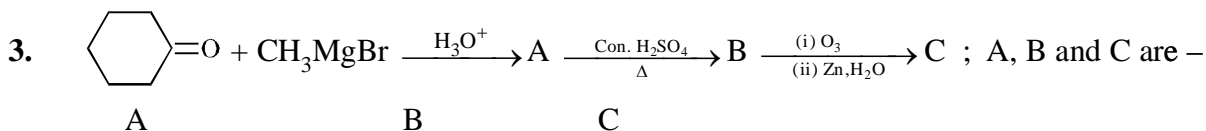
1. When n-butane is heated in the presence of  $\text{AlCl}_3/\text{HCl}$  it will be converted into –  
 (A) Ethane (B) Propane (C) Butene (D) Isobutane

HC0026



- (A) +  $\text{HCHO}$  (B)
- (C) +  $\text{CH}_3\text{CHO}$  (D)

HC0027



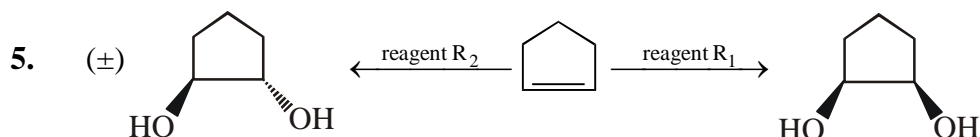
- (A)
- (B)
- (C)
- (D)

HC0028

4. Which has least heat of hydrogenation –

- (A) (B)
- (C) (D)

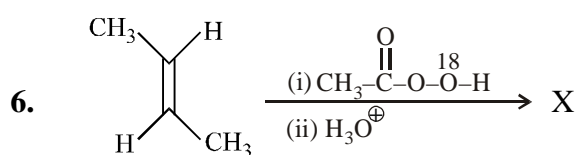
HC0029



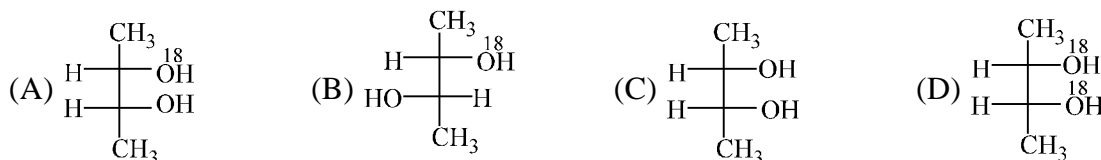
$R_1$  and  $R_2$  respectively are –

- (A) Cold alkaline  $\text{KMnO}_4$ ,  $\text{OsO}_4/\text{H}_2\text{O}_2$   
 (B) Cold alkaline  $\text{KMnO}_4$ ,  $\text{HCO}_3\text{H} / \text{H}_3\text{O}^+$   
 (C) Cold alkaline  $\text{KMnO}_4$ ,  $\text{CH}_3\text{-O-O-CH}_3$   
 (D)  $\text{C}_6\text{H}_5\text{CO}_3\text{H}$ ,  $\text{HCO}_3\text{H} / \text{H}_3\text{O}^+$

HC0030



The probable structure of 'X' is

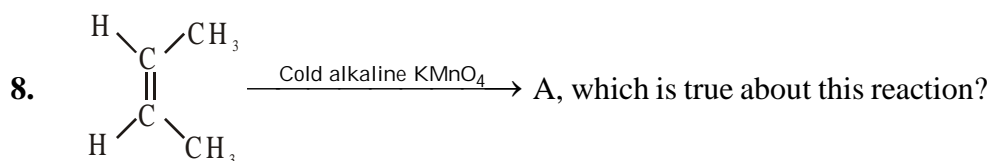


HC0031

7. Which alkene on heating with alkaline  $\text{KMnO}_4$  solution gives acetone and a gas, which turns lime water milky –

- (A) 2-Methyl-2-butene (B) Isobutylene  
 (C) 1-Butene (D) 2-Butene

HC0032



- (A) A is meso 2, 3-butanediol formed by *syn* addition  
 (B) A is meso 2, 3-butanediol formed by *anti* addition  
 (C) A is a racemic mixture of *d* and *l*, 2, 3-butanediol formed by anti addition  
 (D) A is a racemic mixture of *d* and *l* 2,3-butanediol formed by *syn* addition

HC0033

9. Mixture of one mole each of ethene and propyne on reaction with Na will form  $\text{H}_2$  gas at S.T.P. –

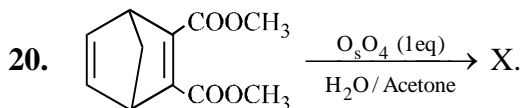
- (A) 22.4 L (B) 11.2 L (C) 33.6 L (D) 44.8 L

HC0034

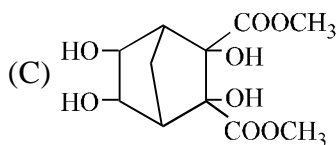
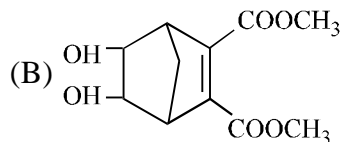
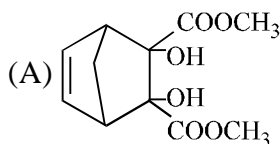
10.  $B \xleftarrow{\text{Lindlar's catalyst}} R-C\equiv C-R \xrightarrow{Na/NH_3} A$   
 A and B are geometrical isomers –  
 (A) A is trans, B is cis (B) A and B both are cis  
 (C) A and B both are trans (D) A is cis, B is trans  
**HC0035**
11. A mixture of  $CH_4$ ,  $C_2H_4$  and  $C_2H_2$  gaseous are passed through a Wolf bottle containing ammonical cuprous chloride. The gas coming out is  
 (A) Methane (B) Acetylene  
 (C) Mixture of methane and ethylene (D) original mixture  
**HC0036**
12. Which of the following reagents cannot be used to locate the position of triple bond in  $CH_3-C\equiv C-CH_3$   
 (A)  $Br_2/CCl_4$  (B)  $O_3/H_2O$  (C)  $Cu_2Cl_2/NH_4OH$  (D)  $KMnO_4/H^+$   
**HC0037**
13. In the presence of strong bases, triple bonds will migrate within carbon skeletons by the  
 (A) removal of protons (B) addition of protons  
 (C) removal and readdition of protons (D) addition and removal of protons.  
**HC0038**
14.  $CH_3-CH_2-C\equiv CH \xrightleftharpoons[A]{B} CH_3C\equiv C-CH_3$  ; A and B are –  
 (A) alcoholic KOH and  $NaNH_2$  (B)  $NaNH_2$  and alcoholic KOH  
 (C)  $NaNH_2$  and Lindlar catalyst (D) Lindlar and  $NaNH_2$  catalyst  
**HC0039**
15. If a mixture of iso-octane (70%) & n-heptane (30%) is present in sample. The octane number of this sample is :  
 (A) 40 (B) 70 (C) 30 (D) 85  
**HC0040**
16.  $HC\equiv CH \xrightarrow[Cu_2Cl_2]{NH_4Cl} \text{Product}$   
 Product is –  
 (A)  $Cu-C\equiv C-Cu$  (B)  $H_2C=CH-C\equiv CH$  (C)  $HC\equiv C-Cu$  (D)  $Cu-C\equiv C-NH_4$   
**HC0041**
17. Which of the following process is not good for the preparation of open chain alkane having odd number of carbons :  
 (A) Wurtz process (B) Kolbe electrolysis  
 (C) Corey house synthesis (D) Both (A) & (B)  
**HC0042**
18. How many moles of  $O_2$  required for complete combustion of one mole of propane –  
 (A) 7 (B) 5 (C) 16 (D) 10  
**HC0043**

19. How much volume of air will be needed for complete combustion of 10 lit. of ethane – (Assuming that approx 20% O<sub>2</sub> is present in air)
- (A) 135 lit.                      (B) 35 lit.                      (C) 175 lit.                      (D) 205 lit.

HC0044

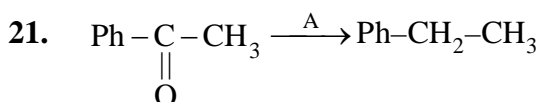


Identify 'X'.



(D) Reaction will not occur

HC0045



A could be:

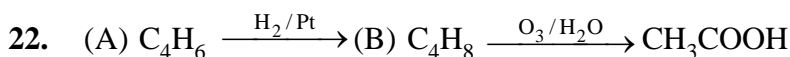
(A) NH<sub>2</sub>NH<sub>2</sub>, glycol/OH<sup>-</sup>, Δ

(B) Zn(Hg)/conc. HCl

(C) Red P/HI

(D)  $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{SH} \quad \text{SH} \end{array}$ ; Raney Ni, H<sub>2</sub>, Δ

HC0046



Hence A and B are

(A) CH<sub>3</sub>C ≡ CCH<sub>3</sub>, CH<sub>3</sub>CH = CHCH<sub>3</sub>(B) CH<sub>2</sub> = CHCH = CH<sub>2</sub>, CH<sub>3</sub>CH = CHCH<sub>3</sub>(C) , CH<sub>3</sub>CH = CHCH<sub>3</sub>

(D) None

HC0047

23. An alkene on ozonolysis yields only ethanal. The ozonolysis of isomer of this alkene yields :

(A) Propanone

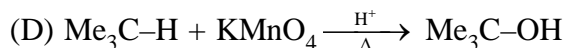
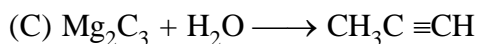
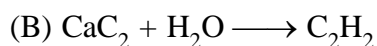
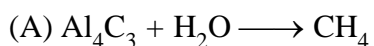
(B) Ethanal

(C) Methanal

(D) Only propanal

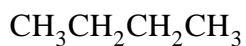
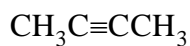
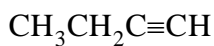
HC0048

24. Which is / are true statements/ reactions?



HC0049

25. Which reagent is the most useful for distinguishing compound I from the rest of the compounds

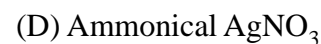
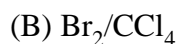
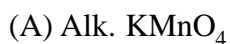


I

II

III

IV

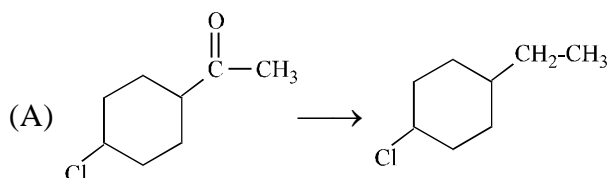


HC0050

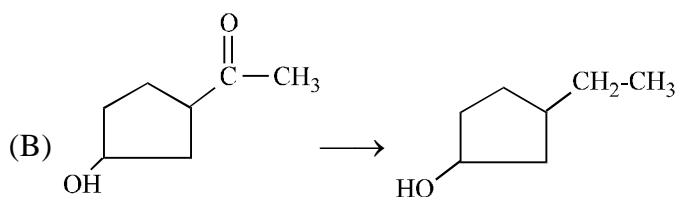
26. Match the column

Column I

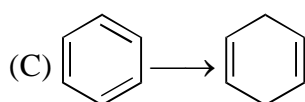
Column II



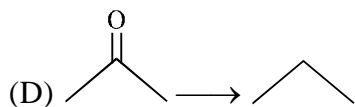
(P) Birch reduction



(Q) Stephen's reduction



(R) Wolf-Kishner reduction

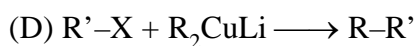
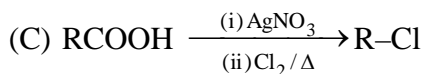
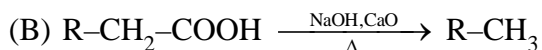
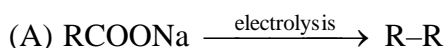


(S) Clemmensen reduction

HC0051

## 27. Match the column

## Column I



## Column II

(P) Correy-House reaction

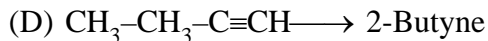
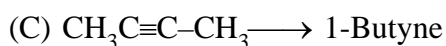
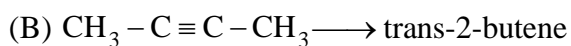
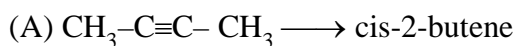
(Q) Kolbe electrolysis

(R) Oakwood degradation / Soda lime process

(S) Hunsdiecker reaction

HC0052

## 28. Column I



## Column II

(P)  $\text{Na/NH}_3(l)$ (Q)  $\text{H}_2/\text{Pd/BaSO}_4$ (R) alc.  $\text{KOH}, \Delta$ (S)  $\text{NaNH}_2, \Delta$ 

HC0053



## EXERCISE # (J-MAINS)

1. 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly [AIEEE-2005]
- (1) 2-bromo-2-methylbutane (2) 1-bromo-2-methylbutane  
(3) 1-bromo-3-methylbutane (4) 2-bromo-3-methylbutane

HC0054

2. Alkyl halides react with dialkyl copper reagent to give [AIEEE-2005]
- (1) alkyl copper halides (2) alkenes  
(3) alkenyl halides (4) alkanes

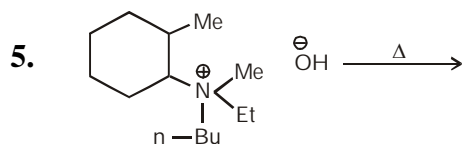
HC0055

3. Reaction of one molecule of HBr with one molecule of 1,3-butadiene at 40°C gives predominantly [AIEEE-2005]
- (1) 1-bromo-2-butene under thermodynamically controlled conditions  
(2) 3-bromobutene under kinetically controlled conditions  
(3) 1-bromo-2-butene under kinetically controlled conditions  
(4) 3-bromobutene under thermodynamically controlled conditions

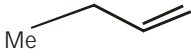
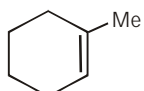
HC0056

4. Acid catalyzed hydration of alkenes except ethene leads to the formation of [AIEEE-2005]
- (1) secondary or tertiary alcohol  
(2) primary alcohol  
(3) mixture of secondary and tertiary alcohols  
(4) mixture of primary and secondary alcohols

HC0057



The alkene formed as a major product in the above elimination reaction is- [AIEEE-2006]

- (1)  (2)  $\text{CH}_2=\text{CH}_2$  (3)  (4) 

HC0058

6. Reaction of trans-2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces- [AIEEE-2006]
- (1) 4-phenyl cyclopentene (2) 2-phenyl cyclopentene  
(3) 1-phenyl cyclopentene (4) 3-phenyl cyclopentene

HC0059

7. Phenyl magnesium bromide reacts with methanol to give- [AIEEE-2006]  
 (1) A mixture of anisole and  $Mg(OH)Br$   
 (2) A mixture of benzene and  $Mg(OMe)Br$   
 (3) A mixture of toluene and  $Mg(OH)Br$   
 (4) A mixture of phenol and  $Mg(Me)Br$   
**HC0060**
8. Which of the following reactions will yield, 2, 2-dibromopropane [AIEEE-2007]  
 (1)  $CH_3-C\equiv CH + 2HBr \longrightarrow$  (2)  $CH_3CH=CHBr + HBr \longrightarrow$   
 (3)  $CH\equiv CH + 2HBr \longrightarrow$  (4)  $CH_3-CH=CH_2 + HBr \longrightarrow$   
**HC0061**
9. In the following sequence of reactions, the alkene affords the compound 'B' :- [AIEEE-2008]  
 $CH_3CH=CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B.$   
 The compound B is  
 (1)  $CH_3CH_2CHO$  (2)  $CH_3COCH_3$  (3)  $CH_3CH_2COCH_3$  (4)  $CH_3CHO$   
**HC0062**
10. The hydrocarbon which can react with sodium in liquid ammonia is [AIEEE-2008]  
 (1)  $CH_3CH_2CH_2C\equiv CCH_2CH_2CH_3$  (2)  $CH_3CH_2C\equiv CH$   
 (3)  $CH_3CH=CHCH_3$  (4)  $CH_3CH_2C\equiv CCH_2CH_3$   
**HC0063**
11. The treatment of  $CH_3MgX$  with  $CH_3C\equiv C-H$  produces [AIEEE-2008]  
 (1)  $CH_3-CH=CH_2$  (2)  $CH_3C\equiv C-CH_3$  (3)  $CH_3-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}-CH_3$  (4)  $CH_4$   
**HC0064**
12. The main product of the following reaction is [AIEEE-2010]  
 $C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{Conc. H_2SO_4} ?$   
 (1)  $\begin{array}{l} H_5C_6CH_2CH_2 \\ H_3C \end{array} \begin{array}{l} \diagdown \\ \diagup \end{array} C = CH_2$  (2)  $\begin{array}{l} H_5C_6 \\ H \end{array} \begin{array}{l} \diagdown \\ \diagup \end{array} C = C \begin{array}{l} \diagup \\ \diagdown \end{array} \begin{array}{l} H \\ CH(CH_3)_2 \end{array}$   
 (3)  $\begin{array}{l} C_6H_5CH_2 \\ H \end{array} \begin{array}{l} \diagdown \\ \diagup \end{array} C = C \begin{array}{l} \diagup \\ \diagdown \end{array} \begin{array}{l} CH_3 \\ CH_3 \end{array}$  (4)  $\begin{array}{l} C_6H_5 \\ H \end{array} \begin{array}{l} \diagdown \\ \diagup \end{array} C = C \begin{array}{l} \diagup \\ \diagdown \end{array} \begin{array}{l} CH(CH_3)_2 \\ H \end{array}$   
**HC0065**
13. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is :- [AIEEE-2010]  
 (1) Ethene (2) Propene (3) 1-Butene (4) 2-Butene  
**HC0066**

14. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of :- [AIEEE-2011]

(1) an isopropyl group (2) an acetylenic triple bond  
(3) two ethylenic double bonds (4) a vinyl group

HC0067

15. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds :- [AIEEE-2011]

(1) 2-Methyl-1-pentene (2) 1-Pentene  
(3) 2-Pentene (4) 2-Methyl-2-pentene

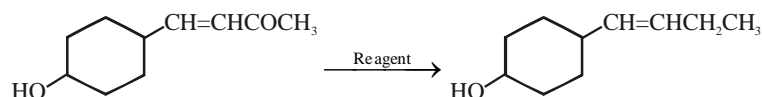
HC0068

16. 2-Hexyne gives trans-2-Hexene on treatment with :- [AIEEE-2012]

(1)  $\text{LiAlH}_4$  (2)  $\text{Pt}/\text{H}_2$  (3)  $\text{Li}/\text{NH}_3$  (4)  $\text{Pd}/\text{BaSO}_4$

HC0069

17. In the given transformation, which of the following is the most appropriate reagent ? [AIEEE-2012]



(1)  $\text{NaBH}_4$  (2)  $\text{NH}_2\text{NH}_2, \overset{\ominus}{\text{O}}\text{H}$  (3)  $\text{Zn} - \text{Hg} / \text{HCl}$  (4)  $\text{Na}, \text{Liq. NH}_3$

HC0070

18. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is :- (JEE MAIN OFFLINE 2013)

(1) 2-Butyne (2) 2-Butene (3) Acetylene (4) Ethene

HC0071

19. The number and type of bonds in  $\text{C}_2^{2-}$  ion in  $\text{CaC}_2$  are: (JEE MAIN ONLINE 2014)

(1) Two  $\sigma$  bonds and one  $\pi$  - bond (2) Two  $\sigma$  bonds and two  $\pi$  - bonds  
(3) One  $\sigma$  bond and two  $\pi$  - bonds (4) One  $\sigma$  bond and one  $\pi$  - bond

HC0072

20. In the hydroboration - oxidation reaction of propene with diborane,  $\text{H}_2\text{O}_2$  and  $\text{NaOH}$ , the organic compound formed is : (JEE MAIN ONLINE 2014)

(1)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (2)  $(\text{CH}_3)_3\text{COH}$  (3)  $\text{CH}_3\text{CHOHCH}_3$  (4)  $\text{CH}_3\text{CH}_2\text{OH}$

HC0073

21. Which one of the following class of compounds is obtained by polymerization of acetylene ?

(JEE MAIN ONLINE 2014)

(1) Poly-ene (2) Poly-yne (3) Poly-amide (4) Poly-ester

HC0074

22. The gas liberated by the electrolysis of Dipotassium succinate solution is :

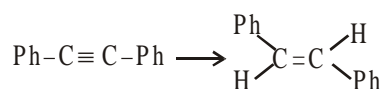
(JEE MAIN ONLINE 2014)

- (1) Ethyne                      (2) Ethene                      (3) Propene                      (4) Ethane

HC0075

23. The reagent needed for converting


(JEE MAIN ONLINE 2014)



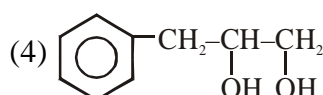
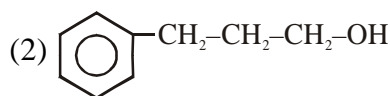
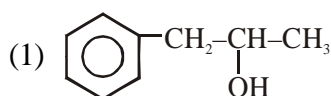
is :

- (1)  $\text{H}_2/\text{Lindlar Cat.}$                       (2) Cat. Hydrogenation  
(3)  $\text{LiAlH}_4$                                       (4)  $\text{Li}/\text{NH}_3$

HC0076

24.   $\text{CH}_2-\text{CH}=\text{CH}_2$  on mercuration- demercuration produces the major product :-

(Jee Main online 2014)



HC0077

25. The major product obtained in the photo catalysed bromination of 2-methylbutane is :-

(Jee Main online 2014)

- (1) 2-bromo-2-methylbutane                      (2) 2-bromo-3-methylbutane  
(3) 1-bromo-2-methylbutane                      (4) 1-bromo-3-methylbutane

HC0078

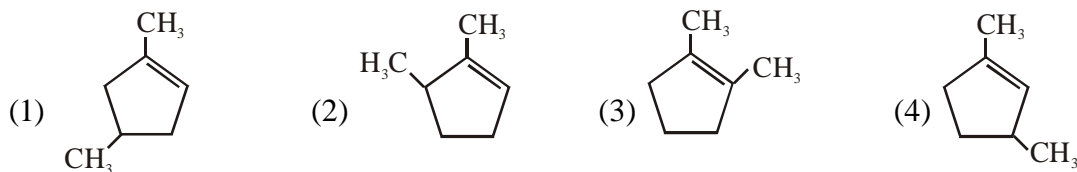
26. In the presence of peroxide,  $\text{HCl}$  and  $\text{HI}$  do not give anti-Markownikoff's addition to alkenes because

(Jee Main online 2014)

- (1) All the steps are exothermic in  $\text{HCl}$  and  $\text{HI}$   
(2) One of the steps is endothermic in  $\text{HCl}$  and  $\text{HI}$   
(3)  $\text{HCl}$  is oxidizing and the  $\text{HI}$  is reducing  
(4) Both  $\text{HCl}$  and  $\text{HI}$  are strong acids

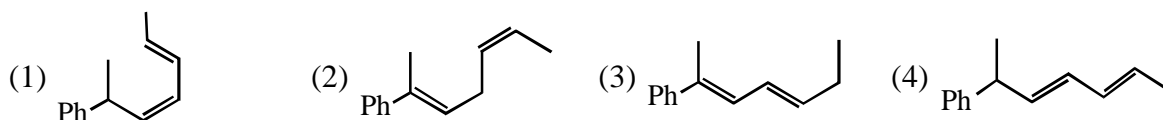
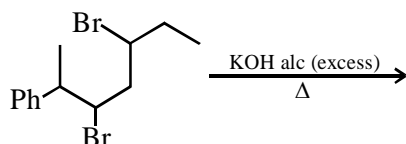
HC0079

27. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? (Jee Main offline 2015)



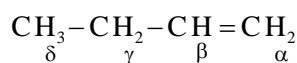
HC0080

28. The major product of the following reaction is (Jee Main (Jan) 2019)



HC0081

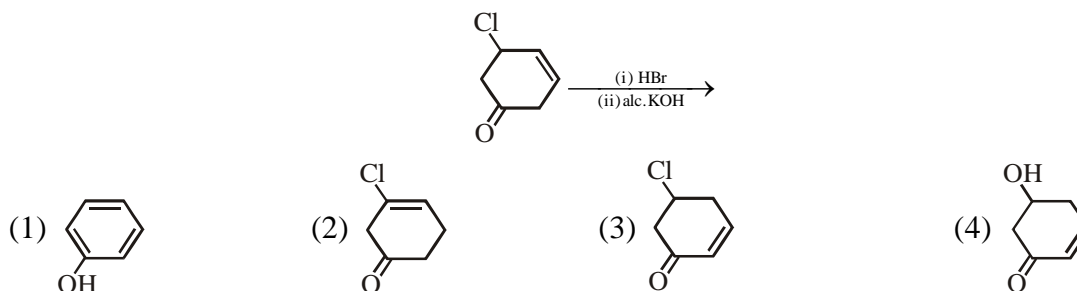
29. Which hydrogen in compound (E) is easily replaceable during bromination reaction in presence of light: (Jee Main (Jan) 2019)



- (1)  $\beta$  - hydrogen (2)  $\gamma$  - hydrogen (3)  $\delta$  - hydrogen (4)  $\alpha$  - hydrogen

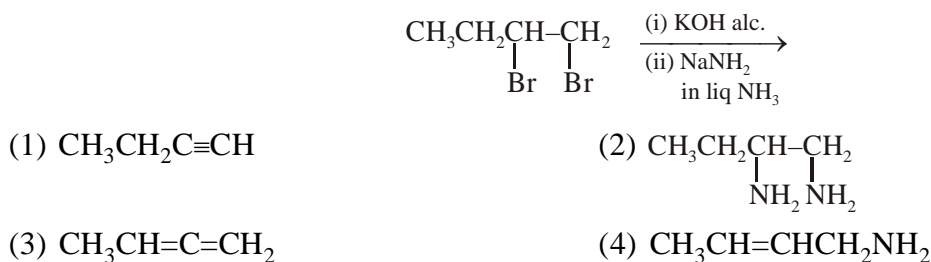
HC0082

30. The major product of the following reaction is: (Jee Main (Jan) 2019)



HC0083

31. The major product of the following reaction is: (Jee Main (Jan) 2019)



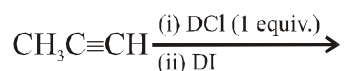
HC0084

32. Which one of the following alkenes when treated with HCl yields majorly an anti Markovnikov product? (Jee Main (April) 2019)

- (1)  $F_3C - CH = CH_2$  (2)  $Cl - CH = CH_2$   
 (3)  $CH_3O - CH = CH_2$  (4)  $H_2N - CH = CH_2$

HC0085

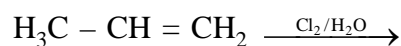
33. The major product of the following reaction is : (Jee Main (April) 2019)



- (1)  $CH_3CD(Cl)CHD(I)$  (2)  $CH_3CD_2CH(Cl)(I)$   
 (3)  $CH_3CD(I)CHD(Cl)$  (4)  $CH_3C(I)(Cl)CHD_2$

HC0086

34. The major product of the following addition reaction is : (Jee Main (April) 2019)



- (1)  $CH_3 - \underset{\substack{| \\ Cl}}{CH} - \underset{\substack{| \\ OH}}{CH_2}$  (2)  $H_3C - \underset{\substack{| \\ OH}}{CH} - \underset{\substack{| \\ Cl}}{CH_2}$  (3)  $H_3C - \triangle$  (4)  $\begin{array}{c} O \\ || \\ H_3C - C - CH_3 \end{array}$

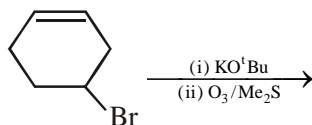
HC0087

35. But-2-ene on reaction with alkaline  $KMnO_4$  at elevated temperature followed by acidification will give : (Jee Main (April) 2019)

- (1) one molecule of  $CH_3CHO$  and one molecule of  $CH_3COOH$   
 (2)  $CH_3 - \underset{\substack{| \\ OH}}{CH} - \underset{\substack{| \\ OH}}{CH} - CH_3$   
 (3) 2 molecules of  $CH_3COOH$   
 (4) 2 molecules of  $CH_3CHO$

HC0088

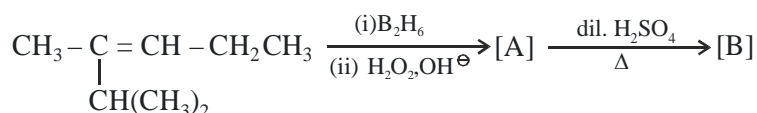
36. The major product(s) obtained in the following reaction is/are : (Jee Main (April) 2019)



- (1) O=CCCC=CC=O
- (2) O=CCCC=O and O=CC=O
- (3) O=CCC(OtBu)CC=O
- (4) O=CCC=O

HC0089

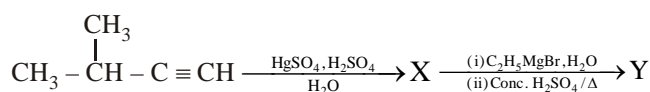
37. The major product [B] in the following sequence of reactions is :- (Jee Main (April) 2020)



- (1) CC(C)C(=O)CC                      (2) CC(C)C=C
- (3) CC(C)C=CC                      (4) CC(C)C=CC

HC0090

38. The major product (Y) in the following reactions is : (Jee Main (April) 2020)



- (1) CC(C)C(=O)C                      (2) CC(C)C=C
- (3) CC(C)C=C                      (4) CC(C)C=C

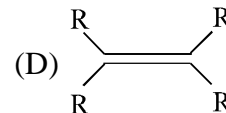
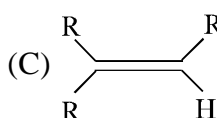
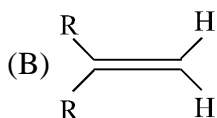
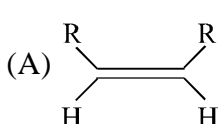
HC0091

## EXERCISE # JEE ADVANCE

1. Propyne and propene can be distinguished by – [IIT -2000]  
 (A) conc.  $\text{H}_2\text{SO}_4$  (B)  $\text{Br}_2$  in  $\text{CCl}_4$  (C) dil.  $\text{KMnO}_4$  (D)  $\text{AgNO}_3$  in ammonia

HC0092

2. Which one of the following alkenes will react fastest with  $\text{H}_2$  under catalytic hydrogenation condition [IIT -2000]



HC0093

3. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkene because – [IIT -2001]

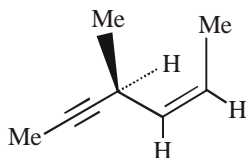
- (A) both are highly ionic (B) one is oxidising and the other is reducing  
 (C) one of the step is endothermic in both the cases (D) All the steps are exothermic in both cases

HC0094

4. The reaction of propene with  $\text{HOCl}$  proceeds via the addition of – [IIT '2001]  
 (A)  $\text{H}^+$  in first step (B)  $\text{Cl}^+$  in first step  
 (C)  $\text{OH}^-$  in first step (D)  $\text{Cl}^+$  and  $\text{OH}^-$  in single step

HC0095

5.



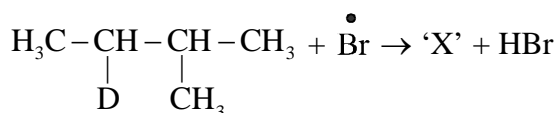
Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives –

[IIT '2001]

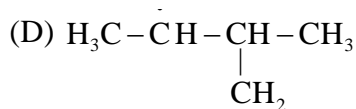
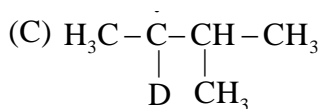
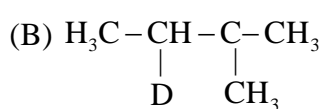
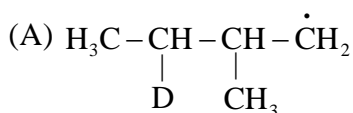
- (A) An optically active compound (B) An optically inactive compound  
 (C) A racemic mixture (D) A diastereomeric mixture

HC0096

6. Consider the following reactions – [IIT '2002]



Identify the structure of the major product 'X'



HC0097



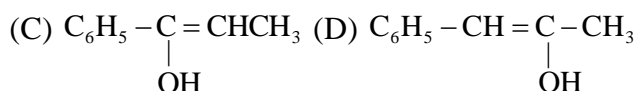
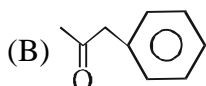
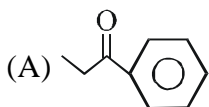
7. The nodal plane in the  $\pi$ -bond of ethene is located in – [IIT '2002]
- (A) The molecular plane  
 (B) A plane parallel to the molecular plane  
 (C) A plane perpendicular to the molecular plane which contains the carbon-carbon  $\sigma$ -bond at right angle  
 (D) A plane perpendicular to the molecular plane which contains the carbon-carbon  $\sigma$ -bond

HC0098

8. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne- [IIT '2002]
- (A) Bromine,  $\text{CCl}_4$  (B)  $\text{H}_2$ , Lindlar catalyst  
 (C) Dilute  $\text{H}_2\text{SO}_4$ ,  $\text{HgSO}_4$  (D) Ammonical  $\text{Cu}_2\text{Cl}_2$  solution

HC0099

9.  $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} \text{A}$  [IIT '2003]



HC0100

10. [IIT '2003]

Number of compounds in X will be:

[IIT '2003]

- (A) 2 (B) 3 (C) 4 (D) 5

HC0101

11. 2-hexyne can be converted into trans-2-hexene by the action of : [IIT '2004]
- (A)  $\text{H}_2$ -Pd-BaSO<sub>4</sub> (B) Li in liq.  $\text{NH}_3$  (C)  $\text{H}_2$ -PtO<sub>2</sub> (D)  $\text{NaBH}_4$

HC0102

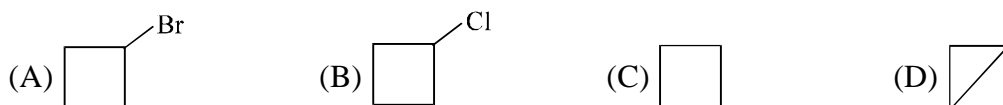
12. Cyclohexene is best prepared from cyclohexanol by which of the following: [IIT '2004]
- (A) conc.  $\text{H}_3\text{PO}_4$  (B) conc.  $\text{HCl}/\text{ZnCl}_2$  (C) conc.  $\text{HCl}$  (D) conc.  $\text{HBr}$

HC0103

13. When Phenyl Magnesium Bromide reacts with tert. butanol, which of the following is formed? [IIT '2005]
- (A) Tert. butyl methyl ether (B) Benzene  
 (C) Tert. butyl benzene (D) Phenol

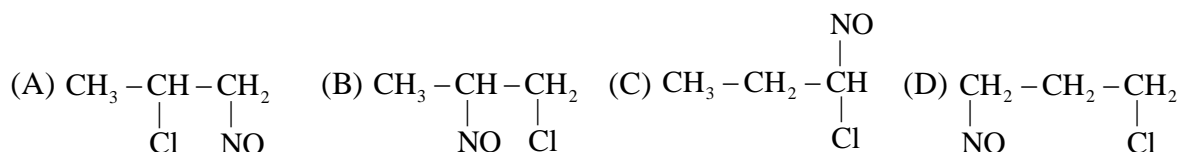
HC0104

14. 1-Bromo-3-chlorocyclobutane when treated with two equivalents of Na, in the presence of ether which of the following will be formed? [IIT '2005]



HC0105

15.  $\text{CH}_3\text{-CH=CH}_2 + \text{NOCl} \rightarrow \text{P}$   
Identify the adduct. [IIT 2006]



HC0106

16. The number of stereoisomers obtained by bromination of trans-2-butene is [IIT 2007]



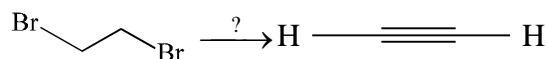
HC0107

17. The number of structural isomers for  $\text{C}_6\text{H}_{14}$  is [IIT 2007]



HC0108

18. The reagent(s) for the following conversion, [IIT 2007]



is / are

- (A) alcoholic KOH  
(B) alcoholic KOH followed by  $\text{NaNH}_2$   
(C) aqueous KOH followed by  $\text{NaNH}_2$   
(D)  $\text{Zn} / \text{CH}_3\text{OH}$

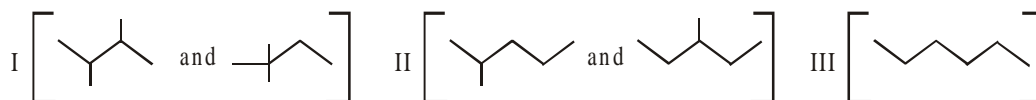
HC0109

19. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are [IIT-2010]

- (A)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$   
(B)  $\text{BrCH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$   
(C)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{C}\equiv\text{CH}$   
(D)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$

HC0110

20. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. [IIT-2014]



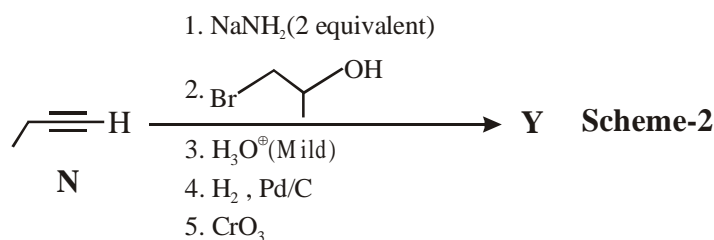
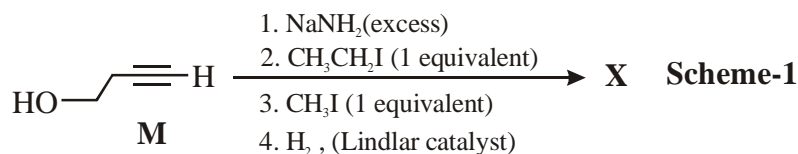
The correct order of their boiling point is

- (A) I > II > III      (B) III > II > I      (C) II > III > I      (D) III > I > II

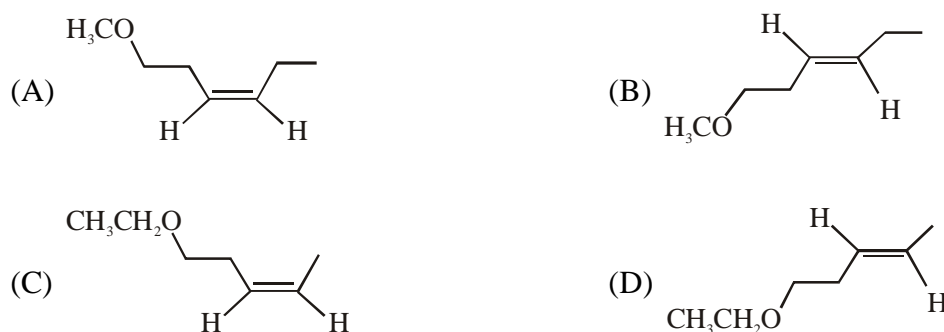
HC0111

Paragraph For Question 21 and 22

Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both the schemes. [IIT-2014]



21. The product X is -

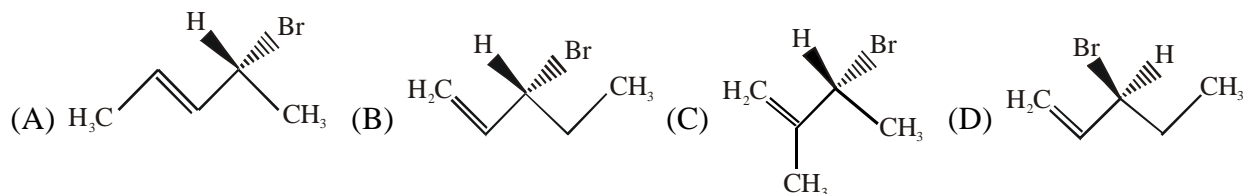


HC0112

22. The correct statement with respect to product Y is -
- (A) It gives a positive Tollens test and is a functional isomer of X
- (B) It gives a positive Tollens test and is a geometrical isomer of X
- (C) It gives a positive Iodoform test and is a functional isomer of X
- (D) It gives a positive Iodoform test and is a geometrical isomer of X

HC0113

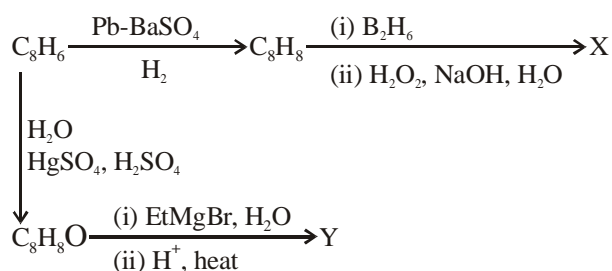
23. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are) [IIT-2015]



**Paragraph For Questions 24 and 25**

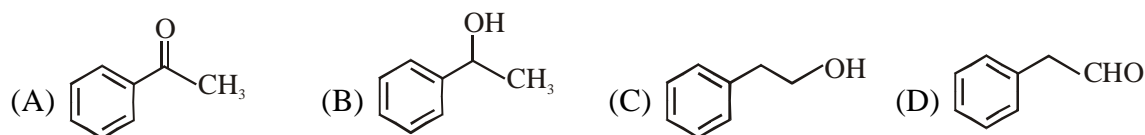
In the following reaction

[IIT-2015]



HC0114

24. Compound X is :



HC0115

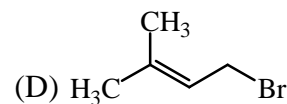
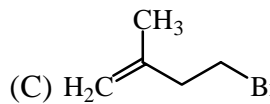
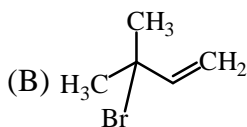
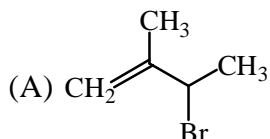
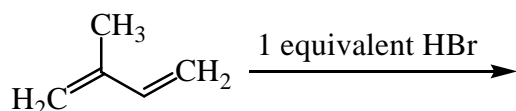
25. The major compound Y is :



HC0116

26. In the following reaction, the major product is -

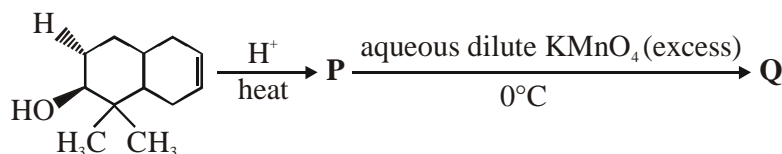
[IIT-2015]



HC0117

27. The number of hydroxyl group(s) in Q is

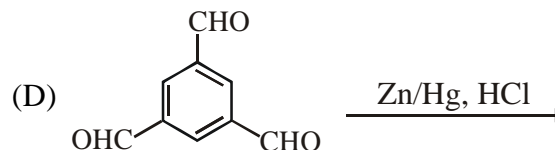
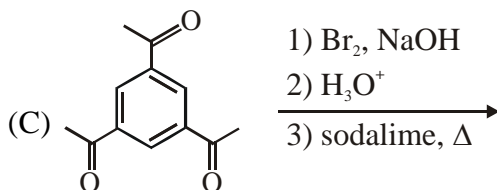
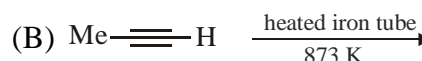
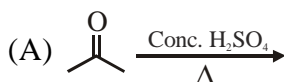
[IIT-2015]



HC0118

28. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)

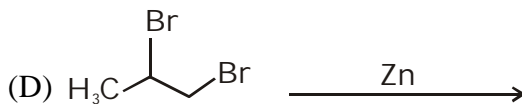
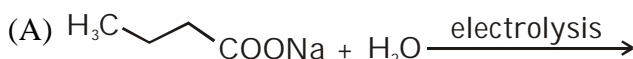
[IIT-2018]



HC0119

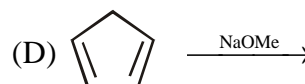
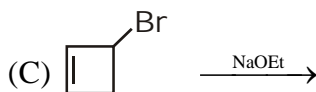
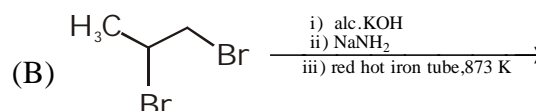
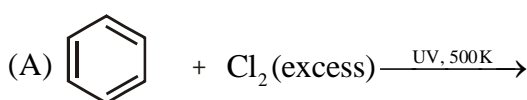
29. Which of the following reactions produce(s) propane as a major product?

[IIT-2019]



HC0120

30. Choose the correct option(s) that give(s) an aromatic compound as the major product.



[IIT-2019]

HC0121

## ANSWER-KEY

## EXERCISE # O-1

- |         |         |         |         |
|---------|---------|---------|---------|
| 1. (A)  | 2. (C)  | 3. (B)  | 4. (C)  |
| 5. (C)  | 6. (B)  | 7. (A)  | 8. (D)  |
| 9. (D)  | 10. (C) | 11. (D) | 12. (C) |
| 13. (C) | 14. (B) | 15. (C) |         |

## EXERCISE # O-2

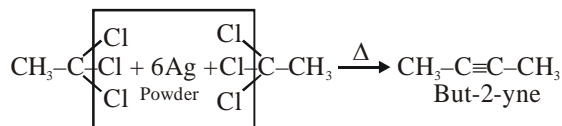
- |                                  |                                   |            |          |
|----------------------------------|-----------------------------------|------------|----------|
| 1. (B)                           | 2. (A,B,C,D)                      | 3. (A,B)   | 4. (B,C) |
| 5. (B,C,D)                       | 6. (A,C)                          | 7. (A,B,D) | 8. (A,C) |
| 9. (A)→P ; (B)→R ; (C)→S ; (D)→Q | 10. (A)→R ; (B)→S ; (C)→Q ; (D)→P |            |          |

## EXERCISE # S-1

- |                                   |                                     |             |               |
|-----------------------------------|-------------------------------------|-------------|---------------|
| 1. (D)                            | 2. (B)                              | 3. (A)      | 4. (C)        |
| 5. (B)                            | 6. (A)                              | 7. (B)      | 8. (A)        |
| 9. (B)                            | 10. (A)                             | 11. (C)     | 12. (A)       |
| 13. (C)                           | 14. (A)                             | 15. (B)     | 16. (B)       |
| 17. (D)                           | 18. (B)                             | 19. (C)     | 20. (B)       |
| 21. (A,B,C,D)                     | 22. (A,B)                           | 23. (A,B,C) | 24. (A,B,C,D) |
| 25. (D)                           | 26. (A)→S ; (B)→R ; (C)→P ; (D)→R,S |             |               |
| 27. (A)→Q ; (B)→R ; (C)→S ; (D)→P | 28. (A)→Q ; (B)→P ; (C)→S ; (D)→R   |             |               |

## EXERCISE # J-MAINS

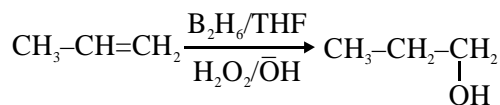
- |         |         |         |         |         |
|---------|---------|---------|---------|---------|
| 1. (1)  | 2. (4)  | 3. (1)  | 4. (1)  | 5. (2)  |
| 6. (4)  | 7. (2)  | 8. (1)  | 9. (4)  | 10. (2) |
| 11. (4) | 12. (2) | 13. (4) | 14. (4) | 15. (4) |
| 16. (3) | 17. (2) |         |         |         |
| 18. (1) |         |         |         |         |



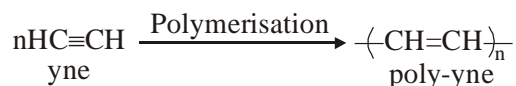
19. (3)



20. (1)



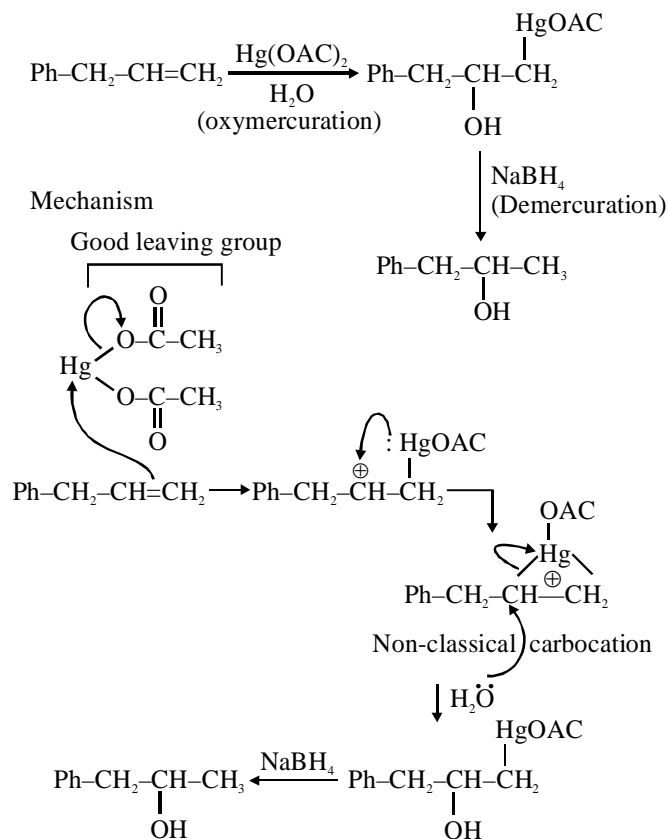
21. (2)



22. (2)

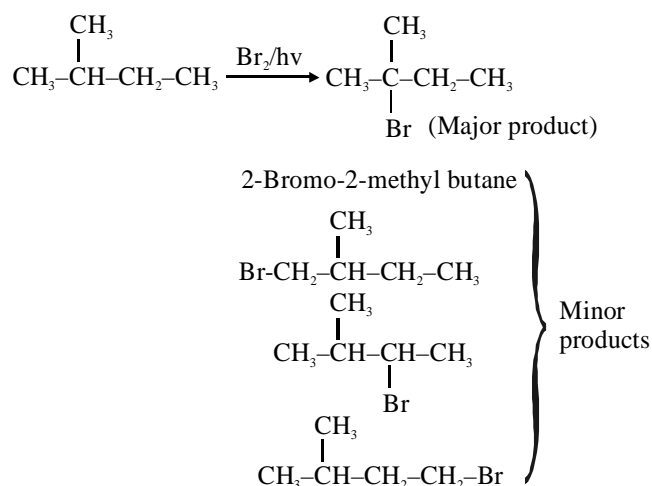
23. (4)

24. (1)



Rearrangement of carbocation formed is not possible due to formation of cyclic non-classical carbocation.

25. (1)



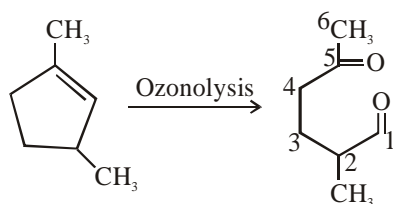
Relectivity ratio for bromination is

1° : 2° : 3° :: 1 : 82 : 1600

Hence 3° product will be major product.

26. (2)

27. (4)



5-Keto-2-Methylhexanal

28. Ans. (3)

29. Ans. (2)

30. Ans. (1)

31. Ans. (1)

32. Ans. (1)

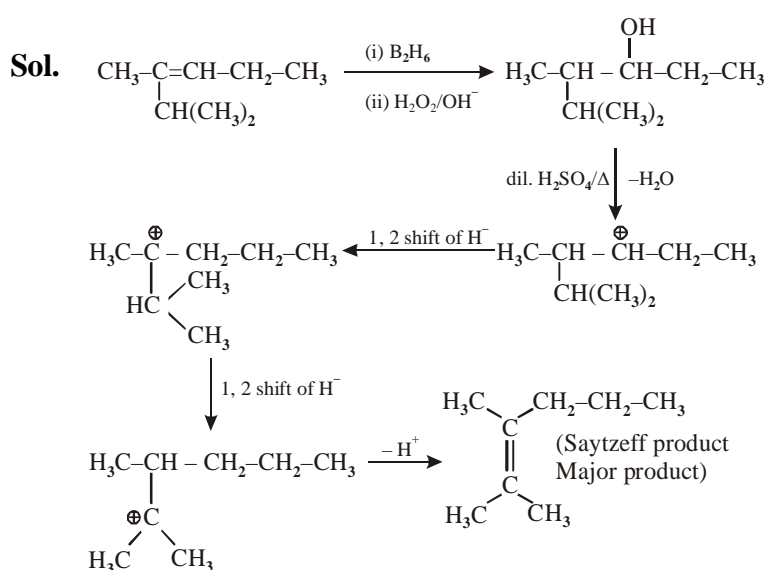
33. Ans. (4)

34. Ans. (2)

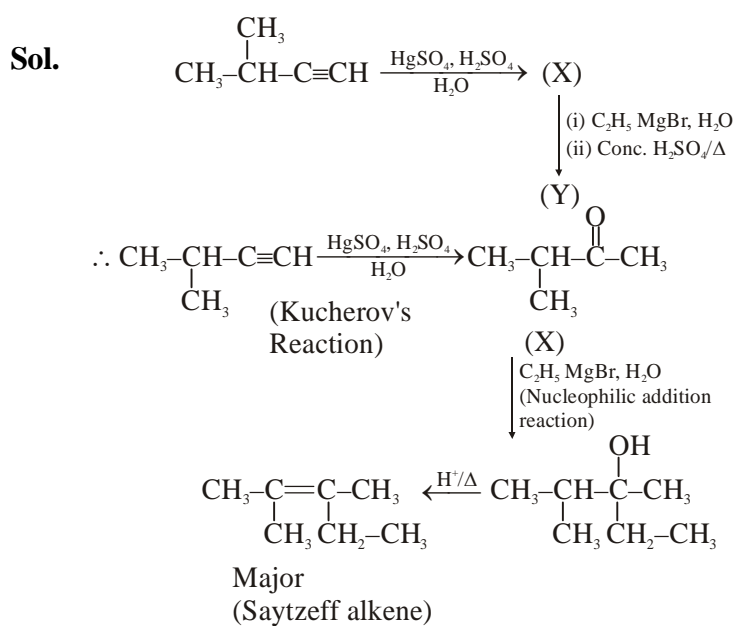
35. Ans. (3)

36. Ans. (2)

37. Ans. (1)



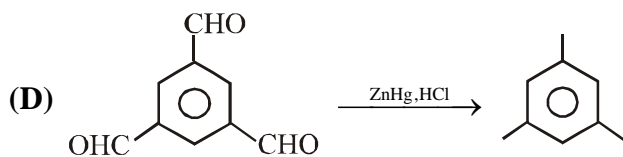
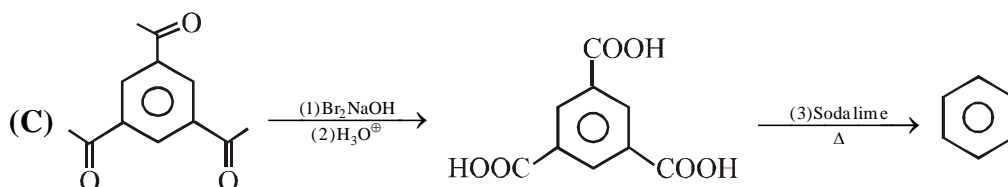
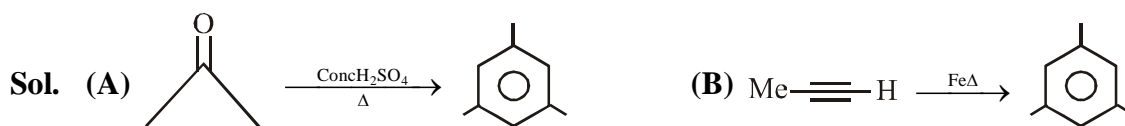
38. Ans. (3)





EXERCISE # JEE ADVANCE

- |             |         |           |         |         |
|-------------|---------|-----------|---------|---------|
| 1. (D)      | 2. (A)  | 3. (C)    | 4. (B)  | 5. (B)  |
| 6. (B)      | 7. (A)  | 8. (D)    | 9. (A)  | 10. (B) |
| 11. (B)     | 12. (A) | 13. (B)   | 14. (D) | 15. (A) |
| 16. (A)     | 17. (C) | 18. (B)   | 19. (D) | 20. (B) |
| 21. (A)     | 22. (C) | 23. (B,D) | 24. (C) | 25. (D) |
| 26. (D)     | 27. (4) |           |         |         |
| 28. (A,B,D) |         |           |         |         |



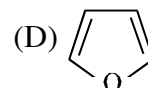
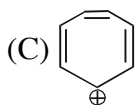
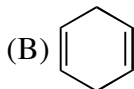
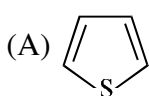
29. Ans. (B,C)

30. Ans. (B,D)

## AROMATIC COMPOUNDS

## EXERCISE # O-I

1. Which of the following is not an aromatic compound :



AH0001

2. Which of the following group is divalent:

(A) Benzoyl

(B) Benzyl

(C) Benzal

(D) p-Tolyl

AH0002

3. Benzene is a resonance hybrid mainly of two Kekule structures. Hence :

(A) Half of the molecules correspond to one structure, and half of the second structure

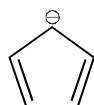
(B) At low temperatures benzene can be separated into two structures

(C) Two structures make equal contribution to resonance hybrid

(D) An individual benzene molecule changes back and forth between two structures

AH0003

4. How many  $\pi$  electron are there in the following species :



(A) 2

(B) 4

(C) 6

(D) 8

AH0004

5. The number of benzylic hydrogen atoms in ethylbenzene is:

(A) 3

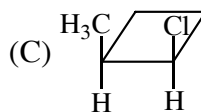
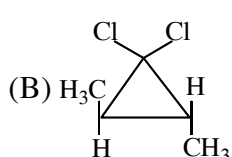
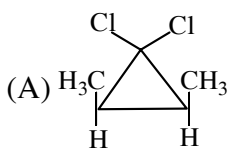
(B) 5

(C) 2

(D) 7


AH0005

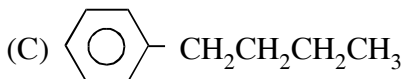
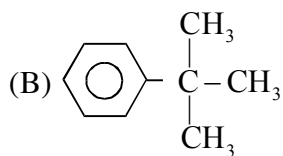
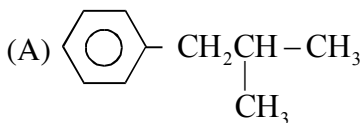
6. Trans-Butene-2  $\xrightarrow[\text{Solvent}]{\text{CHCl}_3 / \text{KOH}}$  Product



(D) Both (A) &amp; (B)

AH0006

7.  +  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{AlCl}_3}$  hydrocarbon (X) major product X is:



(D) None is correct

AH0007

8. In the sulphonation, acetylation and formylation of benzene the group of effective electrophiles would be :



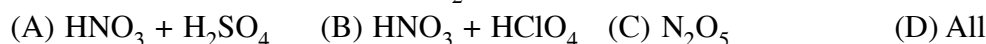
AH0008

9. o/p ratio in highest for nitration of which of the following compound ?



AH0009

10. Which can be used to generate  $\text{NO}_2^+$  in nitration of benzene ring



AH0010

11. For the electrophilic substitution reaction involving nitration, which of the following sequence regarding the rate of reaction is true?

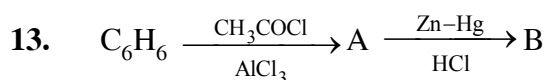


AH0011

12. For the electrophilic substitution reaction involving sulphonation, which of the following sequence regarding the rate of reaction is true?



AH0012

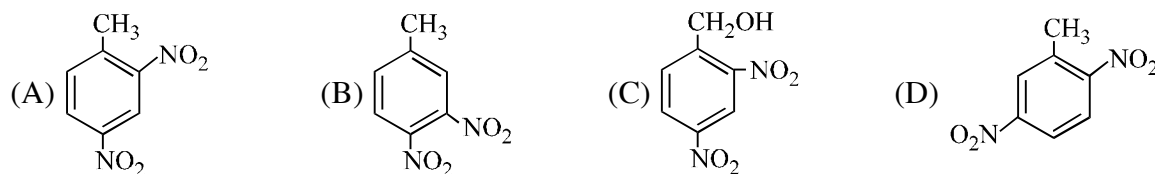


The end product in the above sequence is:



AH0013

14. p-Nitrotoluene on further nitration gives:



AH0014

15. Reaction of  $\text{SO}_3$  is easier in:



AH0015

16. Which order is correct for the decreasing reactivity to ring monobromination of the following compounds:

(I)  $C_6H_5CH_3$       (II)  $C_6H_5COOH$       (III)  $C_6H_6$       (IV)  $C_6H_5NO_2$   
 (A) I > II > III > IV      (B) I > III > II > IV      (C) II > III > IV > I      (D) III > I > II > IV

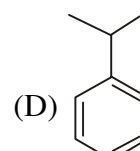
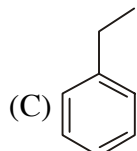
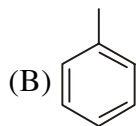
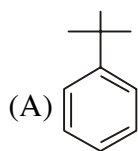
AH0016

17. The highest yield of m-product is possible by the electrophilic substitution of the following:

(A)  $C_6H_5CH_3$       (B)  $C_6H_5CH_2COOC_2H_5$   
 (C)  $C_6H_5CH(COOC_2H_5)_2$       (D)  $C_6H_5C(COOC_2H_5)_3$

AH0017

18. Which of the following will undergo sulphonation at fastest rate ?



AH0018

19. Aniline under acidic medium, when chlorinated, produces:

(A) o-Chloro aniline      (B) m-Chloro aniline  
 (C) p-Chloro aniline      (D) Mixture of ortho and para-chloro aniline

AH0019

20. When sulphonilic acid ( $p-H_2NC_6H_4SO_3H$ ) is treated with excess of bromine water, the product is:

(A) Tribromo product      (B) Dibromo product  
 (C) Monobromo product      (D) Tetrebromo product

AH0020

21. In a reaction of  $C_6H_5Y$ , the major product (>60%) is m-isomer, so the group Y is:

(A)  $-COOH$       (B)  $-Cl$       (C)  $-OH$       (D)  $-NH_2$

AH0021

22. An aromatic compound of molecular formula  $C_6H_4Br_2$  was nitrated then three isomers of formula  $C_6H_3Br_2NO_2$  were obtained. The original compound is:

(A) o-Dibromobenzene      (B) m-Dibromobenzene  
 (C) p-Dibromobenzene      (D) Both A & C

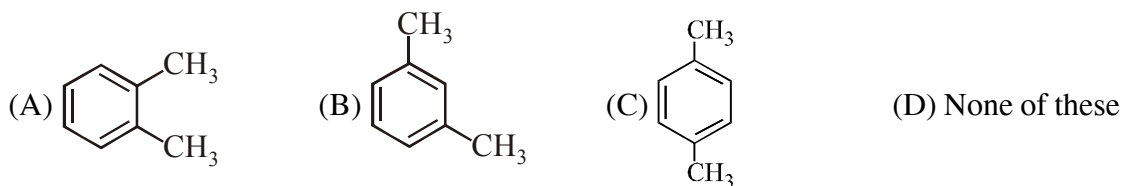
AH0022

23. Which of the following is most reactive towards sulphonation?

(A) m-Xylene      (B) o-Xylene      (C) Toluene      (D) p-Xylene

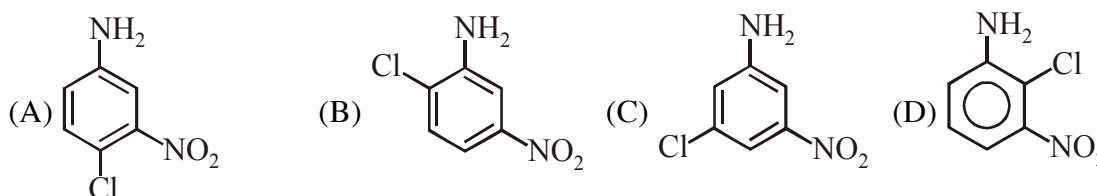
AH0023

24. Ring nitration of dimethyl benzene results in the formation of only one nitro dimethyl benzene. The dimethyl benzene is:



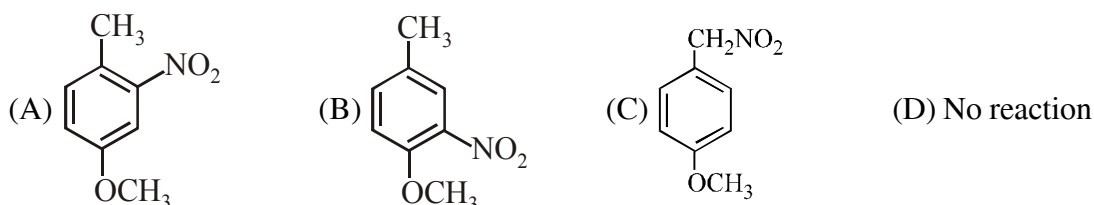
AH0024

25. If meta-nitroaniline is chlorinated, the major product is:



AH0025

26. If p-methoxy toluene is nitrated, the major product is:



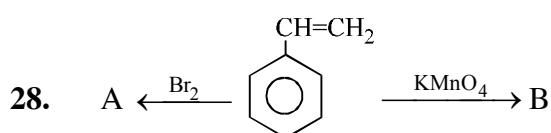
AH0026

27.  $C_6H_5CH_3 \xrightarrow{CrO_2Cl_2} A \xrightarrow{H_2O} B$

The functional group present in B and name of the reaction would be

- (A)  $-CHO$ , Gattermann aldehyde synthesis (B)  $-CHO$ , Etard reaction  
(C)  $-COCH_3$ , Friedel Crafts reaction (D)  $-CHO$ , Oxo reaction

AH0027

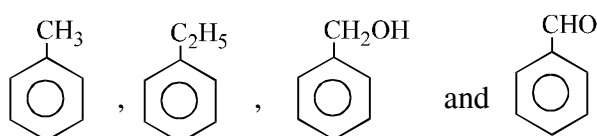


Compound A and B respectively are:

- (A) o-Bromostyrene, benzoic acid (B) p-Bromostyrene, benzaldehyde  
(C) m-Bromostyrene, benzaldehyde (D) Styrene dibromide, benzoic acid

AH0028

29. If the mixture of the following four aromatic compounds on oxidation by strong oxidising agent gives:



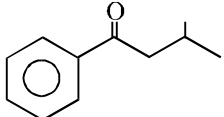
- (A) Mixture of  $C_6H_5CH_2OH + C_6H_5COOH$  (B) Mixture of  $C_6H_5CHO + C_6H_5COOH$   
(C) Only  $C_6H_5COOH$  (D) None of the above

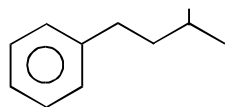
AH0029

30. Which of the following is/are produced when a mixture of benzene vapour and oxygen is passed over  $V_2O_5$  catalyst at 775 K?

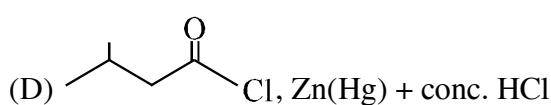
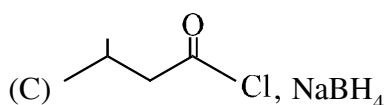
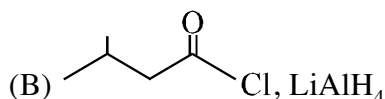
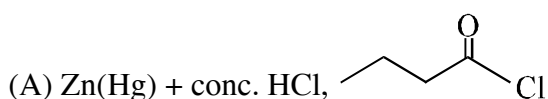
- (A) Oxalic acid      (B) Glyoxal      (C) Fumaric acid      (D) Maleic anhydride

AH0030

31. Benzene on reaction with 'A' forms  which on reaction with 'B' forms

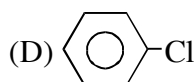
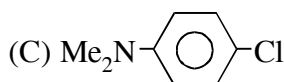
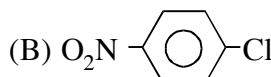
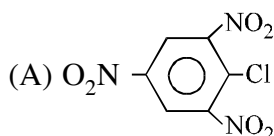


'A' and 'B' are:



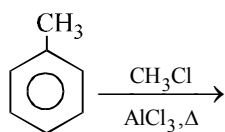
AH0031

32. Which chloroderivative of benzene among the following would undergo-hydrolysis most readily with  $NaOH$  to furnish the corresponding hydroxy derivative.



AH0032

33. Major product of this reaction will be :



- (A) o-Xylene      (B) p-Xylene      (C) Both      (D) m-Xylene

AH0033

34. For preparing monoalkyl benzene, acylation process is preferred than direct alkylation because

- (A) In alkylation, a poisonous gas is evolved  
 (B) In alkylation, large amount of heat is evolved  
 (C) In alkylation, polyalkylated product is formed  
 (D) Alkylation is very costly

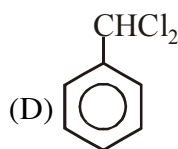
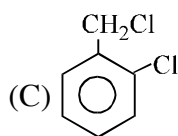
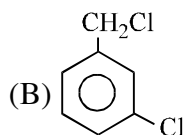
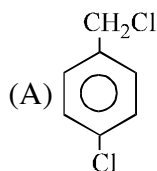
AH0034

35. Phenol and ethanol are distinguished by the reaction with


- (A) Red litmus      (B)  $NaHCO_3$       (C)  $FeCl_3$       (D) Na

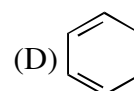
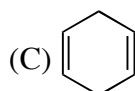
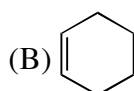
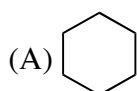
AH0035

36. An aromatic compound 'A'  $C_7H_6Cl_2$ , gives AgCl on bonding with alcoholic  $AgNO_3$  solution, and yields  $C_7H_7OCl$  on treatment with sodium hydroxide. 'A' on oxidation gives a mono chlorobenzoic acid which affords only one mononitro derivative. The compound A is:

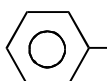


AH0036

37.  +  $H_2 \xrightarrow[\text{High pressure}]{Ni, \text{ high temp.}}$  (A). Which of the following can be isolated as the product of this reaction.



AH0037

38. Chloral +   $\xrightarrow{\text{Conc. } H_2SO_4}$  product. The product is:

(A) Lindane

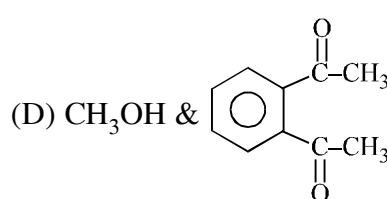
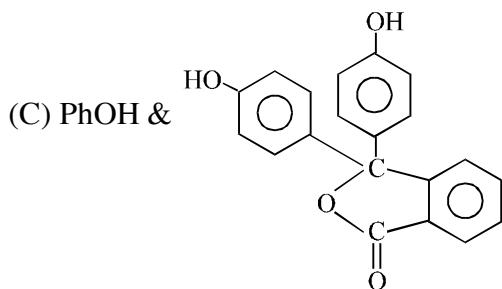
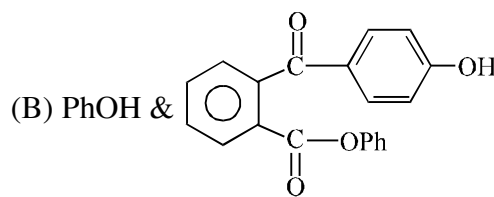
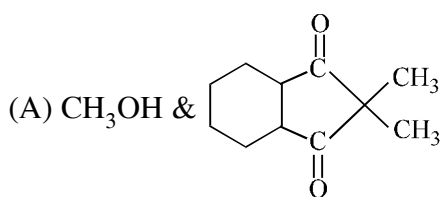
(B) DDT

(C) Teflon

(D) Ethanep perchlorate

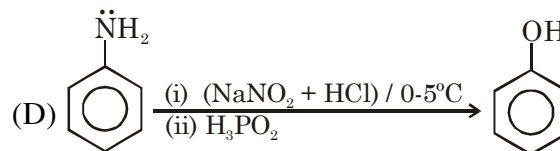
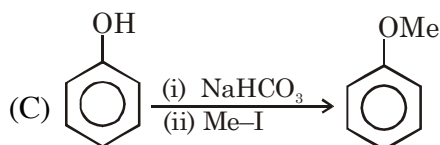
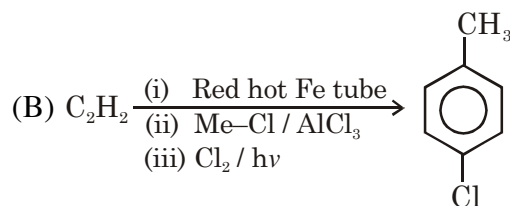
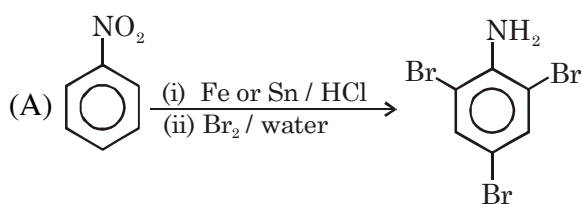
AH0038

39. Acetophenone  $\xrightarrow{HCO_3H}$  A  $\xrightarrow{H_3O^+}$  B + C  $\xrightarrow[H^+]{\text{Phthalic Anhydride}}$  Indicator (D) ; C & D are

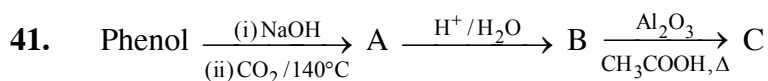


AH0039

40. Select the reaction giving correct major product :



AH0040

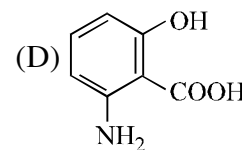
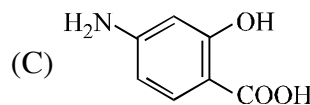
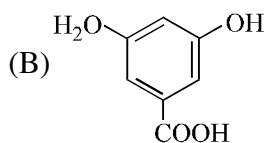
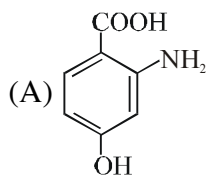


In this reaction, the end product C is:

- (A) Salicylaldehyde (B) Salicylic acid (C) Phenyl acetate (D) Aspirin

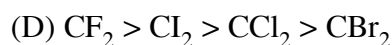
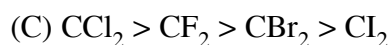
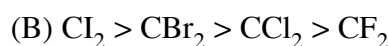
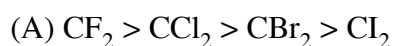
AH0041

42. m-Aminophenol on treatment with NaOH and CO<sub>2</sub> gives which of the following as major product?



AH0042

43. Stability order of following singlet halocarbene is



AH0043



## EXERCISE # O-II

1. In which of the following reaction t-butylbenzene is formed:

- (A) Benzene + iso-butyl chloride,  $\text{AlCl}_3$       (B) Benzene +  $(\text{CH}_3)_2\text{C}=\text{CH}_2 \xrightarrow{\text{BF}_3 \cdot \text{HF}}$   
 (C) Benzene + t-butyl alcohol  $\xrightarrow{\text{H}_2\text{SO}_4}$       (D) Benzene +  $(\text{CH}_3)_2\text{C}=\text{CH}_2 \xrightarrow{\text{AlCl}_3}$

AH0044

2. The replacement of a hydrogen atom in benzene by alkyl group can be brought about with the following reagents :

- (A) Alkyl chloride and  $\text{AlCl}_3$       (B) Alkene and  $\text{AlCl}_3$   
 (C) Alkanol and alkali      (D) Alkanol and acid

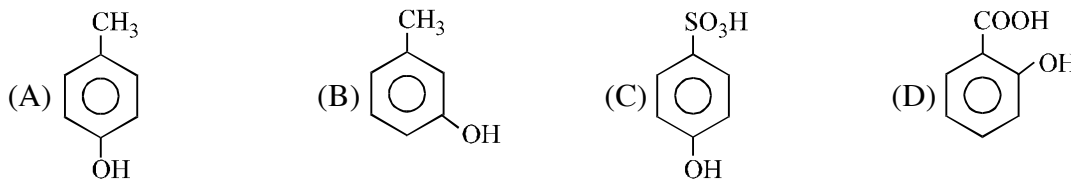
AH0045

3. Benzene reacts with n-propyl chloride in the presence of anhydrous  $\text{AlCl}_3$  to give predominantly:

- (A) n-Propylbenzene      (B) Isopropylbenzene  
 (C) 3-Propyl-1-chlorobenzene      (D) Cumene

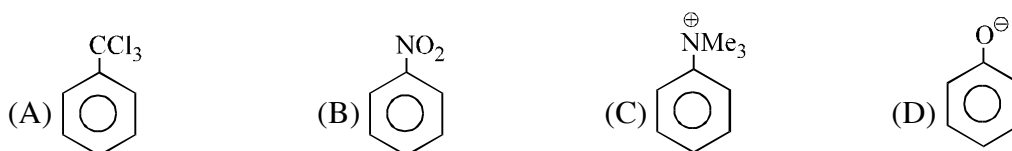
AH0046

4. The structure of the compound that gives a tribromo derivative on treatment with bromine water is:



AH0047

5. Electrophilic attack of  $\text{NO}_2^\oplus$  at meta position is observed in:



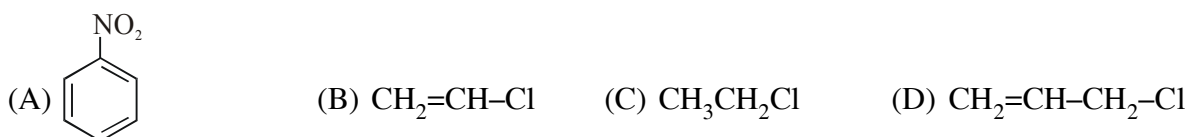
AH0048

6. The good method for converting benzene into n-propyl benzene is:

- (A)  $\text{C}_6\text{H}_6 + \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{Anhyd. AlCl}_3$   
 (B)  $\text{C}_6\text{H}_6 + \text{CH}_3\text{CH}_2\text{COCl} + \text{Anhyd. AlCl}_3$  and then treatment with  $\text{Zn/Hg/HCl}$   
 (C)  $\text{C}_6\text{H}_6 + \text{CH}_3\text{CH}_2\text{COCl} + \text{Anhyd. AlCl}_3$  and then treatment with  $\text{H}_2 \text{ Ni}$   
 (D)  $\text{C}_6\text{H}_6 + \text{Anhyd. AlCl}_3 + \text{cyclopropane}$

AH0049

7. Which of the following can be used as reagent in Friedel Crafts reaction?



AH0050

8. Of the species PhSR,  $\text{PhSR}=\text{O}$ ,  $\text{PhSR}=\text{O}=\text{O}$  and  $\text{Ph}-\text{S}(=\text{O})_2-\text{OR}$  the meta-substituted product is obtained from

- (A) PhSR                      (B)  $\text{PhSR}=\text{O}$                       (C)  $\text{PhSR}=\text{O}=\text{O}$                       (D)  $\text{Ph}-\text{S}(=\text{O})_2-\text{OR}$

AH0051

9. Amongst the following, the moderately activating group is

- (A)  $-\text{NHR}$                       (B)  $-\text{NHCOCH}_3$                       (C)  $-\text{O}-\overset{\text{R}}{\parallel}{\text{C}}-\text{R}$                       (D)  $-\text{CH}_3$

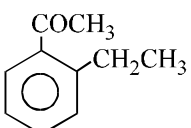
AH0052

10. False statement is / are :

- (A) Although benzene contains three double bonds, normally it does not undergo addition reaction.  
 (B) m-Chlorobromobenzene is an isomer of m-bromochlorobenzene.  
 (C) In benzene, carbon uses all the three p orbitals for hybridization.  
 (D) An electron donating substituent in benzene orients the incoming electrophilic group to the meta position.



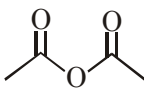
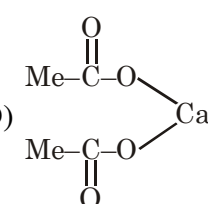
AH0053

11. Benzoic acid may be prepared by the oxidation of:

- (A)                       (B)   
 (C)                       (D) 

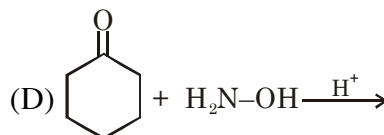
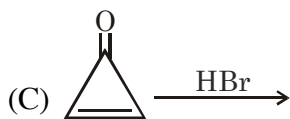
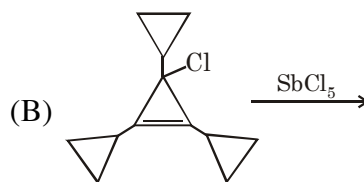
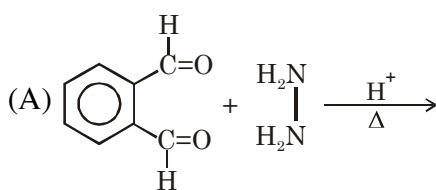
AH0054

12. Identify reactions give ketone product ?

- (A)  +  $\text{R}-\text{C}(\text{OEt})_3 \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{BF}_3}$
- (B)  +   $\xrightarrow[\text{AlCl}_3]{\text{Anhydrous}}$
- (C)  $\text{PhMgBr} + \text{Me}-\text{C}\equiv\text{N} \xrightarrow{\text{H}_3\text{O}^+}$
- (D)   $\xrightarrow[\Delta]{\text{Dry distillation}}$

AH0055

13. Which of the following reaction(s) will give aromatic product ?



AH0056

14. Which of the following statements is/are not true?

- (A) All ortho-para directing groups activates the ring towards electrophilic substitution.  
 (B) Halobenzene is ortho para directing but deactivating in nature  
 (C) All meta-directing groups have  $\pi$ -bond on the atom directly attached to the ring  
 (D) All meta directing groups are deactivating.

AH0057

15. Which of the following is not an ortho-para directing group?

- (A)  $\text{CF}_3$                       (B)  $\text{CCl}_3$                       (C)  $-\text{CH}=\text{CH}-\text{COOH}$     (D)  $-\text{N}\equiv\text{C}$

AH0058

16. Which of the following does not gives Friedel-Crafts reaction?



AH0059

17. Which of the following reactions of benzene proves the presence of three carbon-carbon double bonds in it :

- (A) Formation of a triozonide  
 (B) Hydrogenation of benzene to cyclohexane  
 (C) Formation of  $\text{C}_6\text{H}_6\text{Cl}_6$  by addition of chlorine  
 (D) Formation of nitrobenzene on heating benzene with a mixture of concentrated nitric acid and sulphuric acid

AH0060

18. Which of the following are classified as aromatic ?

- (A) 1, 2, 3-Triphenylcyclopropenium cation    (B) Cyclooctatetraenyl dianion  
 (C) Azulene    (D) Annulene [10]

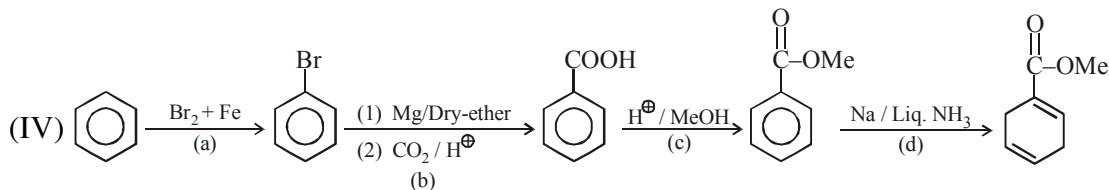
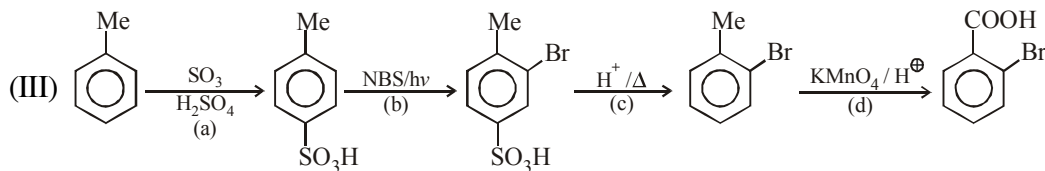
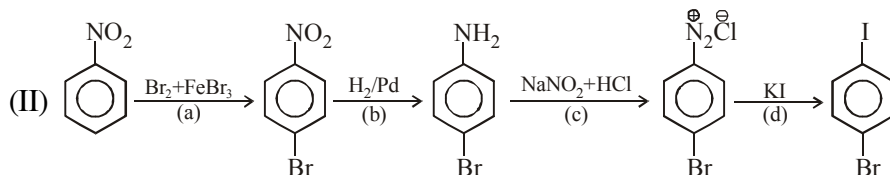
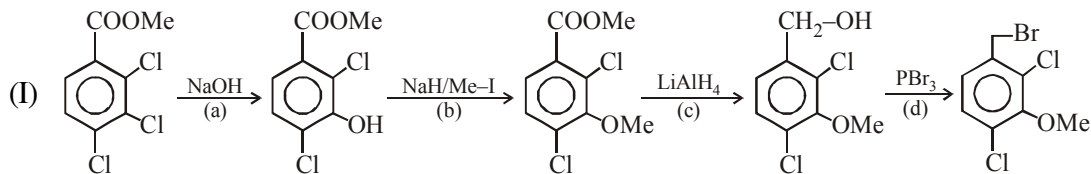
AH0061

19. Which of the following is/are name of 1,2,3,4,5,6 - hexachloro cyclohexane :

- (A) Lindane (B) Gammexane (C) 666 (D) BHC

AH0062

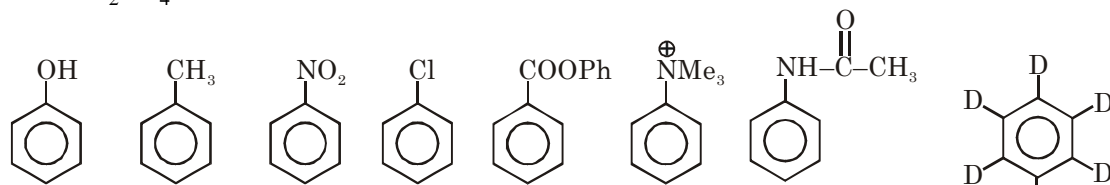
20. Among the following reaction sequences identify incorrect step :



- (A) I-a ; II - b ; III - c ; IV - d (B) I-b ; II - a ; III - d ; IV - d  
(C) I-a ; II - a ; III - b ; IV - d (D) I-b ; II - a ; III - d ; IV - c

AH0063

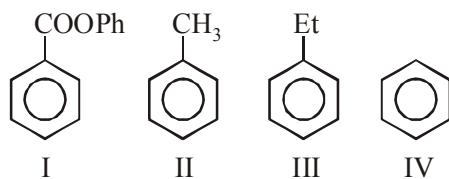
21. How many of following compounds are less reactive than benzene for sulphonation by conc.  $H_2SO_4$  :



- (A) 2 (B) 4 (C) 6 (D) 8

AH0064

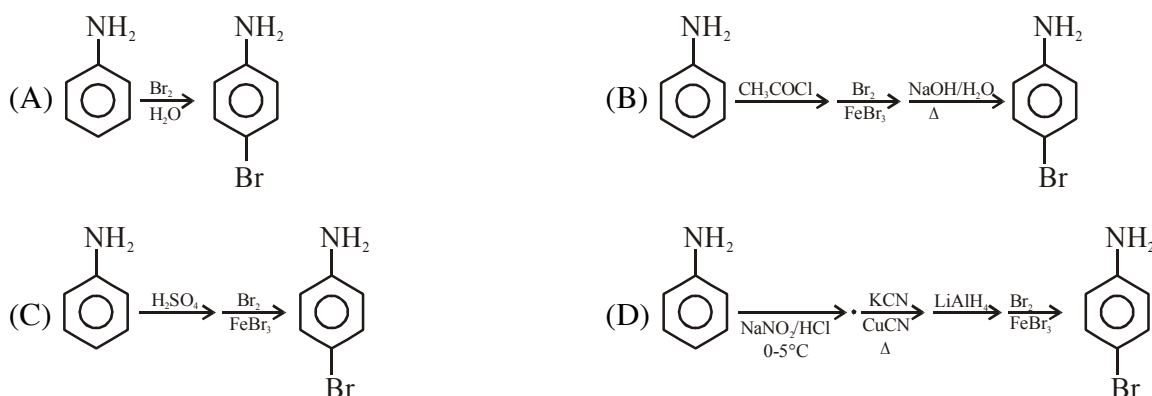
22. Decide the correct order of reactivity of following compounds towards halogenation with  $(Cl_2 + AlCl_3)$ .



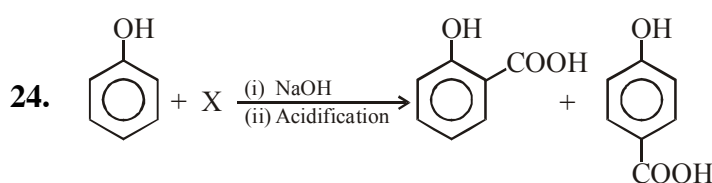
- (A) I > II > III > IV (B) II > III > IV > I (C) III > II > IV > I (D) II > III > I > IV

AH0065

23 Which of the following method(s) is/are not used to prepare p-bromo aniline as major product :



AH0066

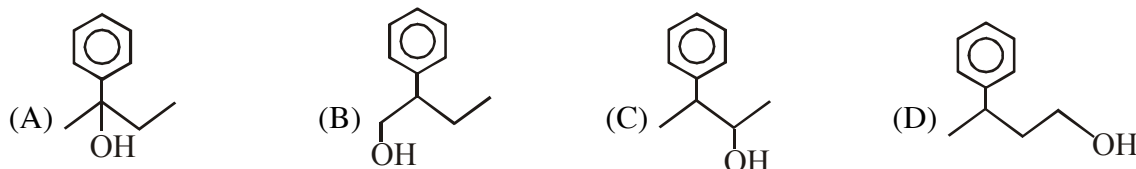
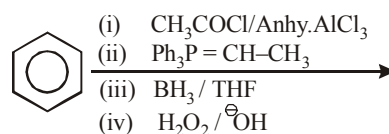


X is/are -

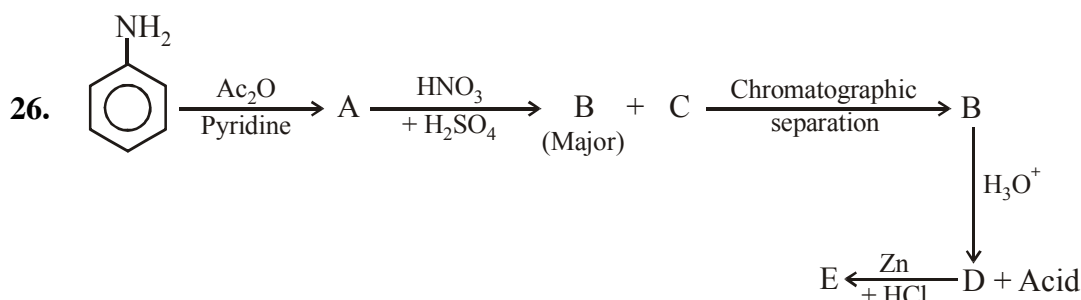
- (A)  $\text{CHCl}_3$       (B)  $\text{CCl}_4$       (C)  $\text{CO}_2$       (D)  $\text{HCOOH}$

AH0067

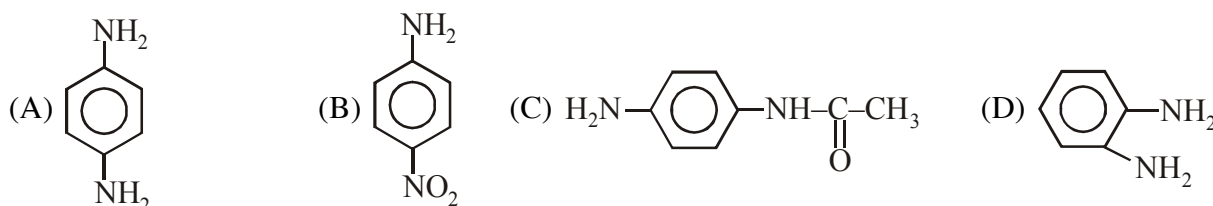
25. Which product is/are not obtained in following reaction.



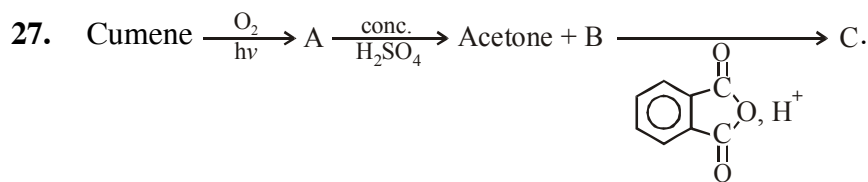
AH0068



E is :



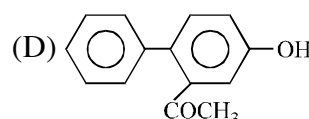
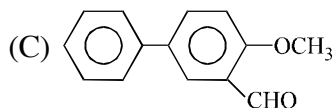
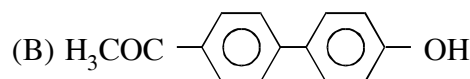
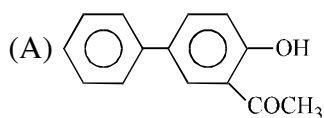
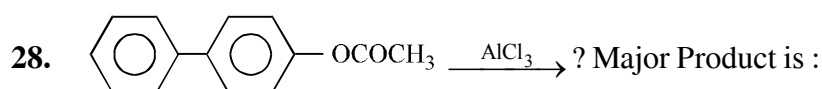
AH0069



Identify correct statement :

- (A) Product C is phenolphthalein indicator
- (B) Product B gives CO<sub>2</sub> effervescence with NaHCO<sub>3</sub>
- (C) Product A formation involves carbocation intermediate
- (D) Product B gives no colour with neutral FeCl<sub>3</sub>

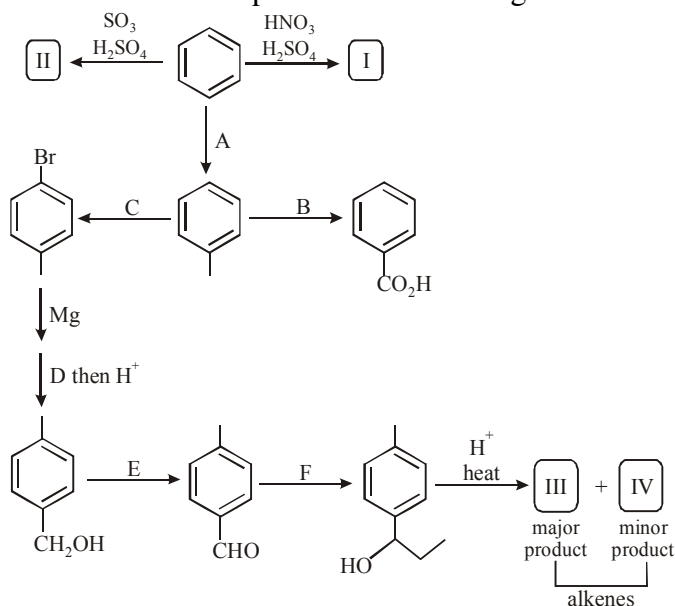
AH0070



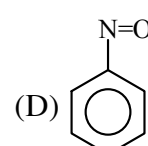
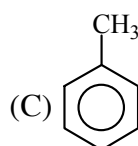
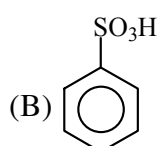
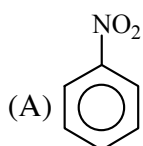
AH0071

Paragraph for 29 to 30

Identify reagent used and intermediate products in following conversion.

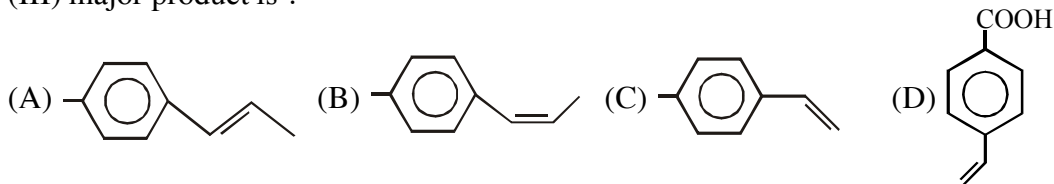


29. Identify II product -



AH0072

30. (III) major product is ?



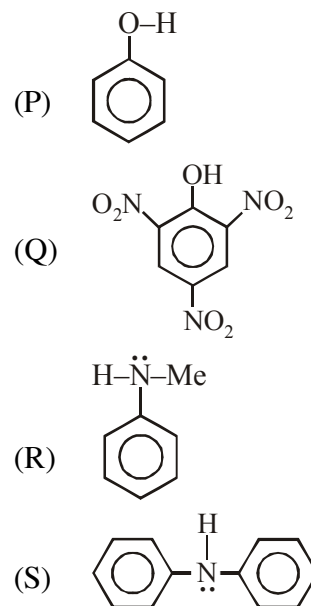
AH0072

31. Match the following :

**Column-I**  
(Properties)

- (A)  $\text{CO}_2 \uparrow$  is evolved from  $\text{NaHCO}_3$
- (B) Gives libermann nitroso test
- (C) Gives yellow oily liquid with  $\text{NaNO}_2 + \text{HCl}$
- (D) Evolve a colourless gas with active metals

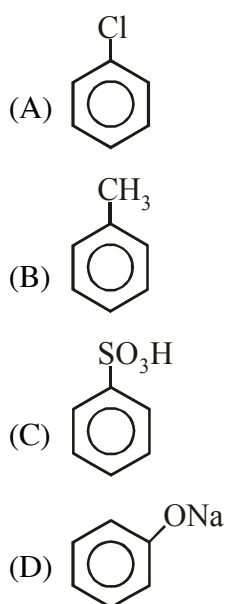
**Column-II**  
(Compound)



AH0073

32. Match the following :

**Column I**  
(Compound)



**Column II**  
(Properties)

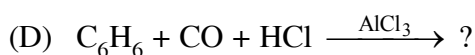
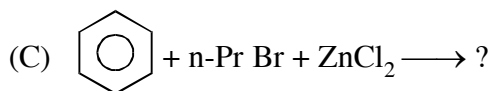
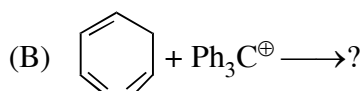
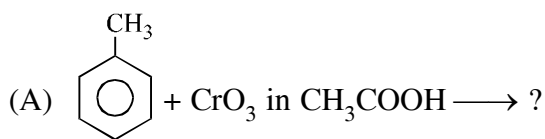
- (P) o-p directing
- (Q) m-directing
- (R) Activating towards electrophile
- (S) Deactivating towards electrophile

AH0074

33. Match the column :

Column I

(Reaction)



Column II

(Product & its property)

(P) Tropylium ion

(Q) Benzaldehyde

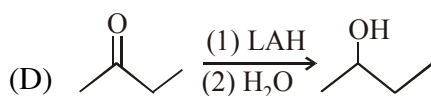
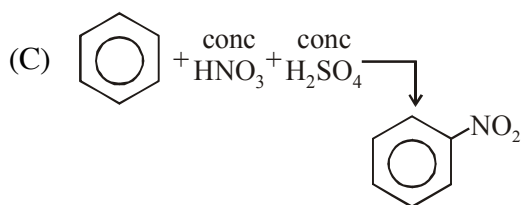
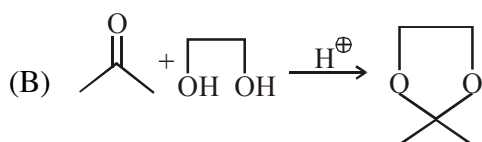
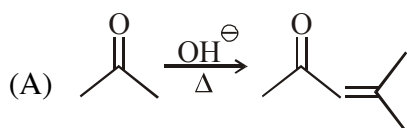
(R) Product can oxidise by KMnO<sub>4</sub>/H<sup>+</sup>

(S) Aromatic product obtained

AH0075

34. Column - I

(Reactions)



Column - II

(Intermediate formed or type of reaction)

(P) Product obtained as racemic mixture

(Q) Substitution reaction

(R) Nu<sup>⊖</sup> Addition takes place during reaction

(S) Carbocation intermediate

(T) Carbanion intermediate

AH0076

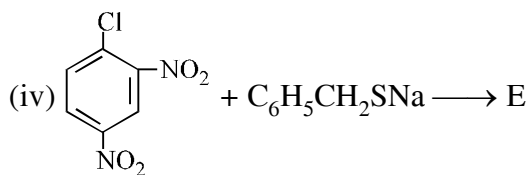
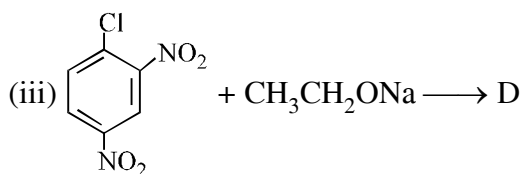
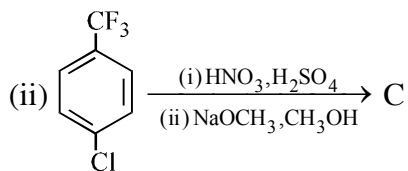
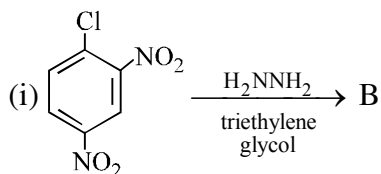


## EXERCISE # S-I

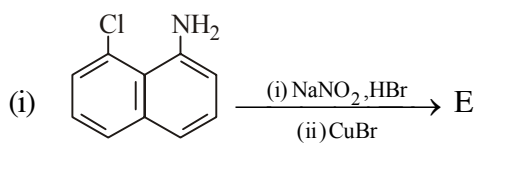
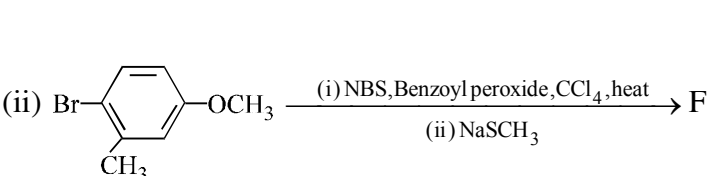
1. Write the most stable resonating structure for the cyclohexadienyl anion formed by reaction of methoxide ion with o-fluoronitrobenzene.

AH0077

2. Write the principal organic product in each of the following reactions:



AH0078

3. (i)  (ii) 

AH0079

4. Reaction of 1,2,3-tribromo-5-nitrobenzene with sodium ethoxide in ethanol gave a single product,  $C_8H_7Br_2NO_3$ , in quantitative yield. Suggest a reasonable structure for this compound.

AH0080

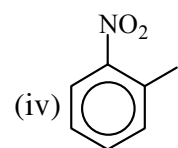
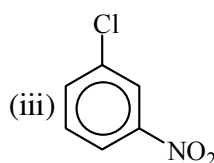
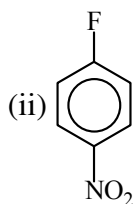
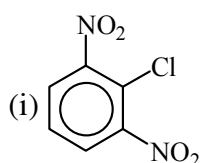
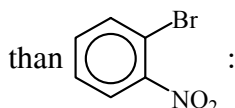
5. Compare the given characteristics of aniline and cyclohexanamine :

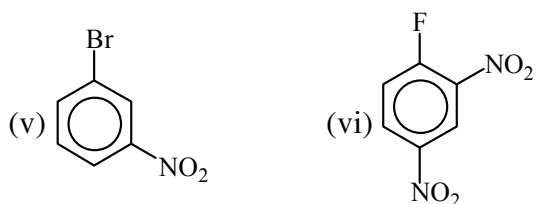
- Both are primary amine
- Both can be acylated by  $RCOCl$
- Both reacts with  $CHCl_3/KOH$
- Both reacts with  $NaNO_2 + HCl$  at  $0-5^\circ C$
- Both reacts with  $PhSO_2Cl$  to give a compound which is soluble in  $KOH$
- Both gives coupling reaction with phenol
- Both gives electrophilic substitution reaction

How many of the given characteristics are correct?

AH0081

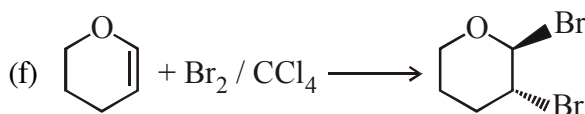
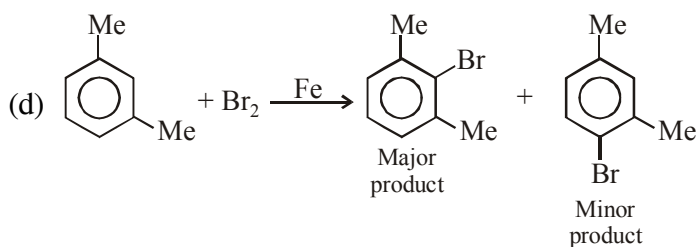
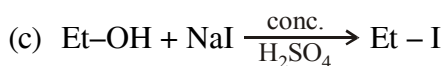
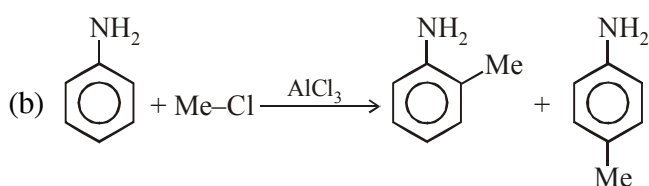
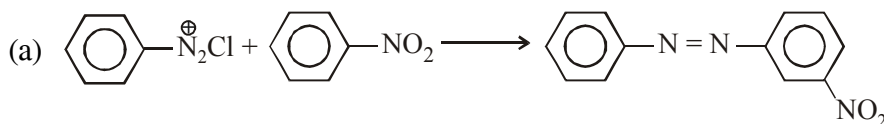
6. Number of compounds which can show faster rate of nucleophilic substitution of halogen



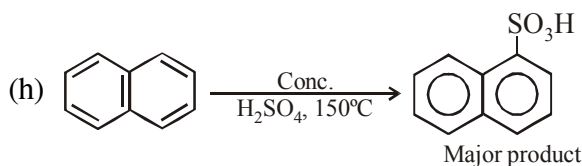
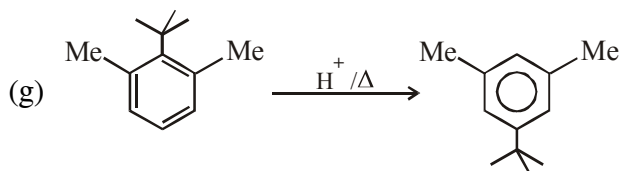


AH0082

7. Identify total number of reactions incorrectly match with its product ?



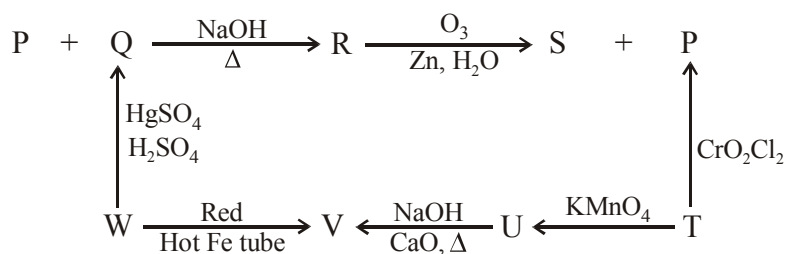
100 % product [Stereo specific reactions] / 100 % उत्पाद [ त्रिविम् विशिष्ट अभिक्रिया ]



AH0083

## Paragraph for No. 8 to 9

For given reaction sequence molecular formula for compound 'U' is  $C_7H_6O_2$  & P gives negative Fehling test.

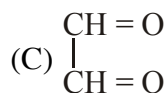
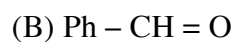
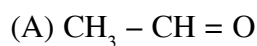


8. Compound which is not a hydrocarbon

- (A) W                      (B) R                      (C) T                      (D) V

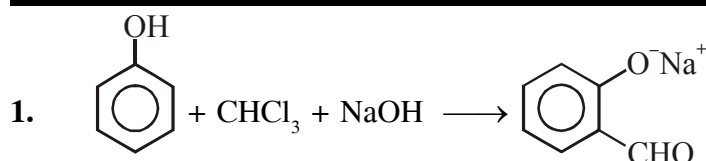
AH0084

9. Compound S is :



AH0084

EXERCISE # (MAINS)



The electrophile involved in the above reaction is

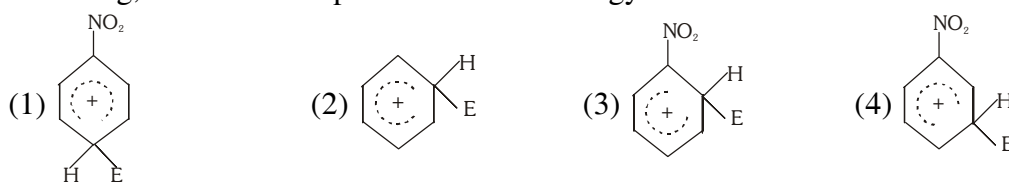
[AIIEE-2006]

- (1) dichlorocarbene ( $:\text{CCl}_2$ ) (2) trichloromethyl anion ( $\ominus\text{CCl}_3$ )  
 (3) formyl cation ( $\oplus\text{CHO}$ ) (4) dichloromethyl cation ( $\oplus\text{CHCl}_2$ )

AH0085

2. The electrophile,  $\text{E}^\oplus$  attacks the benzene ring to generate the intermediate  $\sigma$ -complex. Of the following, which  $\sigma$ -complex is of lowest energy ?

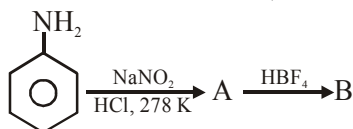
[AIIEE-2008]



AH0086

3. In the chemical reactions,

[AIIEE-2010]

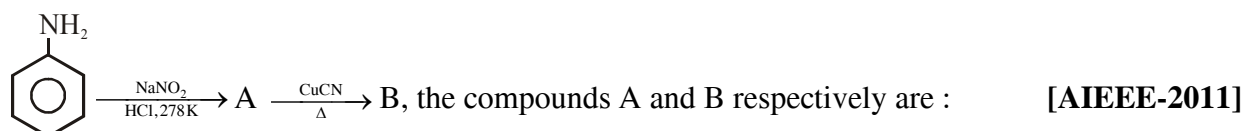


the compounds 'A' and 'B' respectively are :-

- (1) Nitrobenzene and chlorobenzene (2) Nitrobenzene and fluorobenzene  
 (3) Phenol and benzene (4) Benzene diazonium chloride and fluorobenzene

AH0087

4. In the chemical reactions

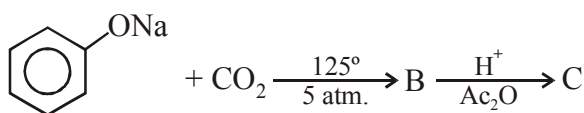


- (1) Fluorobenzene and phenol (2) Benzene diazonium chloride and benzonitrile  
 (3) Nitrobenzene and chlorobenzene (4) Phenol and bromobenzene

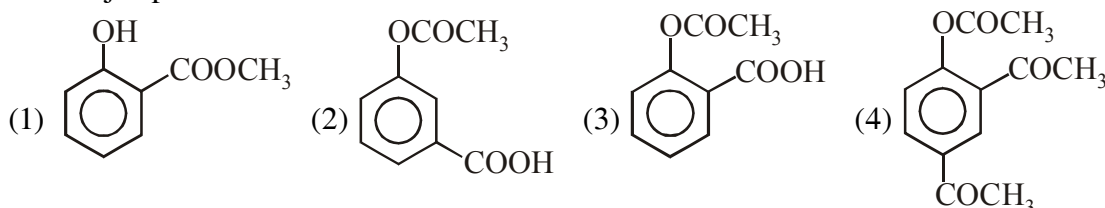
AH0088

5. Sodium phenoxide when heated with  $\text{CO}_2$  under pressure at  $125^\circ\text{C}$  yields a product which on acetylation produces C.

[JEE(Main)-2014]



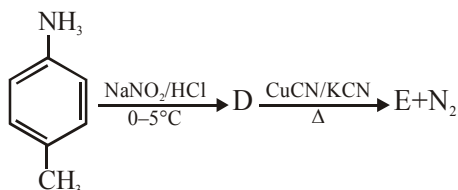
The major product C would be :



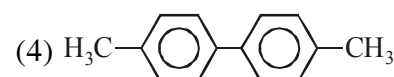
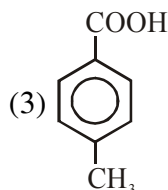
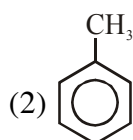
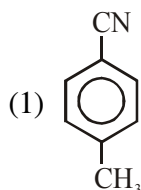
AH0089

6. In the reaction

[IIT-2015]



the product E is :-



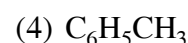
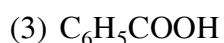
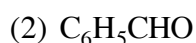
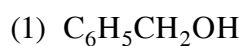
AH0090

[IIT 2015]

7. In the following sequence of reactions :



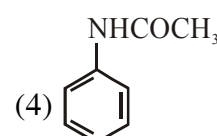
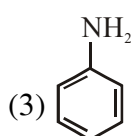
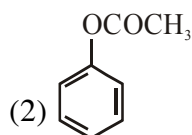
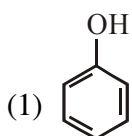
the product C is :-



AH0091

8. Which of the following compounds will significant amount of meta product during mono-nitration reaction ?

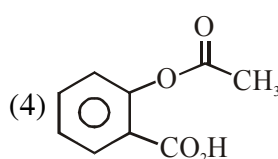
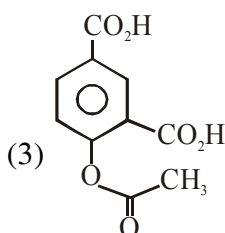
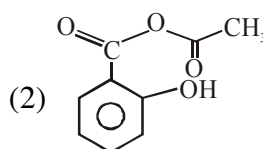
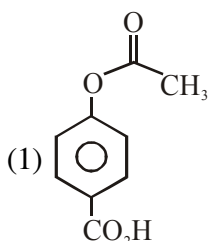
[JEE(Main)-2017]



AH0092

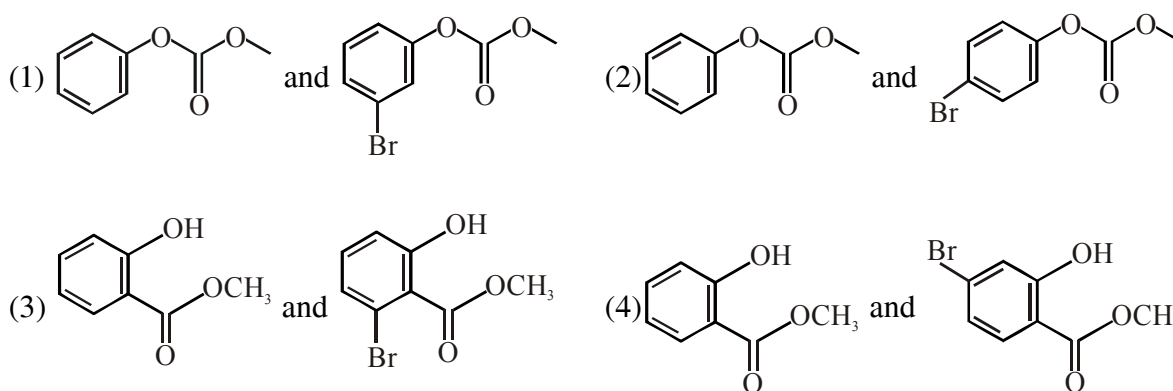
9. Phenol on treatment with  $\text{CO}_2$  in the presence of  $\text{NaOH}$  followed by acidification produces compound X as the major product. X on treatment with  $(\text{CH}_3\text{CO})_2\text{O}$  in the presence of catalytic amount of  $\text{H}_2\text{SO}_4$  produces :

[JEE(Main)-2018]



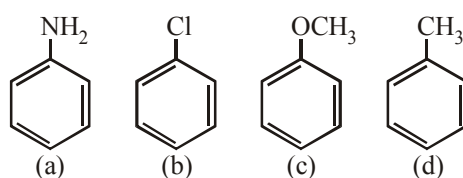
AH0093

10. Phenol reacts with methyl chloroformate in the presence of NaOH to form product A. A reacts with Br<sub>2</sub> to form product B. A and B are respectively : [JEE(Main)-2018]



AH0094

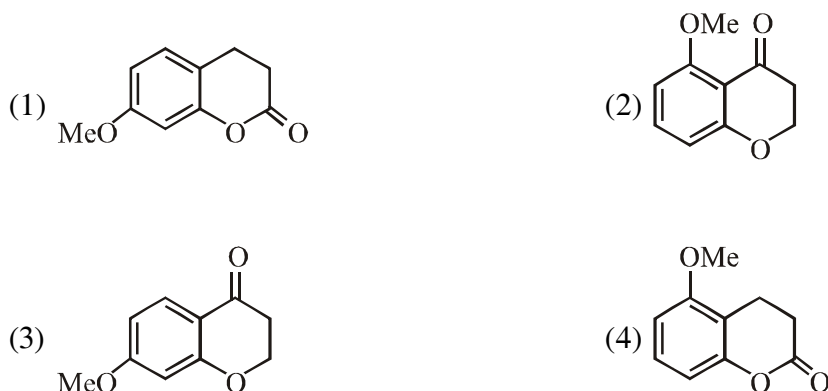
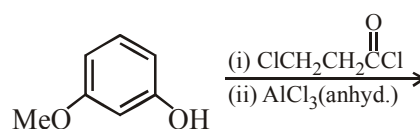
11. The increasing order of nitration of the following compound is :-[JEE(Main)-2018(ONLINE)]



- (1) (b) < (a) < (c) < (d) (2) (b) < (a) < (d) < (c)  
 (3) (a) < (b) < (c) < (d) (4) (a) < (b) < (d) < (c)

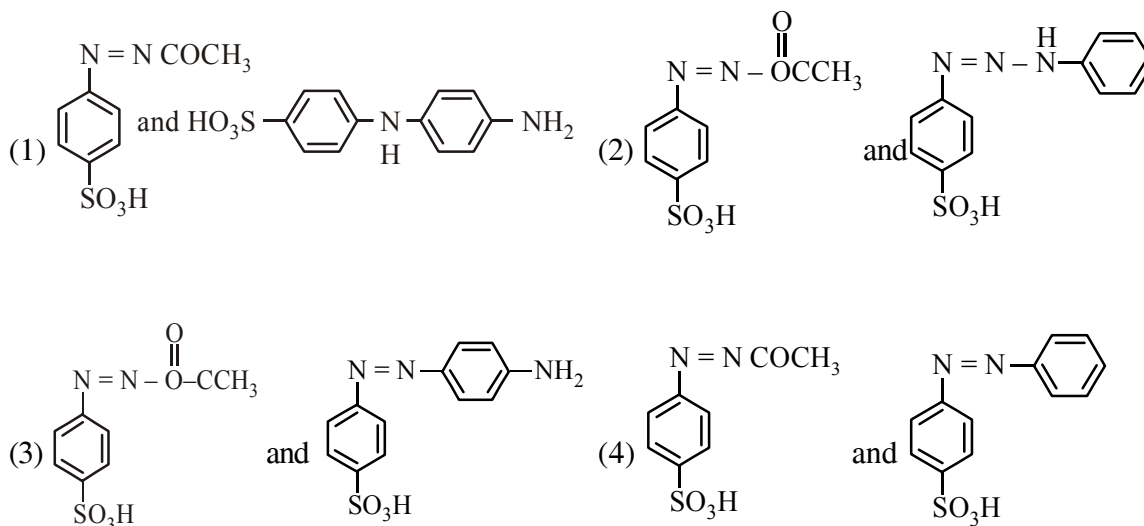
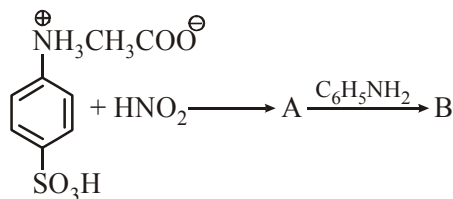
AH0095

12. The major product of the following reaction is : [JEE(Main)-2018(ONLINE)]



AH0096

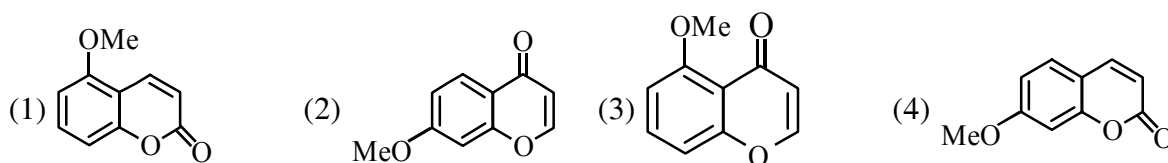
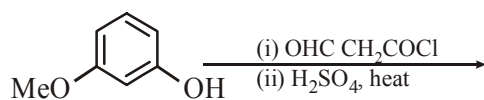
13. Products A and B formed in the following reactions are respectively : [JEE(Main)-2018(ONLINE)]



AH0097

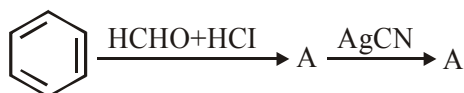
14. The major product of the following reaction is :

[JEE(Main)-2018(ONLINE)]



AH0098

15. The compounds A and B in the following reaction are, respectively: [JEE-Mains (JAN)-2019]

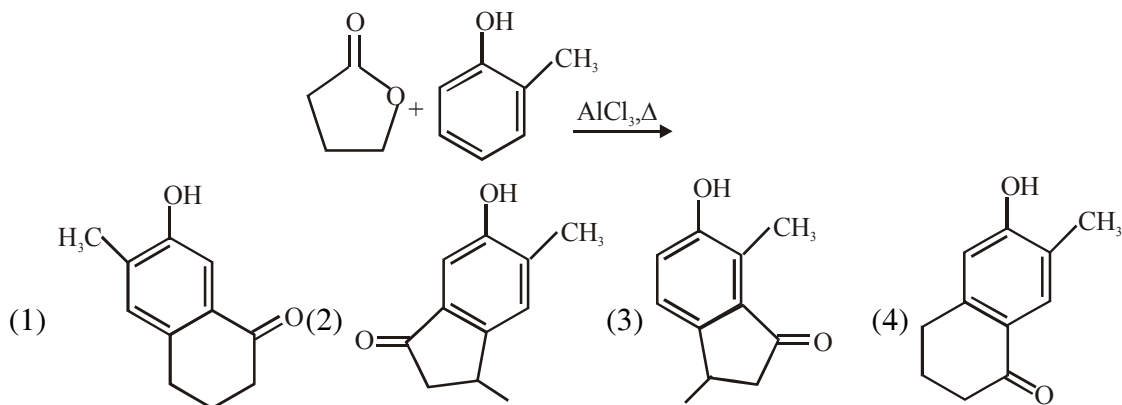


- (1) A = Benzyl alcohol, B = Benzyl isocyanide  
 (2) A = Benzyl alcohol, B = Benzyl cyanide  
 (3) A = Benzyl chloride, B = Benzyl cyanide  
 (4) A = Benzyl chloride, B = Benzyl isocyanide

AH0099

16. The major product of the following reaction is:

[JEE-Mains (JAN)-2019]



AH0100

17. Which of the following compounds is not aromatic ?

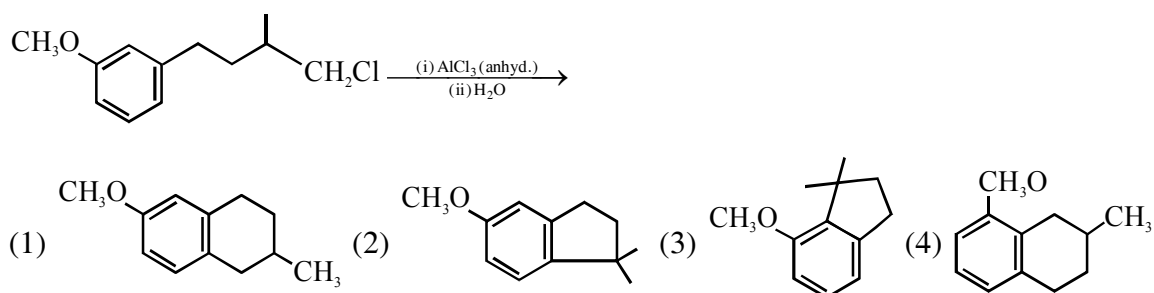
[JEE-Mains (JAN)-2019]



AH0101

18. The major product of the following reaction is:

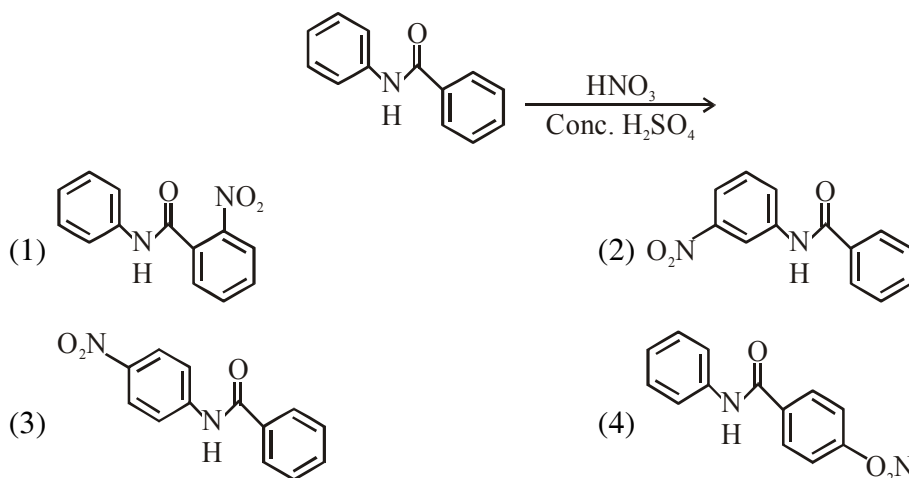
[JEE-Mains (JAN)-2019]



AH0102

19. What will be the major product in the following mononitration reaction ?

[JEE-Mains (JAN)-2019]

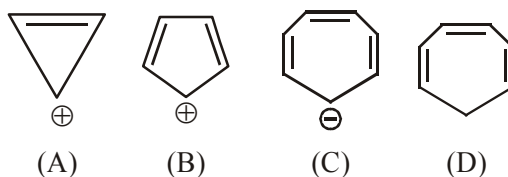


AH0103



20. Which compound(s) out of the following is/are not aromatic ?

[JEE-Mains (JAN)-2019]

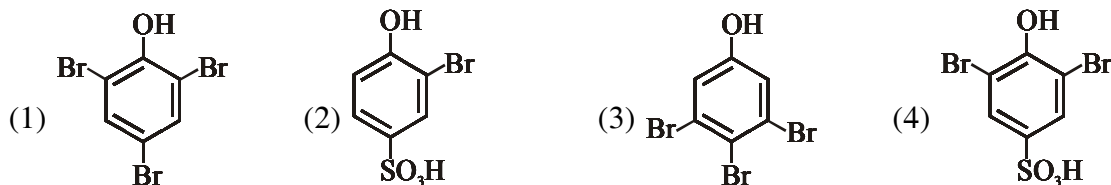
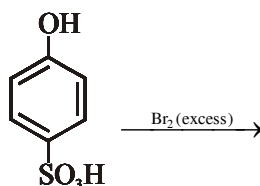


- (1) C and D      (2) B, C and D      (3) A and C      (4) B

AH0104

21. The major product of the following reaction is :

[JEE-Mains (JAN)-2019]



AH0105

22. Which of the following compounds will produce a precipitate with  $\text{AgNO}_3$ ?

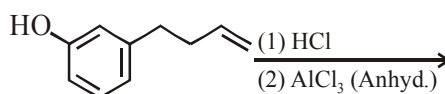
[JEE-Mains (JAN)-2019]



AH0106

23. The major product of the following reaction is :-

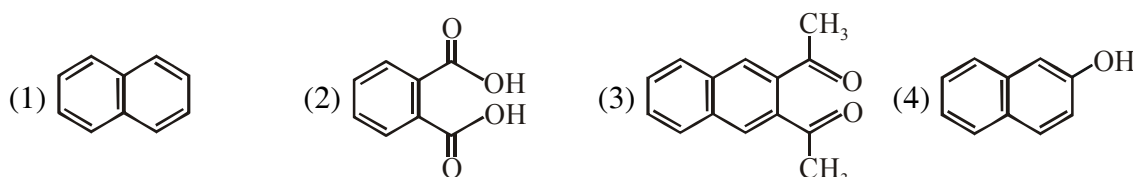
[JEE-Mains (JAN)-2019]



AH0107

24. Among the following four aromatic compounds, which one will have the lowest melting point ?

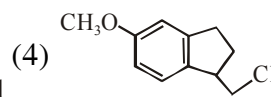
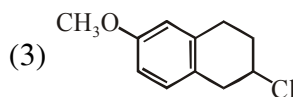
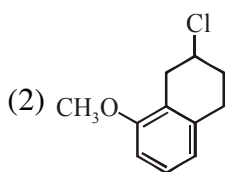
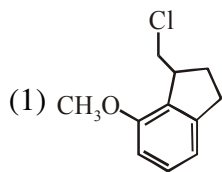
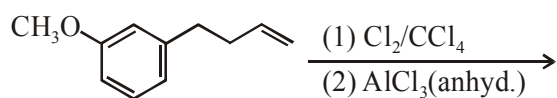
[JEE-Mains (JAN)-2019]



AH0108

25. The major product of the following reaction is :

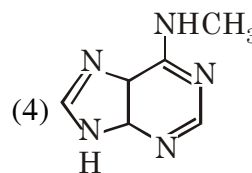
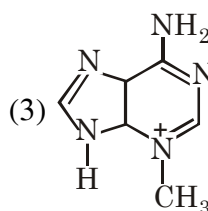
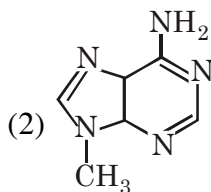
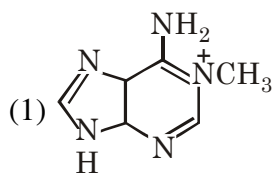
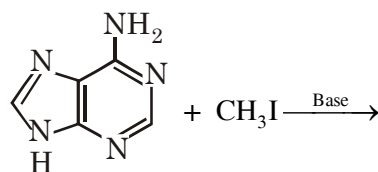
[JEE-Mains (JAN)-2019]



AH0109

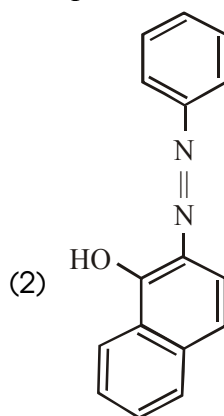
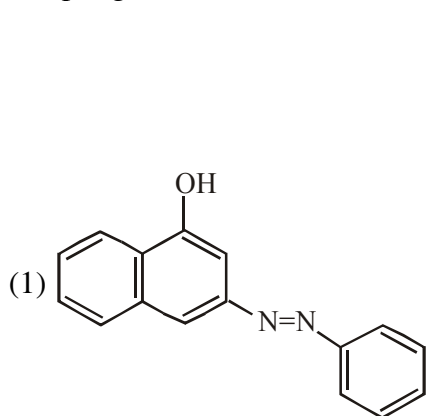
26. The major product in the following reaction is :

[JEE-Mains (April)-2019]

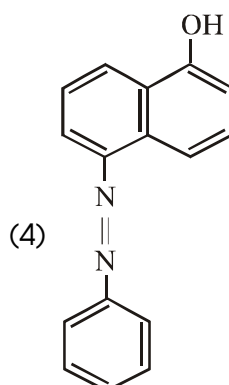
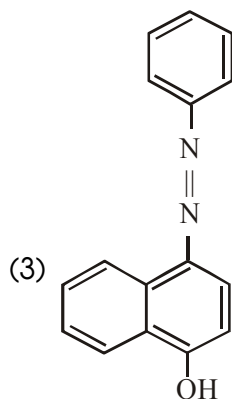


AH0110

27. Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give



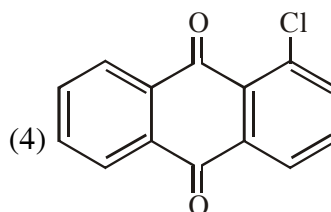
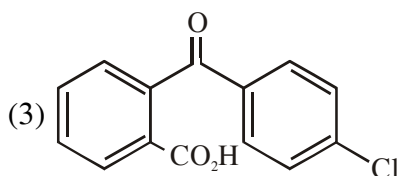
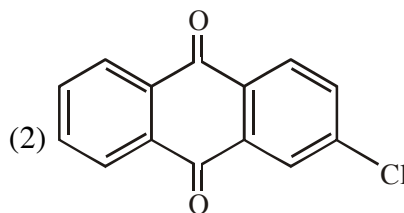
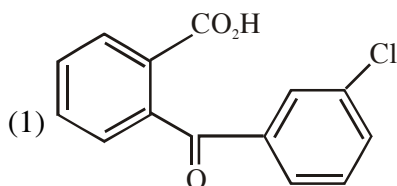
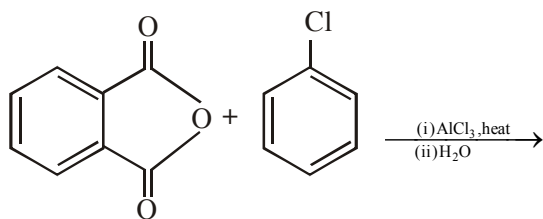
[JEE-Mains (April)-2019]



AH0111

28. The major product of the following reaction is:

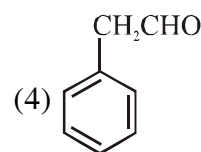
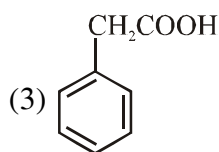
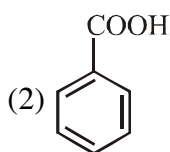
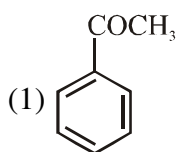
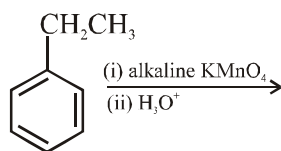
[JEE-Mains (April)-2019]



AH0112

29. The major product of the following reaction is :

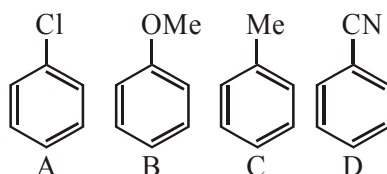
[JEE-Mains (April)-2019]



AH0113

30. The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is :

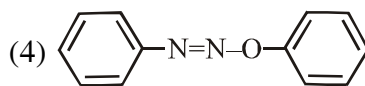
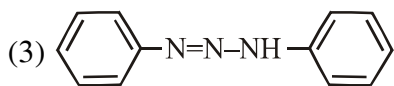
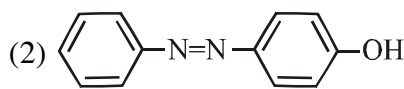
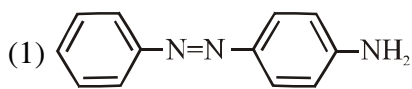
[JEE-Mains (April)-2019]



- (1) D < B < A < C    (2) A < B < C < D    (3) D < A < C < B    (4) B < C < A < D

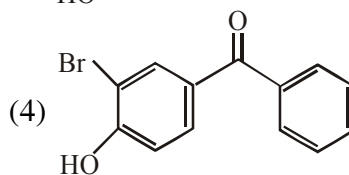
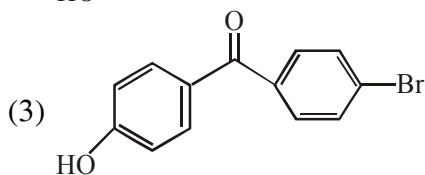
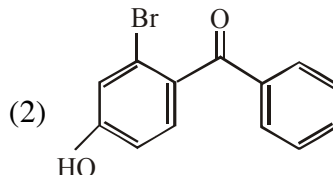
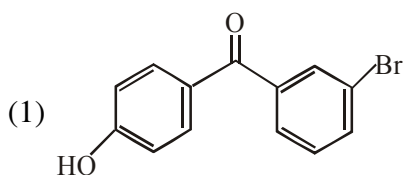
AH0114

31. Aniline dissolved in dilute HCl is reacted with sodium nitrite at 0°C. This solution was added dropwise to a solution containing equimolar mixture of aniline and phenol in dil. HCl. The structure of the major product is : [JEE-Mains (April)-2019]



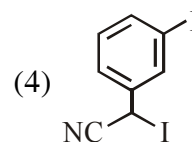
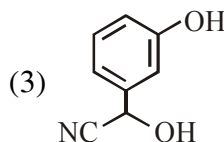
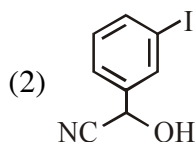
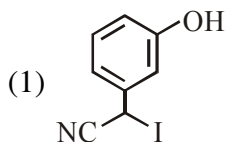
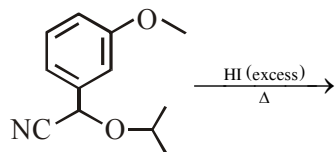
AH0115

32. p-Hydroxybenzophenone upon reaction with bromine in carbon tetrachloride gives: [JEE-Mains (April)-2019]



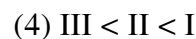
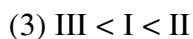
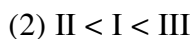
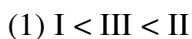
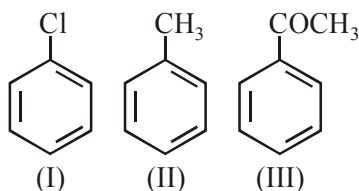
AH0116

33. The major product of the following reaction is : [JEE-Mains (April)-2019]



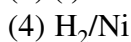
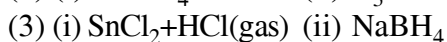
AH0117

34. The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reactions is :- [JEE-Mains (April)-2019]



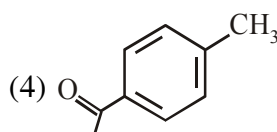
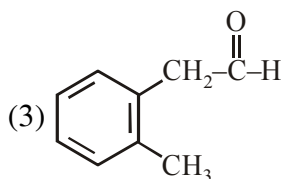
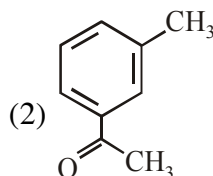
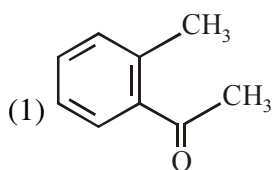
AH0118

35. Which of the following is NOT a correct method of the preparation of benzylamine from cyanobenzene ? [JEE-Mains (April)-2019]



AH0119

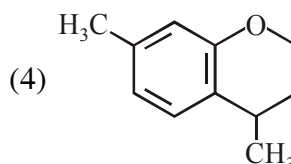
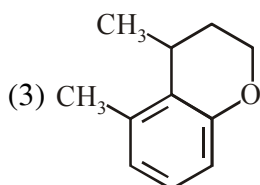
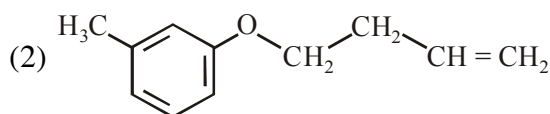
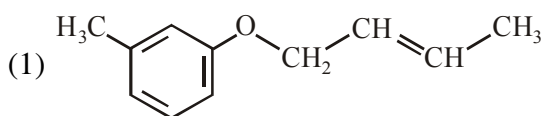
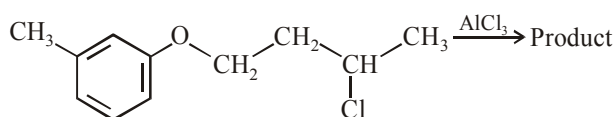
36. Compound A ( $C_9H_{10}O$ ) shows positive iodoform test. Oxidation of A with  $KMnO_4/KOH$  gives acid B ( $C_8H_6O_4$ ). Anhydride of B is used for the preparation of phenolphthalein. Compound A is :-  
[JEE-Mains (April)-2019]



AH0120

37. The major product obtained in the given reaction is :-

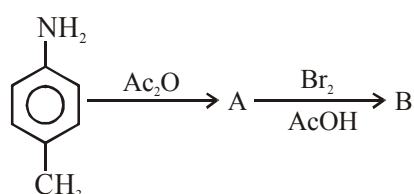
[JEE-Mains (April)-2019]



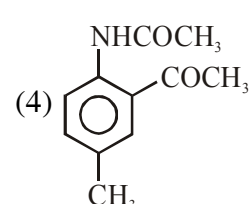
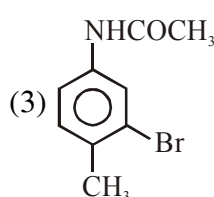
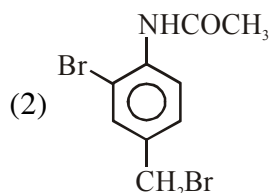
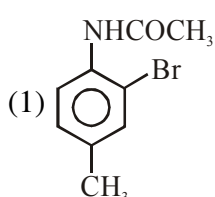
AH0121

38. In the following reaction sequence

[JEE-Mains (Jan)-2020]



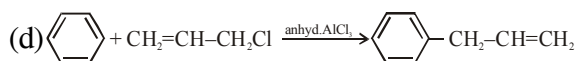
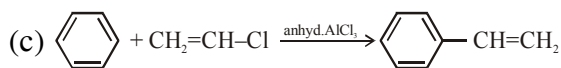
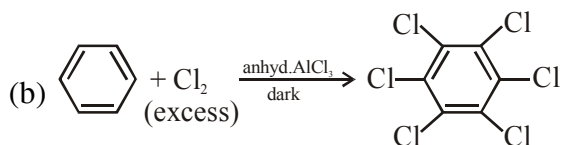
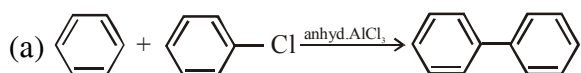
the major products B is -



AH0122

39. Consider the following reactions :

[JEE-Mains (Jan)-2020]



Which of these reactions are possible ?

(1) (a) and (d)

(2) (b) and (d)

(3) (a) and (b)

(4) (b), (c) and (d)

AH0123

40. A solution of m-chloroaniline, m-chlorophenol and m-chlorobenzoic acid in ethyl acetate was extracted initially with a saturated solution of  $\text{NaHCO}_3$  to give fraction A. The left over organic phase was extracted with dilute  $\text{NaOH}$  solution to give fraction B. The final organic layer was labelled as fraction C. Fractions A, B and C, contain respectively :

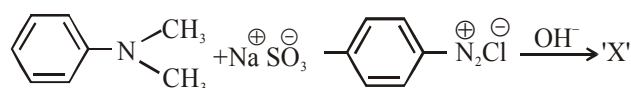
[JEE-Mains (Jan)-2020]

- (1) m-chlorobenzoic acid, m-chloroaniline and m-chlorophenol
- (2) m-chloroaniline, m-chlorobenzoic acid and m-chlorophenol
- (3) m-chlorobenzoic acid, m-chlorophenol and m-chloroaniline
- (4) m-chlorophenol, m-chlorobenzoic acid and m-chloroaniline

AH0124

41. Consider the following reaction :

[JEE-Mains (Jan)-2020]



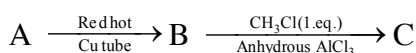
The product 'X' is used :

- (1) in acid base titration as an indicator
- (2) in protein estimation as an alternative to ninhydrin
- (3) in laboratory test for phenols
- (4) as food grade colourant

AH0125

42. In the following sequence of reactions the maximum number of atoms present in molecule 'C' in one plane is \_\_\_\_\_.

[JEE-Mains (Jan)-2020]



(A is a lowest molecular weight alkyne)

AH0126

## EXERCISE # (ADVANCE)

1. The chlorination of toluene in presence of ferric chloride gives predominately: [JEE 1986]

- (A) Benzyl chloride (B) m-Chlorotoluene (C) Benzal chloride (D) *o*- and *p*-Chlorotoluene

AH0127

2. The most basic compound among the following is: [JEE 1990]

- (A) Benzylamine (B) Aniline (C) Acetaniline (D) *p*-Nitro aniline

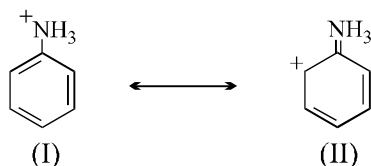
AH0128

3. When nitrobenzene is treated with  $\text{Br}_2$  in presence of  $\text{FeBr}_3$  the major product formed is *m*-bromonitrobenzene. Correct statements are : [JEE 1992]

- (A) The electron density on meta carbon is more than on ortho and para position.  
 (B) The intermediate carbonium ion formed after initial attack of  $\text{Br}^+$  attack the meta position is least destabilized.  
 (C) Loss of aromaticity when  $\text{Br}^+$  attacks at the ortho and para positions and not at meta position  
 (D) Easier loss of  $\text{H}^+$  to regain aromaticity form the meta position than from ortho and para position.

AH0129

4. Choose the correct statement from the ones given below for two aniline in: [JEE 1993]



- (A) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions  
 (B) II is not an acceptable canonical structure because it is non aromatic  
 (C) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons  
 (D) II is an acceptable canonical structure

AH0130

5. Most stable carbonium ion is: [JEE 1995]

- (A)  $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-}^+\text{CH}_2$  (B)  $\text{C}_6\text{H}_5\text{CH}_2^+$   
 (C)  $p\text{-Cl-C}_6\text{H}_4\text{-}^+\text{CH}_2$  (D)  $p\text{-CH}_3\text{O-C}_6\text{H}_4\text{-}^+\text{CH}_2$

AH0131

6. Arrange in order of decreasing trend towards  $\text{S}_{\text{E}}$  reactions: [JEE 1995]

- (I) Chlorobenzene (II) Benzene (III) Anilinium chloride (IV) Toluene  
 (A) II > I > III > IV (B) III > I > II > IV (C) IV > II > I > III (D) I > II > III > IV

AH0132

7. Among the following statements on the nitration of aromatic compounds, the false one is:

- (A) The rate of benzene is almost the same as that of hexadeuterobenzene [JEE 1997]  
 (B) The rate of nitration of toluene is greater than that of benzene.  
 (C) The rate of nitration of benzene is greater than that of hexadeuterobenzene  
 (D) Nitration is an electrophilic substitution reaction

AH0133

8. Nitrobenzene can be prepared from benzene by using a mixture of conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$ . In the nitrating mixture  $\text{HNO}_3$  acts as a: [JEE 1997]

(A) Base (B) Acid (C) Reducing agent (D) Catalyst

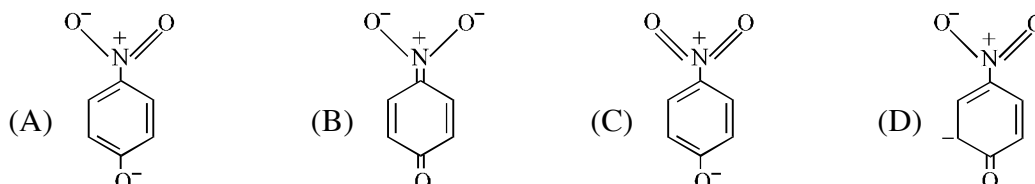
AH0134

9. Benzyl chloride ( $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ) can be prepared from toluene by chlorination with: [JEE 1998]

(A)  $\text{SO}_2\text{Cl}_2\text{h}\nu$  (B)  $\text{SOCl}_2$  (C)  $\text{Cl}_2\text{h}\nu$  (D)  $\text{NaOCl}$

AH0135

10. The most unlikely representation of resonance structure of p-nitrophenoxide ion is: [JEE 1998]



AH0136

11. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives: [JEE 1998]

(A) Diphenyl ether (B) p-hydroxyazobenzene  
(C) Chlorobenzene (D) Benzene

AH0137

12. Toluene, when treated with  $\text{Br}_2/\text{Fe}$ , gives p-bromotoluene as the major product, because the  $\text{CH}_3$  group:

(A) is para directing (B) is meta directing [JEE 1999]  
(C) activates the ring by hyperconjugation (D) deactivates the ring

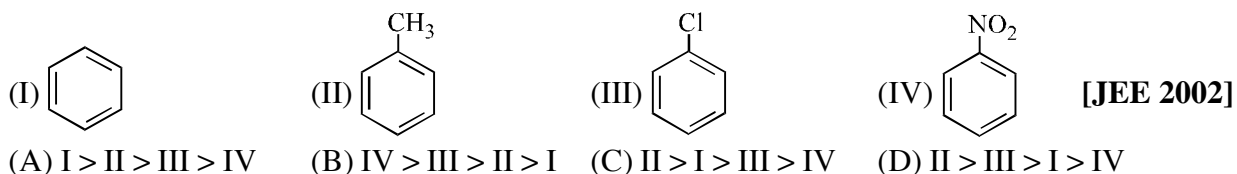
AH0138

13. Amongst the following the strongest base is: [JEE 2000]

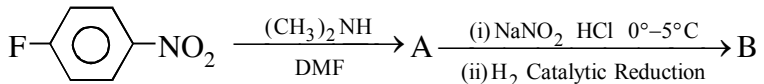
(A)  $\text{C}_6\text{H}_5\text{NH}_2$  (B)  $\text{p-O}_2\text{NC}_6\text{H}_4\text{NH}_2$  (C)  $\text{m-O}_2\text{NC}_6\text{H}_4\text{NH}_2$  (D)  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

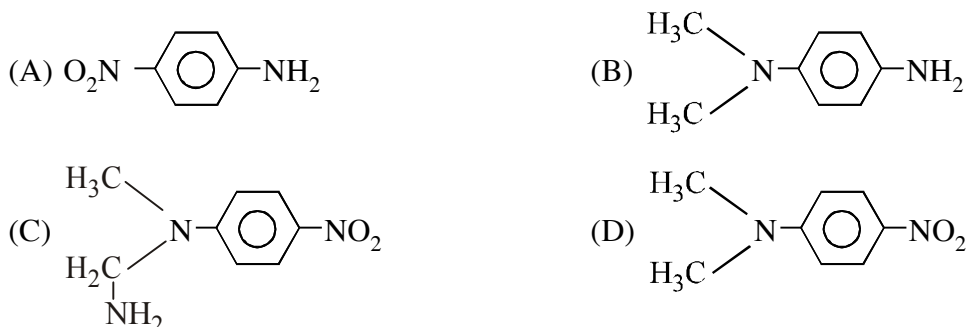
AH0139

14. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds:



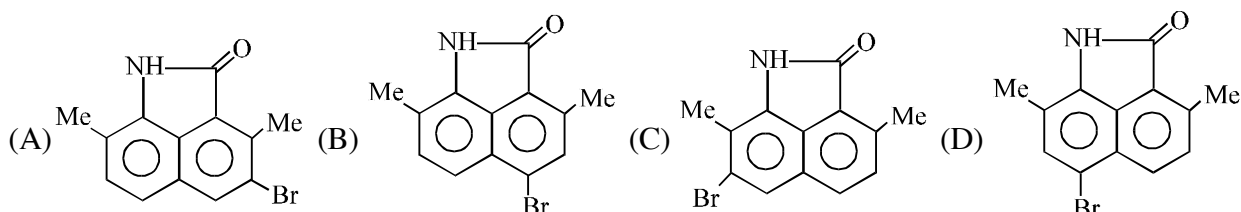
AH0140

15.  [JEE 2003]

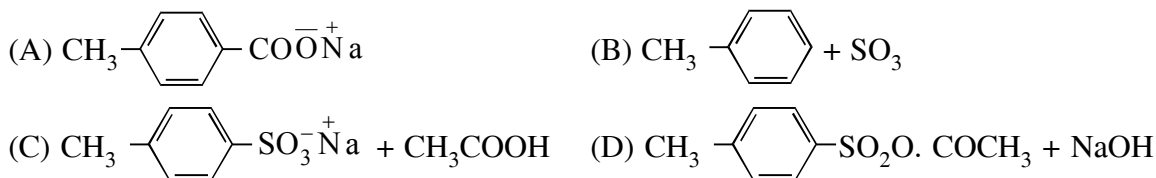
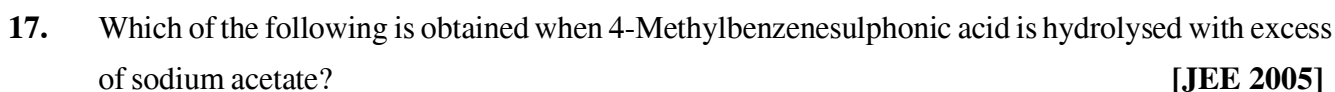


AH0141

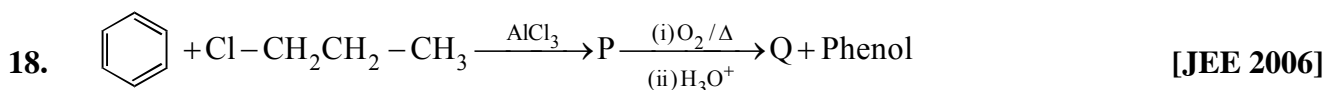




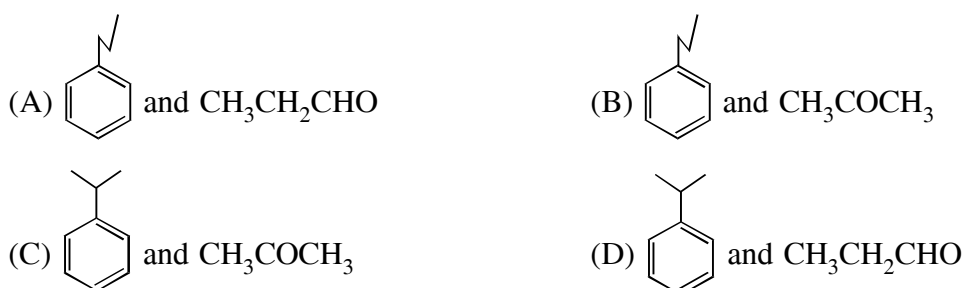
AH0142



AH0143



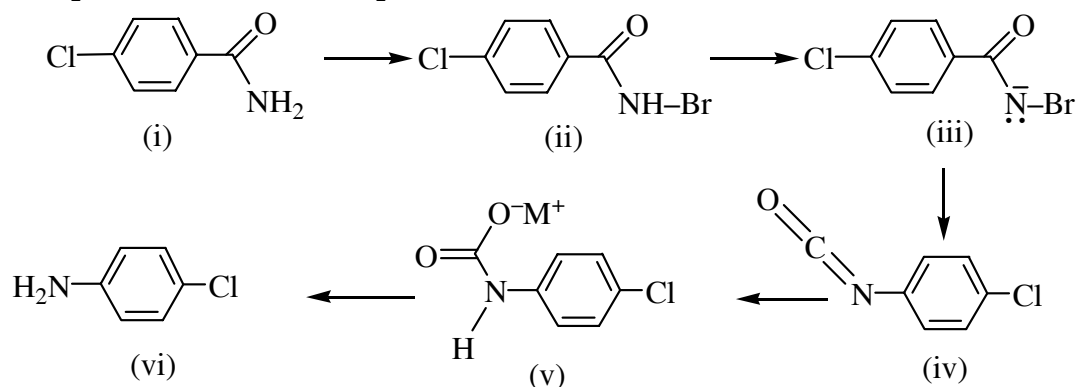
The major products P and Q are



AH0144

## Question No. 19 to 21 ( 3 questions)

## Comprehension I

RCONH<sub>2</sub> is converted into RNH<sub>2</sub> by means of Hofmann bromamide degradation.

In this reaction, RCONHBr is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an intramolecular reaction.

19. How can the conversion of (i) to (ii) be brought about? [JEE 2006]

- (A) KBr (B) KBr + CH<sub>3</sub>ONa (C) KBr + KOH (D) Br<sub>2</sub> + KOH

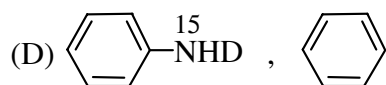
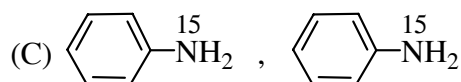
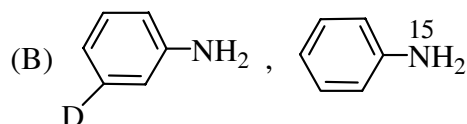
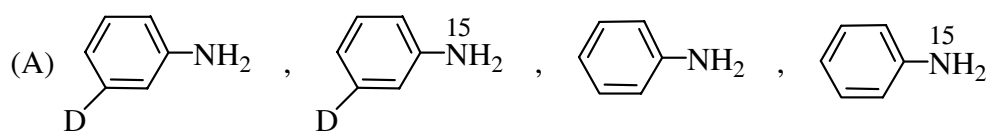
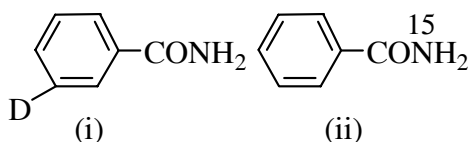
AH0145

20. Which is the rate determining step in Hofmann bromamide degradation? [JEE 2006]

- (A) Formation of (i) (B) Formation of (ii) (C) Formation of (iii) (D) Formation of (iv)

AH0145

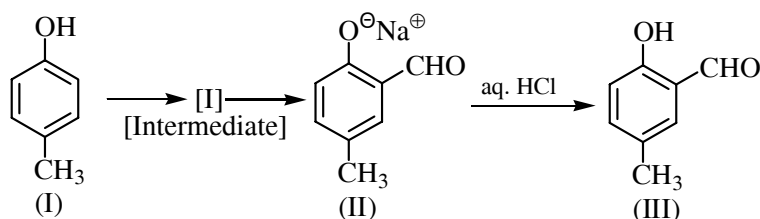
21. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation? [JEE 2006]



AH0145

*Paragraph for Question Nos. 22 to 25 (4 questions)*

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.



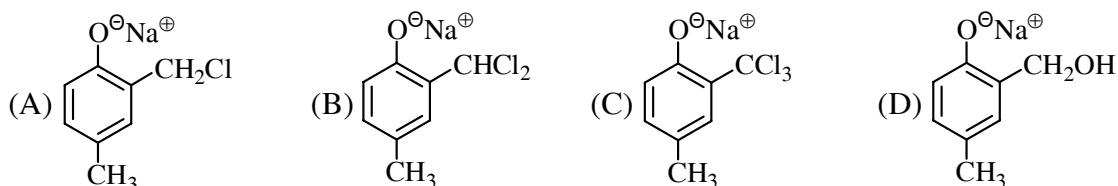
22. Which one of the following reagents is used in the above reaction ? [JEE 2007]
- (A) a NaOH + CH<sub>3</sub>Cl (B) a NaOH + CH<sub>2</sub>Cl<sub>2</sub>  
 (C) a NaOH + CHCl<sub>3</sub> (D) aNaOH + CCl<sub>4</sub>

AH0146

23. The electrophile in this reaction is [JEE 2007]
- (A) :CHCl (B) <sup>+</sup>CHCl<sub>2</sub> (C) :CCl<sub>2</sub> (D) •CCl<sub>3</sub>

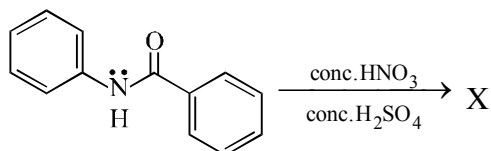
AH0146

24. The structure of the intermediate I is [JEE 2007]

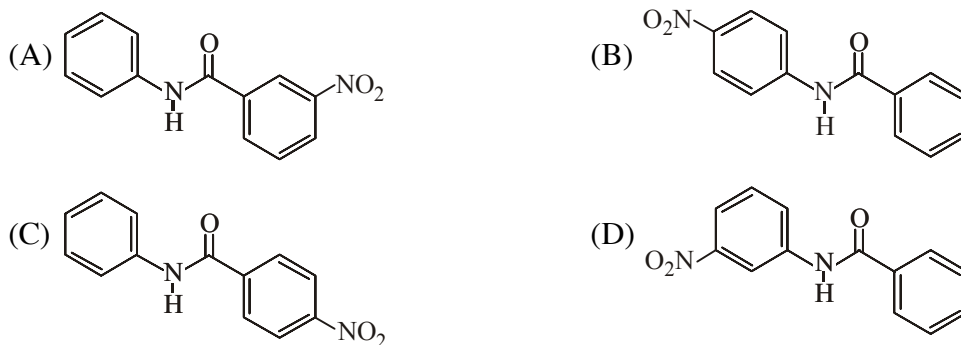


AH0146

25. In the following reaction, [JEE 2007]



the structure of the major product 'X' is



AH0147

26. **Statement - 1 :** Bromobenzene upon reaction with Br<sub>2</sub> / Fe gives 1, 4-dibromobenzene as the major product.

and

**Statement-2 :** In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

- (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1  
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement 1  
 (C) Statement-1 is True, Statement-2 is False  
 (D) Statement-1 is False, Statement-2 is True

[JEE 2008]

AH0148

27. **Statement-1** : Aniline on reaction with  $\text{NaNO}_2 / \text{HCl}$  at  $0^\circ\text{C}$  followed by coupling with  $\beta$ -naphthol gives a dark blue coloured precipitate.

and

**Statement-2** : The colour of the compound formed in the reaction of aniline with  $\text{NaNO}_2 / \text{HCl}$  at  $0^\circ$  followed by coupling with  $\beta$ -naphthol is due to the extended conjugation.

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

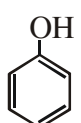
(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement 1

(C) Statement-1 is True, Statement-2 is False

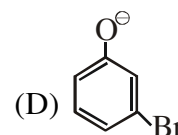
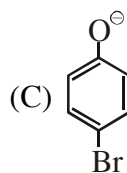
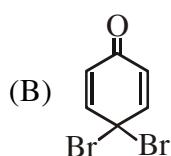
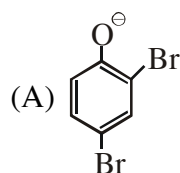
(D) Statement-1 is False, Statement-2 is True

[JEE 2008]

AH0149

28. In the reaction  the intermediate(s) is(are) –

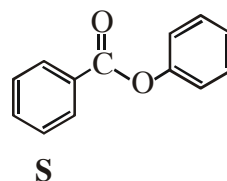
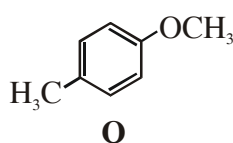
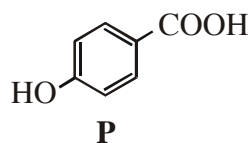
[JEE 2009]



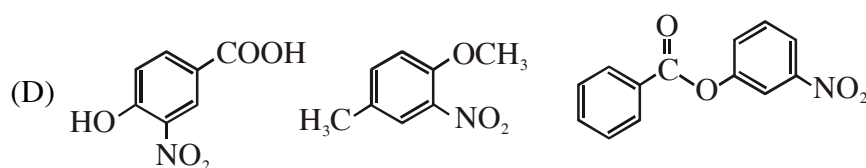
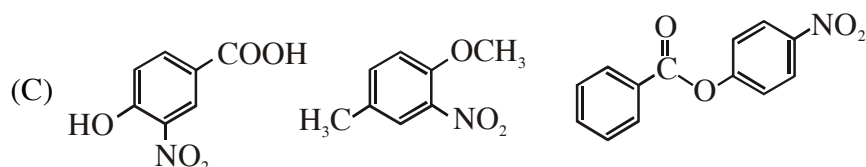
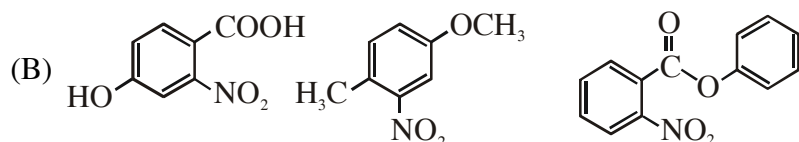
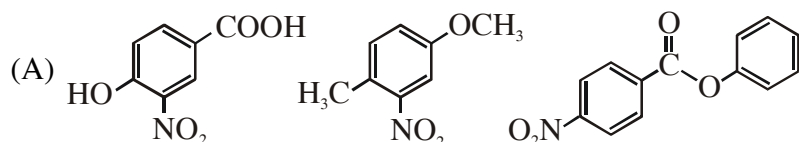
AH0150

29. The compounds P, Q and S

[JEE 2009]



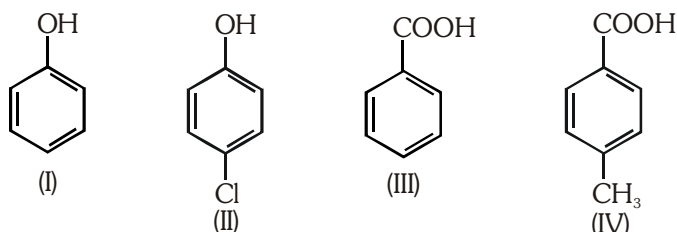
were separately subjected to nitration using  $\text{HNO}_3 / \text{H}_2\text{SO}_4$  mixture. The product formed in each case respectively, is



AH0151

30. The correct acidity order of the following is :

[JEE 2009]



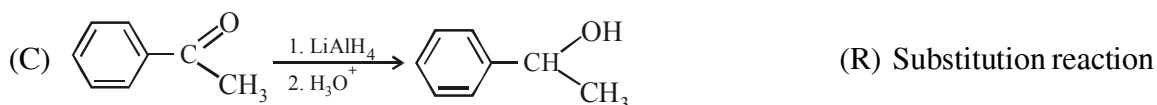
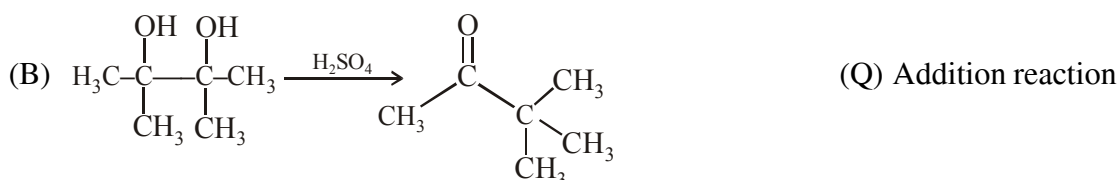
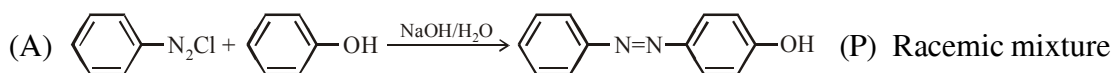
- (A) (III) > (IV) > (II) > (I)      (B) (IV) > (III) > (I) > (II)  
 (C) (III) > (II) > (I) > (IV)      (D) (II) > (III) > (IV) > (I)

AH0152

31. Match the reactions in Column-I with appropriate options in Column-II.

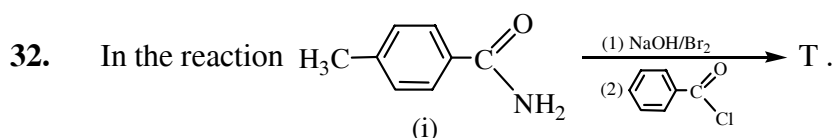
Column-I

Column-II [IIT-JEE-2010]



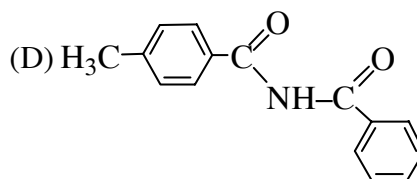
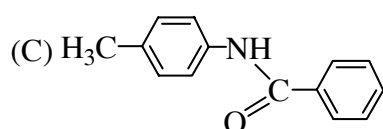
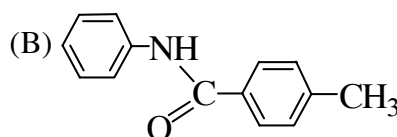
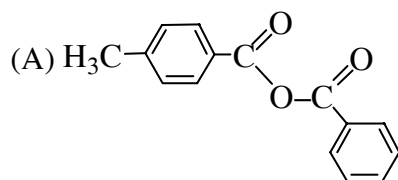
(T) Carbocation intermediate

AH0153



The structure of the Product T is :

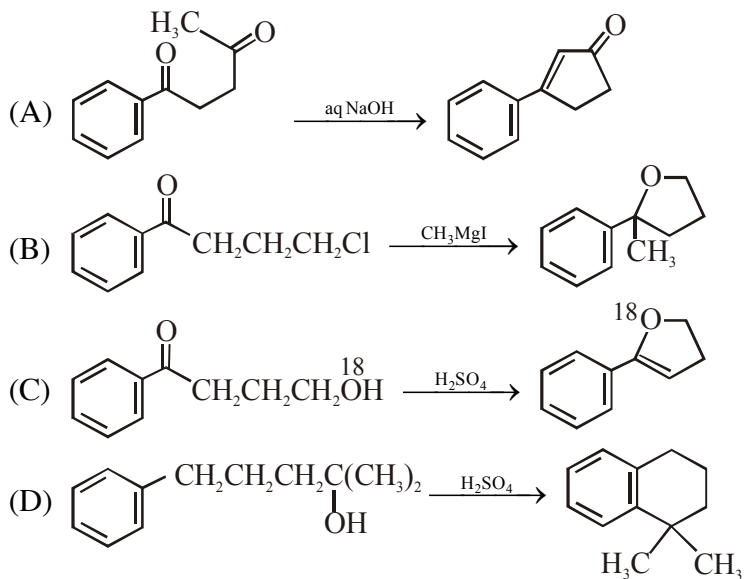
[JEE 2010]



AH0154

33. Match the reactions in **Column-I** with appropriate types of step/reactive intermediate involved in these reactions as given in **Column-II**

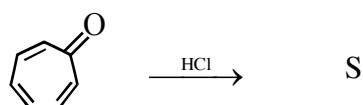
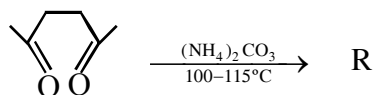
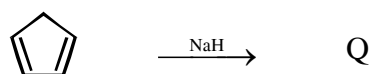
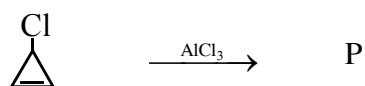
**Column-I**



**Column-II** [IIT-JEE-2012]

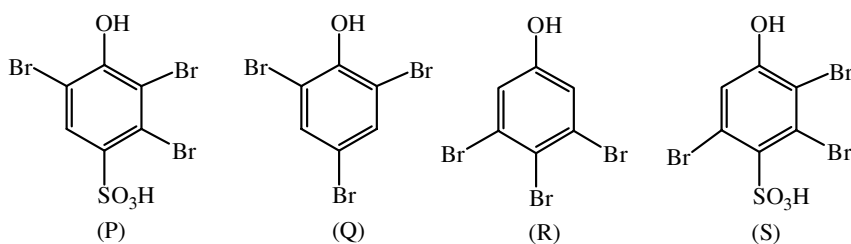
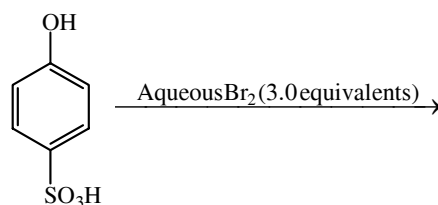
- (P) Nucleophilic substitution  
 (Q) Electrophilic substitution  
 (R) Dehydration  
 (S) Nucleophilic addition  
 (R) Carbanion

34. Among P, Q, R and S, the aromatic compound(s) is / are :



- (A) P (B) Q (C) R (D) S

35. The major product(s) of the following reaction is (are) -



- (A) P (B) Q (C) R (D) S

AH0155

[JEE 2013]

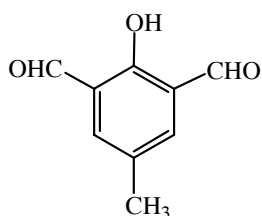
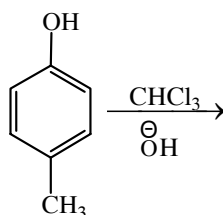
AH0156

[JEE 2013]

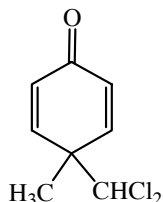
AH0157

36. In the following reaction, the product (s) formed is (are)

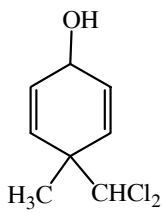
[JEE 2013]



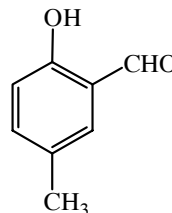
(P)



(Q)



(R)



(S)

(A) P (major)

(B) Q (minor)

(C) R (minor)

(D) S (major)

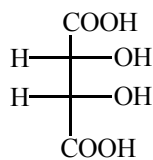
AH0158

**Paragraph for Question 37 and 38**

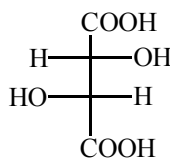
P & Q are isomers of dicarboxylic acid  $\text{C}_4\text{H}_4\text{O}_4$ . Both decolourize  $\text{Br}_2/\text{H}_2\text{O}$ , On heating P forms the cyclic anhydride.

Upon treatment with dilute alkaline  $\text{KMnO}_4$ , P as well as Q could produce one or more than one from S, T and U.

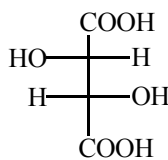
[JEE 2013]



(S)

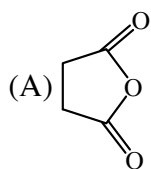
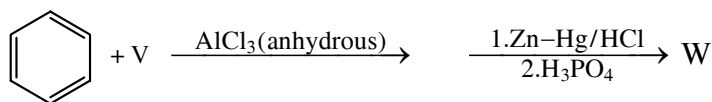
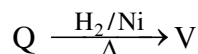


(T)



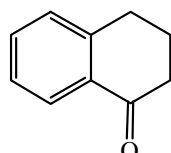
(U)

37. In the following reaction sequences V and W are , respectively -

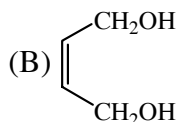


(V)

and

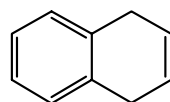


(W)

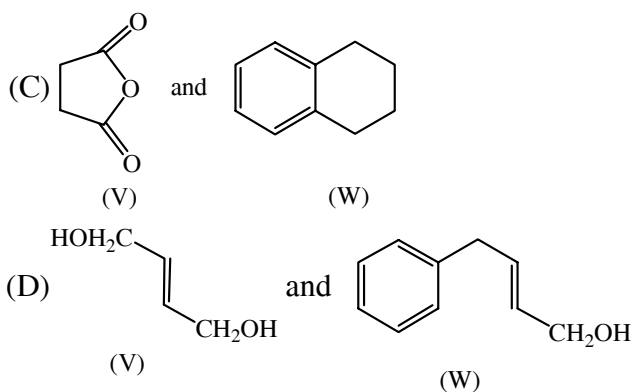


(V)

and



(W)



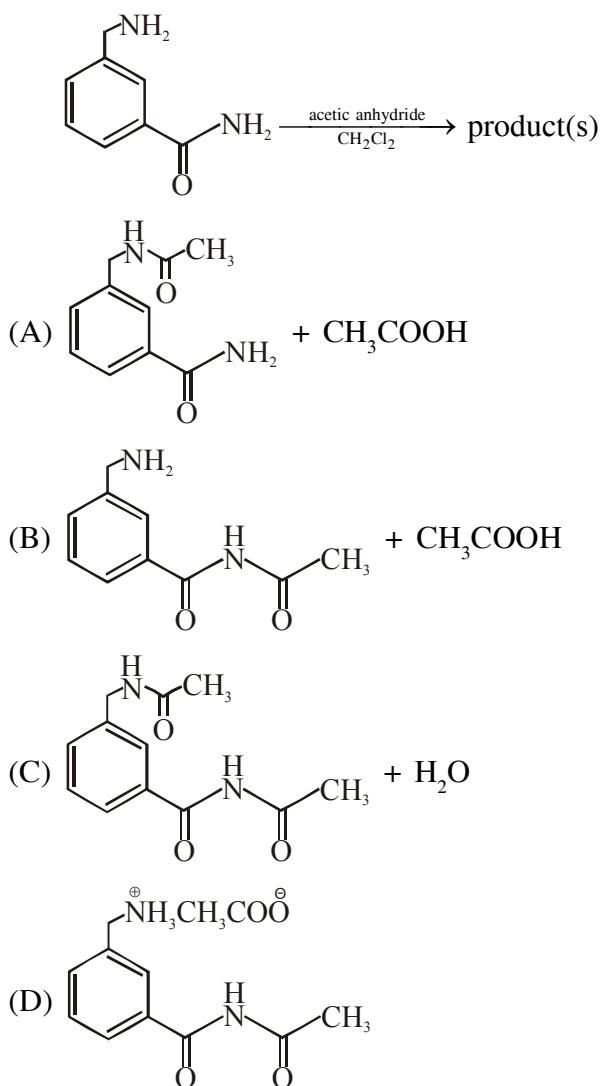
AH0159

38. Compounds formed from P and Q are respectively  
 (A) Optically active S and optically active pair (T, U)  
 (B) Optically inactive S and optically inactive pair (T, U)  
 (C) Optically active pair (T, U) and optically active S  
 (D) Optically inactive pair (T, U) and optically inactive S

AH0159

39. In the reaction shown below, the major product(s) formed is / are :

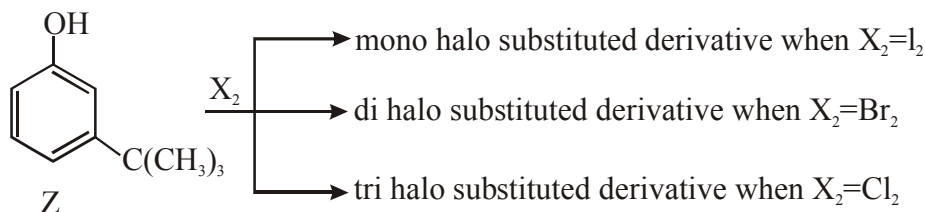
[JEE 2014]



AH0160



40. The reactivity of compound Z with different halogens under appropriate conditions is given below : [JEE 2014]



The observed pattern of electrophilic substitution can be explained by -

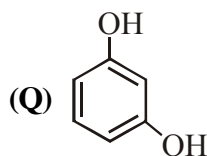
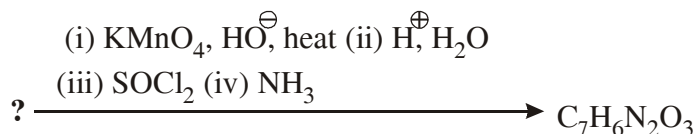
- (A) The steric effect of the halogen  
 (B) The steric effect of the tert-butyl group  
 (C) The electronic effect of the phenolic group  
 (D) The electronic effect of the tert-butyl group
- AH0161
41. Match the four starting materials (P, Q, R, S) given in List I with the corresponding reaction scheme (I, II, III, IV) provided in List - II and select the correct answer using the code given below in lists. [JEE 2014]

**List - I**

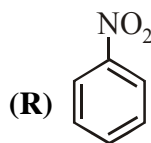
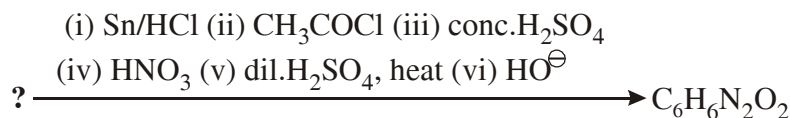


**List - II**

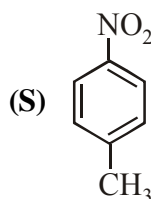
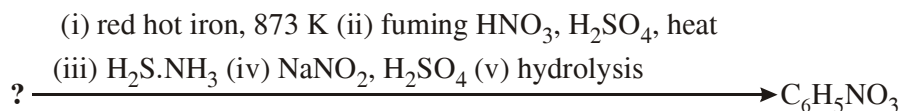
(1) **Scheme I**



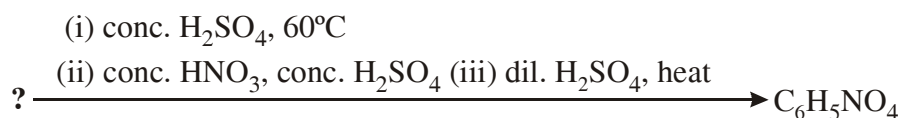
(2) **Scheme II**



(3) **Scheme III**



(4) **Scheme IV**

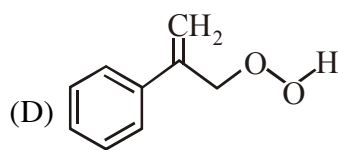
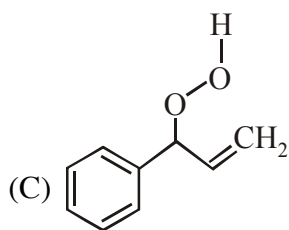
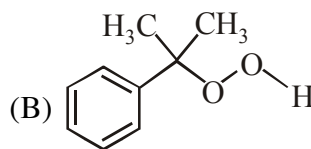
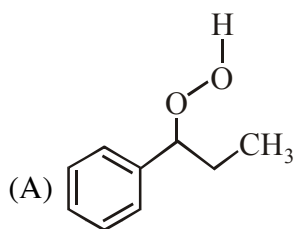
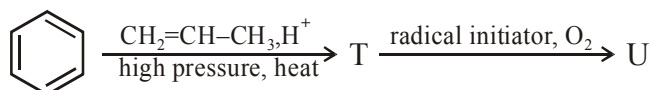


Code :

	P	Q	R	S
(A)	1	4	2	3
(B)	3	1	4	2
(C)	3	4	2	1
(D)	4	1	3	2

42. The major product U in the following reactions is :

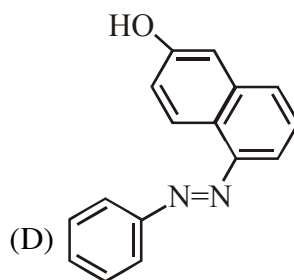
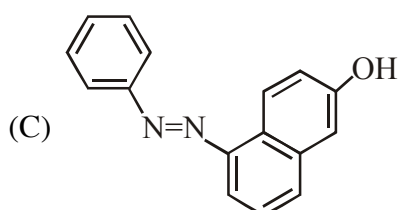
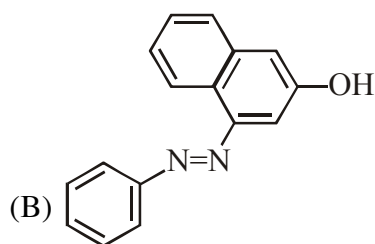
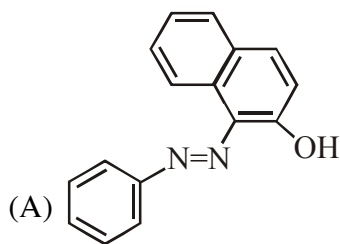
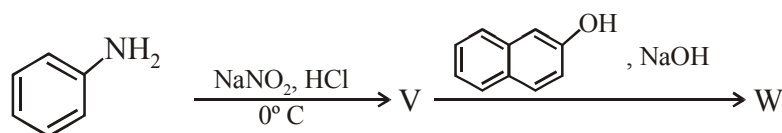
AH0162  
[IIT 2015]



AH0163

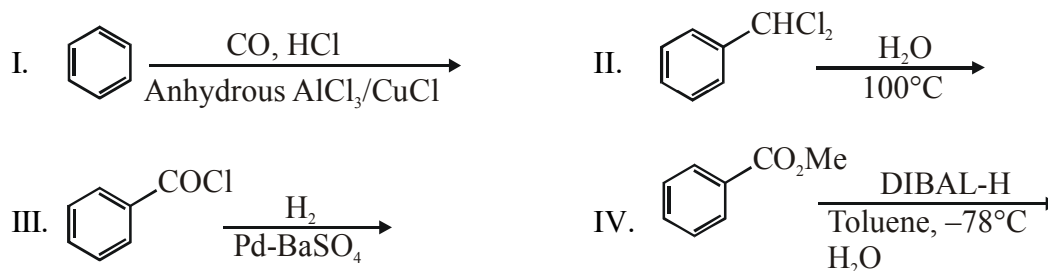
43. In the following reactions, the major product W is :

[IIT 2015]



AH0164

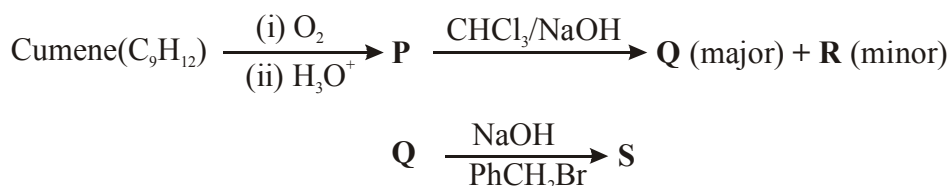
44. Among the following the number of reaction(s) that produce(s) benzaldehyde is : [IIT 2015]



AH0165

45. The correct statement(s) about of the following reaction sequence is(are)

[IIT 2016]

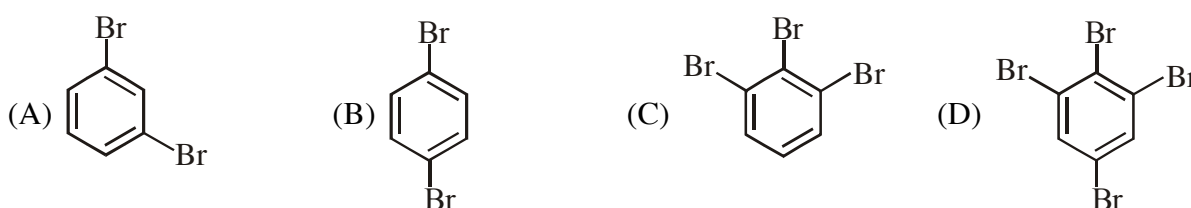
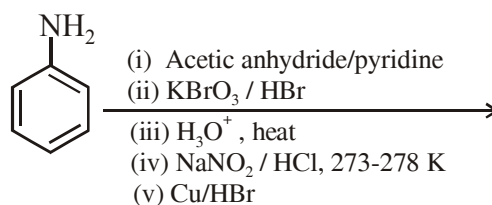


- (A) R is steam volatile  
 (B) Q gives dark violet coloration with 1% aqueous FeCl<sub>3</sub> solution  
 (C) S gives yellow precipitate with 2, 4,-dinitrophenylhydrazine  
 (D) S gives dark violet coloration with 1% aqueous FeCl<sub>3</sub> solution

AH0166

46. The product(s) of the following reaction sequence is(are)

[IIT 2016]



AH0167

47. Among the following reaction(s) which gives (give) tert-butyl benzene as the major product is(are)

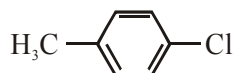
[IIT 2016]



AH0168

48. The IUPAC name(s) of the following compound is(are) :

[IIT 2017]

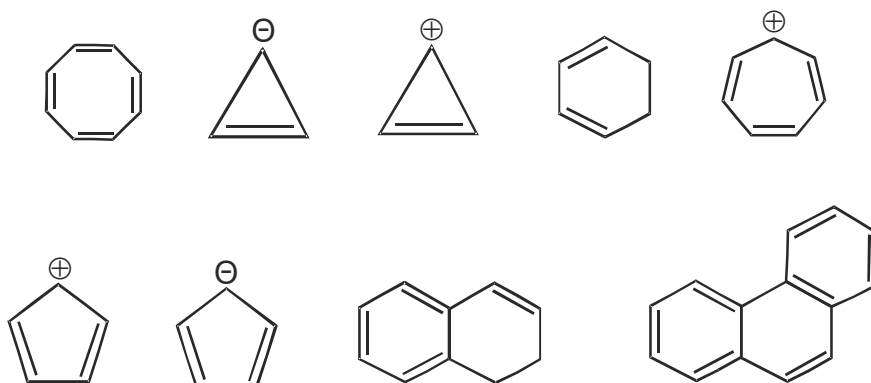


- (A) 4-methylchlorobenzene (B) 4-chlorotoluene  
 (C) 1-chloro-4-methylbenzene (D) 1-methyl-4-chlorobenzene

AH0169

49. Among the following, the number of aromatic compound (s) is :

[IIT 2017]



Answer 50, 51 and 52 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2 and 3 contains starting materials, reaction conditions, , and type of reactions, respectively .

Column 1	Column 2	Column 3
(I) Toluene	(i) NaOH/Br <sub>2</sub>	(P) Condensation
(II) Acetophenone	(ii) Br <sub>2</sub> / hν	(Q) Carboxylation
(III) Benzaldehyde	(iii) (CH <sub>3</sub> CO) <sub>2</sub> O/CH <sub>3</sub> COOK	(R) Substitution
(IV) Phenol	(iv) NaOH/CO <sub>2</sub>	(S) Haloform

AH0170

50. For the synthesis of benzoic acid, the only CORRECT combination is

- (A) (III) (iv) (R) (B) (IV) (ii) (P)  
 (C) (I) (iv) (Q) (D) (II) (i) (S)

AH0171

51. The only CORRECT combination in which the reaction proceeds through radical mechanism is

- (A) (I) (ii) (R) (B) (II) (iii) (R)  
 (C) (III) (ii) (P) (D) (IV) (i) (Q)

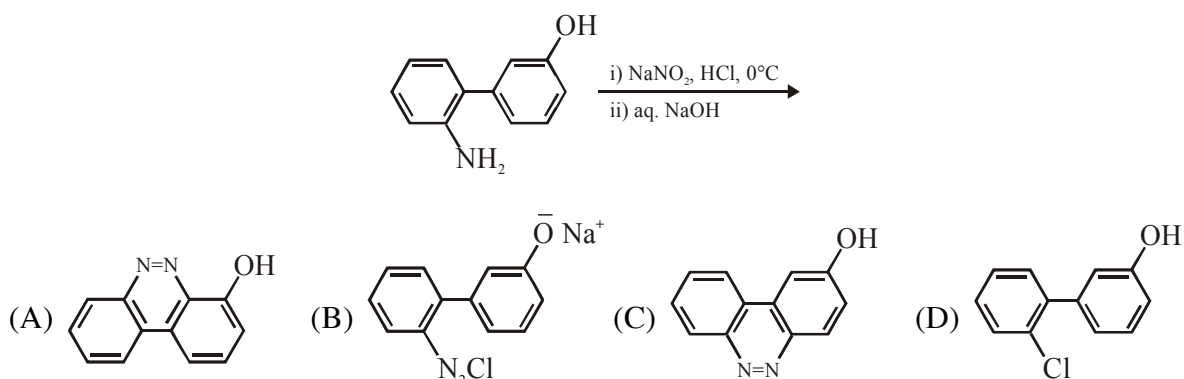
AH0171

52. The only CORRECT combination that gives two different carboxylic acids is

- (A) (IV) (iii) (Q) (B) (III) (iii) (P) (C) (II) (iv) (R) (D) (I) (i) (S)

AH0171

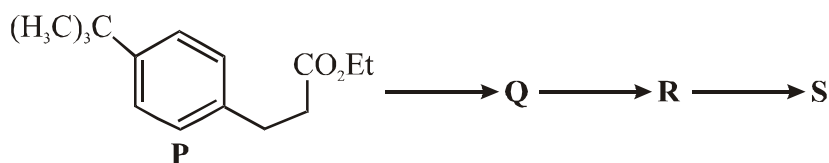
53. The major product of the following reaction is :



AH0172

### Paragraph for 54 & 55

The reaction of compound **P** with  $\text{CH}_3\text{MgBr}$  (excess) in  $(\text{C}_2\text{H}_5)_2\text{O}$  followed by addition of  $\text{H}_2\text{O}$  gives **Q**. The compound **Q** on treatment with  $\text{H}_2\text{SO}_4$  at  $0^\circ\text{C}$  gives **R**. The reaction of **R** with  $\text{CH}_3\text{COCl}$  in the presence of anhydrous  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  followed by treatment with  $\text{H}_2\text{O}$  produces compounds **S**. [Et is ethyl group] [IIT 2017]

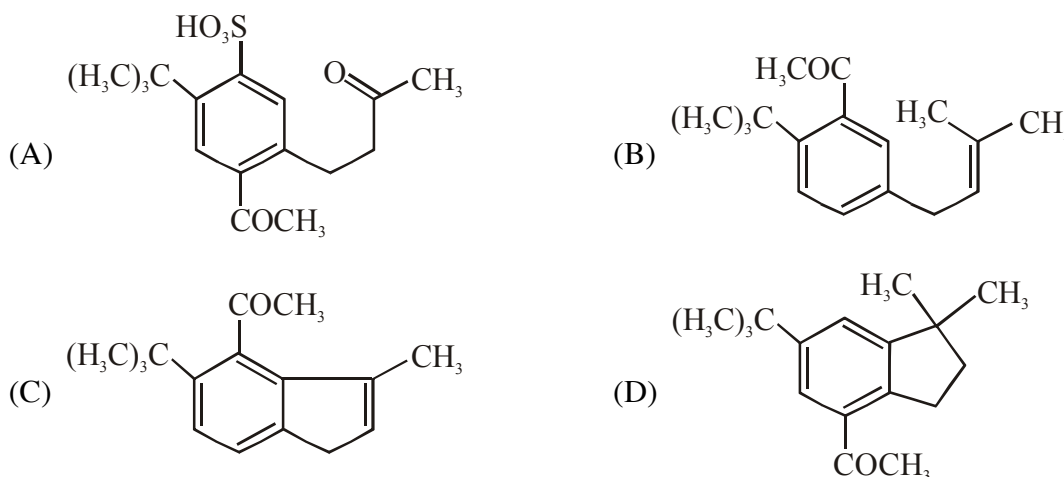


54. The reactions, **Q** to **R** and **R** to **S**, are -

- (A) Dehydration and Friedel-Crafts acylation  
 (B) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation  
 (C) Aromatic sulfonation and Friedel-Crafts acylation  
 (D) Friedel-Crafts alkylation and Friedel-Crafts acylation

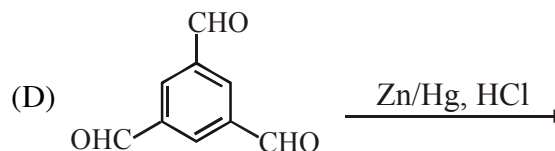
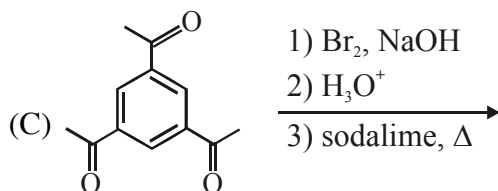
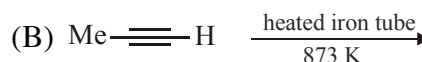
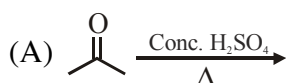
AH0173

55. The product **S** is -



AH0173

56. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are) [IIT 2018]

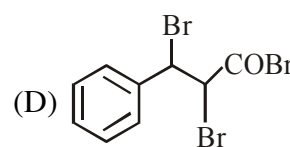
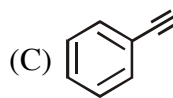
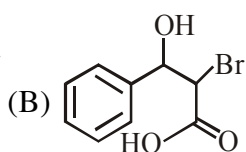
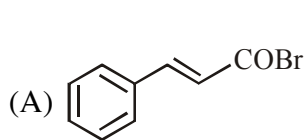


AH0174

### Paragraph "X"

Treatment of benzene with CO/HCl in the presence of anhydrous  $\text{AlCl}_3/\text{CuCl}$  followed by reaction with  $\text{Ac}_2\text{O}/\text{NaOAc}$  gives compound X as the major product. Compound X upon reaction with  $\text{Br}_2/\text{Na}_2\text{CO}_3$ , followed by heating at 473 K with moist KOH furnishes Y as the major product. Reaction of X with  $\text{H}_2/\text{Pd-C}$ , followed by  $\text{H}_3\text{PO}_4$  treatment gives Z as the major product. [IIT 2018] (There are two questions based on PARAGRAPH "X", the question given below is one of them)

57. The compound Y is :-

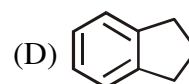
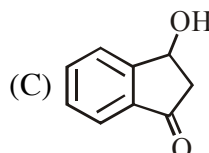
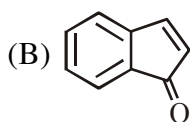
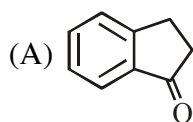


AH0175

### Paragraph "X"

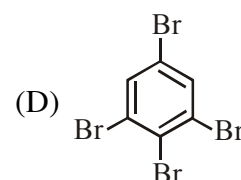
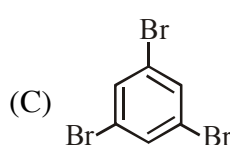
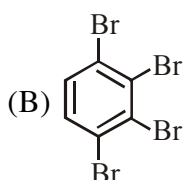
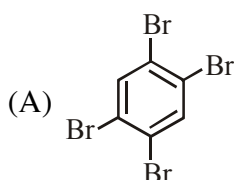
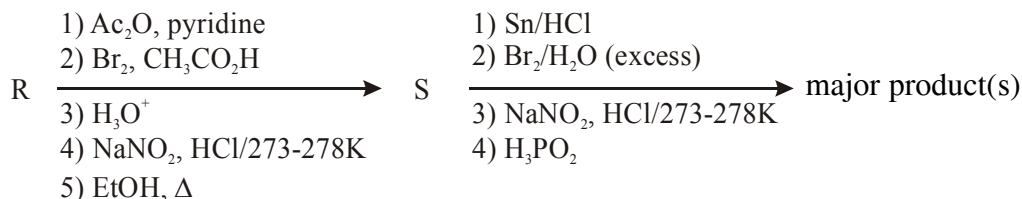
Treatment of benzene with CO/HCl in the presence of anhydrous  $\text{AlCl}_3/\text{CuCl}$  followed by reaction with  $\text{Ac}_2\text{O}/\text{NaOAc}$  gives compound X as the major product. Compound X upon reaction with  $\text{Br}_2/\text{Na}_2\text{CO}_3$ , followed by heating at 473 K with moist KOH furnishes Y as the major product. Reaction of X with  $\text{H}_2/\text{Pd-C}$ , followed by  $\text{H}_3\text{PO}_4$  treatment gives Z as the major product. (There are two question based on PARAGARAPH "X", the question given below is one of them)

58. The compound Z is :-



AH0175

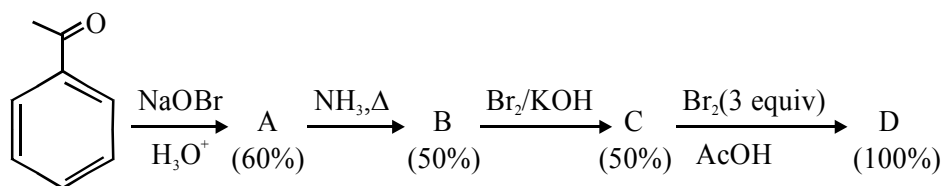
59. Aniline reacts with mixed acid (conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$ ) at 288 K to give P (51%), Q (47%) and R (2%). The major product(s) the following reaction sequence is (are) :- [IIT 2018]



AH0176

60. In the following reaction sequence, the amount of D (in g) formed from 10 moles of acetophenone is \_\_\_\_\_. [IIT 2018]

(Atomic weight in  $\text{g mol}^{-1}$ : H = 1, C = 12, N = 14, O = 16, Br = 80. The yield (%) corresponding to the product in each step is given in the parenthesis)

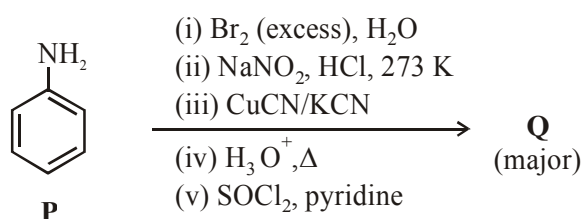


AH0177

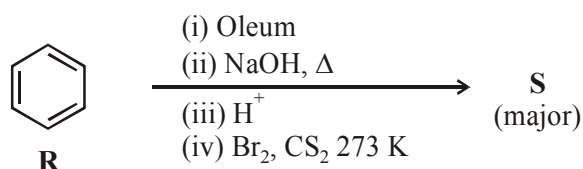
61. Scheme 1 and 2 describe the conversion of P to Q and R to S, respectively. Scheme 3 describes the synthesis of T from Q and S. The total number of Br atoms in a molecule of T is \_\_\_\_\_

Scheme 1 :

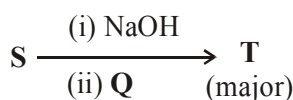
[IIT 2019]



Scheme 2 :



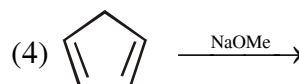
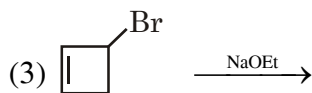
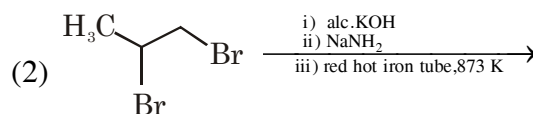
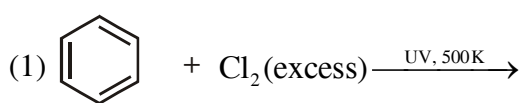
Scheme 3 :



AH0178

62. Choose the correct option(s) that give(s) an aromatic compound as the major product.

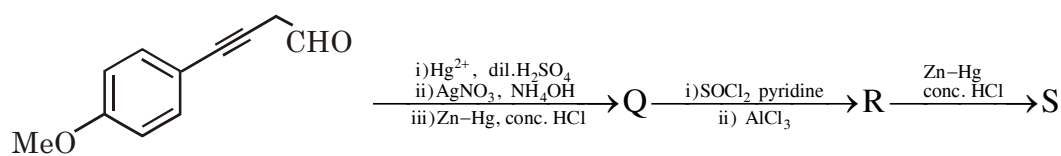
[IIT 2019]



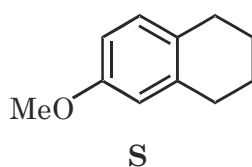
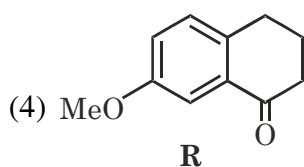
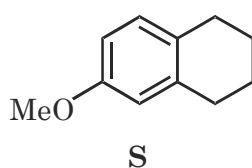
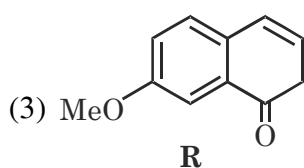
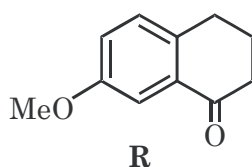
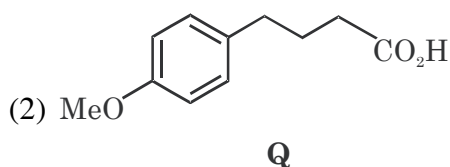
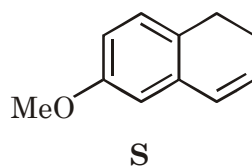
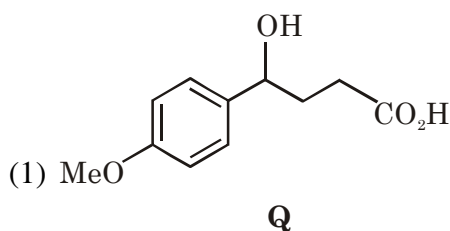
AH0179

63. Choose the correct option(s) for the following reaction sequence

[IIT 2019]



Consider Q, R and S as major products



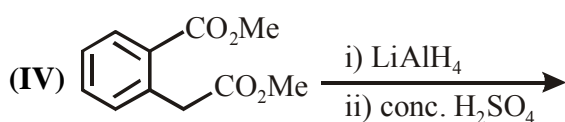
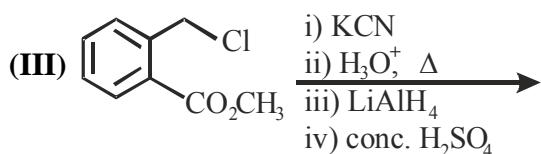
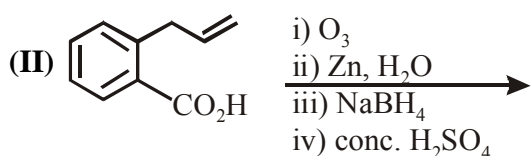
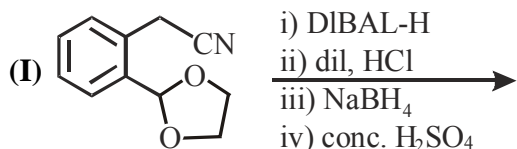
AH0180



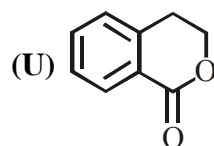
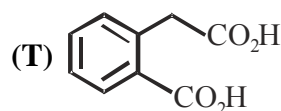
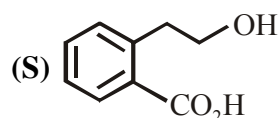
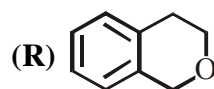
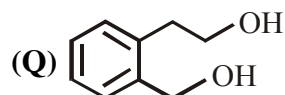
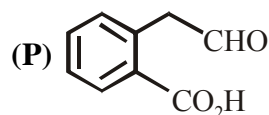
64. Answer the following by appropriately matching the lists based on the information given in the paragraph

List-I includes starting materials and reagents of selected chemical reactions. List-II gives structures of compounds that may be formed as intermediate products and/or final products from the reactions of List-I [IIT 2019]

## List-I



## List-II



Which of the following options has correct combination considering List-I and List-II?

(1) (III), (S), (R)

(2) (IV), (Q), (R)

(3) (III), (T), (U)

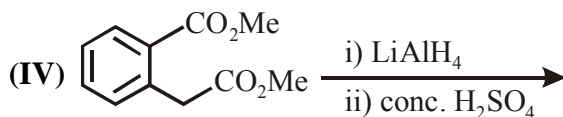
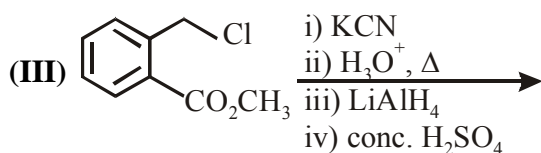
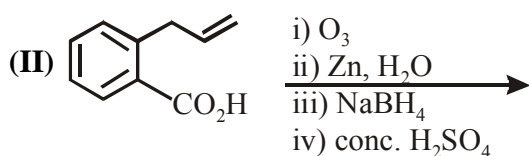
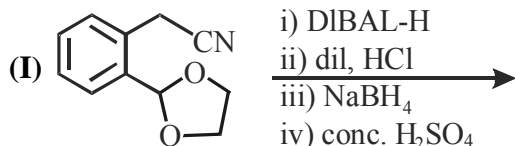
(4) (IV), (Q), (U)

AH0181

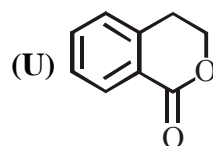
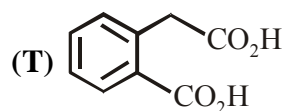
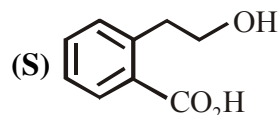
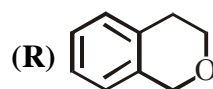
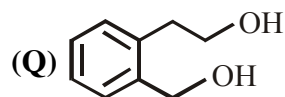
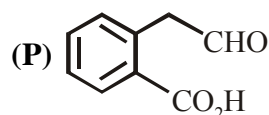
65. Answer the following by appropriately matching the lists based on the information given in the paragraph

List-I includes starting materials and reagents of selected chemical reactions. List-II gives structures of compounds that may be formed as intermediate products and/or final products from the reactions of List-I [IIT 2019]

## List-I



## List-II



Which of the following options has correct combination considering List-I and List-II?

(1) (I), (Q), (T), (U)

(2) (II), (P), (S), (U)

(3) (II), (P), (S), (T)

(4) (I), (S), (Q), (R)

AH0182

## ANSWER-KEY

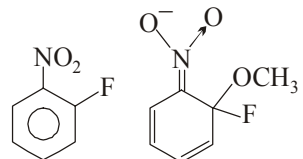
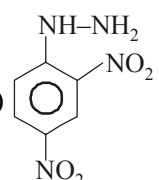
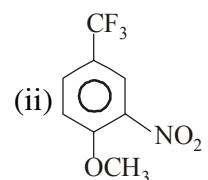
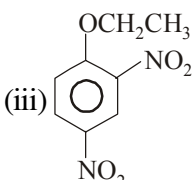
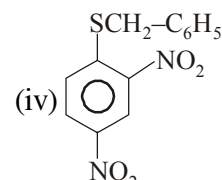
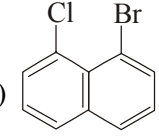
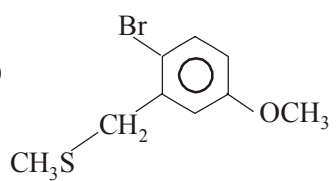
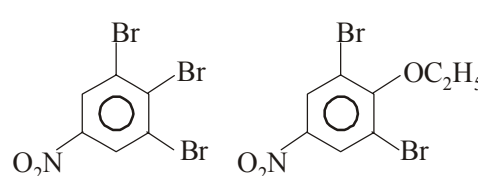
## EXERCISE # O-I

- |              |              |              |              |              |
|--------------|--------------|--------------|--------------|--------------|
| 1. Ans. (B)  | 2. Ans. (C)  | 3. Ans. (C)  | 4. Ans. (C)  | 5. Ans. (C)  |
| 6. Ans. (B)  | 7. Ans. (D)  | 8. Ans. (B)  | 9. Ans. (B)  | 10. Ans. (D) |
| 11. Ans. (C) | 12. Ans. (A) | 13. Ans. (B) | 14. Ans. (A) | 15. Ans. (B) |
| 16. Ans. (B) | 17. Ans. (D) | 18. Ans. (B) | 19. Ans. (B) | 20. Ans. (A) |
| 21. Ans. (A) | 22. Ans. (B) | 23. Ans. (A) | 24. Ans. (C) | 25. Ans. (B) |
| 26. Ans. (B) | 27. Ans. (B) | 28. Ans. (D) | 29. Ans. (C) | 30. Ans. (D) |
| 31. Ans. (D) | 32. Ans. (A) | 33. Ans. (D) | 34. Ans. (C) | 35. Ans. (C) |
| 36. Ans. (A) | 37. Ans. (A) | 38. Ans. (B) | 39. Ans. (C) | 40. Ans. (A) |
| 41. Ans. (D) | 42. Ans. (C) | 43. Ans. (A) |              |              |

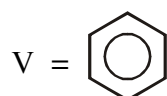
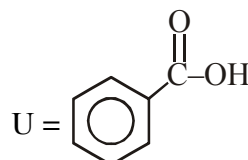
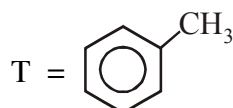
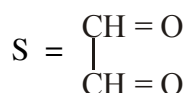
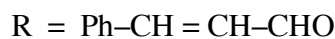
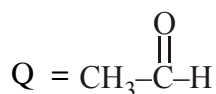
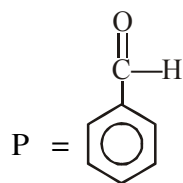
## EXERCISE # O-II

- |  |                  |  |                    |
|--|------------------|--|--------------------|
| 1. Ans. (A,B,C,D)                                    | 2. Ans. (A,B,D)  | 3. Ans. (B,D)                                | 4. Ans. (B,C,D)    |
| 5. Ans. (A,B,C)                                      | 6. Ans. (B,D)    | 7. Ans. (C,D)                                | 8. Ans. (C,D)      |
| 9. Ans. (B,C)  | 10. Ans. (B,C,D) | 11. Ans. (A,B)                               | 12. Ans. (A,B,C,D) |
| 13. Ans. (A,B,C)                                     | 14. Ans. (A,C)   | 15. Ans. (A,B,D)                             | 16. Ans. (B,C,D)   |
| 17. Ans. (A,B,C)                                     | 18. Ans. (A,B,C) | 19. Ans. (A,B,C,D)                           | 20. Ans. (C)       |
| 21. Ans. (B)   | 22. Ans. (A)     | 23. Ans. (A,C,D)                             | 24. Ans. (B,C)     |
| 25. Ans. (A,B,D)                                     | 26. Ans. (A)     | 27. Ans. (A)                                 | 28. Ans. (A)       |
| 29. Ans. (B)   | 30. Ans. (A)     | 31. Ans. (A)-Q;(B)-P,R,S;(C)-R,S;(D)-P,Q,R,S |                    |
| 32. Ans. (A)→P,S ; (B)→P,R ; (C)→Q,S ; (D)→P,R       |                  |  |                    |
| 33. Ans. (A)→Q,R,S ; (B)→P,R,S ; (C)→R,S ; (D)→Q,R,S |                  |  |                    |
| 34. Ans. (A)→R,T ; (B)→R,S ; (C)→Q,S ; (D)→P,R       |                  |  |                    |

## EXERCISE # S-I

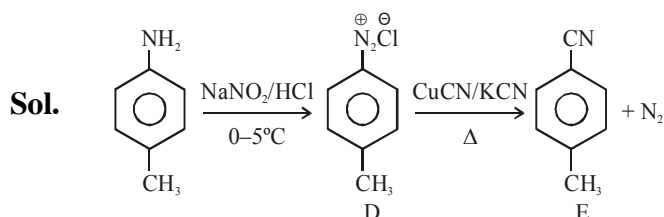
1. Ans. 
2. Ans. (i)  (ii)  (iii)  (iv) 
3. Ans. (i)  (ii) 
4. Ans. 

Solution for No. 8 & 9



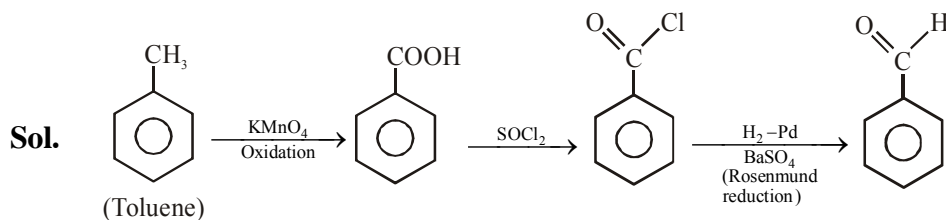
EXERCISE # (MAINS)

1. Ans. (1)      2. Ans. (2)      3. Ans. (4)      4. Ans. (2)  
5. Ans. (3)      6. Ans. (1)



Formation of D is example of Diazotisation  
Formation of E from D is example of Sandmeyer's Reaction

7. Ans. (2)



8. Ans. (3)      9. Ans.(4)      10. Ans.(2)      11. Ans.(4)  
12. Ans.(1)      13. Ans.(3)      14. Ans.(4)      15. Ans. (4)  
16. Ans. (1)      17. Ans. (3)      18. Ans. (2)      19. Ans. (3)  
20. Ans. (2)      21. Ans. (1)      22. Ans. (4)      23. Ans. (2)  
24. Ans. (1)      25. Ans.(4)      26. Ans. (Bonus)      27. Ans. (3)  
28. Ans. (3)      29. Ans. (2)      30. Ans. (3)      31. Ans. (1)

32. Ans. (4)

33. Ans. (1)

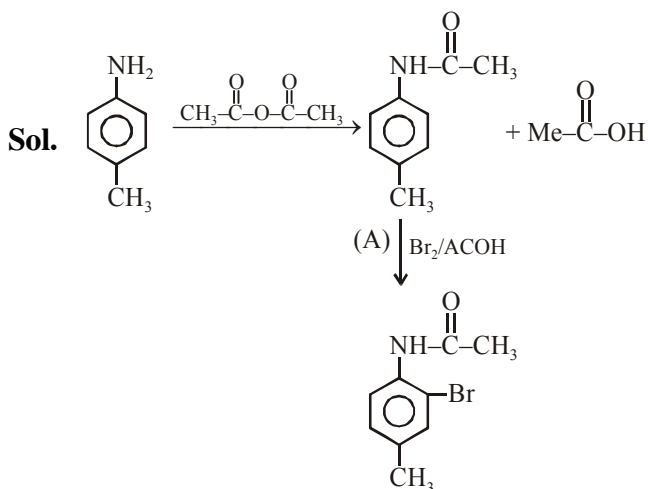
34. Ans.(3)

35. Ans. (1)

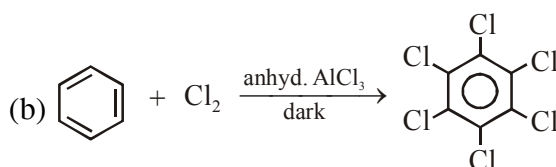
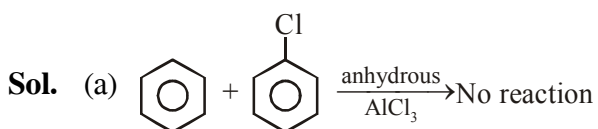
36. Ans. (1)

37. Ans. (4)

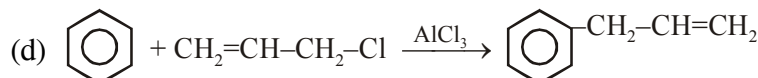
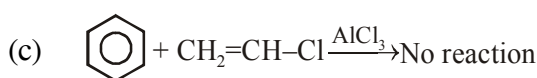
38. Ans. (1)



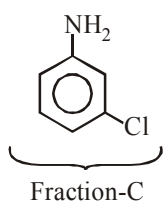
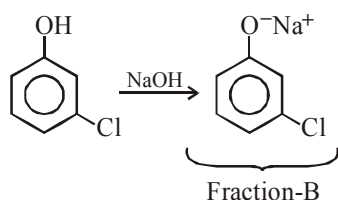
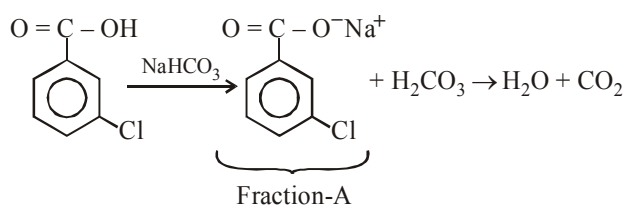
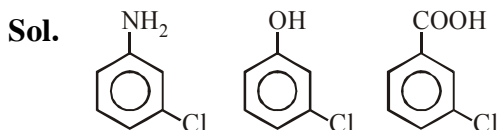
39. Ans. (2)



(electrophilic substitution)

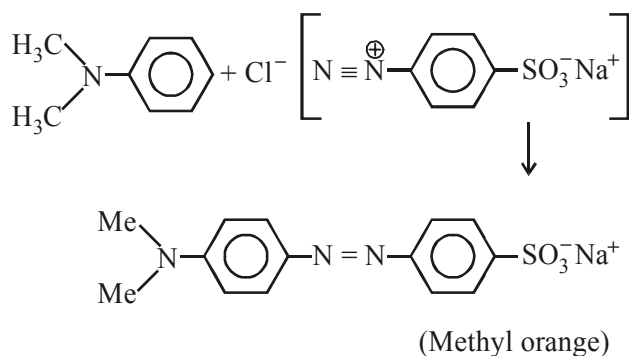


40. Ans. (3)



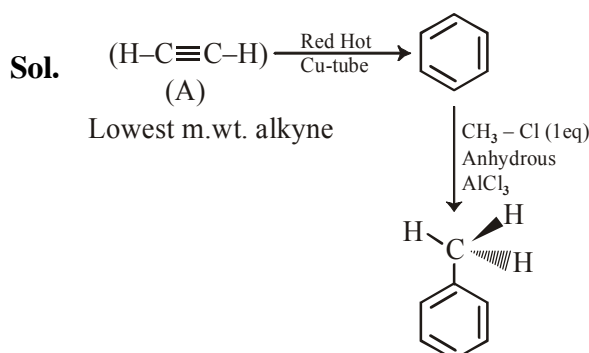
41. Ans. (1)

Sol.



It is an acid base indicator

42 Ans. (13)



Total 13 atom are present in same plane (7 carbon & 6 hydrogen atoms.)

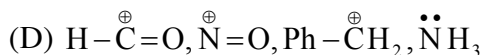
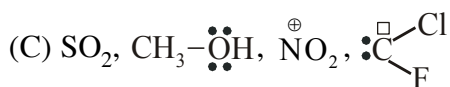
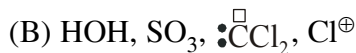
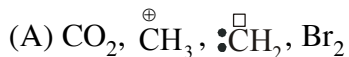
**EXERCISE # (ADVANCE)**

- |   |                  |                  |                  |
|---|------------------|------------------|------------------|
| 1. Ans. (D)   | 2. Ans. (A)      | 3. Ans. (A,B)    | 4. Ans. (C)      |
| 5. Ans. (D)   | 6. Ans. (C)      | 7. Ans. (C)      | 8. Ans. (A)      |
| 9. Ans. (A,C)   | 10. Ans. (C)     | 11. Ans. (B)     | 12. Ans. (A,C)   |
| 13. Ans. (D)  | 14. Ans. (C)     | 15. Ans. (B)     | 16. Ans. (D)     |
| 17. Ans. (C)  | 18. Ans. (C)     | 19. Ans. (D)     | 20. Ans. (D)     |
| 21. Ans. (B)  | 22. Ans. (C)     | 23. Ans. (C)     | 24. Ans. (B)     |
| 25. Ans. (B)  | 26. Ans. (C)     | 27. Ans. (D)     | 28. Ans. (A,B,C) |
| 29. Ans. (C)  | 30. Ans. (A)     |                  |                  |
| 31. Ans. (A)→R, S, T ; (B)→T ; (C)→P, Q ; (D)→R             |                  |                  | 32. Ans. (C)     |
| 33. Ans. (A)→(R,S,T) ; (B)→(P, S) ; (C)→(R, S) ; (D)→(Q, R) |                  |                  |                  |
| 34. Ans. (A,B,C,D)  | 35. Ans. (B)     | 36. Ans. (B,D)   | 37. Ans. (A)     |
| 38. Ans. (B)  | 39. Ans. (A)     | 40. Ans. (A,B,C) | 41. Ans. (C)     |
| 42. Ans. (C)  | 43. Ans. (A)     | 44. Ans. (4)     | 45. Ans. (B,C)   |
| 46. Ans. (B)  | 47. Ans. (B,C,D) | 48. Ans. (B,C)   | 49. Ans. (5)     |
| 50. Ans. (D)  | 51. Ans. (A)     | 52. Ans. (B)     | 53. Ans. (C)     |
| 54. Ans. (B)  | 55. Ans. (D)     | 56. Ans.(A,B,D)  | 57. Ans.(C)      |
| 58. Ans.(A)   | 59. Ans.(D)      | 60. Ans.(495)    | 61. Ans. (4.00)  |
| 62. Ans. (2,4)  | 63. Ans. (2,4)   | 64. Ans. (2)     | 65. Ans. (2)     |

## HALOGEN DERIVATIVES

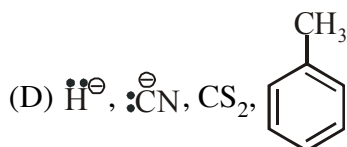
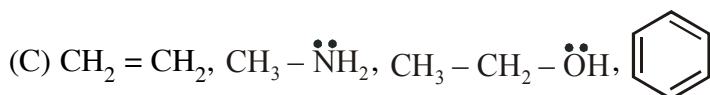
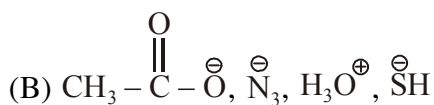
### EXERCISE # O-I (MAINS ORIENTED)

1. Identify set of electrophiles :



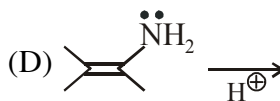
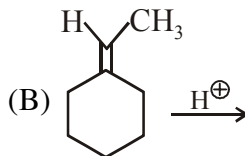
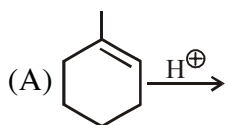
HD0001

2. Identify set of nucleophiles :



HD0002

3. Which of the following will form 2° carbocation?



HD0003

4. Incorrect statement about carbocation is :

(A) It is lewis acid

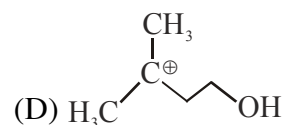
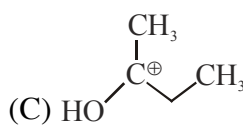
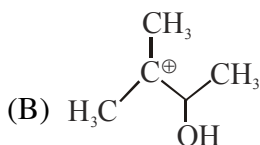
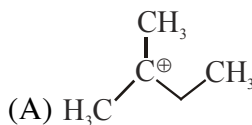
(B) It has 6 electrons in valency shell

(C) It is electrophile

(D) It is always trigonal planer

HD0004

5. Which of the following carbocation is most stable ?



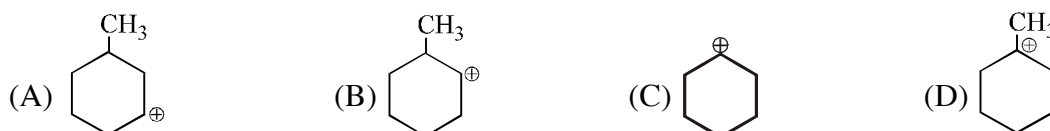
HD0005

6. Which carbocation is least likely to be formed as an intermediate ?



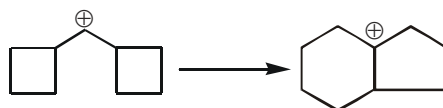
HD0006

7. Which one of the following carbocation would you expect to rearrange :



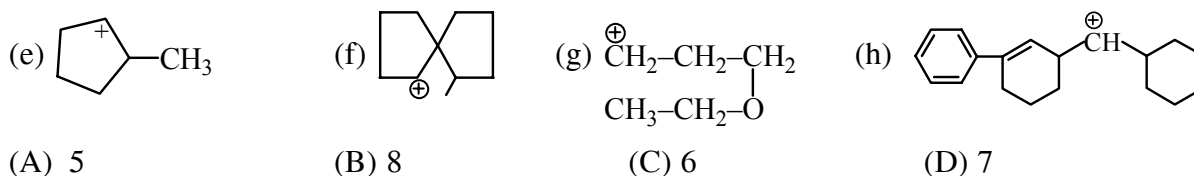
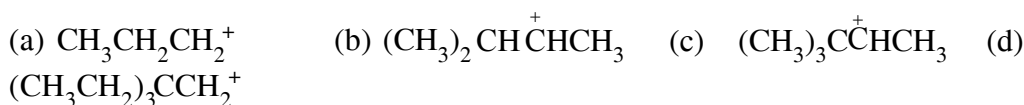
HD0007

8. How many 1,2-shifts are involved during the course of following reaction :



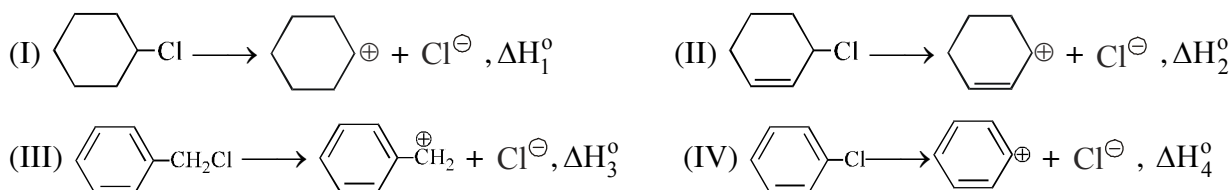
HD0008

9. How many following carbocation undergo re-arrangement -

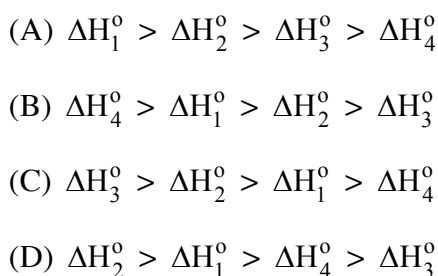


HD0009

10. For the reactions




The correct decreasing order of enthalpies of reaction for producing carbocation is :

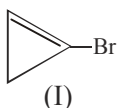


HD0010



11. -Br, which is not the correct statement :

- (A) I is more soluble in water than bromocyclopropane
- (B) I gives pale yellow ppt. on addition with aq.  $\text{AgNO}_3$
- (C) I is having lower dipole moment than bromocyclopropane

(D) I is more ionic than 

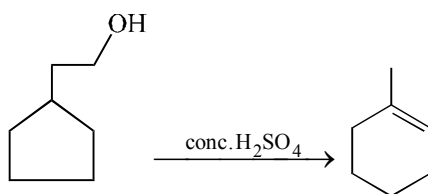
HD0011

12. A solution of (–)-1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of  $\text{SbCl}_5$ , due to the formation of :-

- (A) carbanion
- (B) Carbene
- (C) carbocation
- (D) free radical

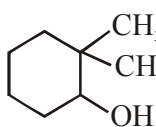
HD0012

13. How many 1,2-Shifts of carbocation intermediate are involved during the course of following reaction :



- (A) 1
- (B) 2
- (C) 3
- (D) 4

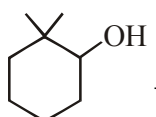
HD0013

14.   $\xrightarrow[\Delta]{\text{H}^+}$  (X) (Major product)

Major product (X) is :

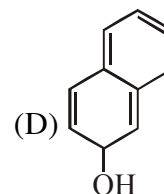
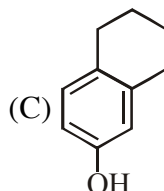
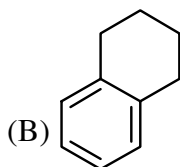
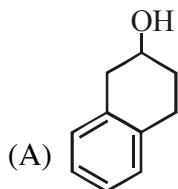
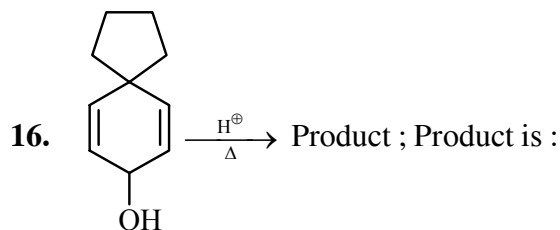
- (A) 
- (B) 
- (C) 
- (D) 

HD0014

15.   $\xrightarrow[5^\circ\text{C}]{\text{H}^+}$  P. The product P is :

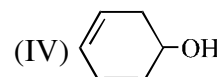
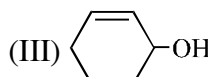
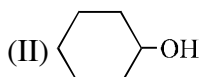
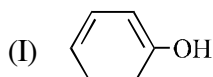
- (A) 
- (B) 
- (C) 
- (D) 

HD0015



HD0016

17. Among the given compounds, the correct order of rate of dehydration is :



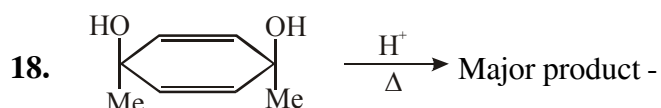
(A) I < II < III < IV

(B) II < III < IV < I

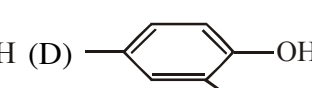
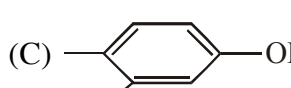
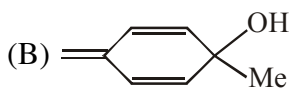
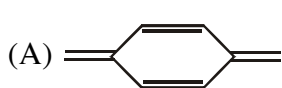
(C) I < III < IV < II

(D) I < II < III = IV

HD0017

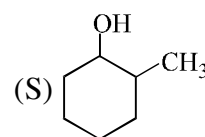
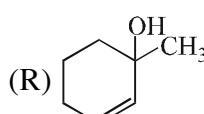
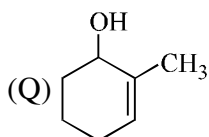
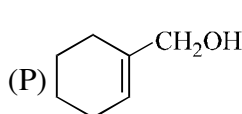


Major product is :



HD0018

19. Identify the correct order of rate of dehydration when given compounds are treated with conc.  $\text{H}_2\text{SO}_4$  :



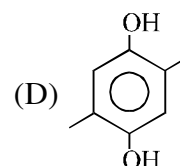
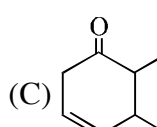
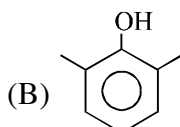
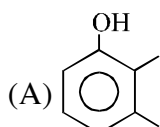
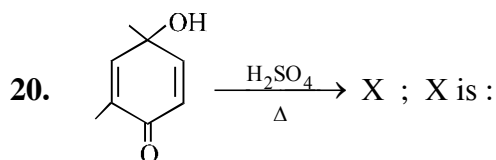
(A) P > Q > R > S

(B) Q > P > R > S

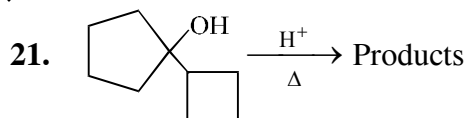
(C) R > Q > P > S

(D) R > Q > S > P

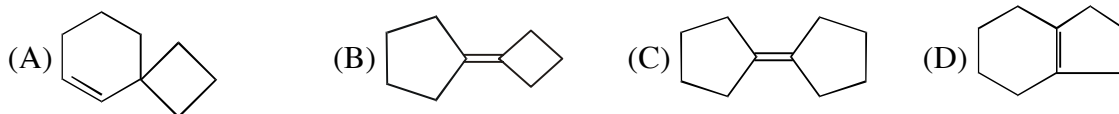
HD0019



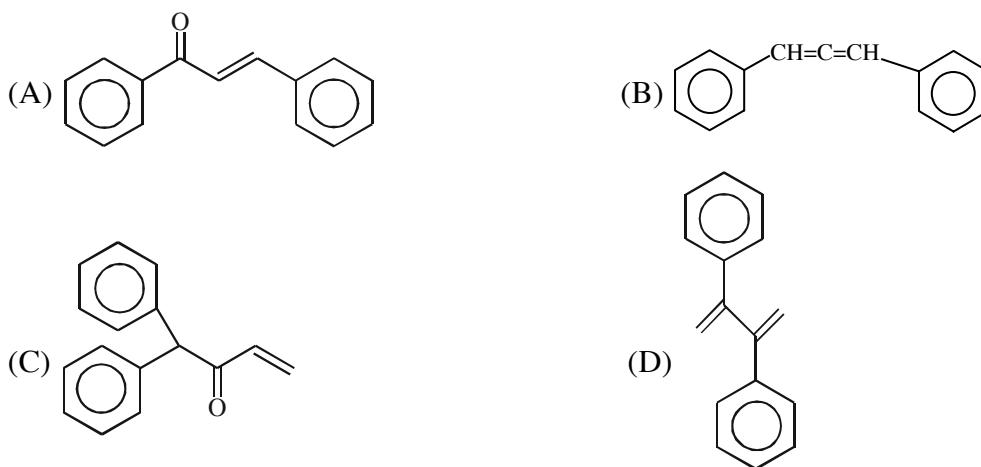
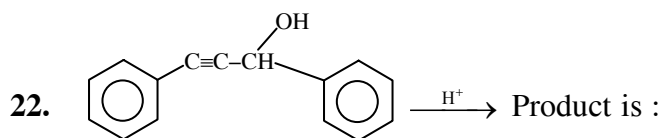
HD0020



Major products is :

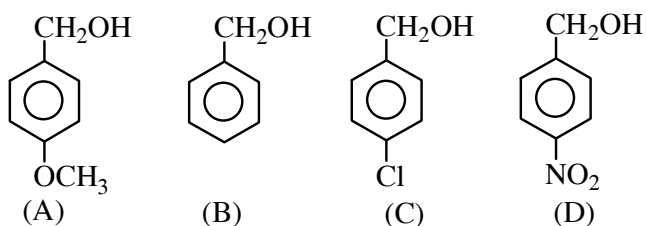


HD0021



HD0022

23. What is the decreasing order of rate of reaction with HBr for the following benzyl alcohol and its derivative :



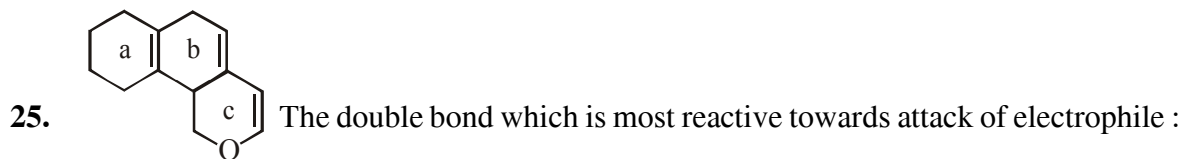
(A) A > C > D > B (B) A > B > D > C (C) D > C > B > A (D) A > B > C > D

HD0023

24. Which will dehydrate at fastest rate by  $H_3PO_4$  :

- (A) 2-methyl butan-2-ol (B) 3-methyl butan-2-ol  
 (C) Butan-1-ol (D) 2-methyl butan-1-ol

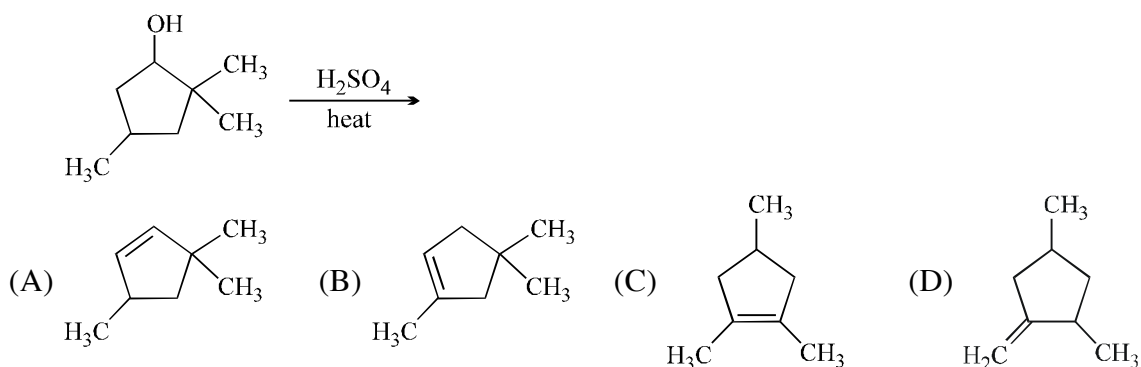
HD0024



- (A) a (B) b (C) c (D) None

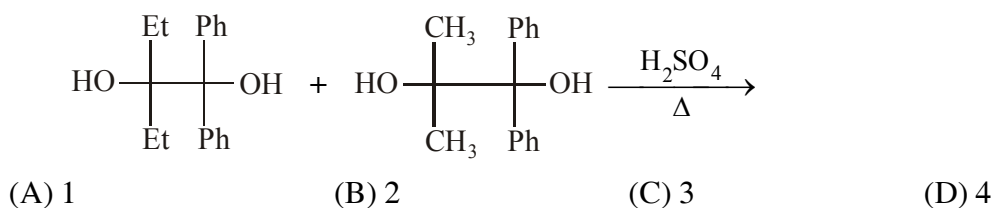
HD0025

26. The major product formed in the following reaction is :



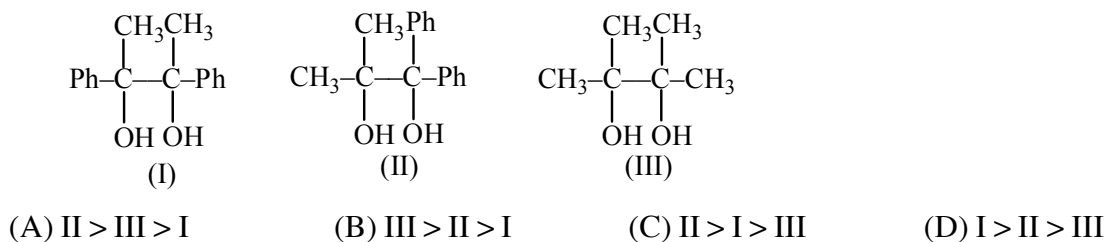
HD0026

27. How many products are obtained in the given reaction :

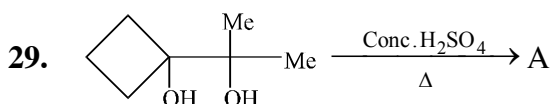


HD0027

28. Compare rate of reaction towards pinacol pinacolone rearrangement.

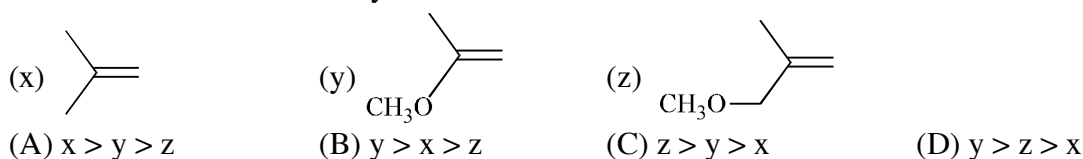


HD0028



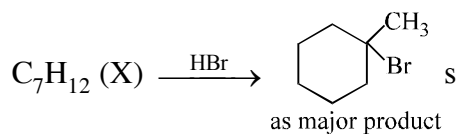
HD0029

30. What is the order of reactivity with HBr :

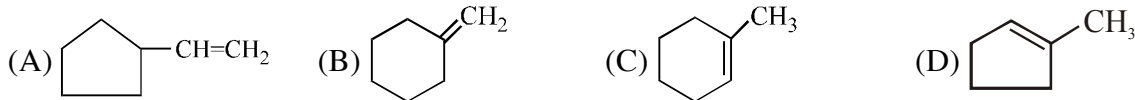


HD0030

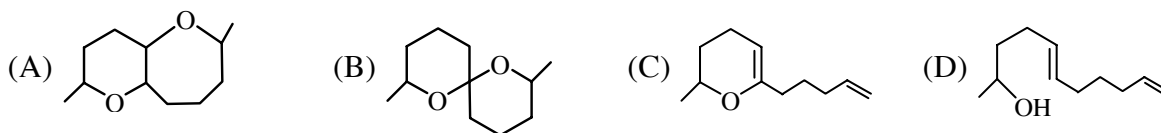
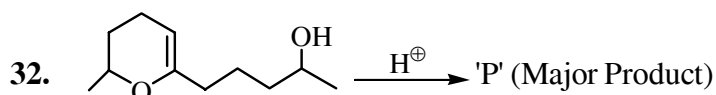
31. In the given reaction



(X) can not be :

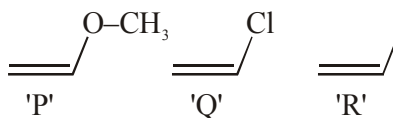


HD0031



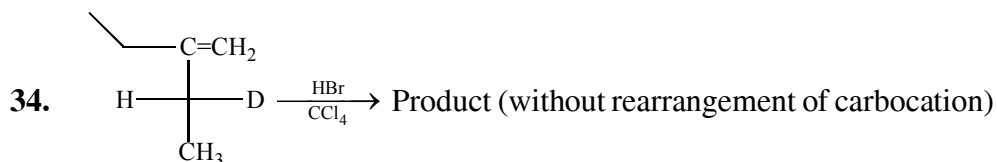
HD0032

33. Arrange the following compounds in decreasing order of electrophilic addition :



(A) P > Q > R (B) P > R > Q (C) R > P > Q (D) R > Q > P

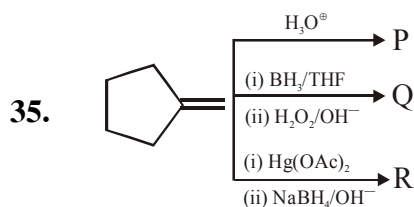
HD0033



What is stereochemistry of product :

(A) Racemic mixture (B) Optically inactive  
(C) Mixture of diastereomers (D) Meso product

HD0034

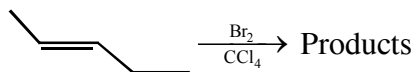


Correct statement regarding products P, Q & R

(A) Product P & R are same (B) Product Q & R are same  
(C) P & Q are functional isomers (D) Product P, Q & R all are different

HD0035

36. Select the incorrect statement about the product mixture in the following reaction :



- (A) It is optically active  
 (B) It is racemic mixture  
 (C) It is a resolvable mixture  
 (D) It is a mixture of erythro compounds

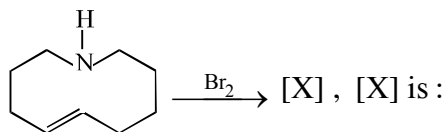
HD0036

37. If P & Q are the major products then P & Q are respectively :

- (A) ;   
 (B) ;   
 (C) ;   
 (D) ;

HD0037

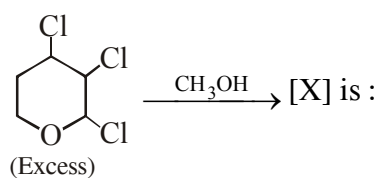
38. In the given reaction :



- (A) (B) (C) (D)

HD0038

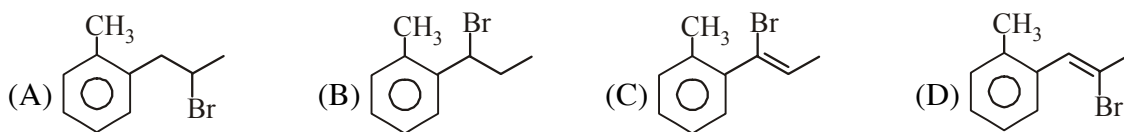
39. In the given reaction:



- (A) (B) (C) (D)

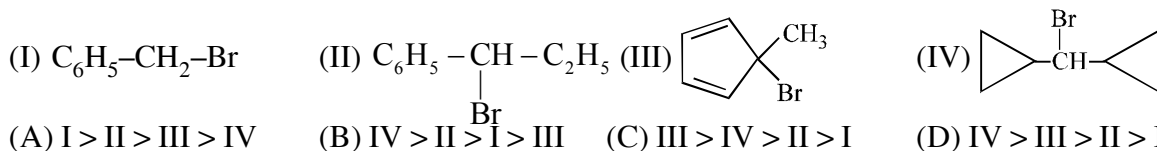
HD0039

40. Which compound undergoes hydrolysis by the  $S_N1$  mechanism at the fastest rate?



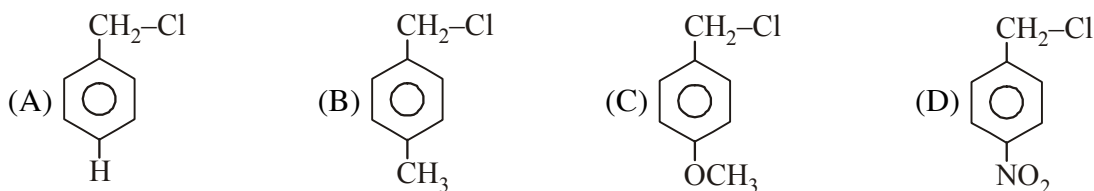
HD0040

41. Arrange the following compounds in decreasing order of their reactivity for hydrolysis reaction



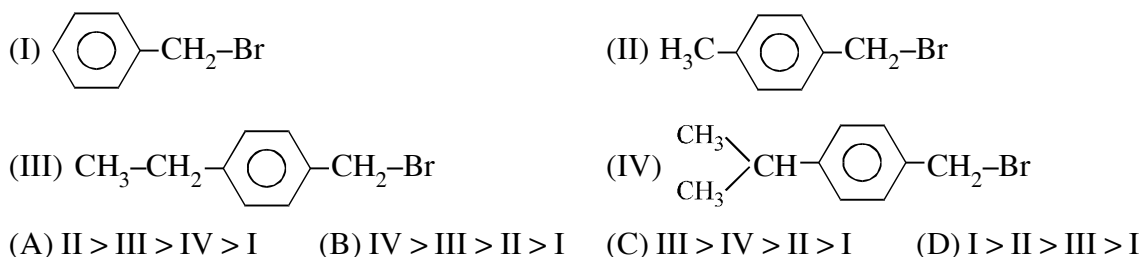
HD0041

42. Which of the following is most reactive toward  $S_N1$  reaction.



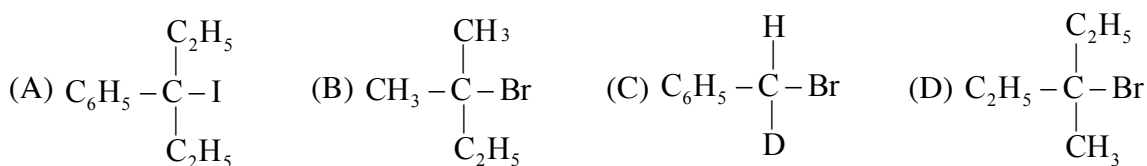
HD0042

43. Arrange the following compounds in order of decreasing rate of hydrolysis for  $S_N1$  reaction:



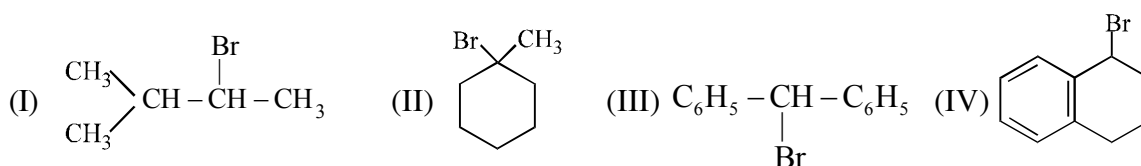
HD0043

44. Which one of the following compounds will give enantiomeric pair on treatment with HOH?



HD0044

45. Consider the  $S_N1$  solvolysis of the following halides in aqueous formic acid:

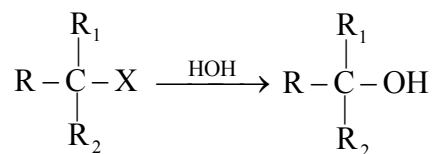


Decide decreasing order of reactivity of above alkyl halide?

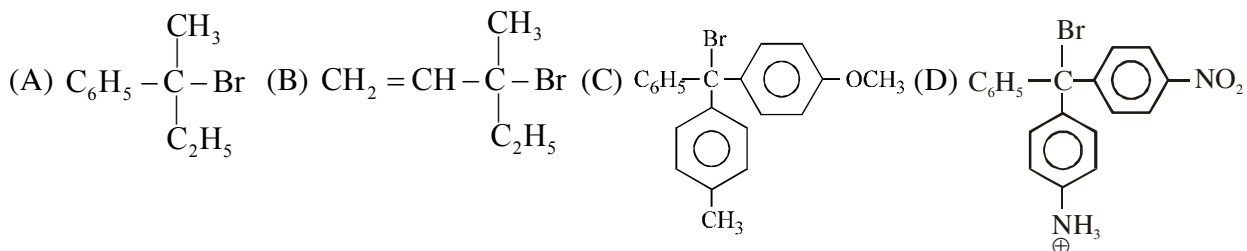


HD0045

46. For the given reaction

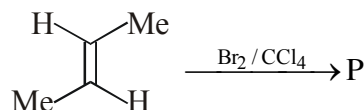


Which substrate will give maximum racemisation?



HD0046

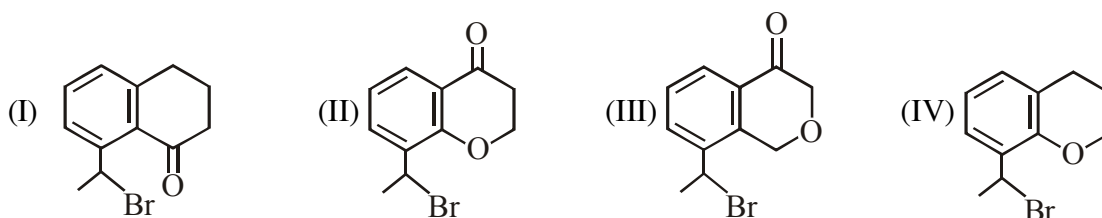
47. Select incorrect statements about the product (P) of the reaction :



- (A) P is optically inactive due to internal compensation  
 (B) P is optically inactive due to the presence of plane of symmetry in the molecule  
 (C) The structure of P can have three optical isomers possible.  
 (D) P can have four possible optical isomers.

HD0047

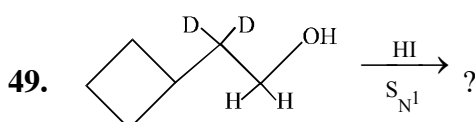
48. Consider the following molecules :



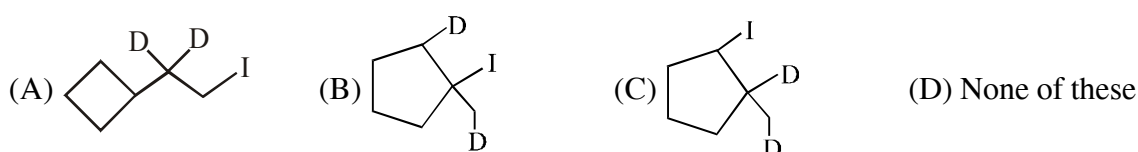
The correct decreasing ease of hydrolysis of alkyl halide is :

- (A) II > III > IV > I (B) II > IV > III > I (C) II > I > III > IV (D) IV > II > III > I

HD0048

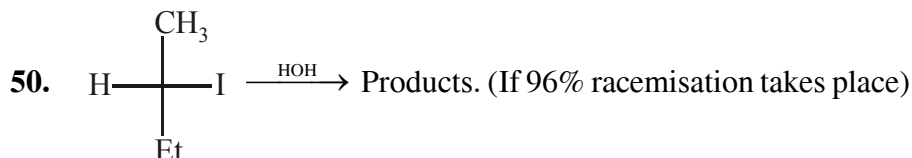


Major product is:



HD0049



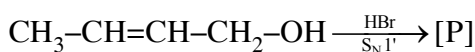


Find out the correct statement about the reaction.

- (A) Among the products 48% S and 48% R configuration containing molecules are present  
 (B) Among the products 50% S and 50% R configuration containing molecules are present  
 (C) Among the products 48% S and 52% R configuration containing molecules are present  
 (D) Among the products 52% S and 48% R configuration containing molecules are present

HD0050

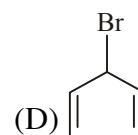
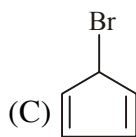
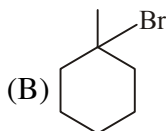
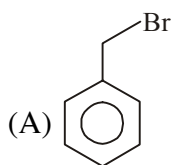
51. In the given reaction the product [P] can be :



- (A)  $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{Br}$  (B)  $\text{CH}_3 - \overset{\text{Br}}{\text{C}} - \text{CH} = \text{CH}_2$   
 (C)  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$  (D)  $\text{CH}_3 - \overset{\text{Br}}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{OH}$

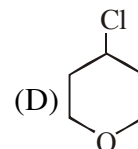
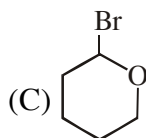
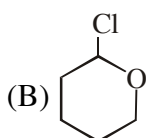
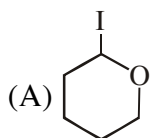
HD0051

52. Which of the following can not give  $\text{S}_\text{N}1$  reaction easily?



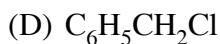
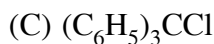
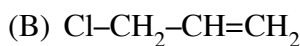
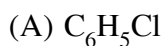
HD0052

53. Which one of the following compounds will be most reactive for  $\text{S}_\text{N}1$  reactions ?



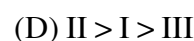
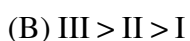
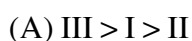
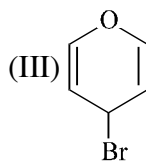
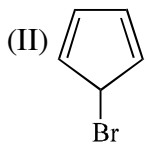
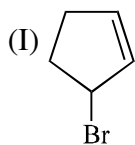
HD0053

54. Which of the following compounds is most rapidly hydrolysed by  $\text{S}_\text{N}1$  mechanism ?



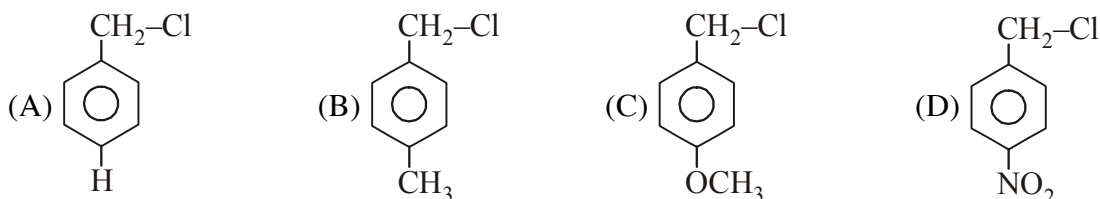
HD0054

55. Among the bromides I-III given below, the order of reactivity in  $\text{S}_\text{N}1$  reaction is:



HD0055

56. Which of the following is most reactive toward  $S_N2$ .



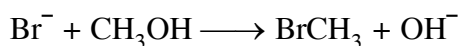
HD0056

57. For reaction  $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$   
the rate of reaction is given by the expression :

- (A) Rate =  $k [CH_3Br]$  (B) Rate =  $k [OH^-]$   
(C) Rate =  $k [CH_3Br][OH^-]$  (D) Rate =  $k [CH_3Br]^0 [OH^-]^0$

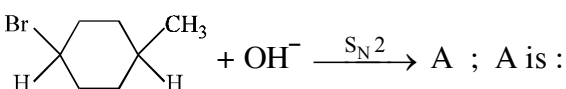
HD0057

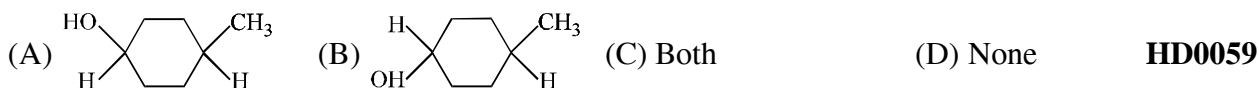
58. Select suitable reason for non-occurrence of the following reaction.



- (A) Attacking nucleophile is stronger one  
(B) Leaving group is a stronger base than nucleophile  
(C) Alcohols are not good substrate for  $S_N$  reaction  
(D) Hydroxide ions are weak bases

HD0058

59.  ; A is :

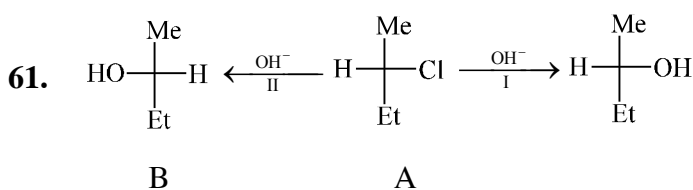


HD0059

60. The reactivity of 2-bromo-2-methylbutane (I), 1-bromopentane (II) and 2-bromopentane (III) towards  $S_N2$  displacement is such that :

- (A)  $I > II > III$  (B)  $I > III > II$  (C)  $II > III > I$  (D)  $II > I > III$

HD0060

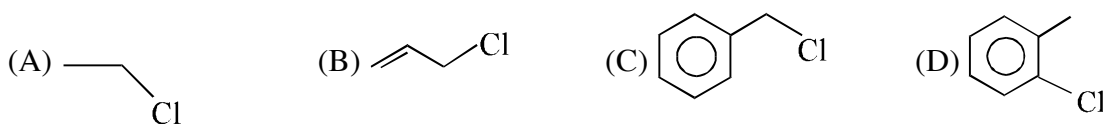


Mechanism involved :

- (A) I can't be  $S_N1$  (B) II can't be  $S_N2$  (C) I  $S_N1$  & II  $S_N2$  (D) I  $S_N2$  & II  $S_N1$

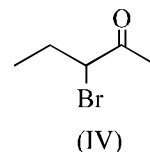
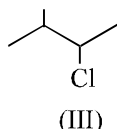
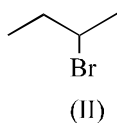
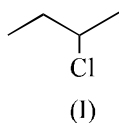
HD0061

62. In which of the following replacement of  $Cl^-$  is most difficult ?



HD0062

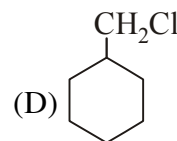
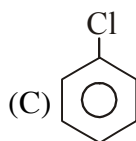
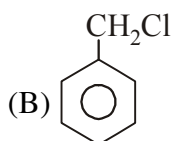
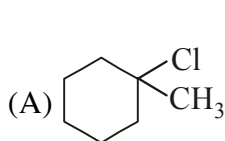
63. Arrange these compounds in order of increasing  $S_N2$  reaction rate :



- (A) III < I < II < IV    (B) III < II < I < IV    (C) IV < III < I < II    (D) III < IV < I < II

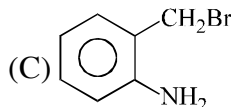
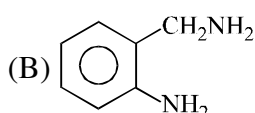
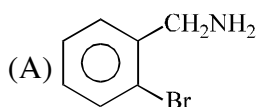
HD0063

64. Which reaction proceeds faster with NaI in DMSO ?



HD0064

65. The major product in the given reaction:  +  $NH_3 \longrightarrow$



(D) All of these

HD0065

66. The given compound  $CH_3-O-CH_2-Br$  gives which one of the following reactions:

(A) Only  $S_N1$

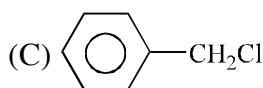
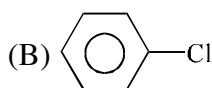
(B) Only  $S_N2$

(C)  $S_N1$  as well as  $S_N2$

(D)  $E_1$  only

HD0066

67. Which will give white ppt. with  $AgNO_3$ ?



(D) Both A & C

HD0067

68. Consider the following groups :

(I)  $-OAc$

(II)  $-OMe$

(III)  $-OSO_2Me$

(IV)  $-OSO_2CF_3$

The order of leaving group nature is:

(A) I > II > III > IV

(B) IV > III > I > II

(C) III > II > I > IV

(D) II > III > IV > I

HD0068

69. When ethyl bromide is treated with moist  $Ag_2O$ , the main product is:

(A) Ethyl ether

(B) Ethanol

(C) Ethoxy ethane

(D) All of these

HD0069

70. When ethyl bromide is treated with dry  $Ag_2O$ , the main product is:

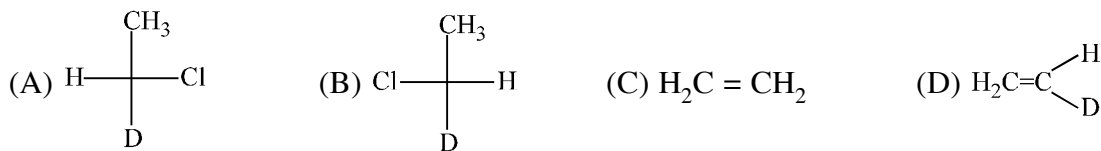
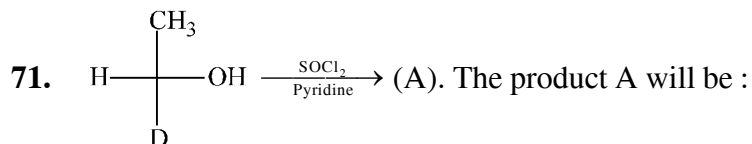
(A) Ethyl ether

(B) Ethanol

(C) Ethoxy ethane

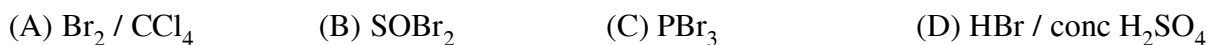
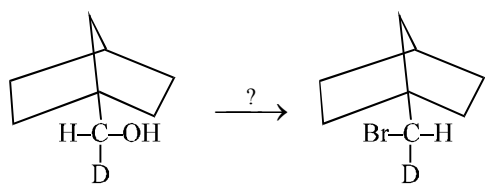
(D) All of these

HD0070



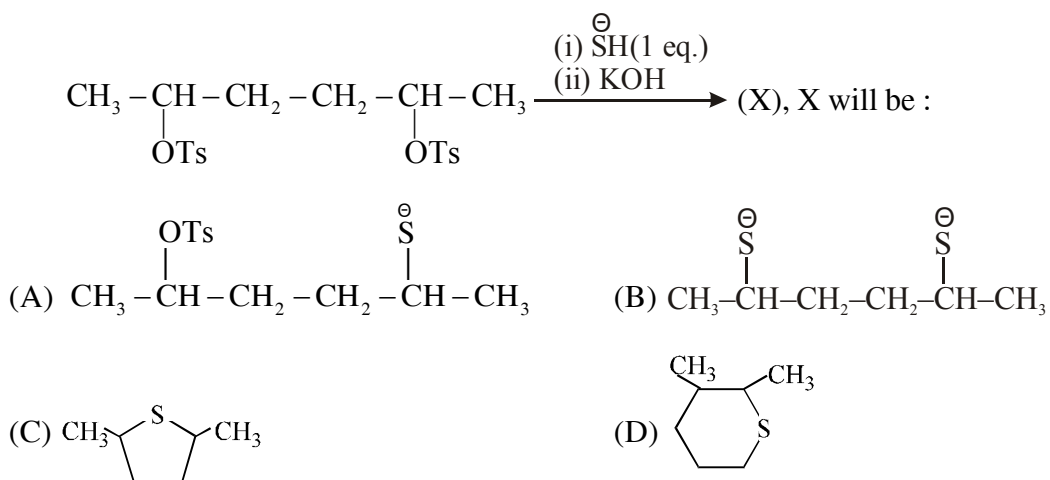
HD0071

72. Which reaction conditions (reagents) is suitable for the following reaction:

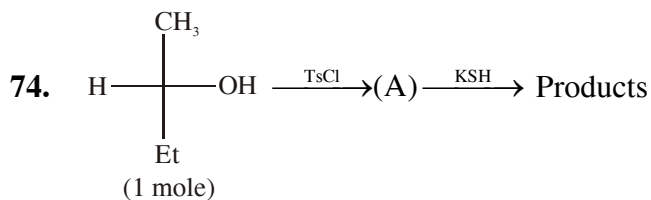


HD0072

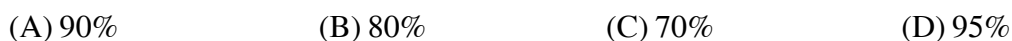
73. In the given reaction



HD0073



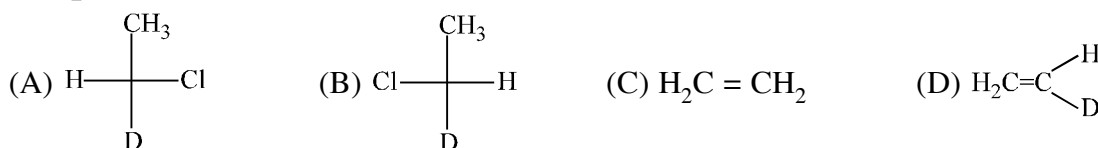
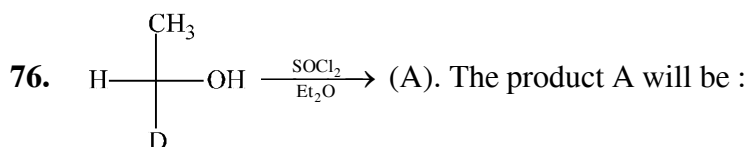
(Assuming all the substrate convert into substitution products containing 0.05 mole of S-configuration) Calculate the percentage of  $\text{S}_{\text{N}}2$  mechanism.



HD0074

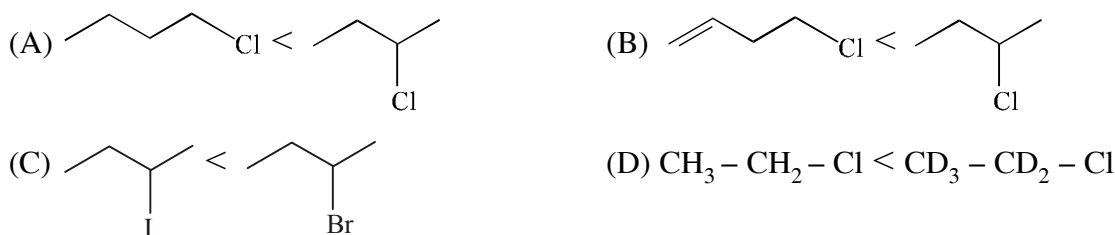
75. The reaction of  $\text{SOCl}_2$  on alkanols to form alkyl chlorides gives good yields because
- (A) Alkyl chlorides are immiscible with  $\text{SOCl}_2$
  - (B) The other products of the reaction are gaseous and escape out
  - (C) Alcohol and  $\text{SOCl}_2$  are soluble in water
  - (D) The reaction does not occurs via intermediate formation of an alkyl chloro sulphite.

HD0075



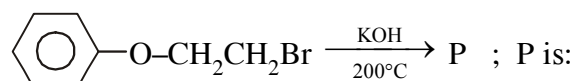
HD0076

77. In the given pairs, which pair represent correct order of rate dehydrohalogenation reaction.

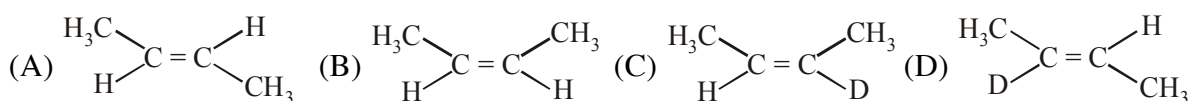
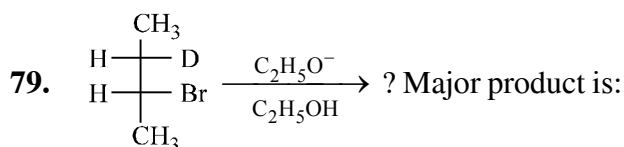


HD0077

78. The product of the reaction

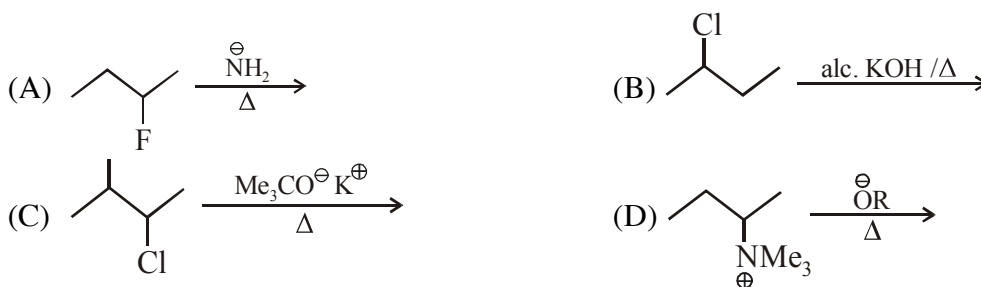


HD0078



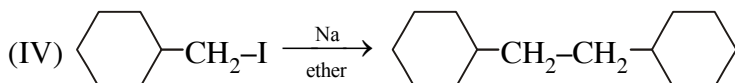
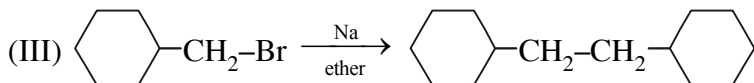
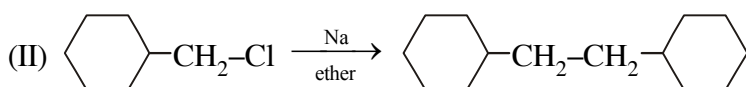
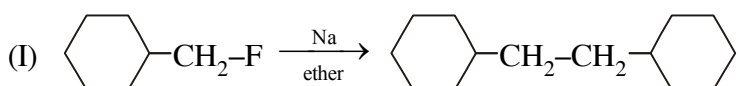
HD0079

80. Which of following reaction(s) produce Saytzeff product as a major product :



HD0080

81. The correct order of rate of following Wurtz reactions :



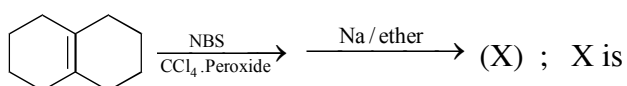
(A) I > II > III > IV

(B) II > I > III > IV

(C) IV > III > II > I

(D) In all rate of Wurtz reaction is same

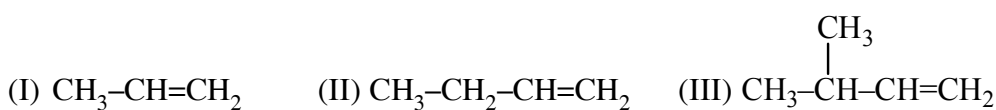
HD0081

82.  (X) ; X is



HD0082

83. Find out the correct order of rate of reaction towards free radical allylic substitution :



(A) I > II > III

(B) II > I > III

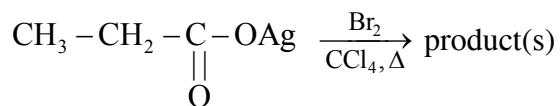
(C) III > II > I

(D) III > I > II

HD0083

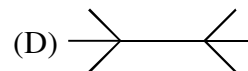
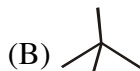
84. What will be the major product, when 2-methyl butane undergoes bromination in presence of light ?  
 (A) 1-Bromo-2-methyl butane (B) 2-Bromo-2-methyl butane  
 (C) 2-Bromo-3-methyl butane (D) 1-Bromo-3-methyl butane **HD0084**

85. Which can not be the possible product of the given reaction ?



- (A)  $\text{CH}_3 - \text{CH}_2 - \text{Br}$  (B)  $\text{CH}_3 - \text{CH}_2 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{O} - \text{CH}_2 - \text{CH}_3$   
 (C)  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$  (D)  $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$  **HD0085**

86. Choose that alkane which cannot give only one monochloro derivative upon reaction with chlorine in sun light :



**HD0086**

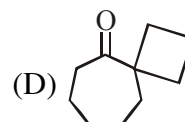
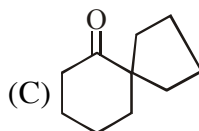
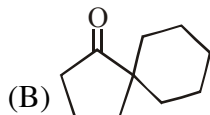
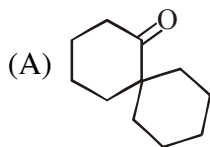
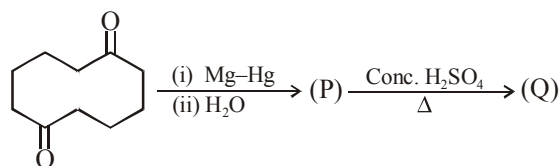
87. 2-chloropentane on halogenation with chlorine gives 2,3, dichloropentane. What will be the structure of free radical species formed in the reaction ?

- (A) Tetrahedral (B) Trigonal planar (C) Square planar (D) Pyramidal **HD0087**

88. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be -

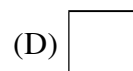
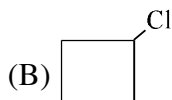
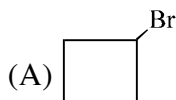
- (A) neopentane (B) propane (C) pentane (D) isopentane **HD0088**

89. Major product (Q) of following reaction is :



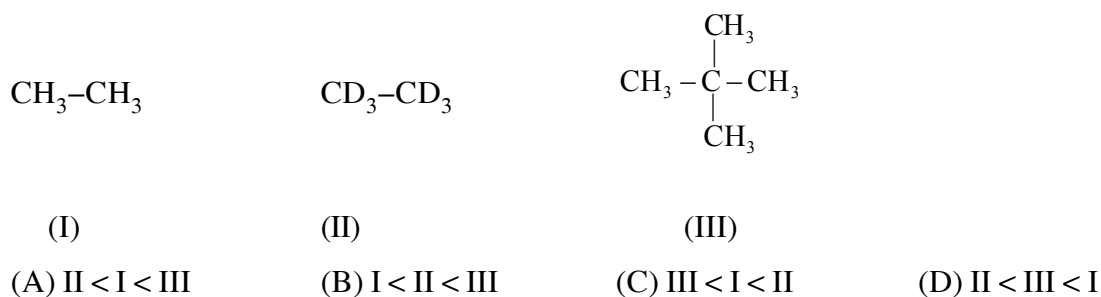
**HD0089**

90. 1-Bromo-3-chloro cyclobutane on reaction with 2-equivalent of sodium in ether gives

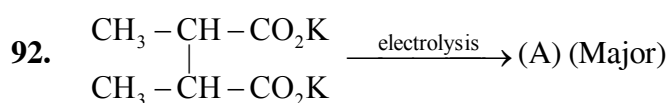


**HD0090**

91. Correct order of rate of photochlorination for following compounds is :



HD0091



Major product (A) of above reaction :



HD0092

93. During the preparation of ethane by Kolbe's electrolytic method using inert electrode the pH of the electrolyte

- (A) Decreases progressively as the reaction proceeds  
 (B) Increases progressively as the reaction proceeds  
 (C) Remains constant throughout the reaction  
 (D) May decrease if concentration of the electrolytes is not very high

HD0093

94. When isobutane is chlorinated in the presence of diffused sunlight, then the product formed is :

- (A) Tertiary butyl chloride in major amount  
 (B) Isobutyl chloride in major amount  
 (C) Both 50 % each  
 (D) n-Butyl chloride, isobutyl chloride and sec-butyl chloride are formed

HD0094

95. Consider the following reactions :



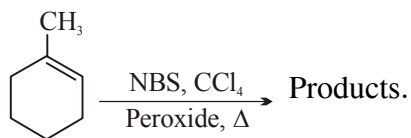
Identify value of X + Y.

- (A) 8 (B) 9 (C) 11 (D) 10

HD0095

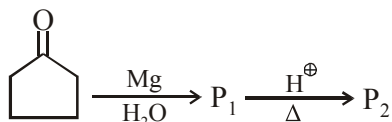


96. Find out the total no. of products (including stereo) in the given reaction :



- (A) 8 (B) 9 (C) 10 (D) 11 **HD0096**

97. Which of the following is not correct about P<sub>2</sub> :

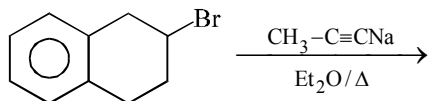


- (A) It is a spiro compound (B) It is a Ketone  
(C) It can show tautomerism (D) Its double bond equivalent is 4 **HD0097**

98. On heating glycerol with excess amount to HI, the product formed is-

- (A) Allyl iodide (B) Isopropyl iodide  
(C) Propylene (D) 1,2,3-tri-iodopropane **HD0098**

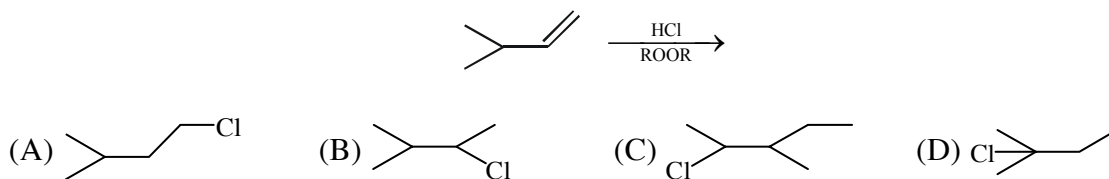
99. In the given reaction:



the products are:

- (A) and (B)   
(C) (D) **HD0099**

100. Major product of the reaction -



**HD0100**

## EXERCISE # O-II

Choose the correct option. One or more than one are correct

1. Rate of  $S_N2$  depends on :

(A) Conc of Nucleophile

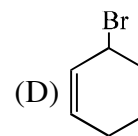
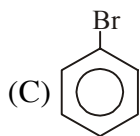
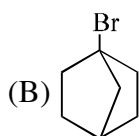
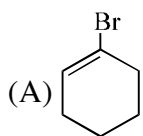
(B) Conc of substrate

(C) Nature of leaving group

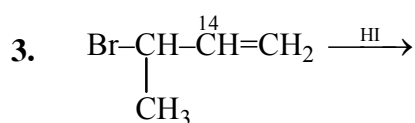
(D) Nature of solvent

HD0101

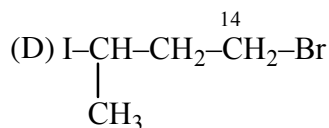
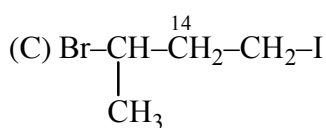
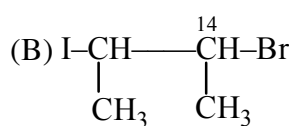
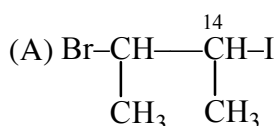
2.  $S_N2$  reaction will be negligible in



HD0102

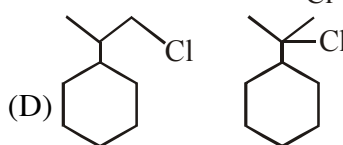
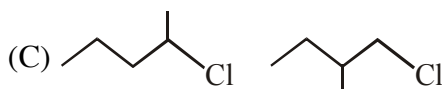
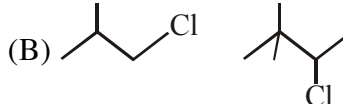
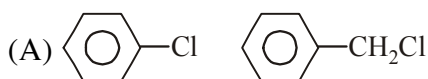


Products which can be obtained during the reaction in good yield :



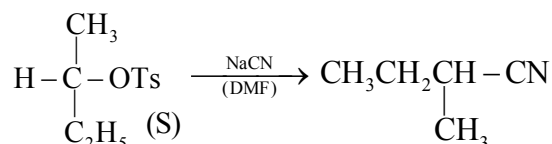
HD0103

4. In the given pair in which pair the first compound is more reactive than second towards  $S_N2$  reaction.



HD0104

5. Consider the given reaction



which of following statements is/are correct for the above reaction.

(A) Product formation takes place due to the breaking of O-Ts

(B) The reaction is  $S_N2$

(C) The reaction is  $S_N1$

(D) Configuration of product is (R)

HD0105

6. Which of the following statements is / are true?

- (A)  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-I}$  will react more readily than  $(\text{CH}_3)_2\text{CHI}$  for  $\text{S}_{\text{N}}2$  reactions.  
 (B)  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Cl}$  will react more readily than  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br}$  for  $\text{S}_{\text{N}}2$  reaction.  
 (C)  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Br}$  will react more readily than  $(\text{CH}_3)_3\text{C-CH}_2\text{-Br}$  for  $\text{S}_{\text{N}}2$  reactions  
 (D)  $\text{CH}_3\text{-O-C}_6\text{H}_4\text{-CH}_2\text{Br}$  will react more readily than  $\text{NO}_2\text{-C}_6\text{H}_5\text{-CH}_2\text{Br}$  for  $\text{S}_{\text{N}}2$  reaction

HD0106

7. Incorrect statement about alkyl halides is / are:

- (A) Tertiary alkyl halides undergo  $\text{S}_{\text{N}}2$  substitutions  
 (B) Alkyl iodides on exposure to sunlight gradually darken  
 (C) Photo iodination is irreversible in presence of  $\text{HIO}_3$   
 (D) A nucleophilic substitution is most difficult in alkyl iodides

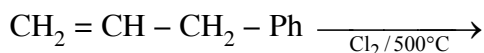
HD0107

8.  $\text{S}_{\text{N}}1$  &  $\text{S}_{\text{N}}2$  is not favourable in

- (A)  $\text{H}_2\text{C}=\text{CH-Cl}$       (B)  $\text{Ph-CH}_2\text{-Cl}$       (C)  $\text{Ph-Cl}$       (D)  $\text{H}_2\text{C}=\text{CH-CH}_2\text{-Cl}$

HD0108

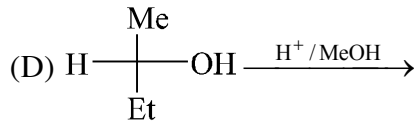
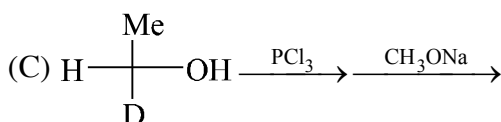
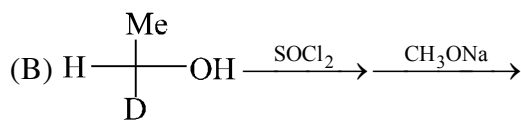
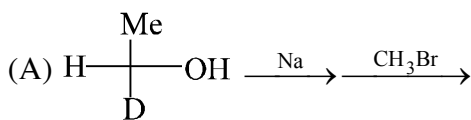
9. Correct statement(s) for the product(s) of following reaction.



- (A) Four different products are formed  
 (B) Two optically active products are formed  
 (C) The optically active compound formed here can also be made by the reaction of  $\text{HCl}$   
 (D) The reaction path is free radical substitution.

HD0109

10. In which of the following reaction configuration about chiral C is retained in the final product



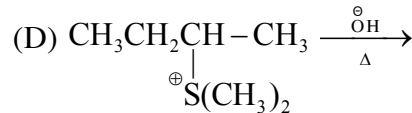
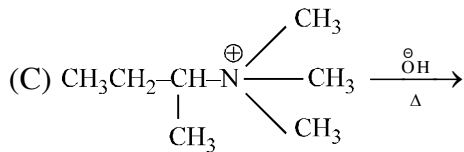
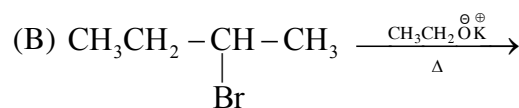
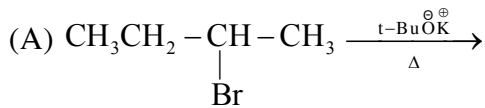
HD0110

11. A gem dichloride is formed in the reaction :

- (A)  $\text{CH}_3\text{CHO}$  and  $\text{PCl}_5$       (B)  $\text{CH}_3\text{COCH}_3$  and  $\text{PCl}_5$   
 (C)  $\text{CH}_2=\text{CH}_2$  and  $\text{Cl}_2$       (D)  $\text{CH}_2=\text{CHCl}$  and  $\text{HCl}$

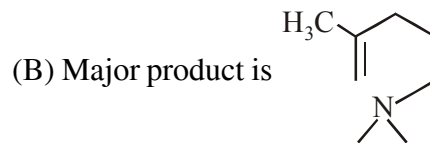
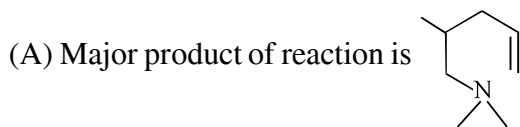
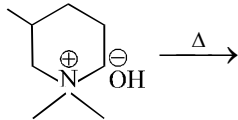
HD0111

12. In which product formation takes place according to Hoffmann's rule



HD0112

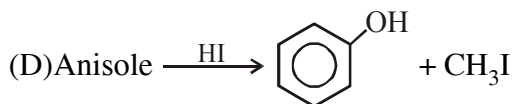
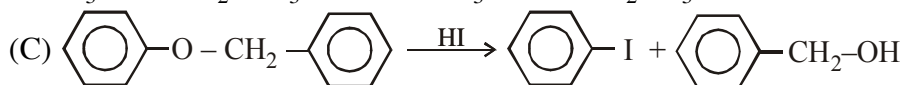
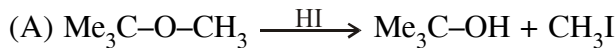
13. Which of following are correct for given reaction



(C) The reaction is thermal elimination reaction (D) The reaction is E<sub>2</sub> reaction

HD0113

14. In which case incorrect products are formed :



HD0114

15. In the given reaction :

Find out the correct statement

(A) It gives total 9 allylic brominated products

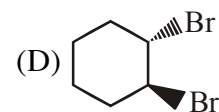
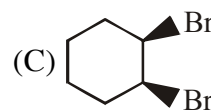
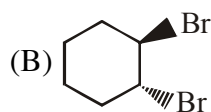
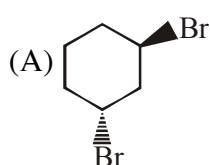
(B) 6 fractions are obtained on fractional distillation of product mixture

(C) Substrate has 7 allylic hydrogens

(D) NBS is a brominating agent for allylic positions

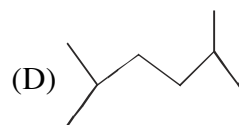
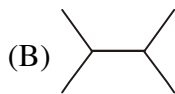
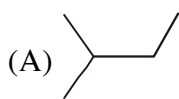
HD0115

16.



HD0116

17. Which of the following can be produced by Wurtz reaction in good yield :



HD0117

18. Products formed when HCl adds to 2,4-hexadiene is :

(A) 4-chloro-2-hexene

(B) 2-chloro-3-hexene

(C) 2-chloro-4-hexene

(D) 1-chloro-2-hexene

HD0118

19. Correct statement among the following is/are :

(A) The rate of hydrolysis of tertiary butyl bromide increases by addition of  $\text{Ag}_2\text{O}$

(B) Aqueous  $\text{Ag}_2\text{O}$  produces nucleophilic  $\text{OH}^-$

(C) The addition of a small amount of oxygen slows down the photochemical chlorination of methane.

(D)  $\text{CH}_3\text{CH}_2\text{Cl}$  is more reactive than  $\text{PhCH}_2\text{Cl}$  for bimolecular nucleophilic substitution reaction

HD0119

20. Incorrect statement among the following is/are :

(A)  $\text{R-OH}$  with  $\text{NaI}$  in the presence of phosphoric acid gives  $\text{R-I}$ , but not in the absence of phosphoric acid

(B) 2-methyl propane on chlorination ( $\text{Cl}_2, h\nu$ ) gives 1-chloro-2-methyl propane while bromination ( $\text{Br}_2, h\nu$ ) gives 2-bromo-2-methyl propane

(C) Usually higher temperature prefers substitution over elimination

(D) Triphenyl chloromethane cannot be hydrolysed

HD0120

21. Correct statements among the following is/are :

(A) Dihaloalkanes having the same type of halogen atoms on same atom are named as alkylidene dihalides

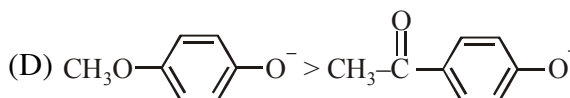
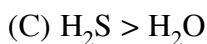
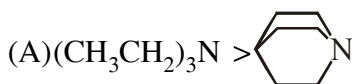
(B) Dihaloalkanes having the same type of halogen atoms on adjacent atoms are named as alkylene dihalides

(C) In common name system gem-dihalides are named as alkylidene halide

(D) In common name system vic-dihalides are named as alkylene halide

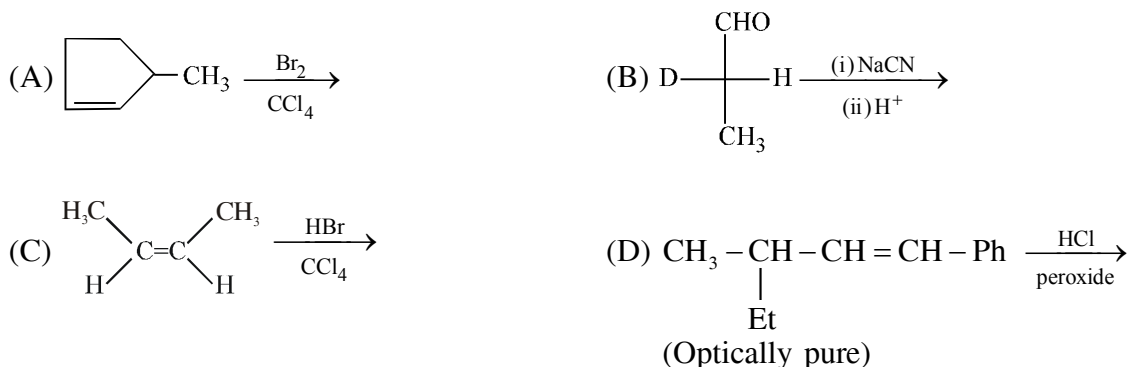
HD0121

22. Which of the following is correct order of nucleophilicity ?



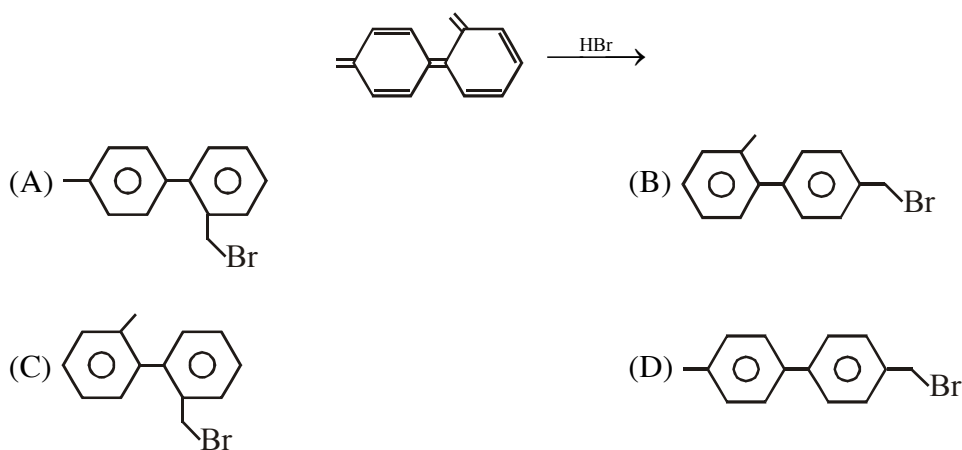
HD0122

23. Which of following reaction products are diastereomer of each other :

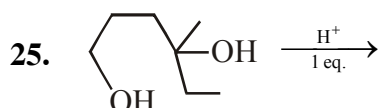


HD0123

24. Product obtained in given reaction in good yield are :



HD0124

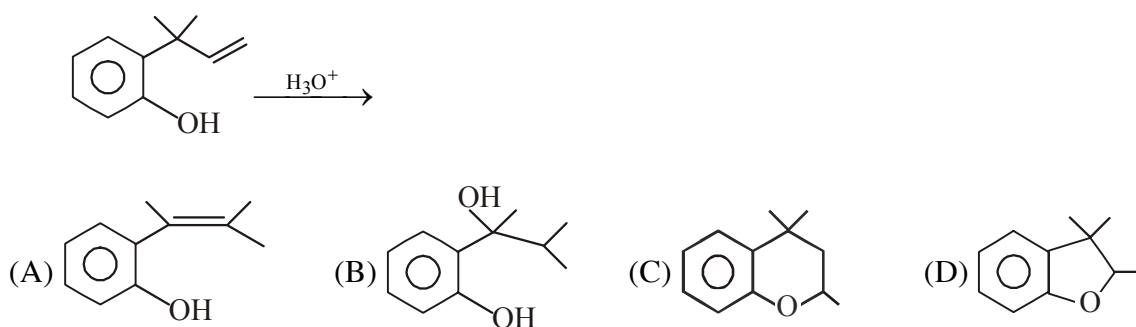


Correct statements for given reaction :

- (A) Product mixture is resolvable  
 (B) Product can be separated by fractional distillation of mixture  
 (C) Two products possible & both are optically active  
 (D) Products are diastereomer

HD0125

26. Which of the following can be formed during this reaction ?



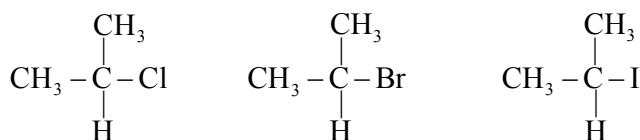
HD0126

27. Select **true** statement(s) :

- (A) Cyclopropane decolorizes bromine water
- (B) In general, bromination is more selective than chlorination.
- (C) The 2,4,6-tri-tert, butylphenoxy radical is resistant to dimerization.
- (D) The radical-catalysed chlorination,  $\text{ArCH}_3 \rightarrow \text{ArCH}_2\text{Cl}$ , occurs faster when Ar = phenyl than when Ar = p-nitrophenyl.

HD0127

28. From left to right, correct statements are :



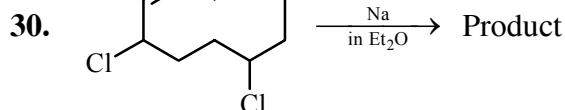
- (A) Rate of  $\text{S}_{\text{N}}1$  mechanism increases in polar protic solvent
- (B) Rate of  $\text{S}_{\text{N}}2$  mechanism increases in DMSO
- (C) Rate of  $\text{E}_2$  mechanism increases
- (D) Rate of  $\text{E}_1$  mechanism increases

HD0128

29. Number of following reactions which produces hydrocarbon as major product ?

- (i)  $\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow[\text{Et}_2\text{O}]{\text{Na}}$
  - (ii)  $\text{CH}_3\text{C}(=\text{O})\text{OK} \xrightarrow{\text{Electrolysis}}$
  - (iii)  $\text{CH}_2(\text{Cl})\text{CH}_2(\text{Cl}) \xrightarrow[\text{dust}]{\text{Zn}}$
  - (iv)  $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2 / \text{H}_2\text{O}}$
  - (v)  $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow[\text{CCl}_4]{\text{Br}_2}$
  - (vi)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \xrightarrow[\text{(ii) CH}_3\text{COOH} / \text{H}_2\text{O}]{\text{(i) B}_2\text{H}_6 - \text{THF}}$
- (A) 2 (B) 4 (C) 5 (D) 6

HD0129

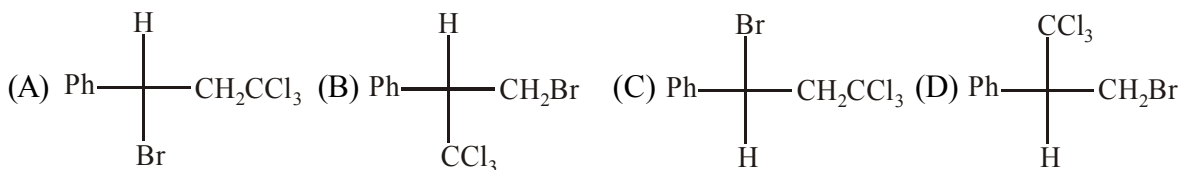


Correct statement is/are :

- (A) odd no. of double bond equivalent in product
- (B) product is bicyclic compound
- (C) product can show geometrical isomerism
- (D) reaction involve carbocation as intermediate

HD0130

31.  $\text{Ph}-\text{CH}=\text{CH}_2 + \text{BrCCl}_3 \xrightarrow{\text{Peroxide}}$  Product is :



HD0131

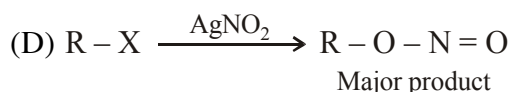
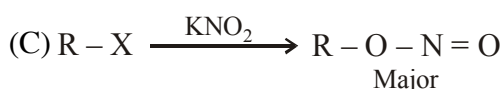
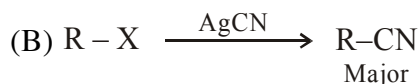
## EXERCISE # S-I

## Comprehension Type :

## Paragraph for Q.No. 01 to 02

Groups like CN &  $[-O-\overset{\cdot\cdot}{N}=O]$  possess two nucleophilic centre and are called ambident nucleophiles. Actually cyanide group is hybrid of two contributing structures and therefore can act as nucleophile in two different ways  $[\overset{\ominus}{C}\equiv N \longleftrightarrow :C=N^{\ominus}]$ . Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage  $[O-\overset{\cdot\cdot}{N}=O]$ .

1. Correct option among the following :



HD0132

2. Incorrect statement



(A) KCN is predominantly ionic in nature

(B) AgCN is mainly covalent in nature

(C) In AgCN, carbon is the donor atom

(D) In AgCN nitrogen is the donor atom

HD0133

3. **Statement-1** : HBr shows antimarkownikoff's addition on propene but not HCl.

**Statement-2** : H-Br is stronger acid than H-Cl.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

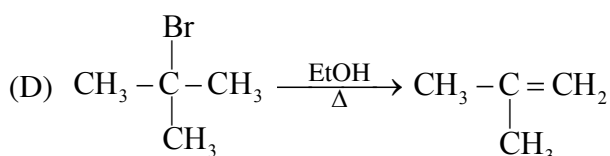
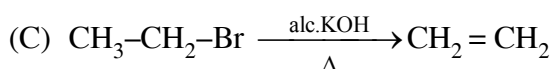
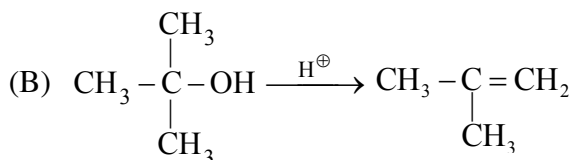
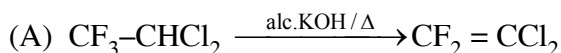
(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

HD0134

4. Match the List I with List II and select the correct answer using the codes given below the Lists.

## List I



## List II

(P) Elimination Reaction

(Q) Carbocation

(R) Carbanion

(S) Free radical

HD0135





## 9. Column - I

(Statements)

- (A) Reactions are concerted  
 (B)  $\text{CH}_3\text{X}$  cannot react  
 (C)  $3^\circ \text{R-X} > 2^\circ \text{R-X} > 1^\circ \text{R-X}$   
 (D)  $\text{R-I}$  reacts faster than  $\text{R-Cl}$

## Column - II

(Consistent path of reaction)

- (P)  $\text{S}_{\text{N}}1$   
 (Q)  $\text{S}_{\text{N}}2$   
 (R)  $\text{E}1$   
 (S)  $\text{E}2$

HD0140

10. Each of the compounds in column A is subjected to further chlorination. Match the following for them :

## Column - A

- (A)  $\text{CHCl}_2\text{-CH}_2\text{-CH}_3$   
 (B)  $\text{CH}_2\text{Cl-CHCl-CH}_3$   
 (C)  $\text{CH}_2\text{Cl-CH}_2\text{-CH}_2\text{-Cl}$   
 (D)  $\text{CH}_3\text{-CCl}_2\text{-CH}_3$   
 (E)  $\begin{array}{c} \text{Cl} \quad \text{Cl} \\ | \quad | \\ \text{CH}_3\text{-C-CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$

## Column - B

- (P) Optically active original compound  
 (Q) Only one trichloro product  
 (R) Three trichloro product.  
 (S) Four trichloro product  
 (T) At least one of the trichloro product is optically active  
 (U) Two trichloro products.

HD0141

## 11. Column - I

(Intermediate)

- (A) Carbocation  
 (B) Carbanion  
 (C) Free radical  
 (D) Octet complete in one of the intermediate

## Column - II

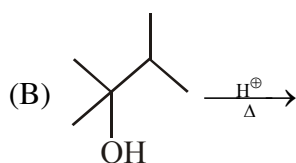
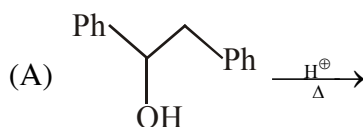
- (P) Kolbey Electrolysis  
 (Q) Wurtz reaction  
 (R) Dehydration of alcohol  
 (S) Monocarboxylic acid with sodalime

HD0142

12. Match the column

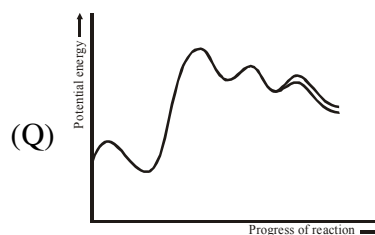
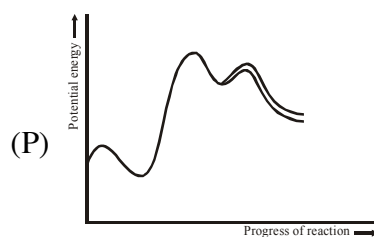
## Column-I

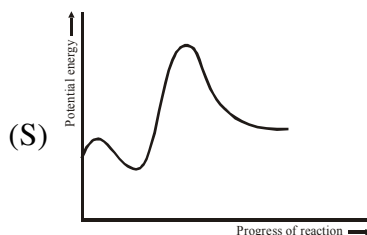
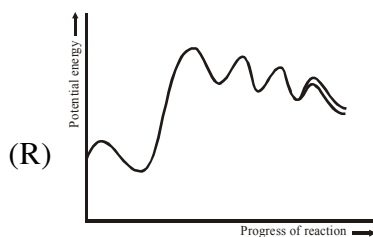
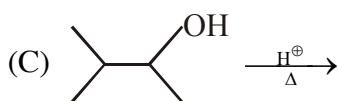
(Reaction)



## Column-II

(Potential energy curve)





HD0143

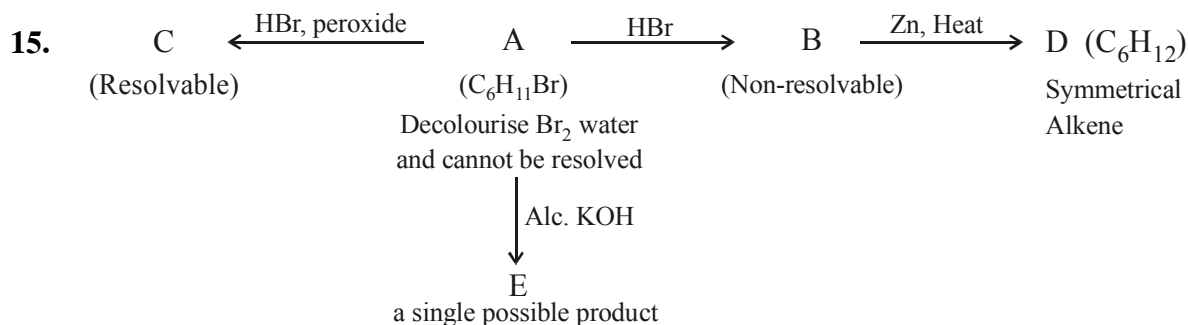
**Subjective Type :**

13. RCl is treated with Li in ether to form R – Li, R – Li reacts with water to form isopentane. R – Cl also reacts with sodium to form 2, 7–dimethyloctane. What is the structure of R – Cl.

HD0144

14. A chloroderivative ‘X’ on reduction gave a hydrocarbon with five carbon atoms in the molecule. When X is dissolved in ether and treated with sodium, 2, 2, 5, 5-tetramethyl hexane is obtained. What is compound X.

HD0145



Identify A, C & E in the sequence of reaction.

HD0146

16. With the help of following data show HBr exhibits the peroxide effect.

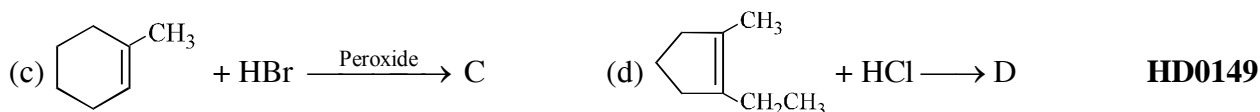
H-X	$\Delta H_1^0/\text{kJ mol}^{-1}$	$\Delta H_2^0/\text{kJ mol}^{-1}$
	$\dot{\text{X}} + \text{CH}_2 = \text{CH}_2 \rightarrow \text{XCH}_2 - \dot{\text{C}}\text{H}_2$	$\text{XCH}_2 - \dot{\text{C}}\text{H}_2 + \text{H-X} \rightarrow \text{XCH}_2\text{CH}_3 + \dot{\text{X}}$
HCl	-67	+ 12.6
HBr	-25.1	- 50.2
HI	+46	-117.1

HD0147

17. Write all the monochlorinated products (including stereo) of isohexane.

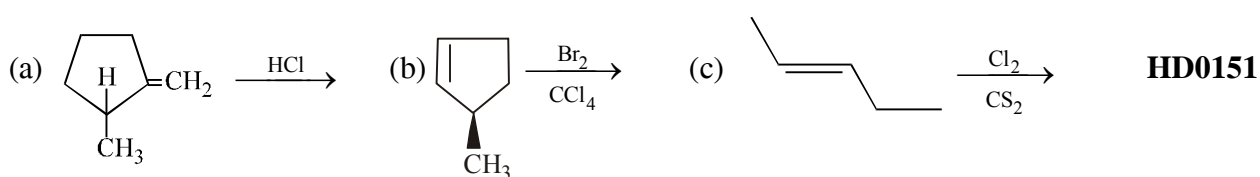
HD0148

18. What are the products of the following reactions ?



19. It required 0.7 g of a hydrocarbon (A) to react completely with  $\text{Br}_2$  (2.0 g) and form a non resolvable product. On treatment of (A) with HBr it yielded monobromo alkane (B). The same compound (B) was obtained when (A) was treated with HBr in presence of peroxide. Write down the structure formula of (A) and (B) and explain the reactions involved. HD0150

20. Complete following reaction :



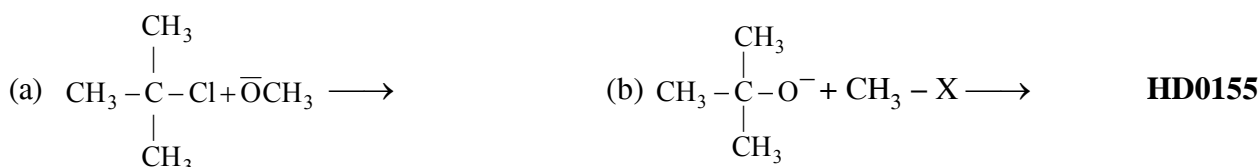
21.  $\text{CH}_3\text{-CH}_2\text{I}$  reacts more rapidly with strong base in comparison to  $\text{CD}_3\text{CH}_2\text{I}$ . HD0152

22.  $\text{CH}\equiv\text{C-CH}_2\text{-CH}=\text{CH}_2$ , adds up HBr to give  $\text{CH}\equiv\text{C-CH}_2\text{-CHBr-CH}_3$  while  $\text{CH}\equiv\text{C-CH}=\text{CH}_2$  adds up HBr to give  $\text{CH}_2=\underset{\text{Br}}{\text{C}}-\text{CH}=\text{CH}_2$  HD0153

23. Predict the product(s) and write the mechanism of the given reaction :



24. What are the products of the following reactions?

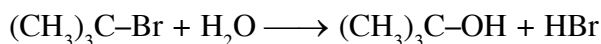


25. A primary alkyl bromide (A),  $\text{C}_4\text{H}_9\text{Br}$ , reacted with alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give an isomer of (A). When (A) was reacted with sodium metal it gave compound (D),  $\text{C}_8\text{H}_{18}$ , which was different from the compound produced when n-butyl bromide was reacted with sodium. Draw the structure of (A) and write equations for all the reactions. HD0156

26. In study of chlorination of propane four products (A,B,C,D) of molecular formula  $\text{C}_3\text{H}_6\text{Cl}_2$  were obtained. On further chlorination of the above products A gave one trichloro product, B gave two whereas C and D gave three each. When optically active C was chlorinated one of trichloro propanes was optically active and remaining two were optically inactive. Identify the structures of A,BC and D, and explain formation of products. HD0157

## EXERCISE # J-MAINS

1. Following reaction :



is an example of-

[AIIEE-2002]

(1) Elimination reaction

(2) Free radical substitution

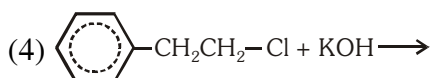
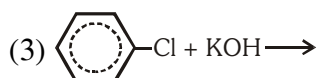
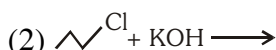
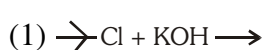
(3) Nucleophilic substitution

(4) Electrophilic substitution

HD0158

2.  $\text{S}_\text{N}^1$  reaction is feasible in-

[AIIEE-2002]



HD0159

3. Bottles containing  $\text{C}_6\text{H}_5\text{I}$  and  $\text{C}_6\text{H}_5\text{-CH}_2\text{I}$  lost their original labels. They were labelled A and B for testing. A and B were separately taken in a test tube and boiled with  $\text{NaOH}$  solution. The end solution in each tube was made acidic with dilute  $\text{HNO}_3$  and then some  $\text{AgNO}_3$  solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment.

[AIIEE-2003]

(1) A was  $\text{C}_6\text{H}_5\text{I}$

(2) A was  $\text{C}_6\text{H}_5\text{CH}_2\text{I}$

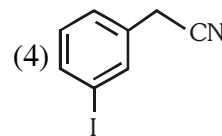
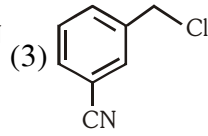
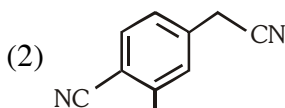
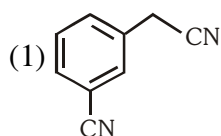
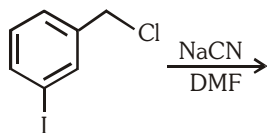
(3) B was  $\text{C}_6\text{H}_5\text{I}$

(4) Addition of  $\text{HNO}_3$  was unnecessary

HD0160

4. The structure of the major product formed in the following reaction is :

[AIIEE-2006]



HD0161

5. Which of the following on heating with aqueous  $\text{KOH}$ , produces acetaldehyde ? [AIIEE-2009]

(1)  $\text{CH}_2\text{ClCH}_2\text{Cl}$

(2)  $\text{CH}_3\text{CHCl}_2$

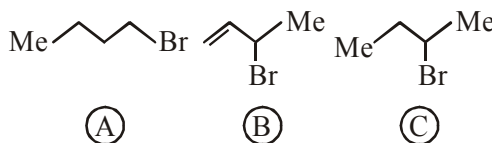
(3)  $\text{CH}_3\text{COCl}$

(4)  $\text{CH}_3\text{CH}_2\text{Cl}$

HD0162

6. Consider the following bromides :-

[AIIEE-2010]



The correct order of  $\text{S}_\text{N}^1$  reactivity is

(1)  $\text{A} > \text{B} > \text{C}$

(2)  $\text{B} > \text{C} > \text{A}$

(3)  $\text{B} > \text{A} > \text{C}$

(4)  $\text{C} > \text{B} > \text{A}$

HD0163

7. In  $S_N^2$  reactions, the correct order of reactivity for the following compounds : [JEE(Main)-2014]  
 $CH_3Cl$ ,  $CH_3CH_2Cl$ ,  $(CH_3)_2CHCl$  and  $(CH_3)_3CCl$  is :

- (1)  $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$   
 (2)  $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$   
 (3)  $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$   
 (4)  $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

HD0164

8. In a nucleophilic substitution reaction : [JEE(Main)-On-Line-2014]



which one of the following undergoes complete inversion of configuration?

- (1)  $C_6H_5CCH_3C_6H_5Br$  (2)  $C_6H_5CHCH_3Br$   
 (3)  $C_6H_5CHC_6H_5Br$  (4)  $C_6H_5CH_2Br$

HD0165

9. The major product obtained in the photo catalysed bromination of 2-methylbutane is :-

- (1) 2-bromo-2-methylbutane  
 (2) 2-bromo-3-methylbutane  
 (3) 1-bromo-2-methylbutane  
 (4) 1-bromo-3-methylbutane

[JEE(Main)-On-Line-2014]

HD0166

10. In the presence of peroxide,  $HCl$  and  $HI$  do not give anti-Markownikoff's addition to alkenes because :- [JEE(Main)-On-Line-2014]

- (1) All the steps are exothermic in  $HCl$  and  $HI$   
 (2) One of the steps is endothermic in  $HCl$  and  $HI$   
 (3)  $HCl$  is oxidizing and the  $HI$  is reducing  
 (4) Both  $HCl$  and  $HI$  are strong acids

HD0167

11. The major product formed when 1,1,1-trichloro-propane is treated with aqueous potassium hydroxide is : [JEE(Main)-On-Line-2014]

- (1) 2-Propanol (2) Propionic acid (3) Propyne (4) 1-Propanol

HD0168

12. The synthesis of alkyl fluoride is best accomplished by : [JEE(Main)-2015]

- (1) Finkelstein reaction (2) Swarts reaction  
 (3) Free radical fluorination (4) Sandmeyer's reaction

HD0169

13. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields :

- (1)  $C_2H_5CH_2\overset{\overset{CH_3}{|}}{C}-OCH_3$  (2)  $C_2H_5CH_2\overset{\overset{CH_3}{|}}{C}=CH_2$  (3)  $C_2H_5CH_2=C\overset{\overset{CH_3}{|}}{CH_3}$

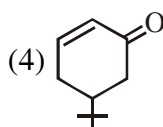
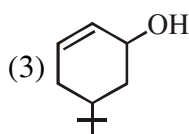
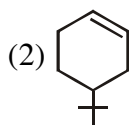
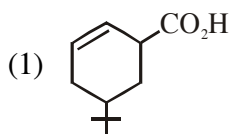
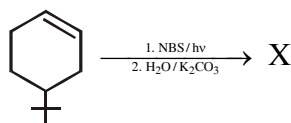
[JEE-MAIN-2016]

- (1) (1) and (2) (2) All of these (3) (1) and (3) (4) (3) only

HD0170

14. The product of the reaction given below is :

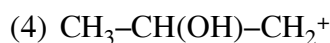
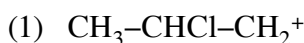
[JEE-MAIN-2016]



HD0171

15. The reaction of propene with HOCl ( $\text{Cl}_2 + \text{H}_2\text{O}$ ) proceeds through the intermediate :

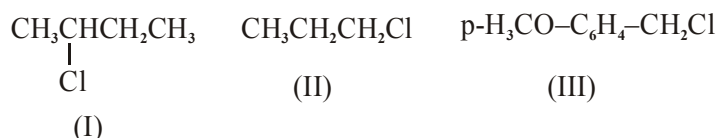
[JEE-MAIN-2016]



HD0172

16. The increasing order of the reactivity of the following halides for the  $\text{S}_{\text{N}}1$  reaction is :

[JEE-MAIN-2017]

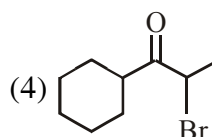
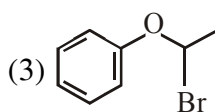
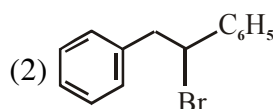
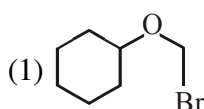


- (1) (III) < (II) < (I)    (2) (II) < (I) < (III)    (3) (I) < (III) < (II)    (4) (II) < (III) < (I)

HD0173

17. Which of the following, upon treatment with tert-BuONa followed by addition of bromine water, fails to decolourize the colour of bromine ?

[JEE-MAIN-2017]



HD0174

18. 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is :

[JEE-MAIN-2017]

(1) Six

(2) Zero

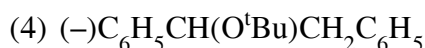
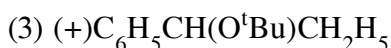
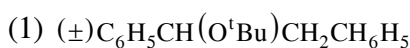
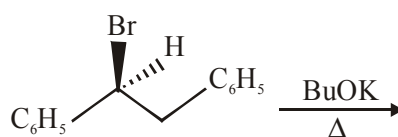
(3) Two

(4) Four

HD0175

19. The major product obtained in the following reaction is :

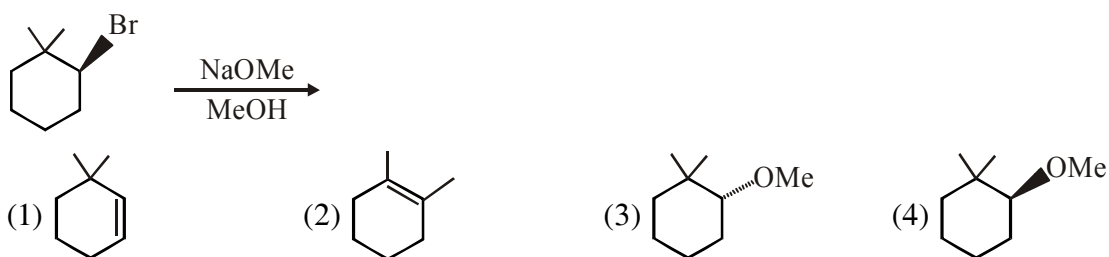
[JEE-MAIN-2017]



HD0176

20. The major product of the following reaction is :

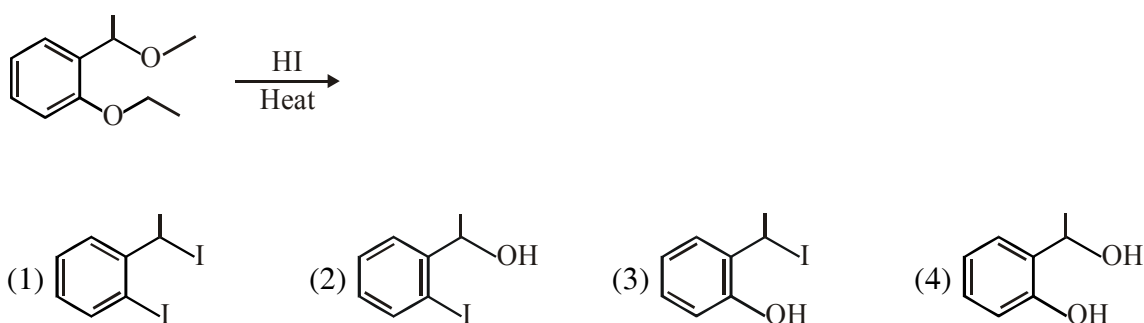
[JEE-MAIN-2018]



HD0177

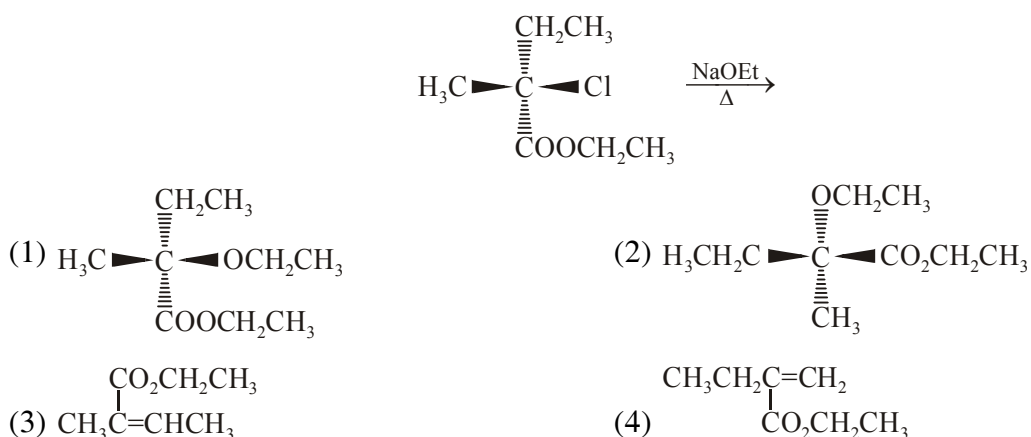
21. The major product formed in the following reaction is :

[JEE-MAIN-2018]



HD0178

22. The major product of the following reaction is: [JEE-MAIN-(January) -2019]



HD0179

23. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is : [JEE-MAIN-(January) -2019]



(1) (B) < (A) < (D) < (C)

(2) (B) < (A) < (C) < (D)

(3) (A) < (C) < (D) < (B)

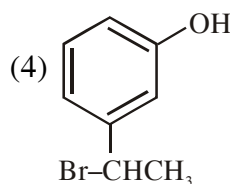
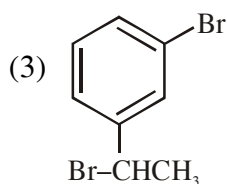
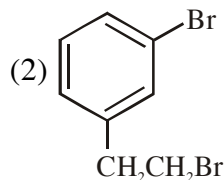
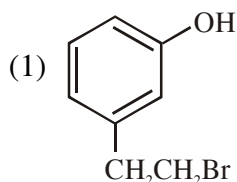
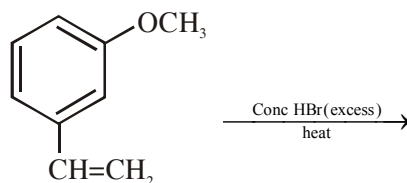
(4) (A) < (B) < (C) < (D)

HD0180



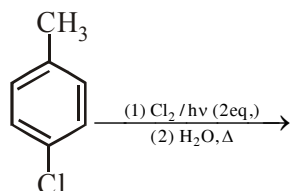
24. The major product of the following reactions:

[JEE-MAIN-(April) -2019]

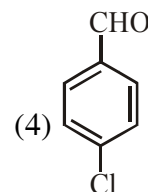
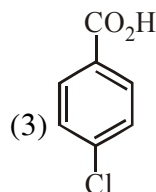
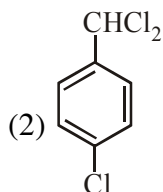
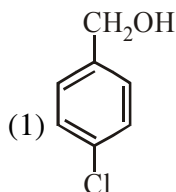


HD0181

25. The major product of the following reaction is:



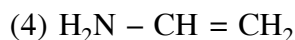
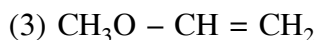
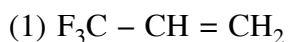
[JEE-MAIN-(April) -2019]



HD0182

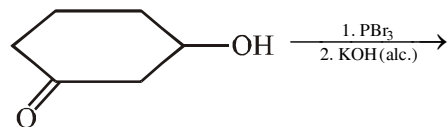
26. Which one of the following alkenes when treated with HCl yields majorly an anti Markovnikov product?

[JEE-MAIN-(April) -2019]

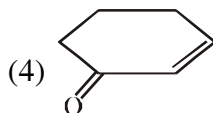
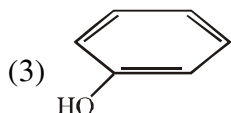
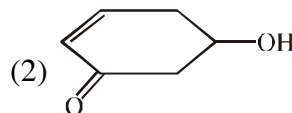
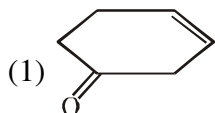


HD0183

27. The major product of the following reaction is :



[JEE-MAIN-(April) -2019]

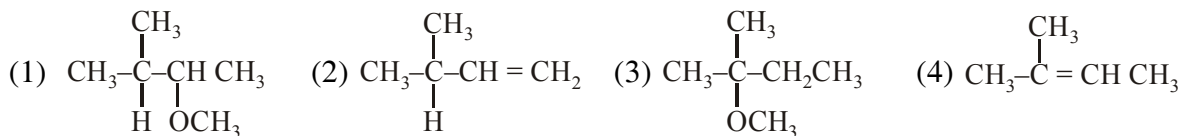
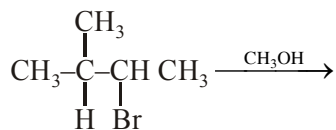


HD0184



32. The major product of the following reaction is :-

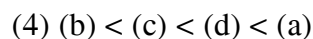
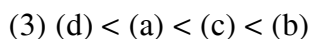
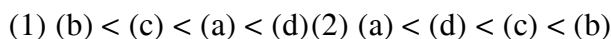
[JEE-MAIN-(April) -2019]



HD0189

33. The increasing order of nucleophilicity of the following nucleophiles is :

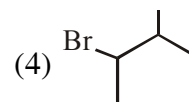
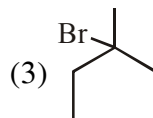
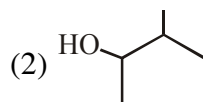
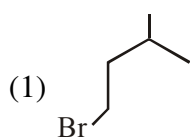
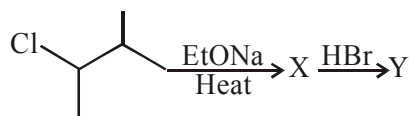
[JEE-MAIN-(April) -2019]



HD0190

34. The major product 'Y' in the following reaction is:

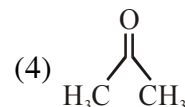
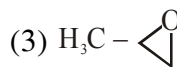
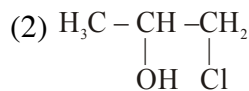
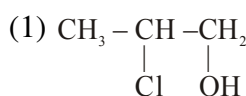
[JEE-MAIN-(April) -2019]



HD0191

35. The major product of the following addition reaction is :

[JEE-MAIN-(April) -2019]



HD0192

36. An 'Assertion' and a 'Reason' are given below. Choose the correct answer from the following options.

**Assertion (A) :** Vinyl halides do not undergo nucleophilic substitution easily.

**Reason (R) :** Even though the intermediate carbocation is stabilized by loosely held  $\pi$ -electrons, the cleavage is difficult because of strong bonding.

[JEE-MAIN-(April) -2019]

- (1) Both (A) and (R) are wrong statements  
 (2) Both (A) and (R) are correct statements and (R) is the correct explanation of (A)  
 (3) Both (A) and (R) are correct statements but (R) is not the correct explanation of (A)  
 (4) (A) is a correct statement but (R) is a wrong statement.

HD0193

37. The reaction of 2, 4-hexadiene with one equivalent of bromine at  $0^\circ\text{C}$  gives a mixture of two compounds 'X' and 'Y'. If 'X' is 4, 5 - dibromohex-2-ene, 'Y' is -

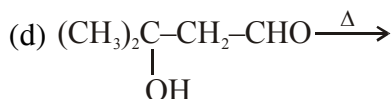
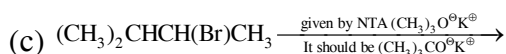
[NSE -2019]

- (1) 2,5-dibromohex-2-ene (2) 2,5-dibromohex-3-ene  
 (3) 2,3-dibromohex-3-ene (4) 3,4-dibromohex-3-ene

HD0194

38. Consider the following reactions :

[JEE-MAIN-2020]



Which of these reaction(s) will not produce Saytzeff product ?

[JEE-MAIN-2020]

- (1) (c) only (2) (a), (c) and (d)  
 (3) (d) only (4) (b) and (d)

HD0195

39. Arrange the following bonds according to their average bond energies in descending order :

C-Cl, C-Br, C-F, C-I

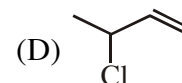
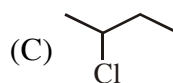
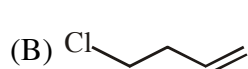
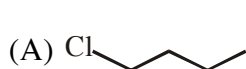
[JEE-MAIN-2020]

- (1) C-I > C-Br > C-Cl > C-F (2) C-Br > C-I > C-Cl > C-F  
 (3) C-F > C-Cl > C-Br > C-I (4) C-Cl > C-Br > C-I > C-F

HD0196

40. The decreasing order of reactivity towards dehydrohalogenation ( $\text{E}_1$ ) reaction of the following compounds is :

[JEE-MAIN-2020]



- (1) B > D > A > C (2) B > D > C > A  
 (3) D > B > C > A (4) B > A > D > C

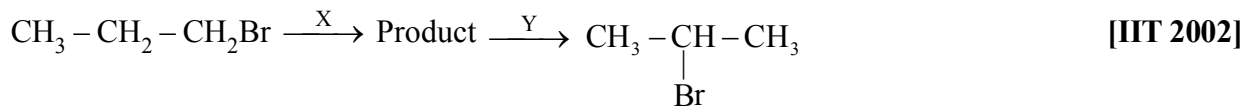
HD0197

EXERCISE # J-ADVANCE (OBJECTIVE)

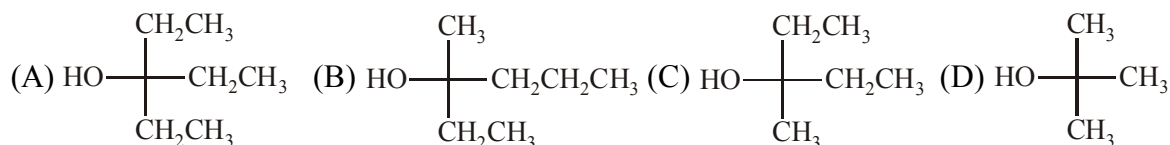
- Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives :  
 (A) o-cresol (B) p-cresol [IIT 1990]  
 (C) 2,4-dihydroxytoluene (D) Benzoic acid HD0198
- Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to [IIT 1990]  
 (A) The formation of less stable carbonium ion (B) Resonance stabilization  
 (C) The inductive effect (D)  $sp^2$  hybridised carbon attached to the halogen  
 HD0199
- 1-Chlorobutane on reaction with alcoholic potash gives : [ITT 1991]  
 (A) 1-butene (B) 1-butanol (C) 2-butene (D) 2-butanol HD0200
- The products of reaction of alcoholic  $AgNO_2$  with ethyl bromide are [IIT 1991]  
 (A) Ethane (B) Ethyl nitrite (C) Nitroethane (D) Ethyl alcohol  
 HD0201
- Arrange the following compounds in order of increasing dipole moment [IIT 1996]  
 Toluene m-dichlorobenzene o-dichlorobenzene p-dichlorobenzene  
 I II III IV  
 (A)  $I < IV < II < III$  (B)  $IV < I < II < III$  (C)  $IV < I < III < II$  (D)  $IV < II < I < III$   
 HD0202
- $(CH_3)_3CMgCl$  reaction with  $D_2O$  produces:  
 (A)  $(CH_3)_3CD$  (B)  $(CH_3)_3OD$  (C)  $(CD_3)_3CD$  (D)  $(CH_3)_3OD$  [IIT 1997]  
 HD0203
- Benzyl chloride ( $C_6H_5CH_2Cl$ ) can be prepared from toluene by chlorination with:  
 (A)  $SO_2Cl_2$  (B)  $SOCl_2$  (C)  $Cl_2, (h\nu)$  (D)  $NaOCl$  [IIT 1998]  
 HD0204
- The order of reactivity of the following alkyl halides for a  $S_N2$  reaction is: [IIT 2000]  
 (A)  $RF > RC > R-Br > R-I$  (B)  $R-F > R-Br > R-Cl > R-I$   
 (C)  $R-Cl > R-Br > RF > RI$  (D)  $R-I > RBr > R-Cl > R-F$  HD0205
- Which of the following has the highest nucleophilicity? [IIT 2000]  
 (A)  $F^-$  (B)  $OH^-$  (C)  $CH_3^-$  (D)  $NH_2^-$  HD0206
- An  $S_N2$  reaction at an asymmetric carbon of a compound always gives. [IIT 2001]  
 (A) an enantiomer of the substance (B) a product with opposite optical rotation  
 (C) a mixture of diastereomers (D) a single stereoisomer HD0207

11. The compound that will react most readily with NaOH to form methanol is [IIT 2001]  
 (A)  $(\text{CH}_3)_4\text{N}^+\text{I}^-$  (B)  $\text{CH}_3\text{OCH}_3$  (C)  $(\text{CH}_3)_3\text{S}^+\text{I}^-$  (D)  $(\text{CH}_3)_3\text{CCl}$  HD0208

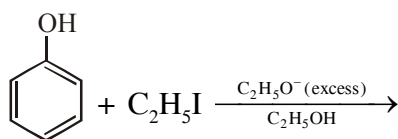
12. Identify the set of reagents / reaction conditions 'X' and 'Y' in the following set of transformation:



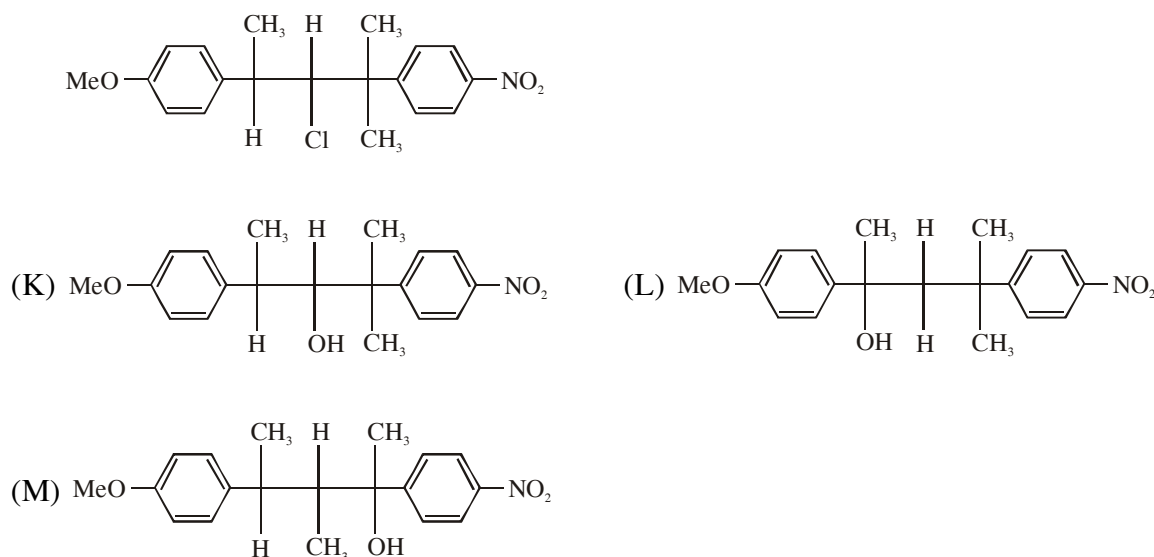
- (A) X = dilute aqueous NaOH, 20°C; Y = HBr / acetic acid, 20°C  
 (B) X = concentrated alcoholic NaOH, 80°C; Y = HBr / acetic acid 20°C  
 (C) X = dilute aqueous NaOH, 20°C; Y =  $\text{Br}_2 / \text{CHCl}_3$ , 0°C  
 (D) X = concentrated alcoholic NaOH, 80°C; Y =  $\text{Br}_2 / \text{CHCl}_3$ , 0°C HD0209
13.  $\text{CH}_3\text{MgBr} + \text{Ethyl ester} \rightarrow$  which can be formed as product. [IIT 2003]  
 (excess)



14. The product of following reaction is [IIT 2003]



- (A)  $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$  (B)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  (C)  $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$  (D)  $\text{C}_6\text{H}_5\text{I}$  HD0211
15. The following compound on hydrolysis in aqueous acetone will give: [IIT 2005]



It mainly gives

- (A) K and L (B) Only K (C) L and M (D) Only M HD0212

16 Match the following:

[IIT 2006]

Column I

- (A)  $\text{CH}_3\text{-CHBr-CD}_3$  on treatment with alc. KOH gives  $\text{CH}_2=\text{CH-CD}_3$  as a major product.  
 (B)  $\text{Ph-CHBr-CH}_3$  reacts faster than  $\text{Ph-CHBr-CD}_3$ .  
 (C)  $\text{Ph-CD}_2\text{-CH}_2\text{Br}$  on treatment with  $\text{C}_2\text{H}_5\text{OD/C}_2\text{H}_5\text{O}^-$  gives  $\text{Ph-CD=CH}_2$  as the major product.  
 (D)  $\text{PhCH}_2\text{CH}_2\text{Br}$  and  $\text{PhCD}_2\text{CH}_2\text{Br}$  react with same rate.

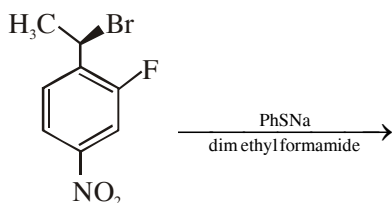
Column II

- (P) E1 reaction  
 (Q) E2 reaction  
 (R) E1cb reaction  
 (S) First order reaction

HD0213

17 The major product of the following reaction is

[IIT 2008]



- (A) (B) (C) (D)

HD0214

18 In the reaction  $\xrightarrow{\text{HBr}}$  the products are

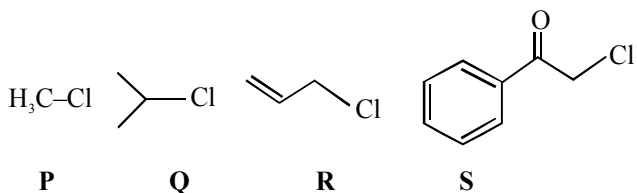
[IIT 2010]

- (A) and  $\text{H}_2$  (B) and  $\text{CH}_3\text{Br}$   
 (C) and  $\text{CH}_3\text{OH}$  (D) and  $\text{CH}_3\text{Br}$

HD0215

19. KI in acetone, undergoes  $\text{S}_{\text{N}}2$  reaction with each of P, Q, R and S. The rates of the reaction vary as -

[IIT 2013]

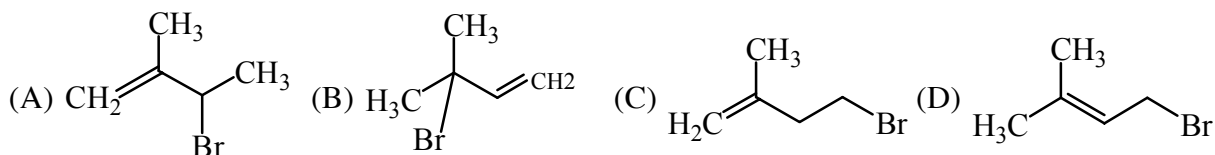
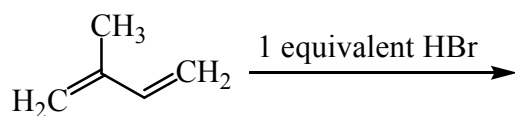


- (A)  $\text{P} > \text{Q} > \text{R} > \text{S}$  (B)  $\text{S} > \text{P} > \text{R} > \text{Q}$  (C)  $\text{P} > \text{R} > \text{Q} > \text{S}$  (D)  $\text{R} > \text{P} > \text{S} > \text{Q}$

HD0216

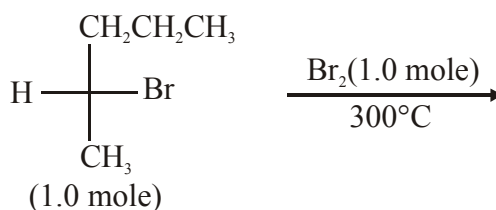
20. In the following reaction, the major product is -

[IIT 2015]



HD0217

21. In the following monobromination reaction, the number of possible chiral products is [IIT 2016]

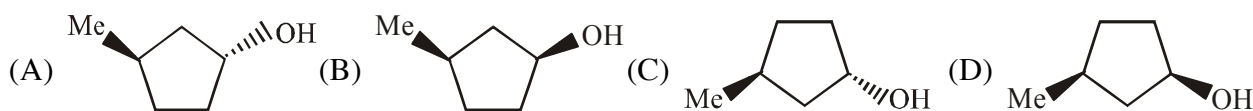
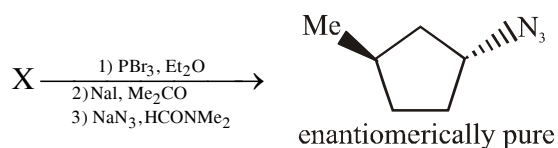


(enantiomerically pure)

HD0218

22. In the following reaction sequence, the correct structure(s) of X is (are)

[IIT-2018]



HD0219

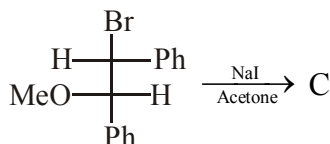


## EXERCISE # J-ADVANCE (SUBJECTIVE)

1. An alkyl halide X of formula  $C_6H_{13}Cl$  on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z ( $C_6H_{12}$ ). Both alkenes on hydrogenation give 2,3-dimethylbutane. Predict the structures of X, Y and Z. [IIT 1996]

HD0220

2. Predict the structure of the intermediates/products in the following reaction sequence – [IIT 1996]



HD0221

3. Which of the following is the correct method for synthesising methyl-t-butyl ether and why?



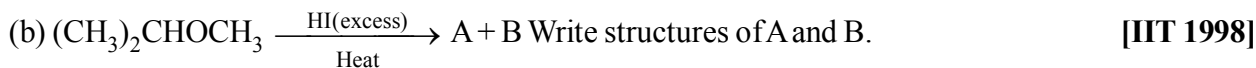
HD0222

4. Write the structures of the products: [IIT 1998]



HD0223

5. (a)  $C_6H_5CH_2\overset{C_6H_5}{\underset{|}{CH}}Cl \xrightarrow[\text{Heat}]{\text{alc. KOH}} A + B$  Write structures of (A) and (B).



HD0224

6. What would be major product? [IIT 2000]

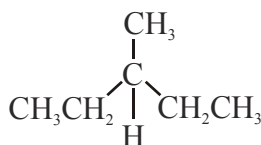


HD0225

7. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is [IIT 2011]

HD0226

8. The maximum number of isomers (including stereoisomers) that are possible on mono-chlorination of the following compounds, is [IIT 2011]



HD0227

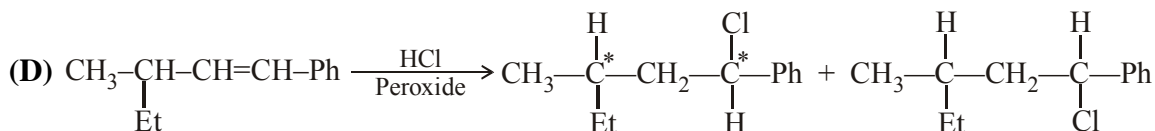
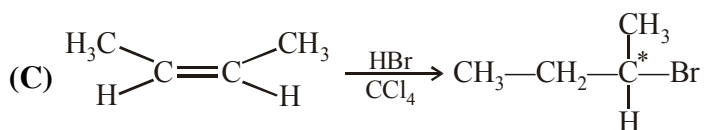
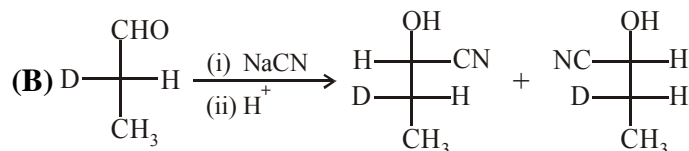
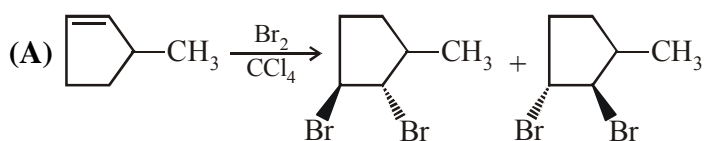
## ANSWER-KEY

## EXERCISE # O-I

- |              |              |              |              |               |
|--------------|--------------|--------------|--------------|---------------|
| 1. Ans. (A)  | 2. Ans. (C)  | 3. Ans. (D)  | 4. Ans. (D)  | 5. Ans. (C)   |
| 6. Ans. (C)  | 7. Ans. (B)  | 8. Ans. (D)  | 9. Ans. (B)  | 10. Ans. (B)  |
| 11. Ans. (C) | 12. Ans. (C) | 13. Ans. (C) | 14. Ans. (A) | 15. Ans. (D)  |
| 16. Ans. (B) | 17. Ans. (A) | 18. Ans. (D) | 19. Ans. (C) | 20. Ans. (D)  |
| 21. Ans. (D) | 22. Ans. (A) | 23. Ans. (D) | 24. Ans. (A) | 25. Ans. (B)  |
| 26. Ans. (C) | 27. Ans. (B) | 28. Ans. (C) | 29. Ans. (D) | 30. Ans. (B)  |
| 31. Ans. (D) | 32. Ans. (B) | 33. Ans. (B) | 34. Ans. (C) | 35. Ans. (A)  |
| 36. Ans. (A) | 37. Ans. (C) | 38. Ans. (D) | 39. Ans. (A) | 40. Ans. (B)  |
| 41. Ans. (B) | 42. Ans. (C) | 43. Ans. (A) | 44. Ans. (C) | 45. Ans. (A)  |
| 46. Ans. (C) | 47. Ans. (D) | 48. Ans. (D) | 49. Ans. (B) | 50. Ans. (C)  |
| 51. Ans. (B) | 52. Ans. (C) | 53. Ans. (A) | 54. Ans. (C) | 55. Ans. (A)  |
| 56. Ans. (D) | 57. Ans. (C) | 58. Ans. (B) | 59. Ans. (B) | 60. Ans. (C)  |
| 61. Ans. (C) | 62. Ans. (D) | 63. Ans. (A) | 64. Ans. (B) | 65. Ans. (A)  |
| 66. Ans. (C) | 67. Ans. (D) | 68. Ans. (B) | 69. Ans. (B) | 70. Ans. (C)  |
| 71. Ans. (B) | 72. Ans. (C) | 73. Ans. (C) | 74. Ans. (A) | 75. Ans. (B)  |
| 76. Ans. (A) | 77. Ans. (A) | 78. Ans. (D) | 79. Ans. (C) | 80. Ans. (B)  |
| 81. Ans. (C) | 82. Ans. (C) | 83. Ans. (C) | 84. Ans. (B) | 85. Ans. (D)  |
| 86. Ans. (C) | 87. Ans. (B) | 88. Ans. (A) | 89. Ans. (C) | 90. Ans. (C)  |
| 91. Ans. (A) | 92. Ans. (C) | 93. Ans. (B) | 94. Ans. (B) | 95. Ans. (A)  |
| 96. Ans. (B) | 97. Ans. (D) | 98. Ans. (B) | 99. Ans. (B) | 100. Ans. (D) |

## EXERCISE #O-II

- |                   |                  |                  |                  |
|-------------------|------------------|------------------|------------------|
| 1. Ans. (A,B,C,D) | 2. Ans. (A,B,C)  | 3. Ans. (A,B)    | 4. Ans. (B,D)    |
| 5. Ans. (B,D)     | 6. Ans. (A,C)    | 7. Ans. (A,C,D)  | 8. Ans. (A,C)    |
| 9. Ans. (A,B,D)   | 10. Ans. (A,C)   | 11. Ans. (A,B,D) | 12. Ans. (A,C,D) |
| 13. Ans. (A,CD)   | 14. Ans. (A,B,C) | 15. Ans. (A,C,D) | 16. Ans. (B, D)  |
| 17. Ans. (B,D)    | 18. Ans. (A,B)   | 19. Ans. (A,B,C) | 20. Ans. (C,D)   |
| 21. Ans. (B,C)    | 22. Ans. (B,C,D) |                  |                  |
| 23. Ans.          |                  |                  |                  |

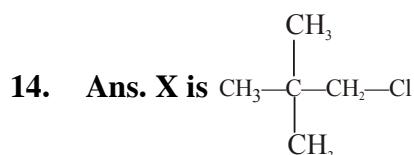


24. Ans. (A,B)      25. Ans. (A,C)      26. Ans. (A,B,D)      27. Ans. (A,B,C,D)  
 28. Ans. (A,B,C,D)      29. Ans. (B)      30. Ans. (A,B,C)      31. Ans. (A,C)

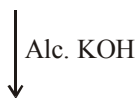
EXERCISE # S-I

1. Ans. (C)      2. Ans. (C)      3. Ans. (B)  
 4. Ans. (A) → P, R ; (B) → P, Q ; (C) → P ; (D) → P, Q  
 5. Ans. (A) → Q ; (B) → P ; (C) → S ; (D) → R  
 6. Ans. (A) → S ; (B) → Q ; (C) → R ; (D) → P  
 7. Ans. (A) → S ; (B) → R, S ; (C) → R ; (D) → P, Q  
 8. Ans. (A) → P, Q, R, S ; (B) → P, R ; (C) → P, T ; (D) → Q, S  
 9. Ans. (A) → Q, S ; (B) → P, R, S ; (C) → P, R, S ; (D) → P, Q, R, S  
 10. Ans. (A) → S, T ; (B) → P, S, T ; (C) → U ; (D) → Q ; (E) → T, U  
 11. Ans. (A) → R ; (B) → Q, S ; (C) → P, Q ; (D) → Q, S  
 12. Ans. (A) → P ; (B) → P ; (C) → Q ; (D) → R  
 13. Ans.

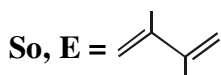
C-I bond being less stable than C-Cl bond and thus on heating heterolytic cleavage of C-I form I<sup>-</sup> which gives yellow precipitate with AgNO<sub>3</sub>.



15. Ans. Molecule A, C<sub>6</sub>H<sub>11</sub>Br has 1 unsaturation

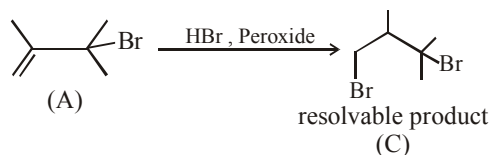


A single possible product, it suggests a symmetrical arrangement



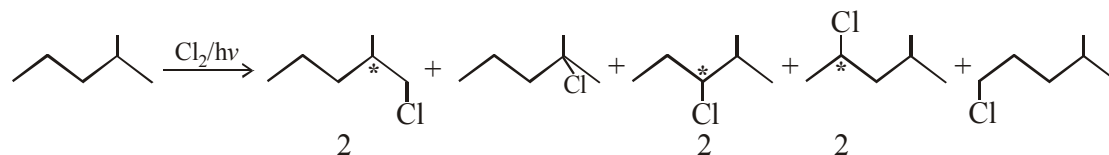
There are only two possibilities of A or structure I can be resolved

while structure II cannot be resolved so 'A' :

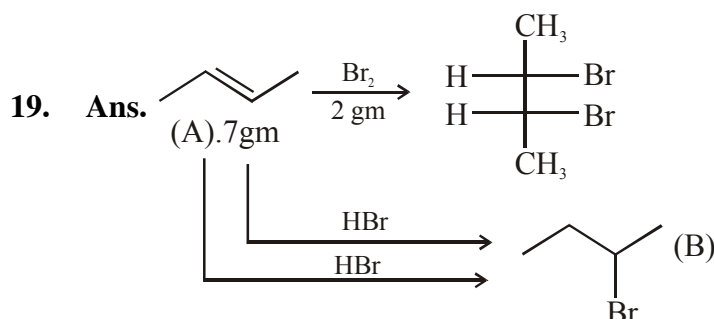
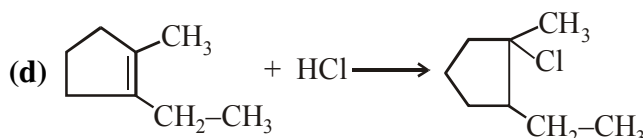
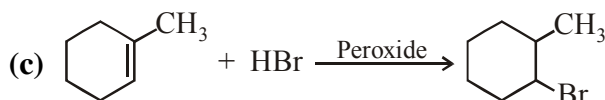
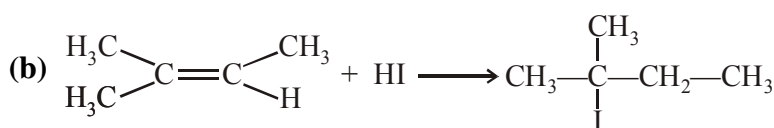


16. Ans. Both step is exothermic with HBr

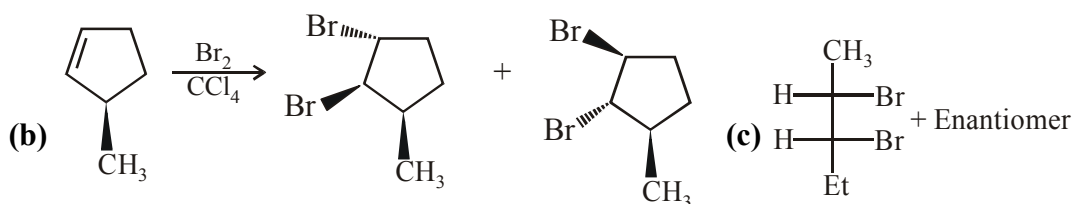
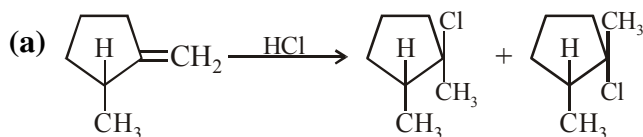
17. Ans.



18. Ans.



20. Ans.

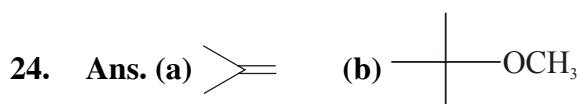
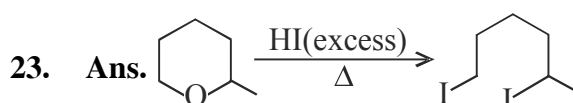


21. Ans.

The elimination of HI (or DI) in presence of strong base shows E2 elimination. The rate determining step involves breaking up of C-H (or C-D) bond. The C-D bond being stronger than C-H and thus elimination is faster in case of  $\text{CH}_3-\text{CH}_2\text{I}$ .

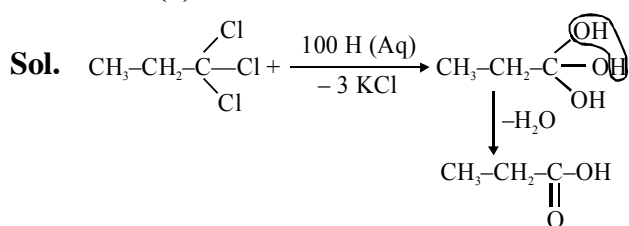
22. Ans.

In second compound  $\pi$  bonds are conjugated so due to resonance given product is formed as major product.



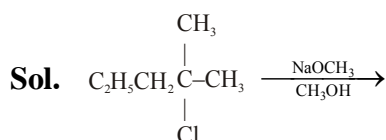


11. Ans. (2)

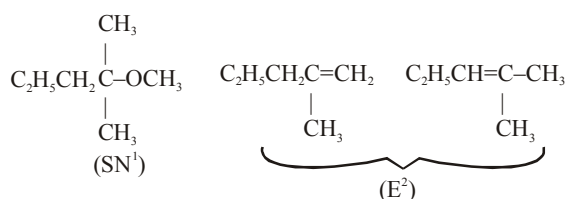


12. Ans. (2)

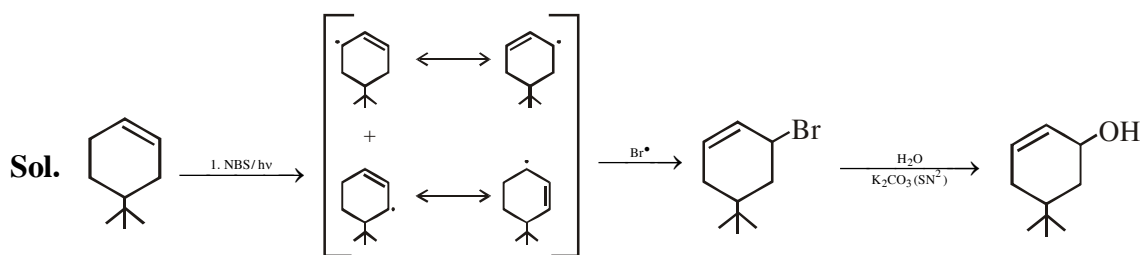
13. Ans. (2)



possible mechanism which takes place is  $\text{E}^2$  &  $\text{SN}^1$  mechanism. Hence possible products are.

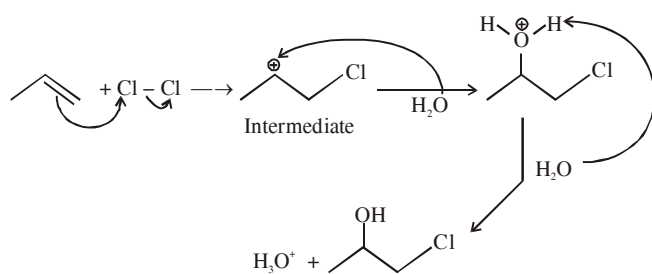


14. Ans. (3)



15. Ans. (3)

Sol.



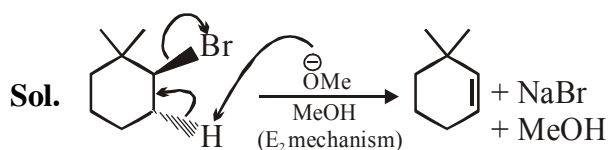
16. Ans. (2)

17. Ans. (1)

18. Ans. (4)

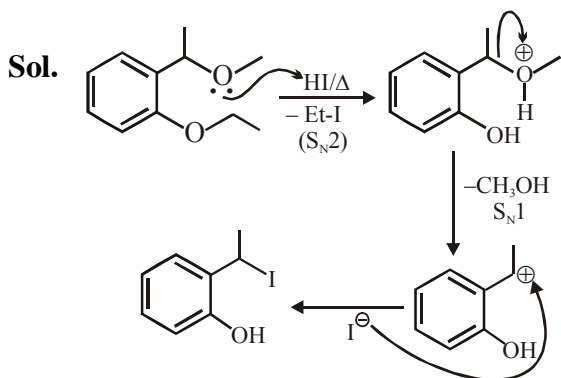
19. Ans. (2)

20. Ans. (1)



Reaction is dehydrohalogenation  $\text{E}^2$ -elimination reaction. Elimination takes place in single step and proceed by formation of transition state from anti position.

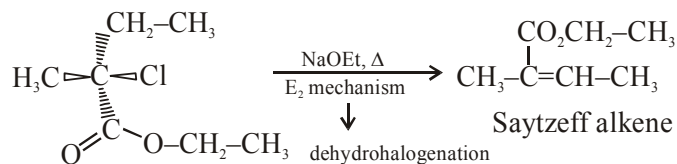
21. Ans. (3)



It is nucleophilic substitution reaction.

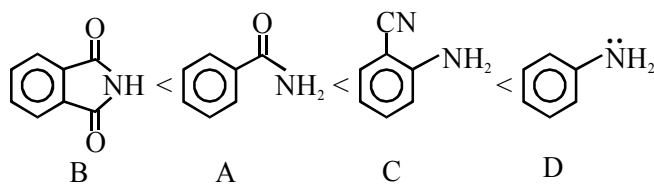
22. Ans. (3)

Sol.



23. Ans. (2)

Sol. Nucleophilicity order



24. Ans.(4)

25. Ans.(4)

26. Ans.(1)

27. Ans.(4)

28. Ans.(4)

29. Ans.(3)

30. Ans.(4)

31. Ans.(3)

32. Ans.(3)

33. Ans.(1)

34. Ans.(3)

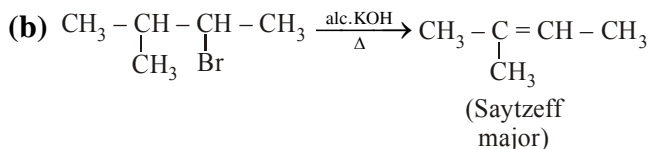
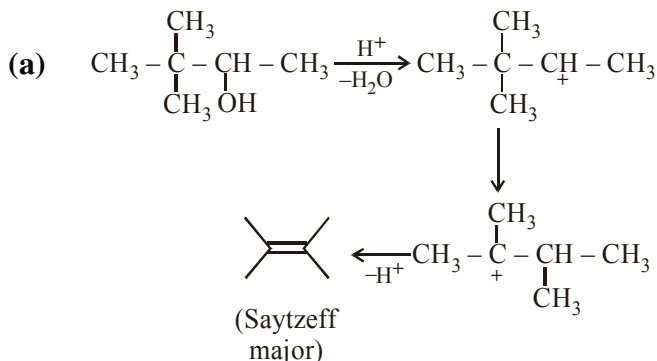
35. Ans.(2)

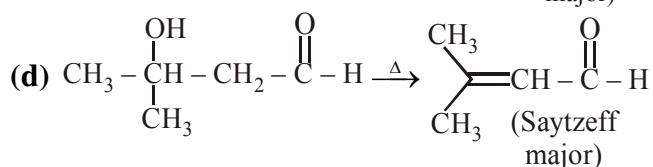
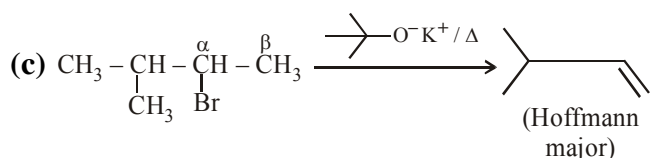
36. Ans.(4)

37. Ans.(2)

38. Ans.(1)

Sol.





$(\text{CH}_3)_3\text{O}^- \text{K}^+$  is incorrect representation of potassium tert-butoxide  $[(\text{CH}_3)_3\text{CO}^- \text{K}^+]$ .

So it is possible that it can be given as Bonus

39. Ans. (3)

Sol. Bond length order in carbon halogen bonds are in the order of  $\text{C} - \text{F} < \text{C} - \text{Cl} < \text{C} - \text{Br} < \text{C} - \text{I}$

Hence, Bond energy order

$\text{C} - \text{F} > \text{C} - \text{Cl} > \text{C} - \text{Br} > \text{C} - \text{I}$

40. Ans. (3)

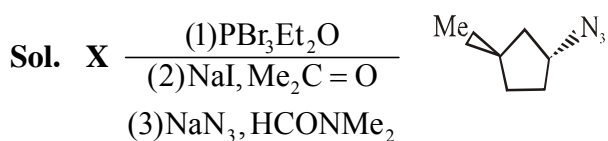
Sol. Reactivity  $\text{D} > \text{B} > \text{C} > \text{A}$


Carbocation formed from D is most stable

Carbocation formed from A is least stable

### EXERCISE # J-ADVANCE\_(OBJECTIVE)

- |  |               |              |              |              |
|--|---------------|--------------|--------------|--------------|
| 1. Ans. (D)  | 2. Ans. (B,D) | 3. Ans. (A)  | 4. Ans. (C)  | 5. Ans. (B)  |
| 6. Ans. (A)  | 7. Ans. (A,C) | 8. Ans. (D)  | 9. Ans. (C)  | 10. Ans. (D) |
| 11. Ans. (A)   | 12. Ans. (B)  | 13. Ans. (D) | 14. Ans. (B) | 15. Ans. (A) |
| 16. Ans. (A) $\rightarrow$ Q ; (B) $\rightarrow$ Q ; (C) $\rightarrow$ R, S ; (D) $\rightarrow$ P, S |               |              |              |              |
| 17. Ans. (A)   | 18. Ans. (D)  | 19. Ans. (B) | 20. Ans. (D) | 21. Ans. (5) |
| 22. Ans. (B)   |               |              |              |              |

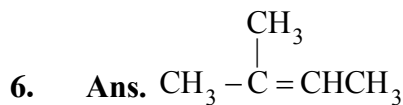
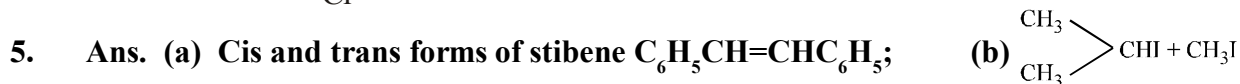
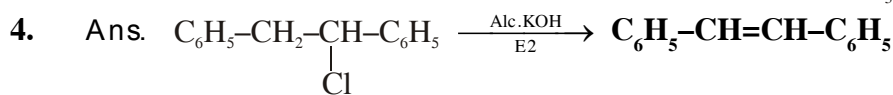
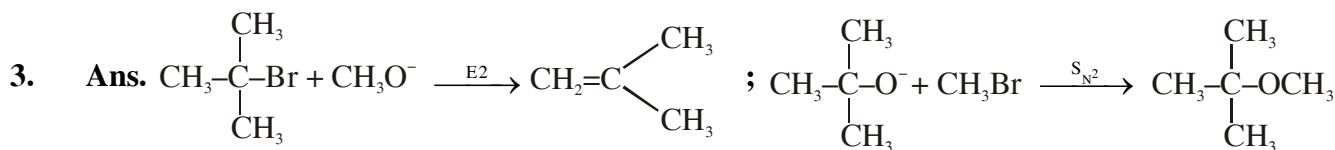


all the three reaction are  $\text{S}_{\text{N}}2$  so X is 

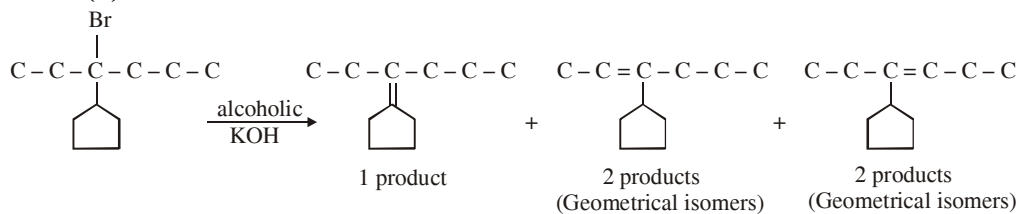
### EXERCISE # J-ADVANCE\_(SUBJECTIVE)

1. Ans. (X) :  $\text{CH}_3 - \underset{\text{Cl}}{\text{C}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$  ; (Y) :  $\text{CH}_2 = \underset{\text{CH}_3}{\text{C}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$  ; (Z) :  $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$

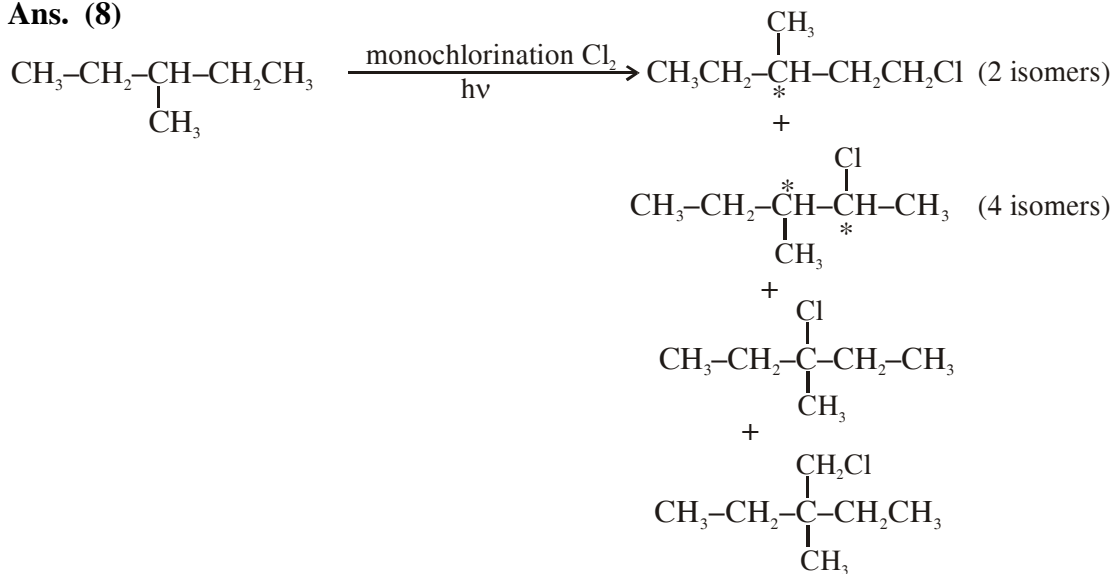




7. Ans. (5)

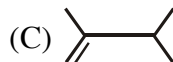
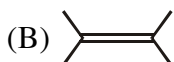
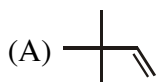
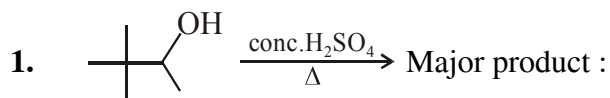


8. Ans. (8)



## ALCOHOL AND ETHER

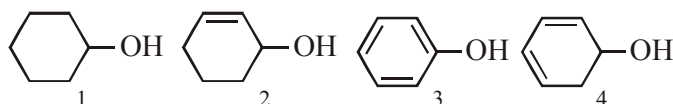
## EXERCISE # O-1



(D) None of these

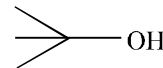
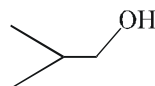
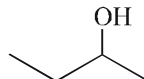
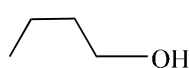
AE0001

2. Correct order of dehydration of following alcohols will be :

(A)  $1 < 2 < 3 < 4$ (B)  $4 > 3 > 1 > 2$ (C)  $4 > 2 > 1 > 3$ (D)  $1 > 3 > 4 > 2$ 

AE0002

3. Dehydration of the isomeric alcohols

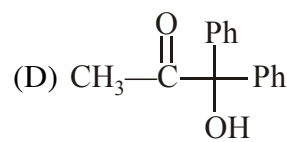
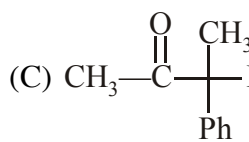
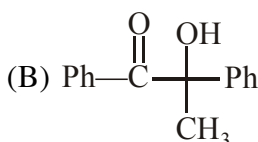
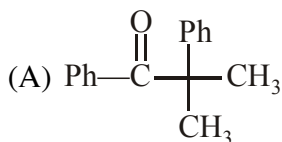
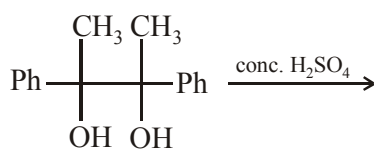


What will be the order of rate of reaction ?

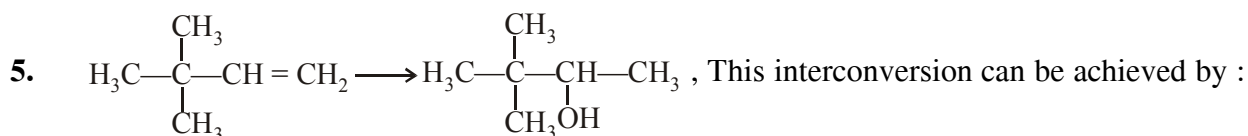
(A)  $\text{IV} > \text{III} > \text{II} > \text{I}$ (B)  $\text{I} > \text{II} > \text{III} > \text{IV}$ (C)  $\text{IV} > \text{II} > \text{III} > \text{I}$ (D)  $\text{II} > \text{IV} > \text{I} > \text{III}$ 

AE0003

4. Find out major product of following reaction.



AE0004



(A) Acid catalysed hydration

(B) Oxymercuration-demercuration

(C) Hydroboration - oxidation

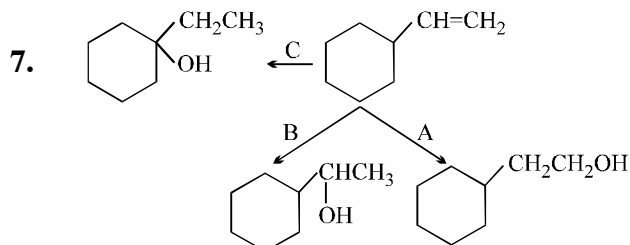
(D) Any method mentioned above

AE0005

6.  $A \xrightarrow[\text{(ii) NaBH}_4, \text{OH}^-]{\text{(i) Hg(OAc)}_2, \text{HOH}}$  1-Methylcyclohexanol. Here A is :



AE0006



Select schemes A, B, C out of

(I) Acid catalysed hydration

(II) HBO

(III) Oxymercuration-demercuration

(A) I in all cases

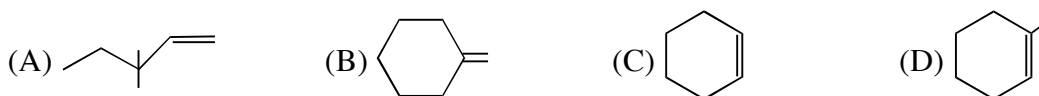
(B) I, II, III

(C) II, III, I

(D) III, I, II

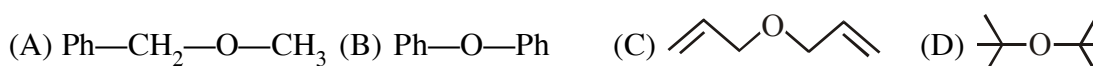
AE0007

8. HBO, oxymercuration-demercuration and acid catalysed hydration will give same product in



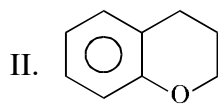
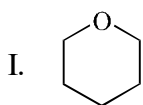
AE0008

9. Which of the following ethers is least reactive to cleavage with conc. HBr ?



AE0009

10. Consider the reaction of HI with the following:



Which forms di-iodide on reaction with HI (excess)?

(A) I and II both

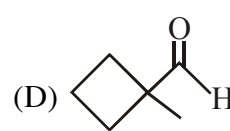
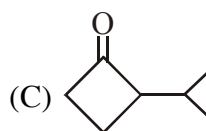
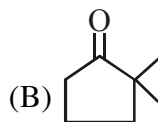
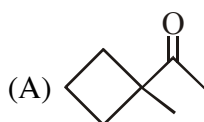
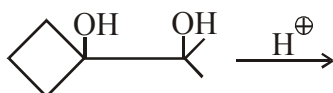
(B) II only

(C) I only

(D) none

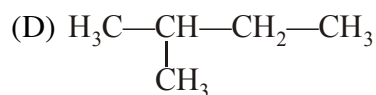
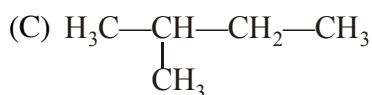
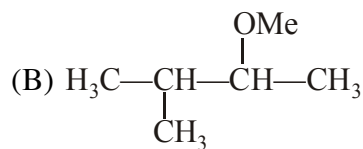
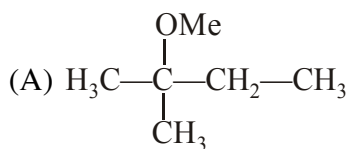
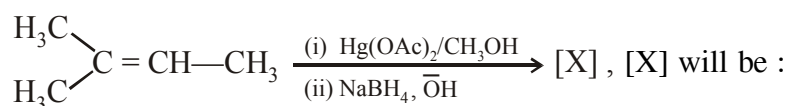
AE0010

11. Find out major product of following reaction.



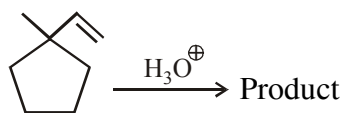
AE0011

12. In the given reaction

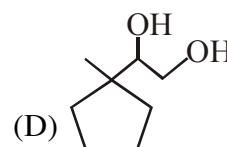
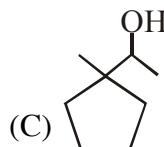
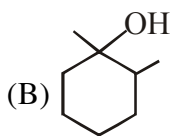


AE0012

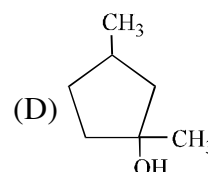
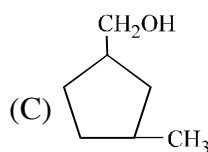
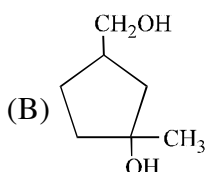
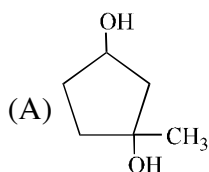
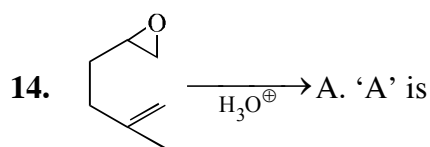
13. In the following reaction



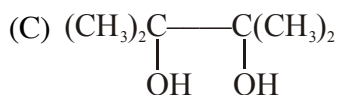
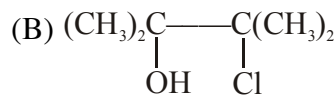
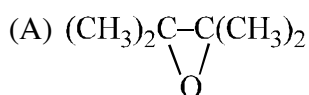
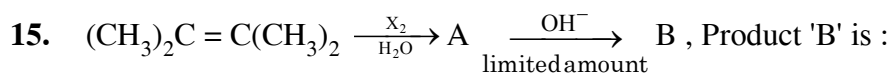
The major product is :



AE0013



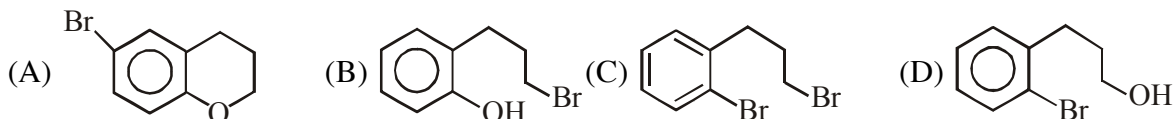
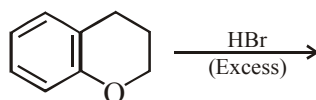
AE0014



(D) None

AE0015

16. Find out correct product of reaction :



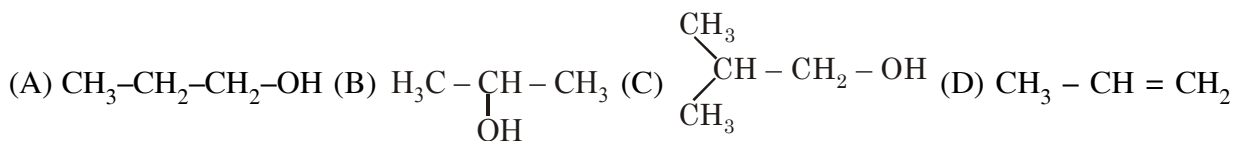
AE0016

17. + HI (1 eq.)  $\longrightarrow$  Product, Product is :



AE0017

18.  $Z \xrightarrow{\text{PCl}_5} X \xrightarrow[\Delta]{\text{Alc.KOH}} Y \xrightarrow{\text{dil. H}_2\text{SO}_4} Z$  ; Z is :



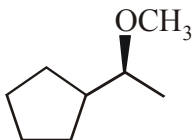
AE0018

19. When 2-chloroethanol is warmed slightly with dilute NaOH, the major product formed is :



AE0019

20. How many total alcohols are form by acidic hydrolysis of following ether.



AE0020

21. Which of the following test can be used to differentiate methyl alcohol and iso-propyl alcohol.



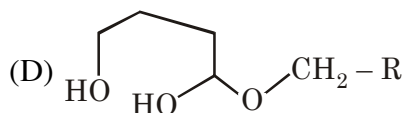
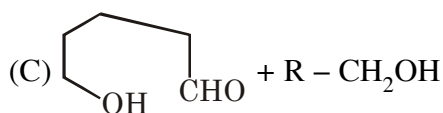
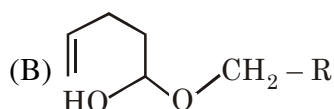
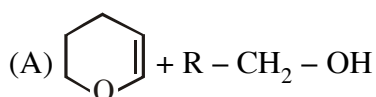
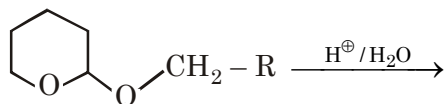
AE0021

22. On reaction of ether with  $\text{BF}_3$ , ether acts as :

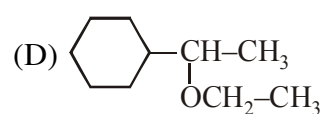
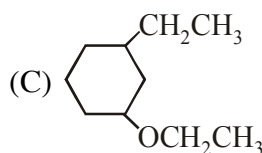
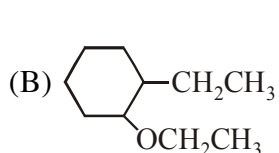
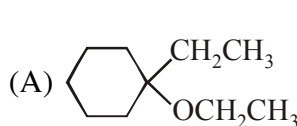
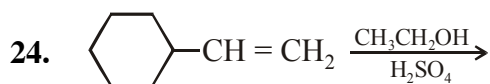
- (A) Electrophile (B) Nucleophile  
(C) Ambiphile (D) None

AE0022

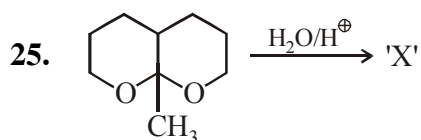
23. Give suitable major product for following reaction



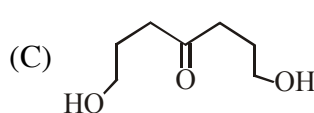
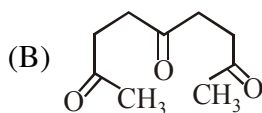
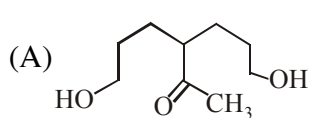
AE0023



AE0024

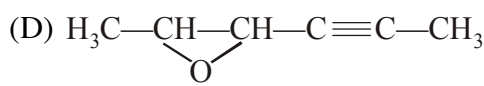
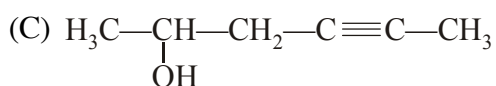
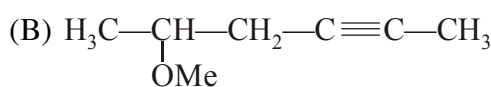
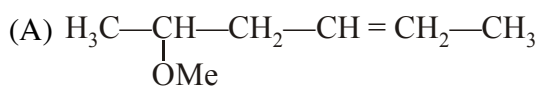
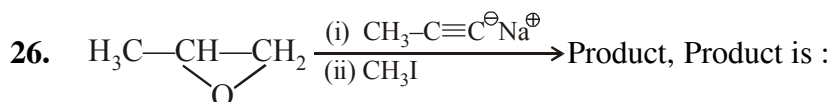


Product 'X' will be :



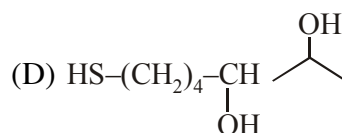
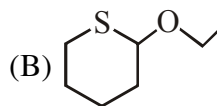
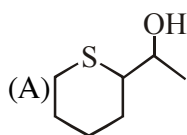
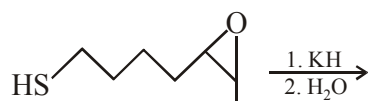
(D) All of these

AE0025



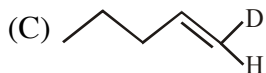
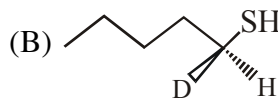
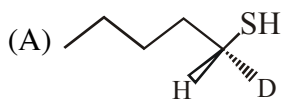
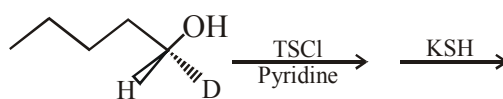
AE0026

27. The product of the reaction is :



AE0027

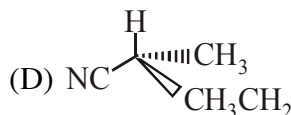
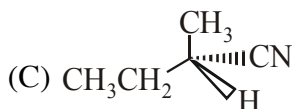
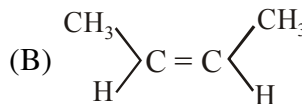
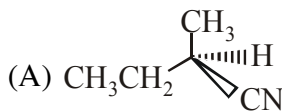
28. Identify the major product of reaction :



(D) No reaction

AE0028

29.  $\text{CH}_3\text{CH}_2-\text{C}(\text{CH}_3)(\text{OH})\text{H} \xrightarrow{\text{PBr}_3} \xrightarrow[\text{DMF}]{\text{KCN}}$  Final product is ?



AE0029

30. Diethyl ether on prolong exposure to air gives :

(A) Ethanol

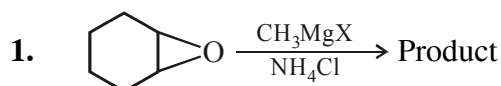
(B) Diethyl peroxide

(C) Diethyl hydroxy peroxide

(D) Ethanoic acid

AE0030

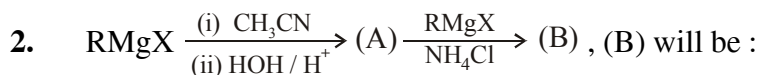
EXERCISE # O-2



What is the product ?

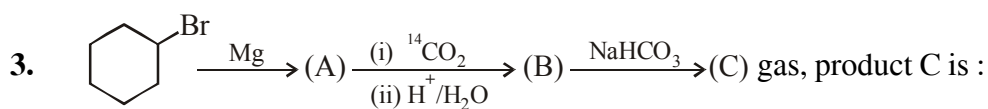
- (A) Enantiomer (B) Diastereoisomer (C) Meso (D) Achiral

AE0031



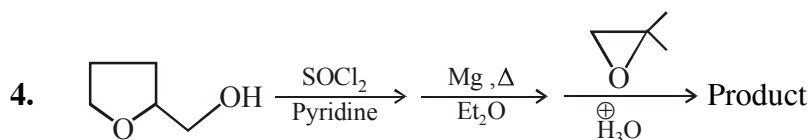
- (A) 1° ROH (B) 2° ROH (C) 3° ROH (D) Alkene

AE0032

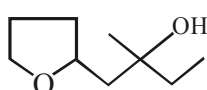
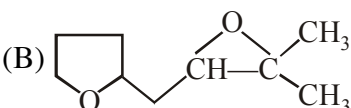
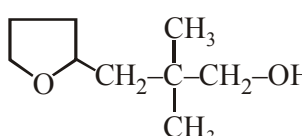
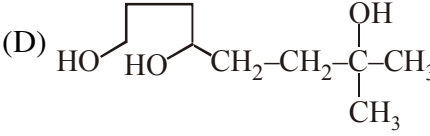


- (A) CO (B)  $^{14}\text{CO}_2$  (C)  $\text{CO}_2$  (D) A mixture  $^{14}\text{CO}_2$  and  $\text{CO}_2$

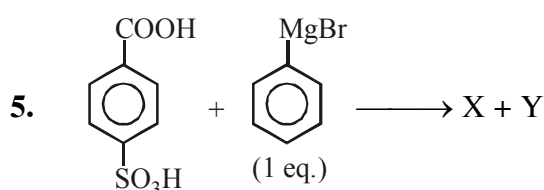
AE0033




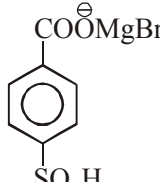

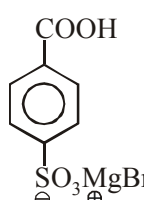

Product of reaction is :

- (A)  (B)   
 (C)  (D) 

AE0034

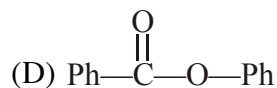
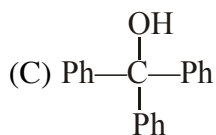
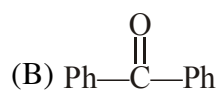
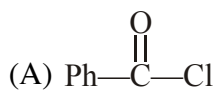
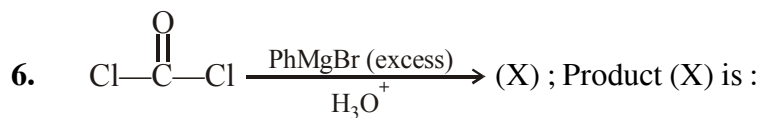


X and Y are respectively :

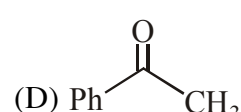
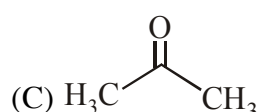
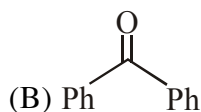
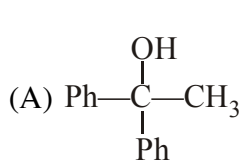
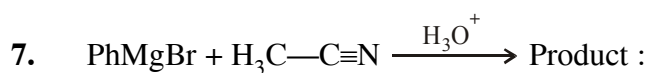
- (A)  only (B)  and   
 (C)  and  (D) None of these

AE0035

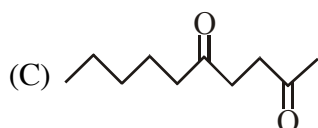
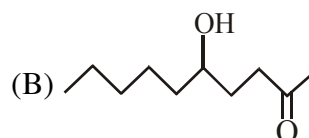
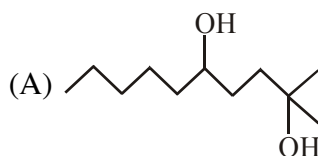
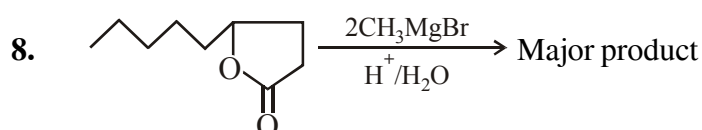




AE0036

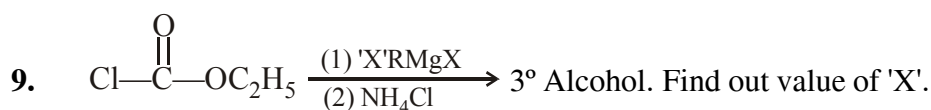


AE0037



(D) No reaction

AE0038



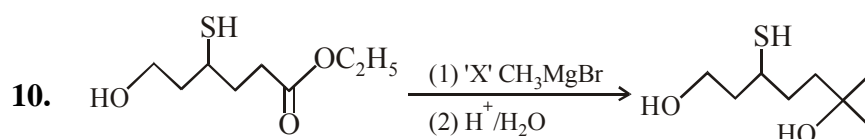
(A) 2

(B) 3

(C) 4

(D) 1

AE0039



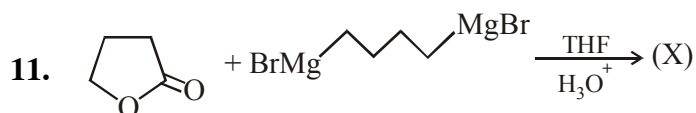
(A) 2

(B) 3

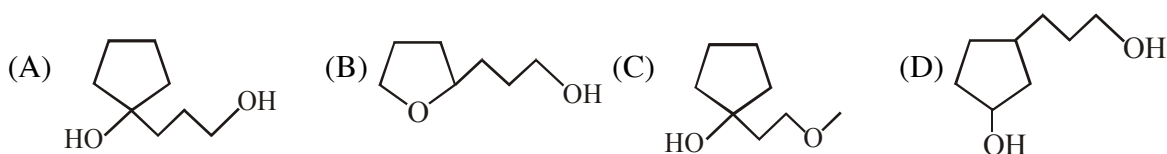
(C) 4

(D) 5

AE0040



Identify (X) :

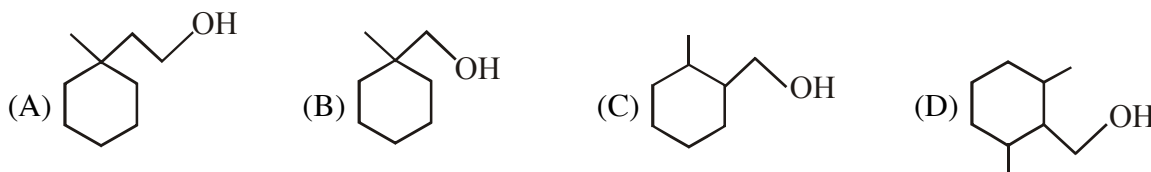
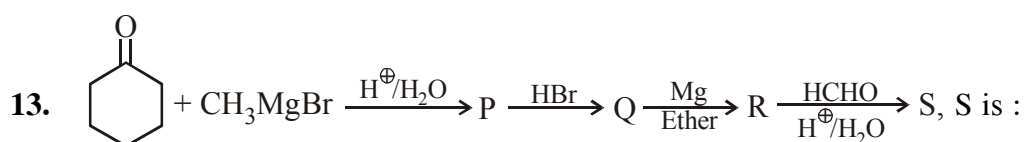


AE0041

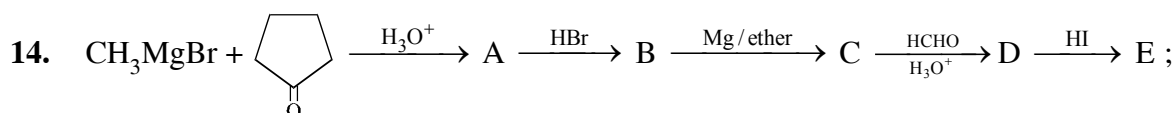
12. If phenyl magnesium bromide and acetaldehyde are the reactants, the product formed after hydrolysis would be :

- (A) Benzyl alcohol (B) 1-Phenylethanol  
(C) 2-Phenylethanol (D) Acetone

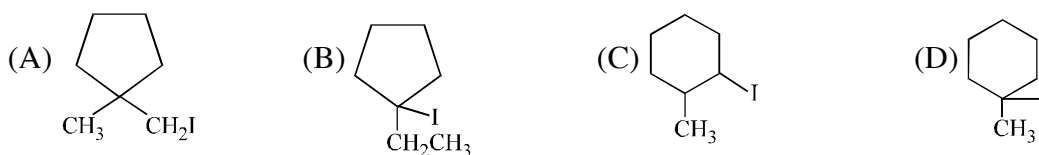
AE0042



AE0043

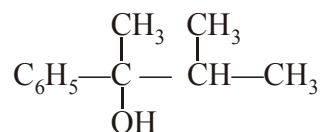


Product E is



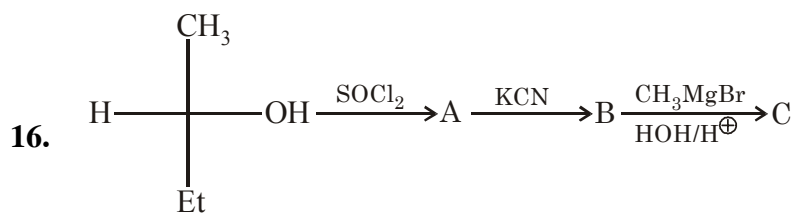
AE0044

15. Which of the following reagents (A to D) would you not select to convert  $C_6H_5COCH_3$  (acetophenone) to the following alcohol ?



- (A)  $CH_3CH_2CH_2MgBr$  and hydrolysis (B)  $CH_3MgBr$  and acid hydrolysis  
(C)  $(CH_3)_2CHMgBr$  and acid hydrolysis (D)  $PhMgBr$  and acid hydrolysis

AE0045

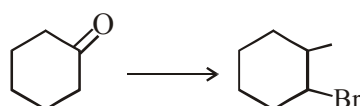


the final product C is :



AE0046

17. Which combination of reagents will not bring about the following conversion ?

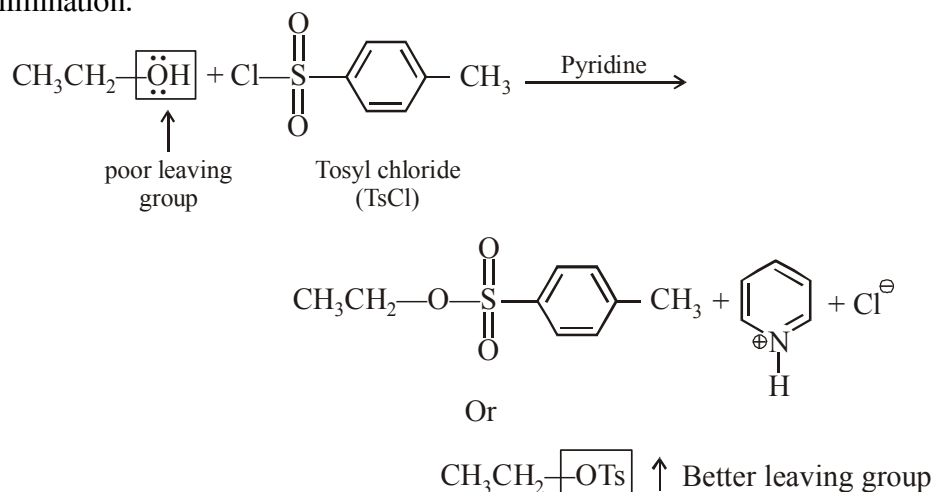


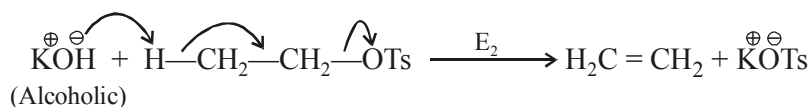
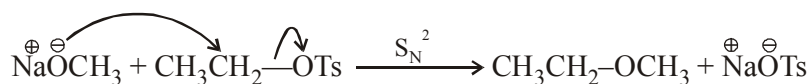
- (A)  $\text{MeMgBr}/\text{H}^{\oplus}$ ,  $\text{H}_2\text{SO}_4/\Delta$ ,  $\text{HBr}/\text{H}_2\text{O}_2$ ,  $h\nu$  (B)  $\text{MeMgBr}/\text{H}^{\oplus}$ ,  $\text{H}_2\text{SO}_4/\Delta$ ,  $\text{HBr}$   
 (C)  $\text{MeMgBr}/\text{H}^{\oplus}$ ,  $\text{HBr}/\text{CCl}_4$  (D)  $\text{MeMgBr}$ ,  $\text{NH}_4\text{Cl}$

AE0047

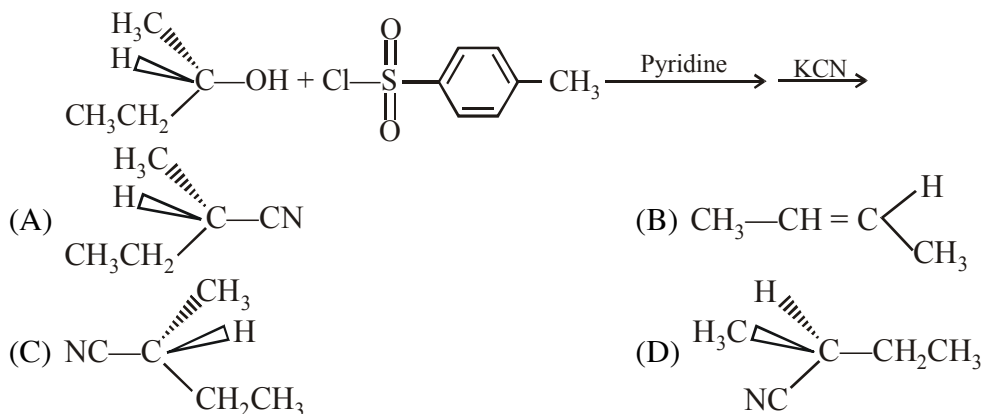
### Paragraph for Q.No. 18 & 19

Alcohols are converted to tosylates by treatment with p-toluene sulfonyl chloride (TsCl) in presence of pyridine. This overall process converts a poor leaving group ( $\text{OH}^-$ ) into better one ( $\text{OTs}^-$ ). A tosylate is a better leaving group because its conjugated acid p-toluene sulfonic acid is strong acid. Because alkyl tosylates have better leaving tendency they undergo both nucleophilic substitution and  $\beta$ -elimination.



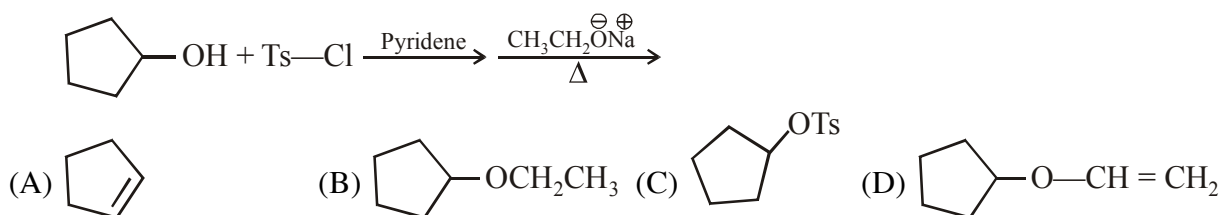


18. Find the major product of following reaction :



AE0048

19. What would be the major product of following reactions ?



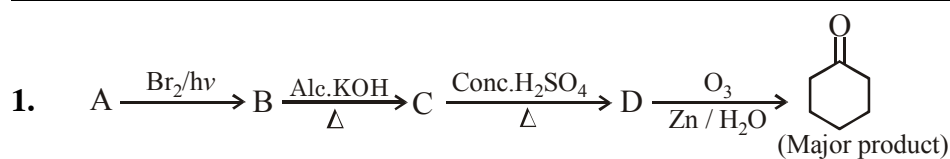
AE0049

20. Which of the following order is incorrect ?

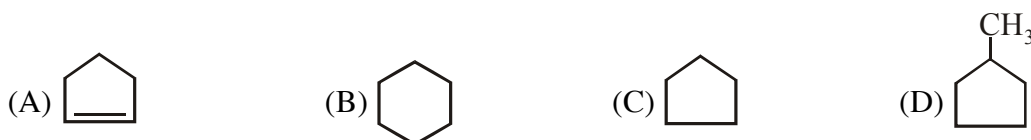
- (A)  $\text{CH}_3-\text{CH}_2-\text{OH} > \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH} > \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$  (Solubility in  $\text{H}_2\text{O}$ )
- (B)  $\text{CH}_3-\text{CH}_2-\text{OH} > \text{CH}_3-\text{O}-\text{CH}_3 > \text{CH}_3-\text{CH}_2-\text{CH}_3$  (Boiling point)
- (C) Pentan-1-ol > Pentanal > Ethoxy ethane (Boiling point)
- (D)  $\text{CH}_3-\text{OH} > \text{CH}_3-\text{CH}_2-\text{OH} > \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$  (Boiling point)

AE0050

## EXERCISE # S-1

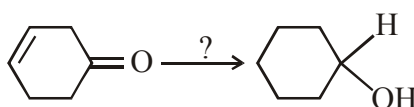


Find out the structure of 'A' :



AE0051

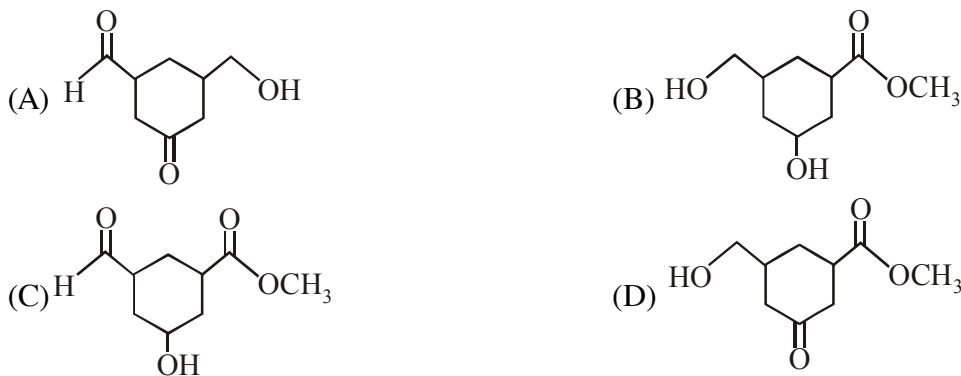
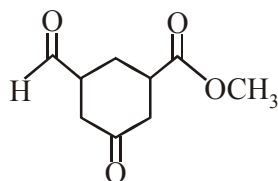
2. Predict the reducing agents in following reaction.



- (A)  $LiAlH_4$  (B)  $NaBH_4$  (C)  $H_2 / Pt, \Delta$  (D) Both (A) and (B)

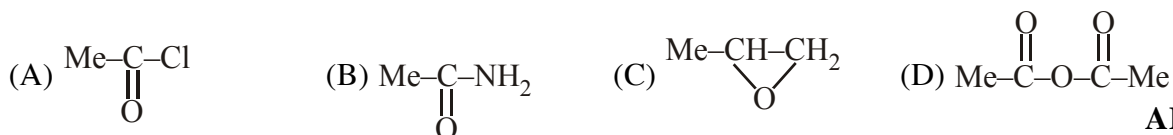
AE0052

3. Find out the product when the following compound react with  $NaBH_4$  :



AE0053

4. Compound which does not give alcohol on reduction by  $LiAlH_4$  is/are ?



AE0054

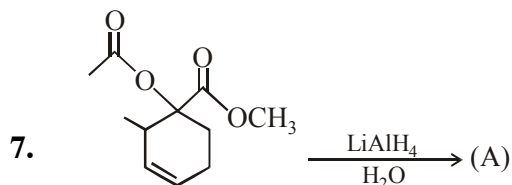
5. Choose the incorrect option ?

- (A) Boiling point increases with increase in carbon due to increase in vander wall forces  
(B) Branching in carbon decreases the boiling point  
(C) High boiling point of alcohols are mainly due to pressure of intermolecular H-bonding  
(D) Methoxymethane has higher boiling point than ethanol & propane

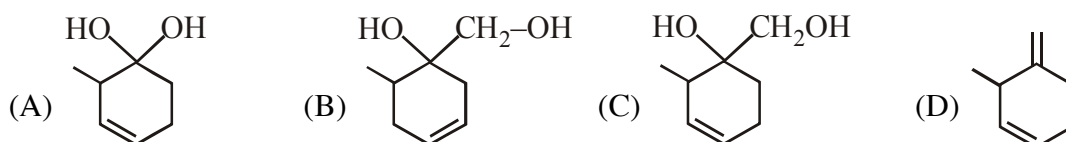
AE0055

6. Ethoxyethane & butan-1-ol are miscible to almost same extent (7.5 & 9 gm per 100 ml water respectively because of :
- (A) Same molecular mass (B) They are isomers  
 (C) Both can form hydrogen bond with water (D) Water is universal solvent

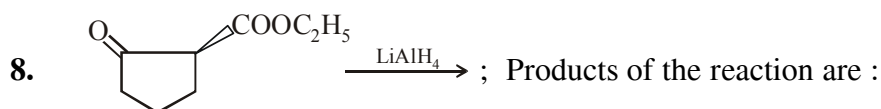
AE0056



Find out 'A' of the reaction



AE0057



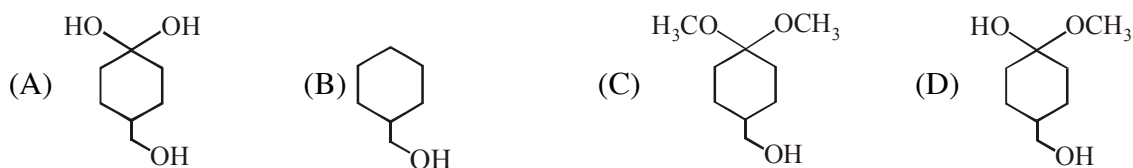
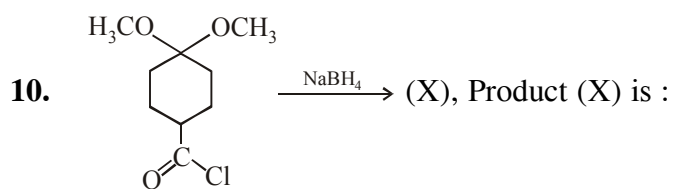
- (A) Racemic (B) Diastereomers  
 (C) Meso (D) Optically pure

AE0058

9. Reduction of  $R-CH_2OH \longrightarrow RCH_3$  can be carried out by :

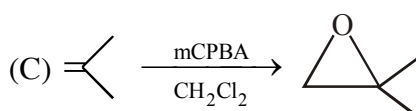
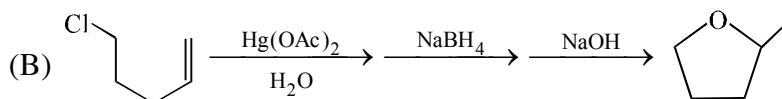
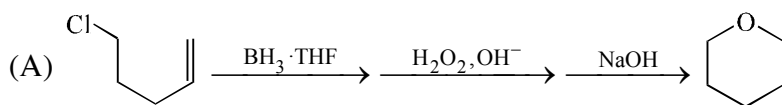
- (A)  $LiAlH_4$  (B)  $H_2 / Ni$   
 (C) Red P + HI (D)  $NaBH_4 / AlCl_3$

AE0059



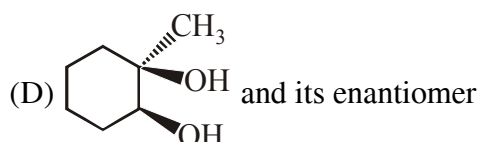
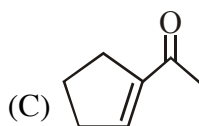
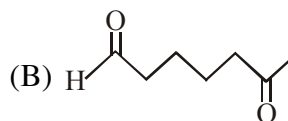
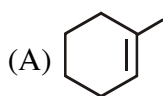
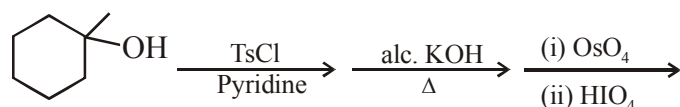
AE0060

11. Select the correct synthesis



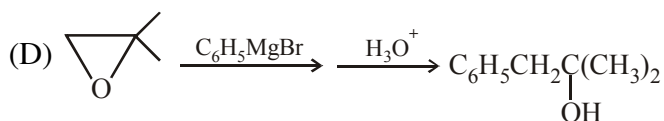
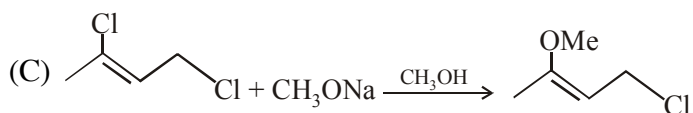
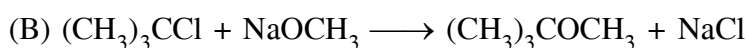
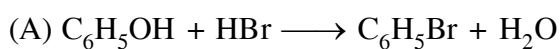
AE0061

12. Identify the final product of following sequence of reactions :



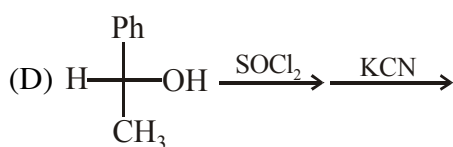
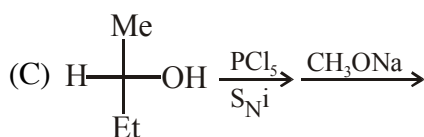
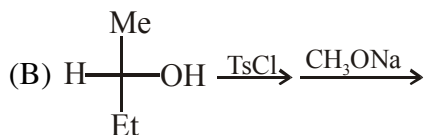
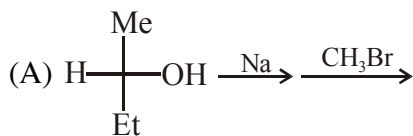
AE0062

13. Which of the following reaction is not possible ?

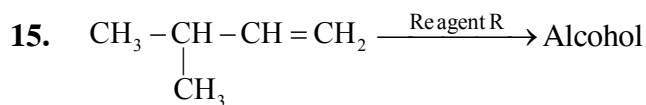


AE0063

14. Which of the following reactions proceeds with inversion of configuration ?



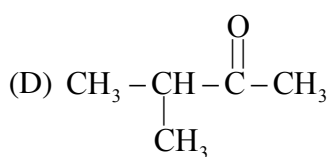
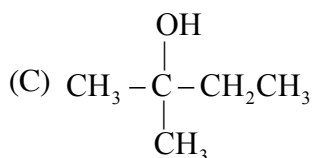
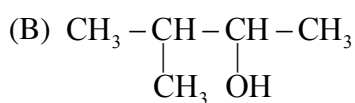
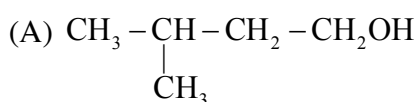
AE0064



which is true about alcohol and Reagent ?

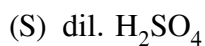
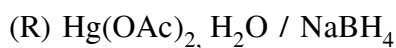
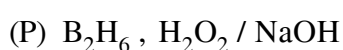
**List-I**

**(Alcohol)**



**List-II**

**(Reagent)**



AE0065



## EXERCISE # J-MAIN

1. In the following sequence of reactions  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{P} + \text{I}_2} \text{A} \xrightarrow[\text{Ether}]{\text{Mg}} \text{B} \xrightarrow{\text{HCHO}} \text{C} \xrightarrow{\text{H}_2\text{O}} \text{D}$ , then compound 'D' is - [AIEEE-2007]  
 (1) Butanal (2) n-Butyl alcohol (3) n-Propyl alcohol (4) Propanal  
**AE0066**
2. A liquid was mixed with ethanol and a drop of concentrated  $\text{H}_2\text{SO}_4$  was added. A compound with a fruity smell was formed. The liquid was :- [AIEEE-2009]  
 (1)  $\text{CH}_3\text{COCH}_3$  (2)  $\text{CH}_3\text{COOH}$  (3)  $\text{CH}_3\text{OH}$  (4)  $\text{HCHO}$   
**AE0067**
3. From amongst the following alcohols the one that would react fastest with conc.  $\text{HCl}$  and anhydrous  $\text{ZnCl}_2$ , is :- [AIEEE-2010]  
 (1) 1-Butanol (2) 2-Butanol  
 (3) 2-Methylpropan-2-ol (4) 2-Methylpropanol  
**AE0068**
4. Consider the following reaction : [AIEEE-2011]  
 $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{SO}_4 \rightarrow$  Produce  
 Among the following, which one cannot be formed as a product under any conditions ?  
 (1) Ethyl-hydrogen sulphate (2) Ethylene (3) Acetylene (4) Diethyl ether  
**AE0069**
5. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism :- [AIEEE-2013]  
 (1) secondary alcohol by  $\text{SN}^1$  (2) tertiary alcohol by  $\text{SN}^1$   
 (3) secondary alcohol by  $\text{SN}^2$  (4) tertiary alcohol by  $\text{SN}^2$   
**AE0070**
6. Allyl phenyl ether can be prepared by heating: (JEE-MAIN-2014)  
 (1)  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Br} + \text{C}_6\text{H}_5\text{ONa}$  (2)  $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{Br} + \text{CH}_3-\text{ONa}$   
 (3)  $\text{C}_6\text{H}_5\text{Br} + \text{CH}_2=\text{CH}-\text{CH}_2-\text{ONa}$  (4)  $\text{CH}_2=\text{CH}-\text{Br} + \text{C}_6\text{H}_5-\text{CH}_2-\text{ONa}$   
**AE0071**
7. In the Victor-Meyer's test, the colour given by  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  alcohols are respectively :-  
 (1) Red, blue, colourless (2) Colourless, red, blue (JEE-MAIN-2014)  
 (3) Red, blue, violet (4) Red, colourless, blue  
**AE0072**

8. Williamson synthesis of ether is an example of (JEE-MAIN-2014)

- (1) Nucleophilic addition (2) Electrophilic substitution  
(3) Nucleophilic substitution (4) Electrophilic addition

AE0073

9. The gas evolved on heating  $\text{CH}_3\text{MgBr}$  in methanol is : [JEE-MAIN-On-line-2016]

- (1) Ethane (2) Propane (3) Methane (4) HBr

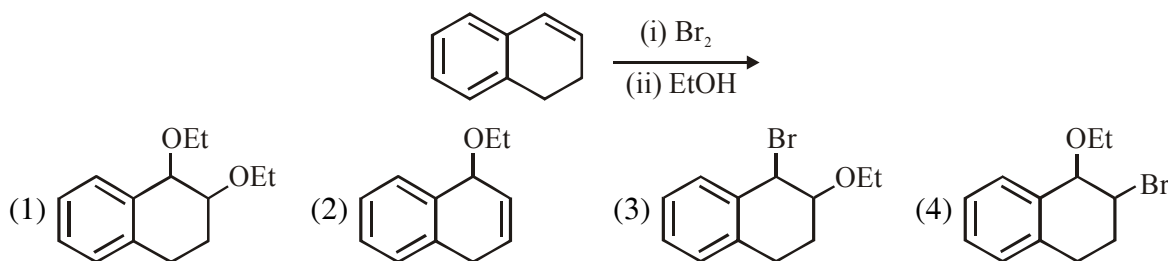
AE0074

10. Bouveault–Blanc reduction reaction involves: [JEE-MAIN-On-line-2016]

- (1) Reduction of an ester with  $\text{Na}/\text{C}_2\text{H}_5\text{OH}$   
(2) Reduction of an ester with  $\text{H}_2/\text{Pd}$   
(3) Reduction of a carbonyl compound with  $\text{Na}/\text{Hg}$  and  $\text{HCl}$   
(4) Reduction of an anhydride with  $\text{LiAlH}_4$

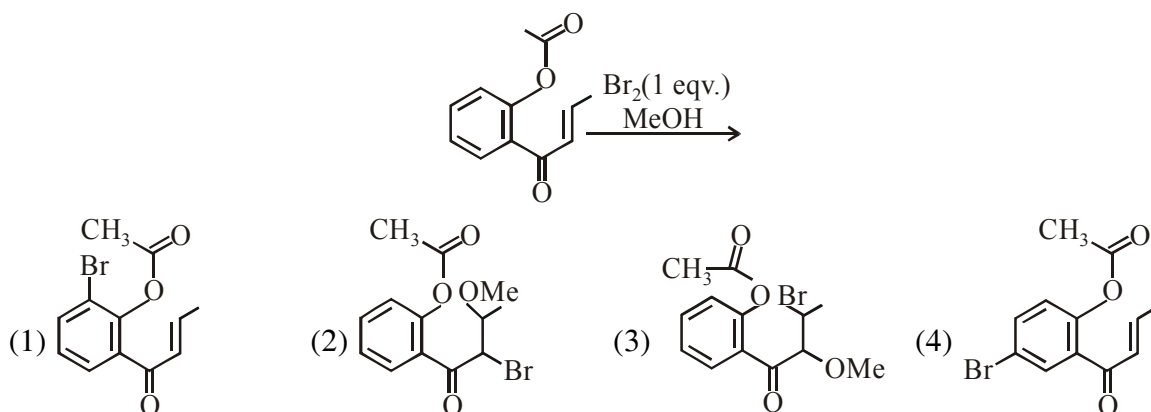
AE0075

11. The major product the following reaction is : [JEE-MAIN-On-line-(Jan)-2019]



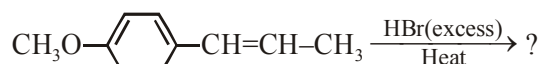
AE0076

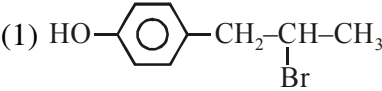
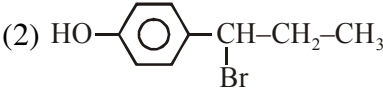
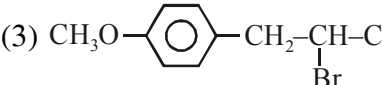
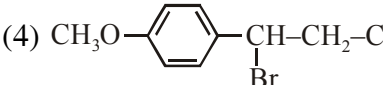
12. The major product obtained in the following conversion is :- [JEE-MAIN-On-line-(Jan)-2019]



AE0077

13. The major product in the following conversion is : [JEE-MAIN-On-line-(Jan)-2019]

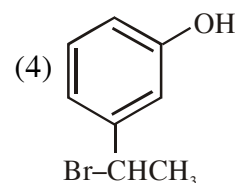
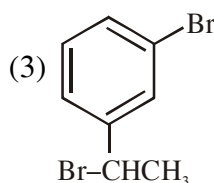
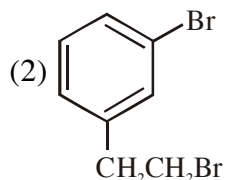
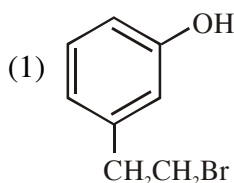
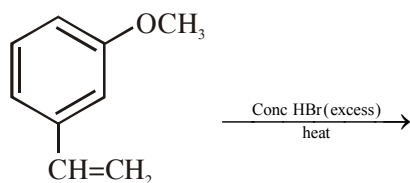


- (1)  (2)   
(3)  (4) 

AE0078

14. The major product of the following reactions:

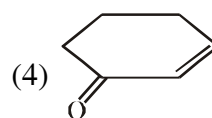
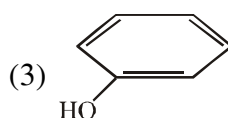
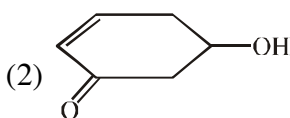
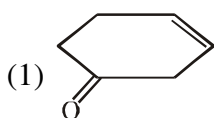
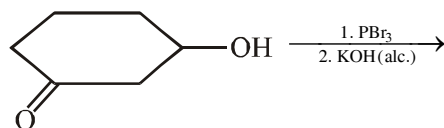
[JEE-MAIN-On-line-(April)-2019]



AE0079

15. The major product of the following reaction is :

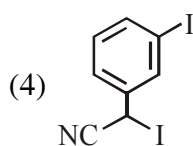
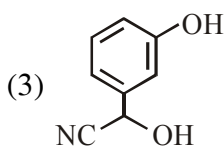
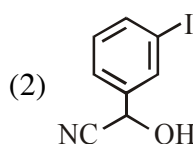
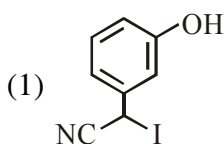
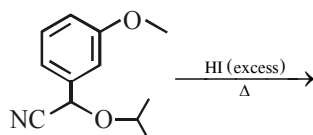
[JEE-MAIN-On-line-(April)-2019]



AE0080

16. The major product of the following reaction is :

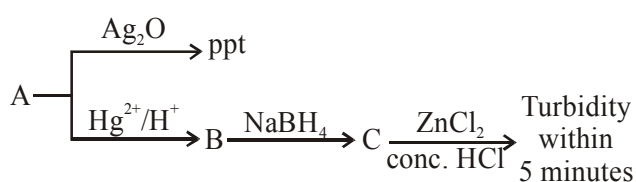
[JEE-MAIN-On-line-(April)-2019]



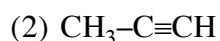
AE0081

17. Consider the following reactions :

[JEE-MAIN-On-line-(April)-2019]



'A' is :



AE0082

18. Heating of 2-chloro-1-phenylbutane with EtOK/EtOH gives X as the major product. Reaction of X with  $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$  followed by  $\text{NaBH}_4$  gives Y as the major product. Y is :

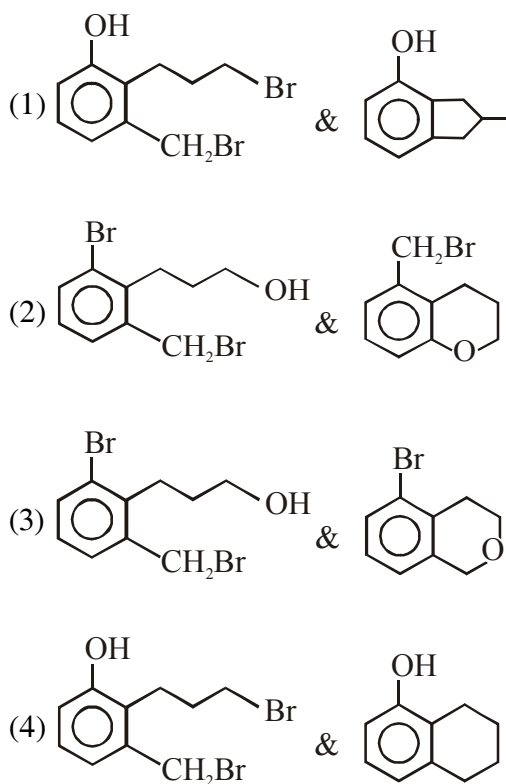
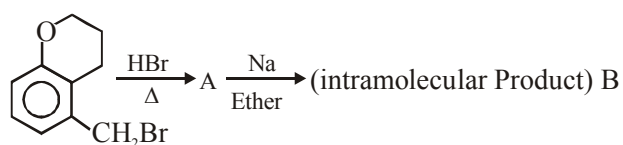
[JEE-MAIN-On-line-(April)-2019]



AE0083

19. In the following reaction sequence, structures of A and B, respectively will be :

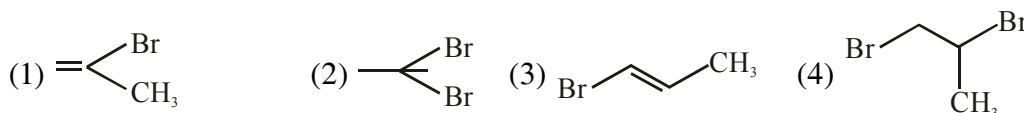
[JEE-MAIN-(Jan)-2020]



AE0084

20. 1-methyl ethylene oxide when treated with an excess of HBr produces :

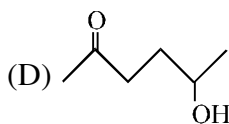
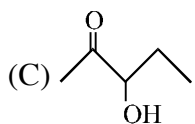
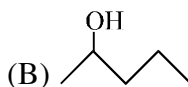
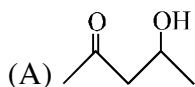
[JEE-MAIN-(Jan)-2020]



AE0085

## EXERCISE # J-ADVANCE

1. Which one of the following will most readily be dehydrated in acidic condition: [JEE 2000]



AE0086

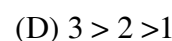
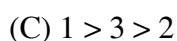
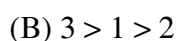
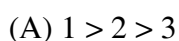
2. Identify the correct order of boiling point of the following compounds: [JEE 2002]



1

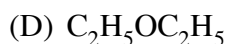
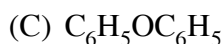
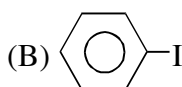
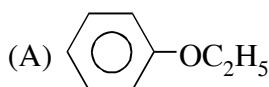
2

3



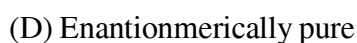
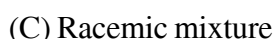
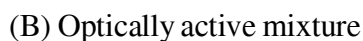
AE0087

3. [JEE 2003]



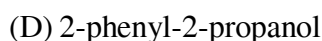
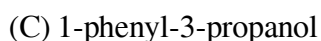
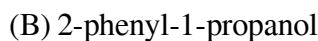
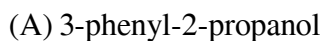
AE0088

4. Reaction of enantiomerically pure acid with 1 chiral carbon and racemic alcohol with 1 chiral carbon gives an ester which is: [JEE 2003]



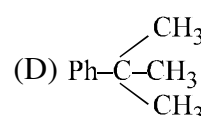
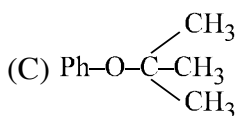
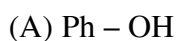
AE0089

5. On acid catalysed hydration, 2-phenyl propene gives: [JEE 2004]

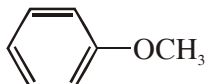


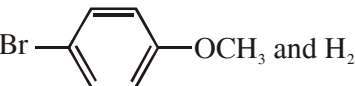



AE0090

6. Phenyl magnesium bromide reacting with t-Butyl alcohol gives [JEE 2005]



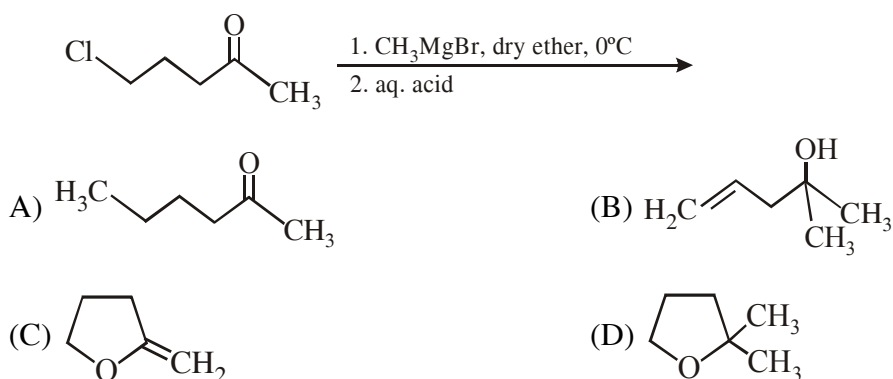
AE0091

7. In the reaction   $\xrightarrow{\text{HBr}}$  the products are [JEE 2010]

- (A)  and  $\text{H}_2$  (B)  and  $\text{CH}_3\text{Br}$
- (C)  and  $\text{CH}_3\text{OH}$  (D)  and  $\text{CH}_3\text{Br}$

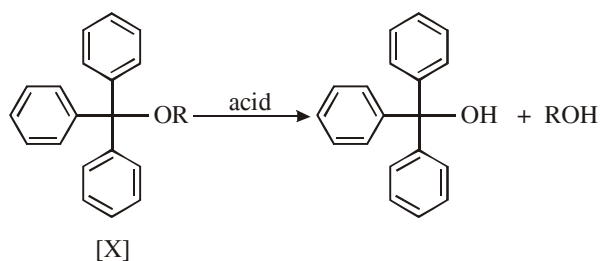
AE0092

8. The major product in the following reaction is



AE0093

9. The acidic hydrolysis of ether (X) shown below is fastest when [JEE 2014]



- (A) one phenyl group is replaced by a methyl group  
 (B) one phenyl group is replaced by a para-methoxyphenyl group  
 (C) two phenyl groups are replaced by two para-methoxyphenyl group  
 (D) no structural change is made to X

AE0094

10. The correct combination of names for isomeric alcohols with molecular formula  $\text{C}_4\text{H}_{10}\text{O}$  is/are [JEE 2014]

- (A) *tert*-butanol and 2-methylpropan-2-ol  
 (B) *tert*-butanol and 1, 1-dimethylethan-1-ol  
 (C) *n*-butanol and butan-1-ol  
 (D) isobutyl alcohol and 2-methylpropan-1-ol

AE0095

**ANSWER-KEY****EXERCISE # O-1**

- |              |              |              |              |
|--------------|--------------|--------------|--------------|
| 1. Ans. (B)  | 2. Ans. (C)  | 3. Ans. (C)  | 4. Ans. (C)  |
| 5. Ans. (B)  | 6. Ans. (D)  | 7. Ans. (C)  | 8. Ans. (C)  |
| 9. Ans. (B)  | 10. Ans. (C) | 11. Ans. (B) | 12. Ans. (A) |
| 13. Ans. (B) | 14. Ans. (B) | 15. Ans. (A) | 16. Ans. (B) |
| 17. Ans. (A) | 18. Ans. (B) | 19. Ans. (D) | 20. Ans. (D) |
| 21. Ans. (C) | 22. Ans. (B) | 23. Ans. (C) | 24. Ans. (A) |
| 25. Ans. (A) | 26. Ans. (B) | 27. Ans. (A) | 28. Ans. (B) |
| 29. Ans. (C) | 30. Ans. (C) |              |              |

**EXERCISE # O-2**

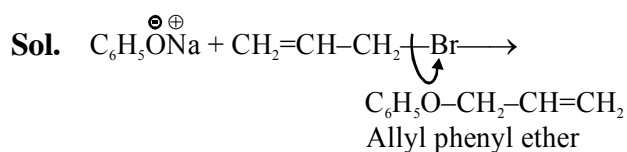
- |                  |              |                  |              |
|------------------|--------------|------------------|--------------|
| 1. Ans. (A)      | 2. Ans. (C)  | 3. Ans. (C)      | 4. Ans. (D)  |
| 5. Ans. (C)      | 6. Ans. (C)  | 7. Ans. (D)      | 8. Ans. (A)  |
| 9. Ans. (B)      | 10. Ans. (C) | 11. Ans. (A)     | 12. Ans. (B) |
| 13. Ans. (B)     | 14. Ans. (D) | 15. Ans. (A,B,D) | 16. Ans. (A) |
| 17. Ans. (B,C,D) | 18. Ans. (C) | 19. Ans. (A)     | 20. Ans. (D) |

**EXERCISE # S-1**

- |                  |                  |                                     |              |
|------------------|------------------|-------------------------------------|--------------|
| 1. Ans. (B)      | 2. Ans. (C)      | 3. Ans. (B)                         | 4. Ans. (B)  |
| 5. Ans. (D)      | 6. Ans. (C)      | 7. Ans. (C)                         | 8. Ans. (B)  |
| 9. Ans. (C)      | 10. Ans. (C)     | 11. Ans. (A,B,C)                    | 12. Ans. (B) |
| 13. Ans. (A,B,C) | 14. Ans. (B,C,D) | 15. Ans. (A)→P; (B)→R; (C)→S; (D)→Q |              |

**EXERCISE # J-MAIN**

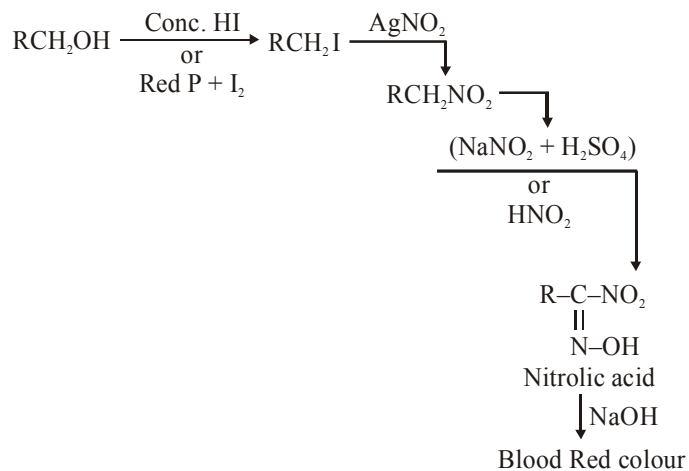
- |             |             |             |             |
|-------------|-------------|-------------|-------------|
| 1. Ans. (3) | 2. Ans. (2) | 3. Ans. (3) | 4. Ans. (3) |
| 5. Ans. (2) |             |             |             |
| 6. Ans. (1) |             |             |             |



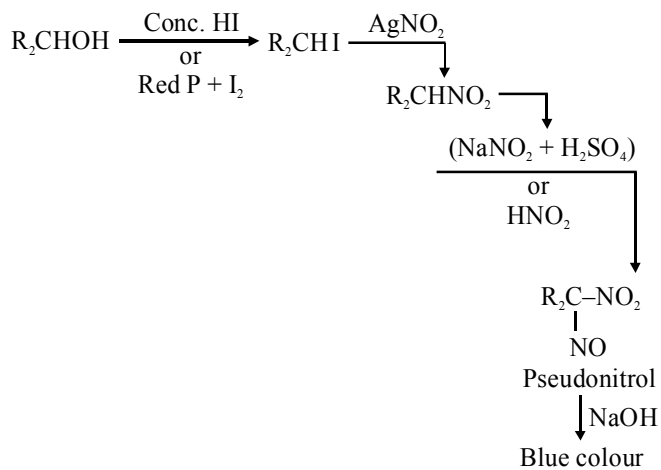
7. Ans. (1)

Sol. Victor Meyer's Test :

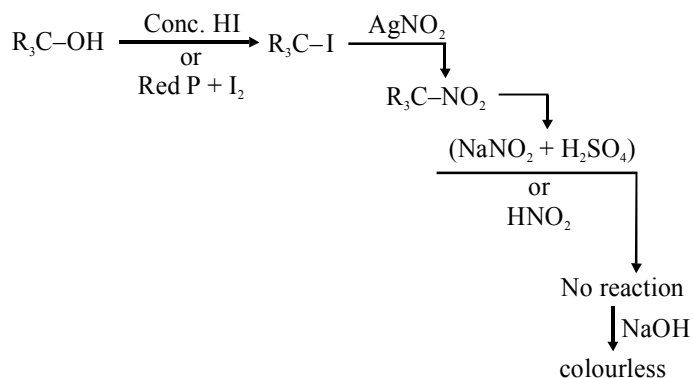
1° Alcohol



2° Alcohol

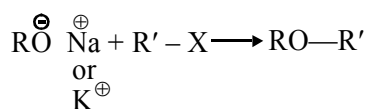


3° Alcohol



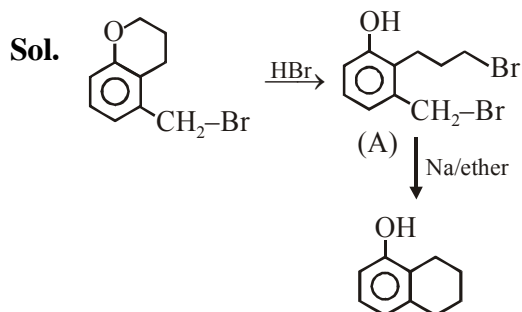
8. Ans.(3)

Sol. Nucleophilic substitution

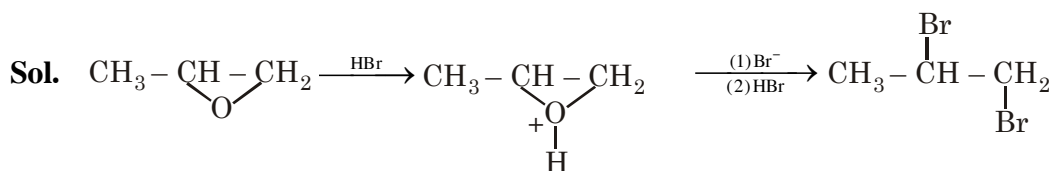




9. Ans. (3)    10. Ans. (1)    11. Ans.(4)    12. Ans. (2)    13. Ans. (2)  
 14. Ans. (4)    15. Ans.(4)    16. Ans. (1)    17. Ans. (2)    18. Ans. (4)  
 19. Ans. (4)

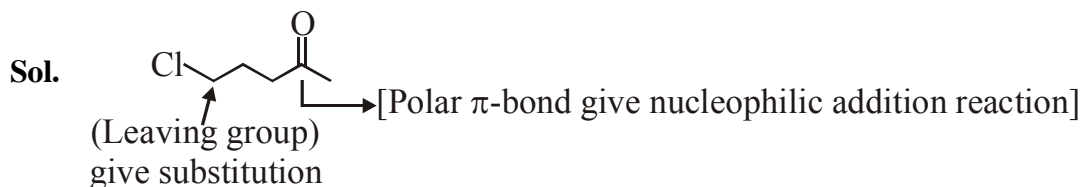


20. Ans.(4)



### EXERCISE # J-ADVANCE

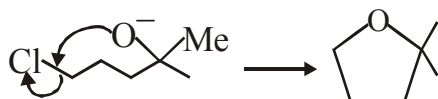
1. Ans. (A)    2. Ans.(B)    3. Ans.(D)    4. Ans. (B)  
 5. Ans. (D)    6. Ans. (B)    7. Ans. (D)  
 8. Ans. (D)



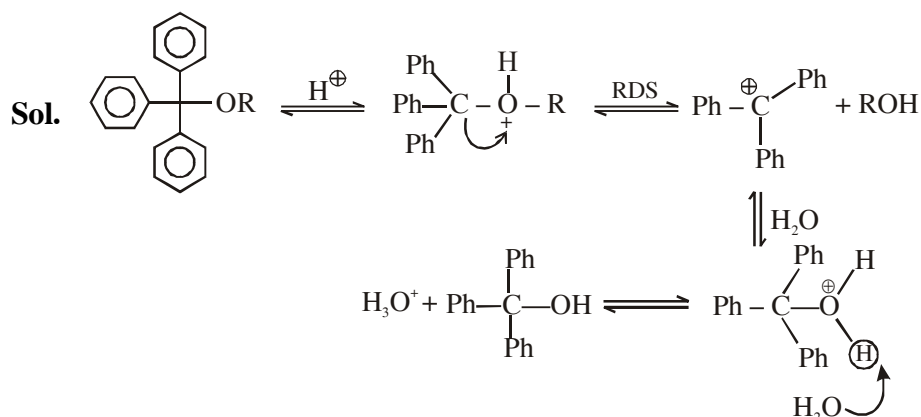
(i) Grignard prefer to give nucleophilic addition on polar  $\pi$ -bond and form anion intermediate.



(ii) In next step anion give intramolecular nucleophilic substitution reaction & form 5 membered ring.



9. Ans. (C)



If 2 Ph groups are substituted by 2 MeO-- groups then carbocation formed in above sequence is more stable and rate of above hydrolysis increases

10. Ans. (A,C,D)

The combination of names for isomeric alcohols with molecular formula  $\text{C}_4\text{H}_{10}\text{O}$  is/are

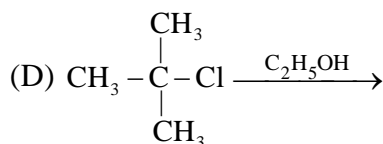
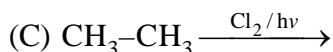
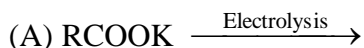
Formula	Names
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	n-butyl alcohol / n-butanol / butan-1-ol
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{OH} \\   \\ \text{CH}_3 \end{array}$	isobutyl alcohol / 2-methyl propan-1-ol
$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\text{OH} \\   \\ \text{CH}_3 \end{array}$	Secondary butyl alcohol / butan-2-ol
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{OH} \\   \\ \text{CH}_3 \end{array}$	Tertiary butyl alcohol / tert butanol / 2-methyl propan-2-ol / 1,1-dimethyl ethan-1-ol

Reference : National Institute of standards and technology (NIST)

CARBOXYLIC ACIDS AND IT'S DERIVATIVE, ALIPHATIC AMINES

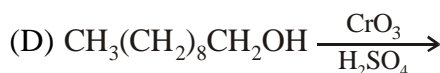
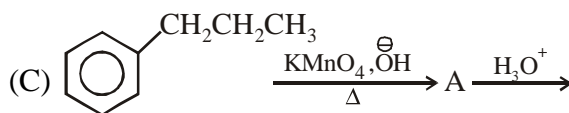
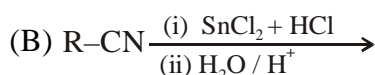
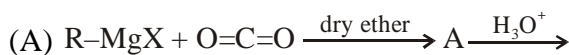
EXERCISE # O-I

1. In which reaction product is hydrocarbon ?



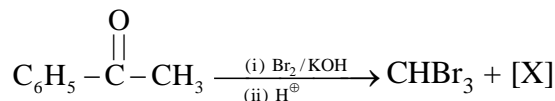
CA0001

2. Which of the following set of reaction can not prepare carboxylic acid as the final product :

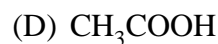
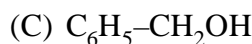
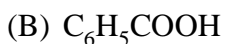
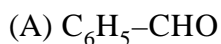


CA0002

3. In the given reaction,

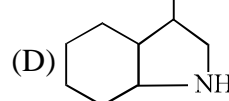
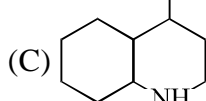
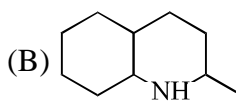
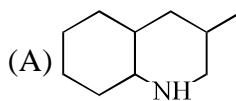
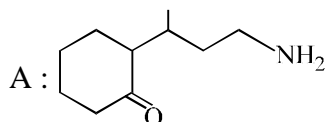


[X] will be :



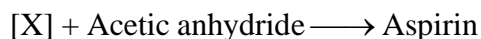
CA0003

4. Reductive amination of A forms:



CA0004

5. In the given reaction :

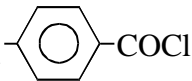
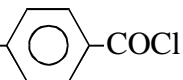
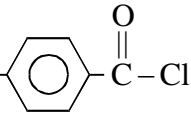


[X] will be :

- (A) Benzoic acid (B) *o*-methoxybenzoic acid  
(C) *o*-Hydroxybenzoic acid (D) *p*-Hydroxybenzoic acid

CA0005

6. Arrange following compounds in decreasing order of reactivity for hydrolysis reaction :

- (I)  $\text{C}_6\text{H}_5\text{COCl}$  (II) 
- (III)  (IV) 
- (A) II > IV > I > III (B) II > IV > III > I  
(C) I > II > III > IV (D) IV > III > II > I

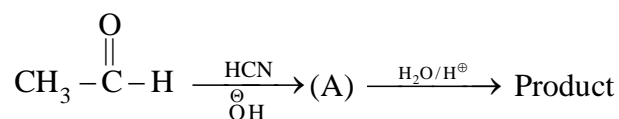
CA0006

7. Which one of the following compounds gives carboxylic acid with  $\text{HNO}_2$ ?

- (A)  $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$  (B)  $\text{C}_6\text{H}_5\text{CONH}_2$   
(C)  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$  (D)  $\text{CH}_3\text{COOC}_2\text{H}_5$

CA0007

8. In the reaction sequence ,

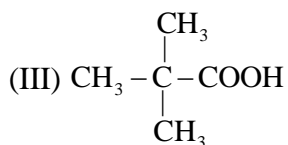
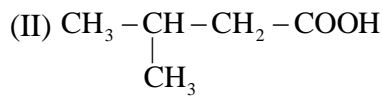
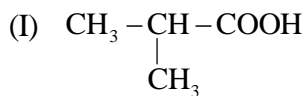


Product will be :

- (A)  $\text{CH}_3-\overset{\text{OH}}{\text{C}}-\text{COOH}$  (B)  $\text{HOOC}-\overset{\text{OH}}{\text{C}}-\text{CH}_3$   
(C) Mixture of  $\text{CH}_3-\overset{\text{OH}}{\text{C}}-\text{COOH}$  and  $\text{HOOC}-\overset{\text{OH}}{\text{C}}-\text{CH}_3$  (D)  $\text{CH}_3-\overset{\text{OH}}{\text{C}}-\text{CONH}_2$

CA0008

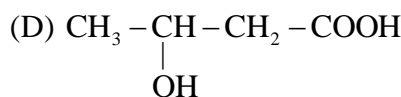
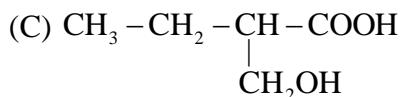
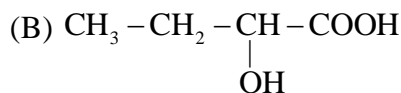
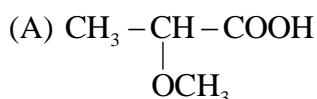
9. Arrange these esters in decreasing order of ease of esterification with  $\text{CH}_3\text{OH}/\text{H}^+$  :



(A) II > I > III > IV      (B) I > II > III > IV      (C) III > IV > II > I      (D) IV > III > II > I

CA0009

10. Which optically active compound on reduction with  $\text{LiAlH}_4$  will give optically inactive compound?



CA0010

11. Which will form lactone on treatment with  $\text{NaOH}$  ?

(A)  $\alpha$ -Bromo acid

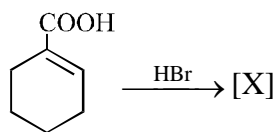
(B)  $\beta$ -Bromo acid

(C)  $\beta$ -Hydroxy acid

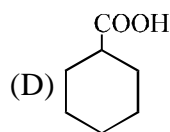
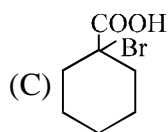
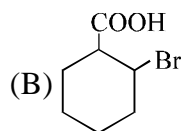
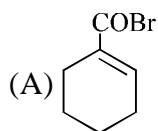
(D)  $\delta$ -Bromo acid

CA0011

12. In the given reaction:

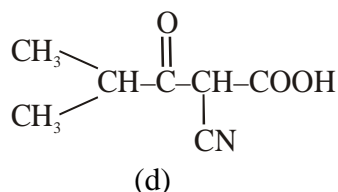
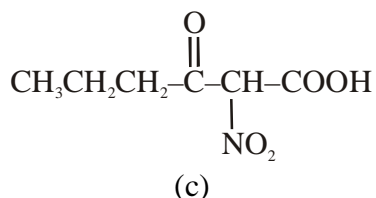
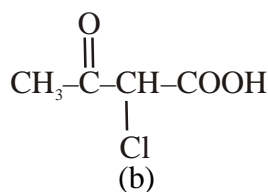
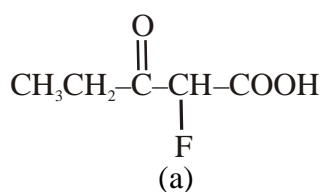


[X] will be :



CA0012

13. Correct order of decarboxylation



(A)  $a > b > c > d$

(B)  $c > d > b > a$

(C)  $c > d > a > b$

(D)  $d > c > a > b$

CA0013

14. N-Ethyl phthalimide on hydrolysis gives:

(A) Methyl alcohol

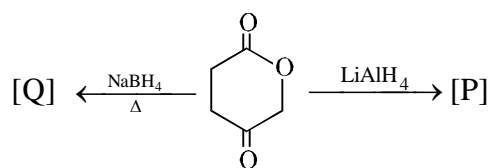
(B) Ethyl amine

(C) Dimethyl amine

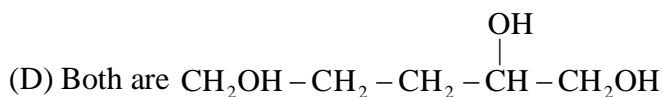
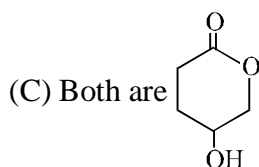
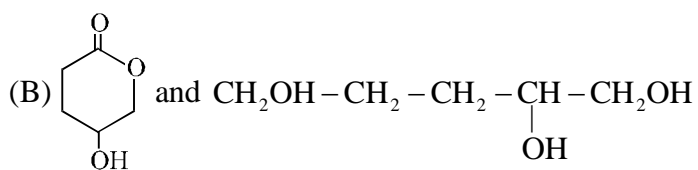
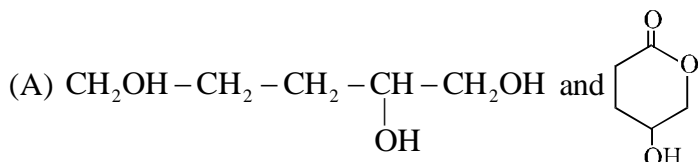
(D) Diethyl amine

CA0014

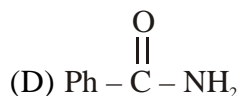
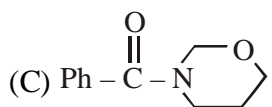
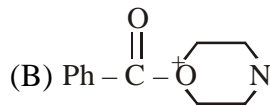
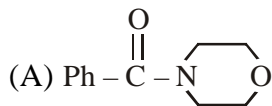
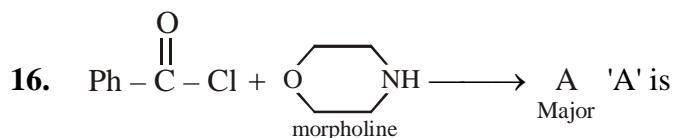
15. In the given reaction:



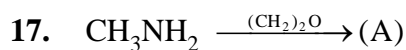
[P] and [Q] respectively be :



CA0015



CA0016



(A) 'A' is more basic than  $\text{CH}_3\text{NH}_2$

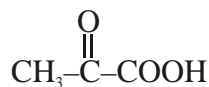
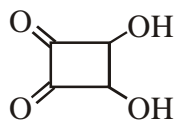
(B) 'A' is less basic than  $\text{CH}_3\text{NH}_2$

(C) 'A' is Ter-amine

(D) None

CA0017

18. Which of the following can released  $\text{CO}_2$  with  $\text{NaHCO}_3$ .



(i)

(ii)

(iii)

(A) (i), (ii) & (iii)

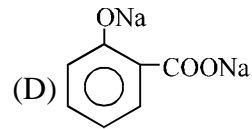
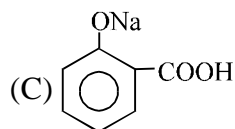
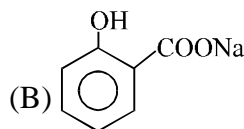
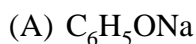
(B) (i) & (ii)

(C) (ii) & (iii)

(D) (i) & (ii)

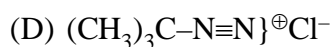
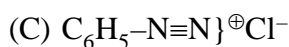
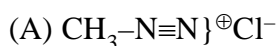
CA0018

19. Sodium bicarbonate reacts with salicylic acid to form :



CA0019

20. Which of the following diazonium salt is relatively stable at  $0-5^\circ\text{C}$ :



CA0020

21. Which is most volatile ?

- (A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  (B)  $(\text{CH}_3)_3\text{N}$  (C)  $\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{NH} \\ \diagup \quad \diagdown \\ \text{CH}_3 \end{array}$  (D)  $\text{CH}_3\text{OH}$

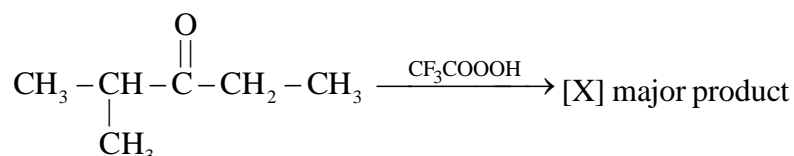
CA0021

22.  $\text{C}_6\text{H}_5\text{CONH}_2 \xrightarrow{\text{Br}_2/\text{OD}^\ominus} \text{P}$ , 'P' is :

- (A)  $\text{C}_6\text{H}_5\text{COND}_2$  (B)  $\text{C}_6\text{H}_5\text{ND}_2$  (C)  $\text{C}_6\text{H}_5\text{NHD}$  (D)  $\text{C}_6\text{H}_5\text{NH}_2$

CA0022

23. In the given reaction:

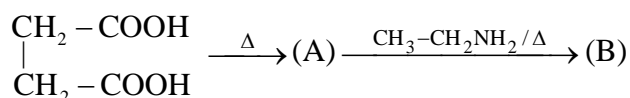


[X] will be:

- (A)  $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{O} - \text{CH} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$  (B)  $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{CH} - \text{C} - \text{O} - \text{CH}_2 - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$
- (C)  $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{OC}(\text{CH}_3)_3 \end{array}$  (D)  $(\text{CH}_3)_3\text{COOCH}_3$

CA0023

24. In the given reaction sequence:

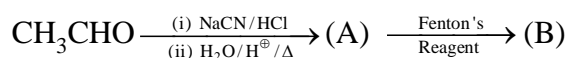


(B) will be:

- (A)  $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2 - \text{C} - \text{NH} - \text{C}_2\text{H}_5 \\ | \\ \text{CH}_2 - \text{C} - \text{NH} - \text{C}_2\text{H}_5 \\ \parallel \\ \text{O} \end{array}$  (B)  $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2 - \text{C} \\ \diagdown \quad \diagup \\ \text{CH}_2 - \text{C} \\ \parallel \\ \text{O} \end{array} \text{N} - \text{C}_2\text{H}_5$
- (C)  $\begin{array}{c} \text{CH}_2 - \text{COOH} \\ | \\ \text{CH}_2 - \text{COOH} \end{array}$  (D)  $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2 - \text{C} - \text{NH} - \text{C}_2\text{H}_5 \\ | \\ \text{CH}_2 - \text{COOH} \end{array}$

CA0024

25. In the given reaction :



(B) will be :

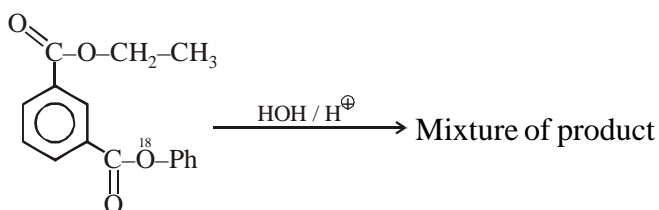
- (A) Acetic acid (B) Oxalic acid (C) Pyruvic acid (D) Citric acid

CA0025



## EXERCISE # O-II

1. Which of the following is/are present in mixture of product :



- (A)  $\text{CH}_3\text{-CH}_2\text{-OH}$       (B)      (C)  $\text{Ph-}^{18}\text{OH}$       (D)

CA0026

2. Mixture of 1°, 2° and 3° amines can be separated by:

- (A) Hinsberg's method      (B) Hofmann's isocyanide test  
(C) Fractional distillation      (D)  $\text{NaNO}_2$  HCl

CA0027

3.  $\text{RCOOR}'$  can be prepared by:

- (A) Esterification of  $\text{RCOOH}$   
(B) Reaction of  $\text{CH}_3\text{CH}=\text{CH}_2$  with methanol  
(C) Baeyer-Villiger oxidation of  $\text{RCOR}'$  with peroxy acid  
(D) reaction of  $\text{RCOCl}$  with  $\text{R}'\text{OH}$

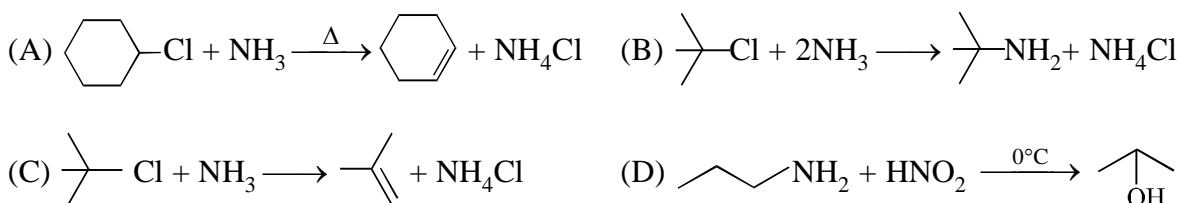
CA0028

4. Which of the following amine reacts with Hinsberg reagent to give base soluble product :-

- (A) Neopentyl amine      (B) sec propyl amine      (C) diethyl amine      (D) ethyl methyl amine

CA0029

5. Which is/are correct reaction(s):



CA0030

6. Which of the following will form acetyl chloride with  $\text{PCl}_5$ ?

- (A)  $\text{MeCOOH}$       (B)  $\text{MeCOOMe}$       (C)  $\text{MeCOOCOMe}$       (D)  $\text{Me-CONH}_2$

CA0031

7. Sodium salt of which compound on electrolysis does not give hydrocarbon:

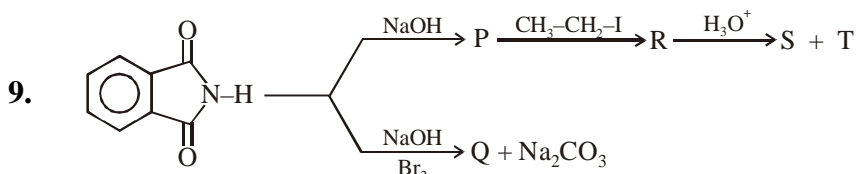
- (A)  $\text{C}_6\text{H}_5\text{COOH}$       (B)  $\text{HCOOH}$       (C)  $\text{Me}_3\text{C-COOH}$       (D)  $\text{COOH-CH=CH-COOH}$

CA0032

8. Among the following, which statement is not correct ?

- (A)  $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$  will not respond to haloform test  
 (B) Schiff's reagent and Schiff's base are different compounds  
 (C) Fehling's solution is a good reagent to detect aromatic aldehydes  
 (D) Both aldehyde and ketone can react with 2,4-dinitrophenylhydrazine reagent

CA0033



If T can evolve effervescence of  $\text{CO}_2$  with a  $\text{NaHCO}_3$ , then correct statement(s) is/are :

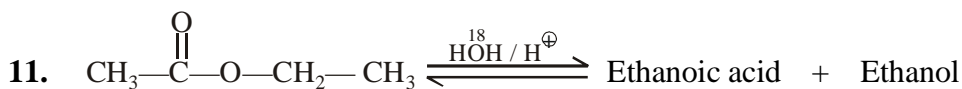
- (A) S & Q can be distinguished by dye azo test  
 (B) T is most acidic among all isomeric benzenoid dicarboxylic acid  
 (C) Q & S can be distinguished by mustered oil test  
 (D) P, Q & T all are soluble in a  $\text{NaHCO}_3$

CA0034

10. Acetic anhydride and ammonia gives the product:

- (A)  $\text{CH}_3\text{CONH}_2$  (B)  $\text{CH}_3\text{CONHCH}_3$  (C)  $\text{CH}_3\text{CN}$  (D)  $\text{CH}_3\text{COONH}_4$

CA0035

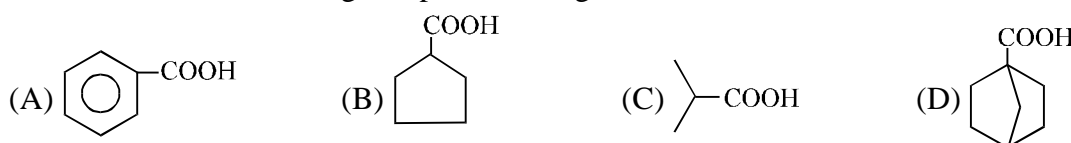


Isotopic oxygen of water will be present with

- (A) Ethanoic acid  
 (B) Ethanol  
 (C) After some time it will also be present in some molecules of ester  
 (D) None of these

CA0036

12. Which one of the following compounds will give HVZ reaction?



CA0037

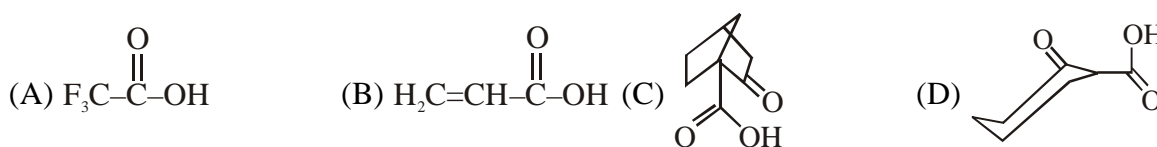
13.  $\text{RCH}_2\text{CONH}_2 + \text{NaOBr} \longrightarrow ?$

Rate of reaction will be faster if 'R' is

- (A)  $\text{CH}_3-$  (B)  $\text{C}_2\text{H}_5-$  (C)  $\text{NO}_2-$  (D)  $\text{CN}-$

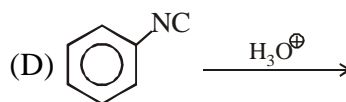
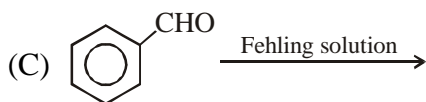
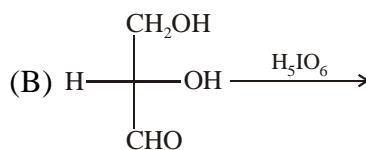
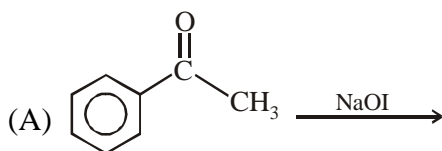
CA0038

14. Which of the following carboxylic acids do not undergo decarboxylation simply on heating ?

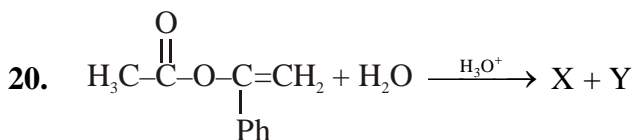


CA0039

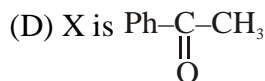
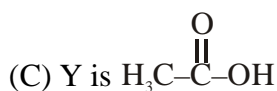
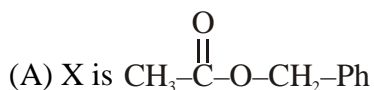
15. Which of the following compounds will give acetic acid with  $\text{KMnO}_4/\text{H}^{\oplus}/\Delta$  :  
 (A)  $\text{CH}_3\text{-CHO}$  (B)  $\text{CH}_3\text{-CH=CH-CH}_3$   
 (C)  $\text{CH}_3\text{-C}\equiv\text{C-CH}_3$  (D)  $\text{CH}_3\text{CH}_2\text{OH}$  CA0040
16. Hofmann degradation is given by:  
 (A) Succinimide (B) Acid chloride (C) Acid anhydride (D) Acetamide CA0041
17. The presence of primary amine can be confirmed by its reaction with :  
 (A)  $\text{HNO}_2$  (B)  $\text{CHCl}_3 + \text{NaOH}$  (C)  $\text{CS}_2 \& \text{HgCl}_2$  (D)  $\text{H}_2\text{SO}_4$  CA0042
18. Total number of compounds which are soluble in hot a NaOH are :  
 (i) Salicylic acid (ii) Aspirine (iii) Carbolic acid (iv) Acetic acid  
 (v) Succinic anhydride (vi) Cyclohexanone (vii) Benzene sulphonamide (viii) Cyclohexene  
 (A) 5 (B) 6 (C) 7 (D) 8 CA0043
19. Number of oxidation reactions in which organic reactant gets oxidised & one of the major product is carboxylic acid/salt :



CA0044

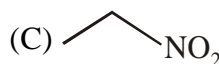
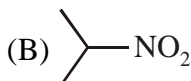
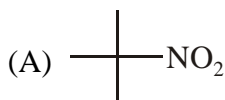


X and Y are :



CA0045

21. Which of the following compound react with  $\text{HNO}_2$  :



CA0046

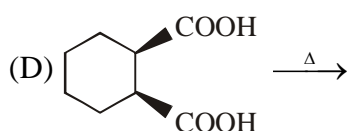
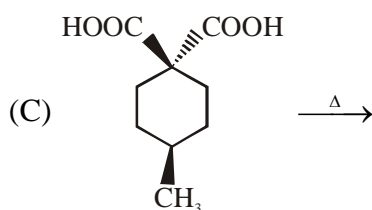
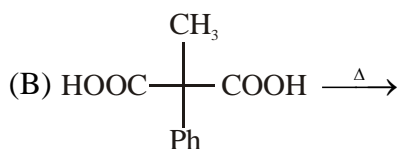
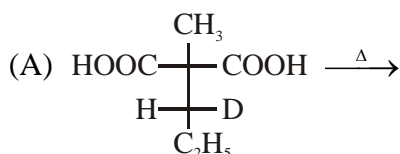
## EXERCISE # S-I

## Matching Type Questions

1. Match the following question :

## Column - I

## (Reaction)



## Column-II

## (Products)

(P) Diastereomers

(Q) Racemic mixture

(R) Meso comp.

(S) CO<sub>2</sub> gas will evolve

CA0047

2. Match the following question :

## Column I

(Organic compounds oxidised by HIO<sub>4</sub>)(A) CH<sub>3</sub>COCHO

(B) 1,2-cyclohexane dione

(C) PhCH(OH)CHO

(D) CH<sub>3</sub>CH<sub>2</sub>CH(OH)COCH<sub>3</sub>

## Column II

(Products of HIO<sub>4</sub> oxidation)

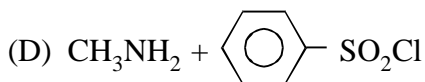
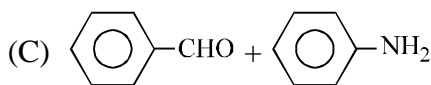
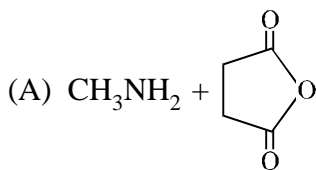
(P) PhCH=O + HCOOH

(Q) CH<sub>3</sub>CH<sub>2</sub>CHO + HOOCCH<sub>3</sub>(R) HOOC(CH<sub>2</sub>)<sub>4</sub>COOH(S) CH<sub>3</sub>COOH + HCOOH

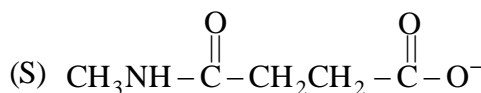
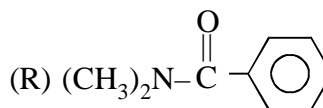
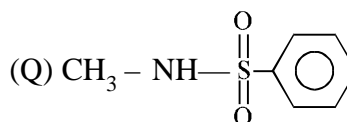
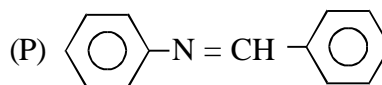
CA0048

3. Match the following question :

**Column I (Reactions)**



**Column II (Products)**

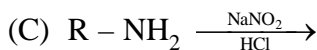
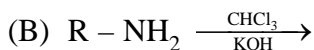


CA0049

4. Match the following question :

**Column I**

(Correct about product)



**Column II**

(P) Product is yellow oily liquid

(Q) Gives red colour with CAN

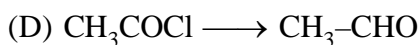
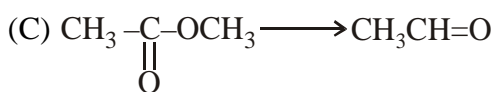
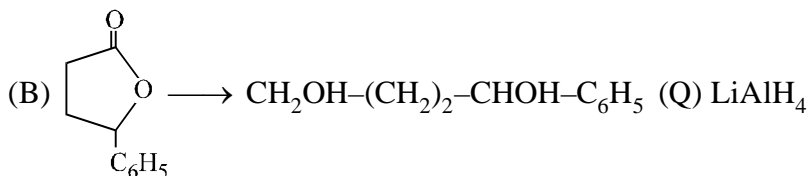
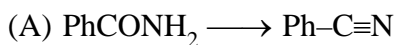
(R) Gives fruity smell with  $\text{CH}_3\text{OH}$

(S) Foul smelling compound is formed.

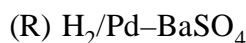
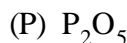
CA0050

5. Match the following question :

**Column I**



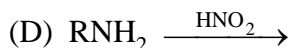
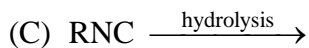
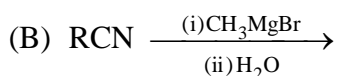
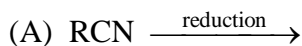
**Column II**



CA0051

6. Match the following question :

**Column I**



**Column II**

(P) 1° Amine

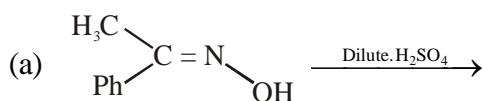
(Q) Alcohol

(R) Ketone

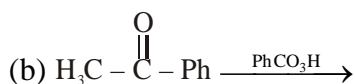
(S) Acid

CA0052

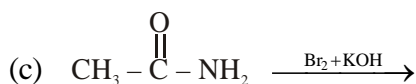
7. Find out number of reactions which involve electron deficient nitrogen [Nitrene character] during reaction mechanism.



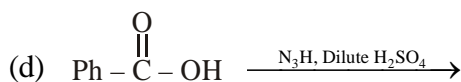
CA0053



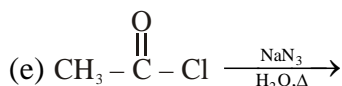
CA0054



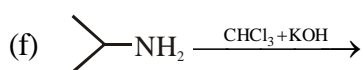
CA0055



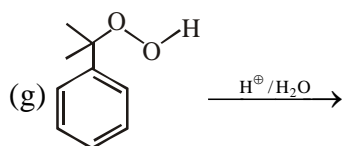
CA0056



CA0057

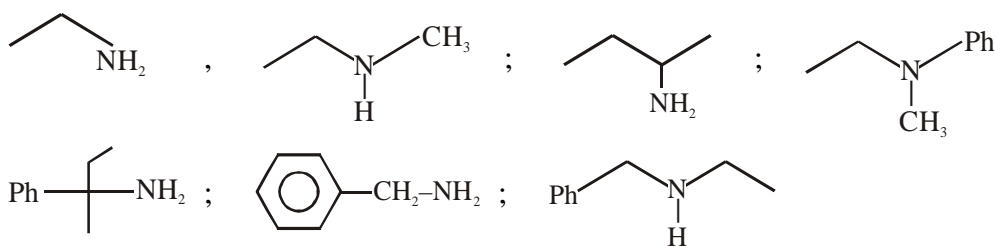


CA0058



CA0059

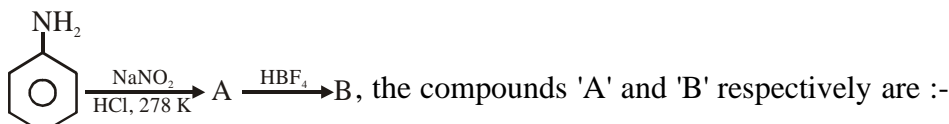
8. Of the following amines how many can be separated by Hoffmann's mustard oil reaction.



CA0060

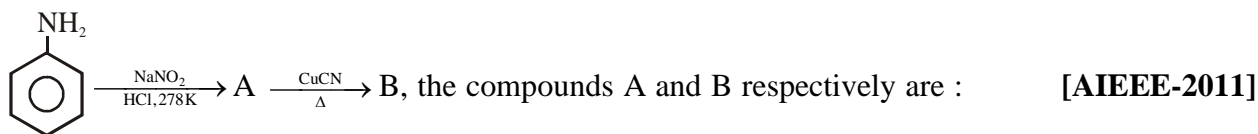


## EXERCISE # JEE-MAIN

1. Reaction - [AIEEE-2002]  
 Primary amine +  $\text{CHCl}_3 + \text{KOH} \rightarrow$  product, here product will be -  
 (1) Cyanide (2) Isocyanide (3) Amine (4) Alcohol  
**CA0066**
2. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is- [AIEEE-2004]  
 (1)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (2)  $\text{Na}_3[\text{Fe}(\text{CN})_6]$  (3)  $\text{Fe}(\text{CN})_3$  (4)  $\text{Na}_4[\text{Fe}(\text{CN})_5]\text{NOS}$   
**CA0067**
3. Which one of the following methods is neither meant for the synthesis nor for separation of amines- [AIEEE-2005]  
 (1) Hofmann method (2) Hinsberg method  
 (3) Curtius reaction (4) Wurtz reaction  
**CA0068**
4. In the chemical reaction,  $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow (\text{A}) + (\text{B}) + 3\text{H}_2\text{O}$ , the compounds (A) and (B) are respectively - [AIEEE-2007]  
 (1)  $\text{C}_2\text{H}_5\text{CN}$  and  $3\text{KCl}$  (2)  $\text{CH}_3\text{CH}_2\text{CONH}_2$  and  $3\text{KCl}$   
 (3)  $\text{C}_2\text{H}_5\text{NC}$  and  $\text{K}_2\text{CO}_3$  (4)  $\text{C}_2\text{H}_5\text{NC}$  and  $3\text{KCl}$   
**CA0069**
5. In the chemical reactions, [AIEEE-2010]  
  
 (1) Nitrobenzene and chlorobenzene  
 (2) Nitrobenzene and fluorobenzene  
 (3) Phenol and benzene  
 (4) Benzene diazonium chloride and fluorobenzene  
**CA0070**



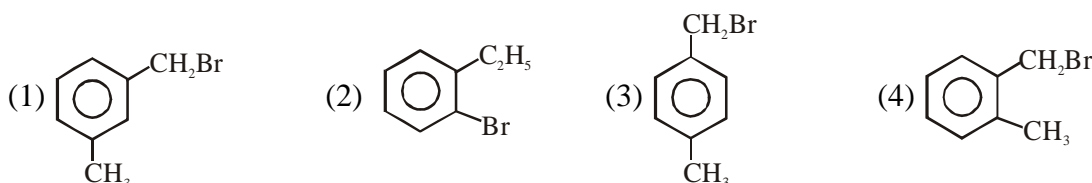
6. In the chemical reactions



- (1) Fluorobenzene and phenol (2) Benzene diazonium chloride and benzonitrile  
 (3) Nitrobenzene and chlorobenzene (4) Phenol and bromobenzene

CA0071

7. Compound (A),  $\text{C}_8\text{H}_9\text{Br}$ , gives a white precipitate when warmed with alcoholic  $\text{AgNO}_3$ . Oxidation of (A) gives an acid (B),  $\text{C}_8\text{H}_6\text{O}_4$ . (B) easily forms anhydride on heating. Identify the compound (A): [AIIEEE-2013]



CA0072

8. An organic compound A upon reacting with  $\text{NH}_3$  gives B. On heating, B gives C. C in presence of KOH reacts with  $\text{Br}_2$  to give  $\text{CH}_3\text{CH}_2\text{NH}_2$ . A is :- [AIIEEE-2013]

- (1)  $\text{CH}_3\text{COOH}$  (2)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$   
 (3)  $\text{CH}_3\text{-CH(CH}_3\text{)-COOH}$  (4)  $\text{CH}_3\text{CH}_2\text{COOH}$

CA0073

9. On heating an aliphatic primary amine with chloroform & ethenolic potassium hydroside the organic compound formed is [AIIEEE-2014]

- (1) An alkyl cyanide (2) An alkyl isocyanide  
 (3) an alkanol (4) an alkanediol

CA0074

10. In the reaction  $\text{CH}_3\text{COOH} \xrightarrow{\text{LiAlH}_4} \text{A} \xrightarrow{\text{PCl}_5} \text{B} \xrightarrow{\text{alc. KOH}} \text{C}$  'C' is [AIIEEE-2014]

- (1) Ethylene (2) Acetyl chloride (3) Acetaldehyde (4) Acetylene.

CA0075

11. In the presence of a small amount of phosphorous, aliphatic carboxylic acids react with chlorine or bromine to yield a compound in which  $\alpha$  - hydrogen has been replaced by halogen. This reaction is known as :

[JEE(Main)-2015]

- (1) Etard reaction (2) Hell - Volhard - Zelinsky reaction  
(3) Wolff - Kischner reaction (4) Rosenmund reaction

CA0076

12. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br<sub>2</sub> used per mole of amine produced are :

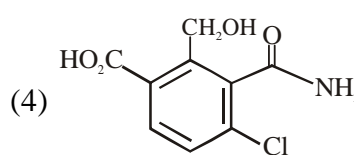
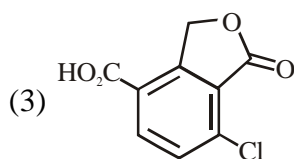
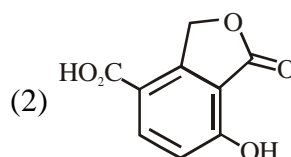
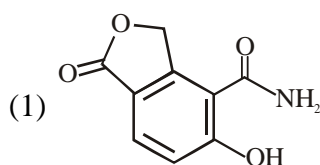
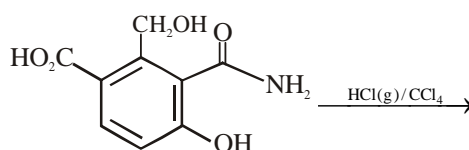
[JEE(Main)-2016]

- (1) Four moles of NaOH and one mole of Br<sub>2</sub>  
(2) One mole of NaOH and one mole of Br<sub>2</sub>  
(3) Four moles of NaOH and two moles of Br<sub>2</sub>  
(4) Two moles of NaOH and two moles of Br<sub>2</sub>

CA0075

13. The major product expected from the following reaction is :

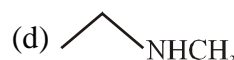
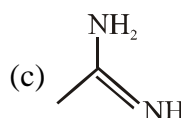
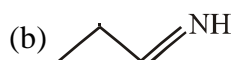
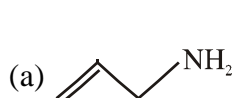
[JEE(Main On-Line)-2017]



CA0078

14. The increasing order of basicity of the following compounds is :

[JEE(Main)-2018]



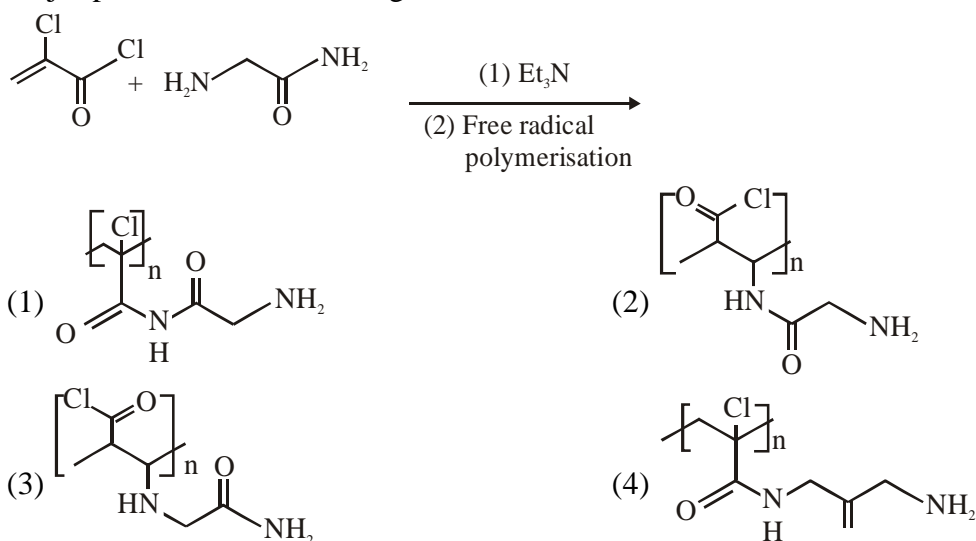
- (1) (b) < (a) < (c) < (d)  
(3) (d) < (b) < (a) < (c)

- (2) (b) < (a) < (d) < (c)  
(4) (a) < (b) < (c) < (d)

CA0079

15. Major product of the following reaction is :

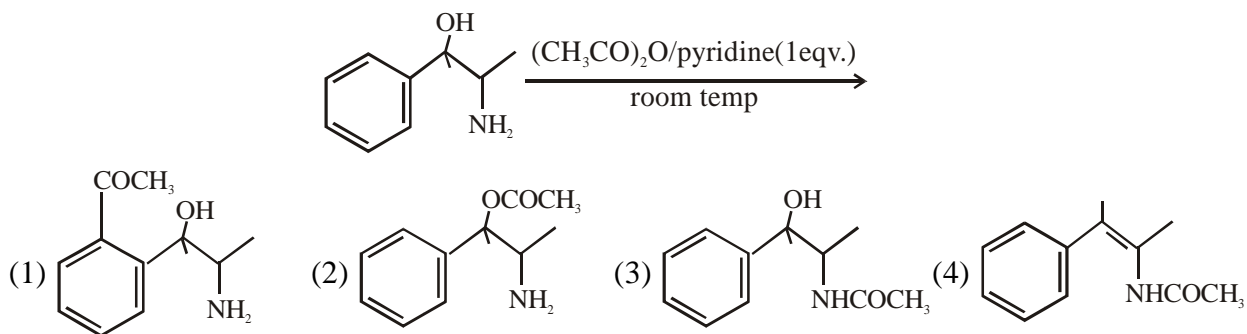
[JEE Main (Jan)-2019]



CA0080

16. The major product obtained in the following reaction is :

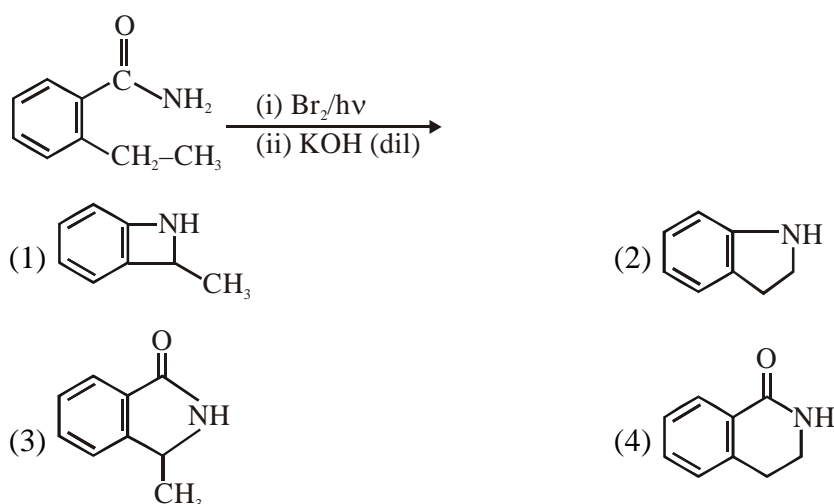
[JEE Main (Jan)-2019]



CA0081

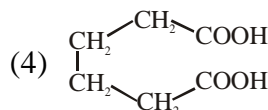
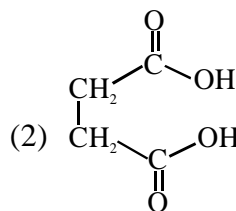
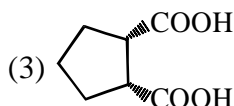
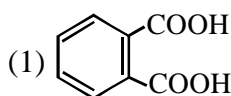
17. The major product of the following reaction is :

[JEE Main (Jan)-2019]



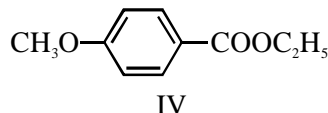
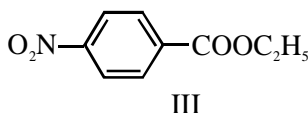
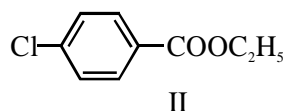
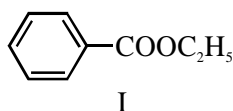
CA0082

18. Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride :  
[JEE Main (Jan)-2019]



CA0083

19. The decreasing order of ease of alkaline hydrolysis for the following esters is :



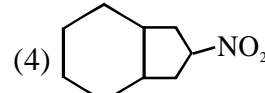
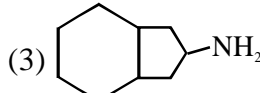
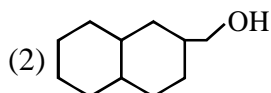
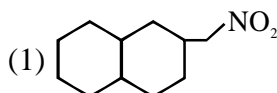
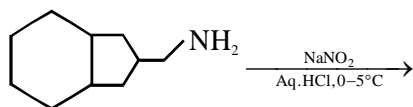
[JEE Main (Jan)-2019]

- (1) IV > II > III > I    (2) III > II > I > IV    (3) III > II > IV > I    (4) II > III > I > IV

CA0084

20. The major product formed in the reaction given below will be :

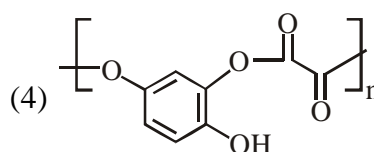
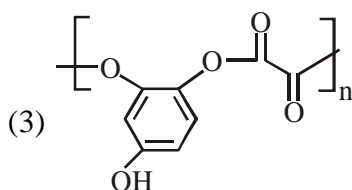
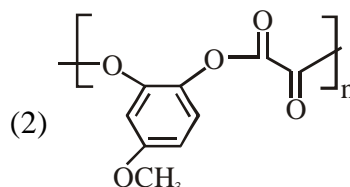
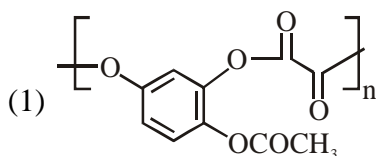
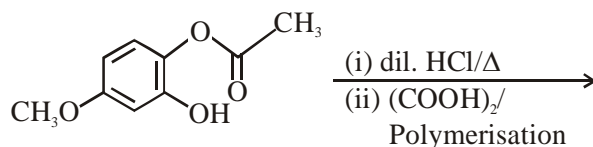
[JEE Main (Jan)-2019]



CA0085

21. The major product of the following reaction is:

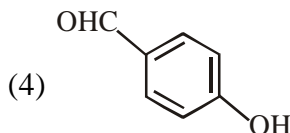
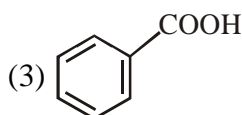
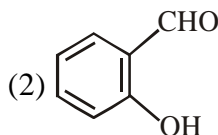
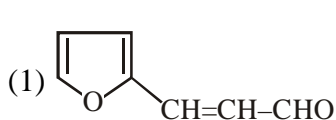
[JEE Main (Jan)-2019]



CA0086

22. An aromatic compound 'A' having molecular formula  $C_7H_6O_2$  on treating with aqueous ammonia and heating forms compound 'B'. The compound 'B' on reaction with molecular bromine and potassium hydroxide provides compound 'C' having molecular formula  $C_6H_7N$ . The structure of 'A' is :

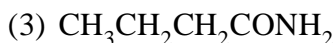
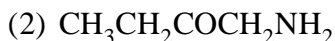
[JEE Main (Jan)-2019]



CA0087

23. A compound 'X' on treatment with  $Br_2/NaOH$ , provided  $C_3H_9N$ , which gives positive carbylamine test. Compound 'X' is :-

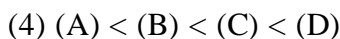
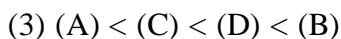
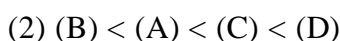
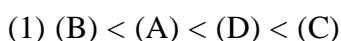
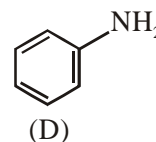
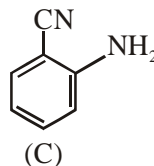
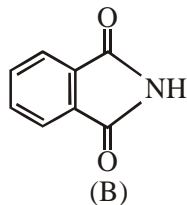
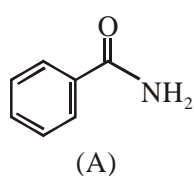
[JEE Main (Jan)-2019]



CA0088

24. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is :

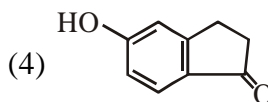
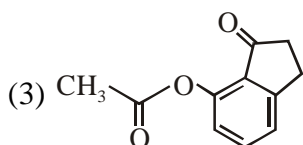
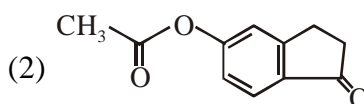
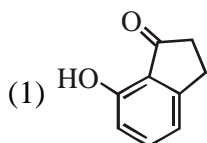
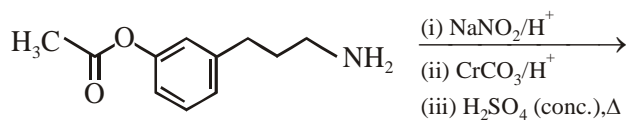
[JEE Main (Jan)-2019]



CA0089

25. The major product of the following reaction is:

[JEE Main (Jan)-2019]



CA0090

26. Which of the following amines can be prepared by Gabriel phthalimide reaction ?

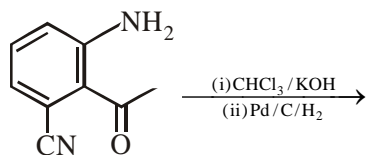
[JEE Main (Apr)-2019]

- (1) Neo-pentylamine (2) n-butylamine (3) triethylamine (4) t-butylamine

CA0091

27. The major product obtained in the following reaction is :

[JEE Main (Apr)-2019]

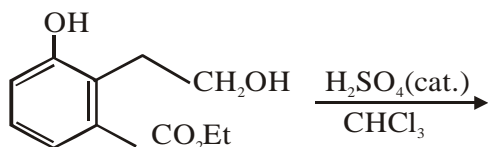


- (1)
- (2)
- (3)
- (4)

CA0092

28. The major product of the following reaction is:

[JEE Main (Apr)-2019]



- (1)
- (2)
- (3)
- (4)

CA0093

29. Hinsberg's reagent is :

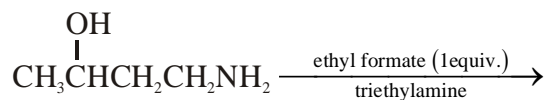
[JEE Main (Apr)-2019]

- (1)  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$  (2)  $\text{C}_6\text{H}_5\text{COCl}$  (3)  $\text{SOCl}_2$  (4)  $(\text{COCl})_2$

CA0094

30. The major product of the following reaction is :

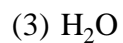
[JEE Main (Apr)-2019]



- (1)
- (2)
- (3)
- (4)

CA0095

31. Ethylamine ( $C_2H_5NH_2$ ) can be obtained from N-ethylphthalimide on treatment with :



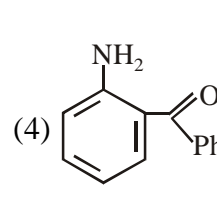
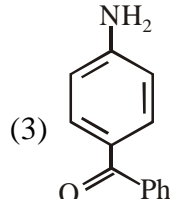
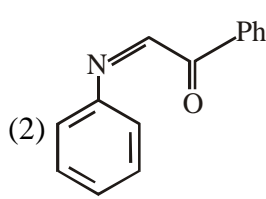
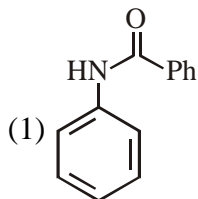
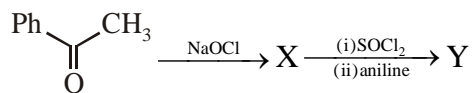
[JEE Main (Apr)-2019]



CA0096

32. The major product 'Y' in the following reaction is:-

[JEE Main (Apr)-2019]

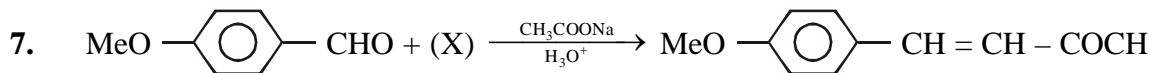


CA0097

## EXERCISE # JEE ADVANCED

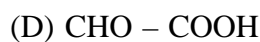
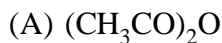
1. Which of the following carboxylic acids undergo decarboxylation easily: [IIT 1995]
- (A)  $C_6H_5CO-CH_2COOH$  (B)  $C_6H_5COCOOH$
- (C)  $C_6H_5\underset{\substack{| \\ OH}}{CH_2}-COOH$  (D)  $C_6H_5\underset{\substack{| \\ NH_2}}{CH_2}-COOH$
- CA0098
2. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to : [IIT 1996]
- (A) Ionization of benzoic acid
- (B) Dimerisation of benzoic acid
- (C) Trimerisation of benzoic acid
- (D) Solvation of benzoic acid
- CA0099
3. When propionic acid is treated with aqueous  $NaHCO_3$ ,  $CO_2$  is liberated. The 'C' of  $CO_2$  comes from. [IIT 1999]
- (A) Methyl group (B) Carboxylic acid group
- (C) methylene group (D) bicarbonate
- CA0100
4. Benzoyl chloride is prepared from benzoic acid by: [IIT 2000]
- (A)  $Cl_2, h\nu$  (B)  $SO_2Cl_2$  (C)  $SOCl_2$  (D)  $Cl_2, H_2O$
- CA0101
5. Which of the following acids has the smallest dissociation constant? [IIT 2002]
- (A)  $CH_3CHFCH_2COOH$  (B)  $FCH_2CH_2COOH$
- (C)  $BrCH_2CH_2COOH$  (D)  $CH_3CHBrCOOH$
- CA0102
6. When benzamide is treated with  $POCl_3$ , the product is: [IIT 2004]
- (A) Benzonitrile (B) Aniline (C) Chlorobenzene (D) Benzylamine
- CA0103





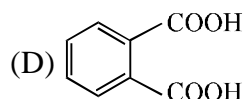
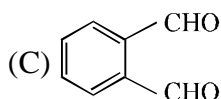
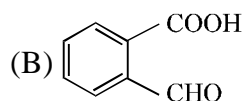
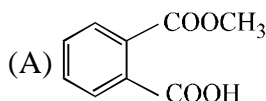
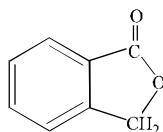
The compound (X) is

[IIT 2005]



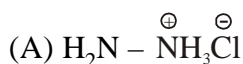
CA104

8. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product? [IIT 2006]

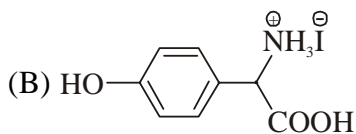


CA105

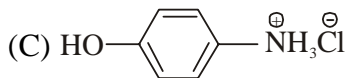
9. Match the compounds in **Column I** with their characteristic test(s)/reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS. **Column-I, Column-II.** [IIT 2008]



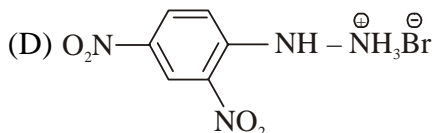
(P) Sodium fusion extract of the compound gives Prussian blue colour with  $\text{FeSO}_4$



(Q) Gives positive  $\text{FeCl}_3$  test



(R) Gives white precipitate with  $\text{AgNO}_3$



(S) Reacts with aldehydes to form the corresponding hydrazone derivative

CA106

10. Match each of the compound in Column I with its characteristic reaction(s) in Column II.

## Column-I

- (A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$   
 (B)  $\text{CH}_3\text{CH}_2\text{OCOCH}_3$   
 (C)  $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2\text{OH}$   
 (D)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

## Column-II

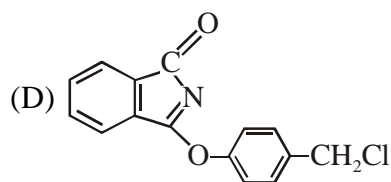
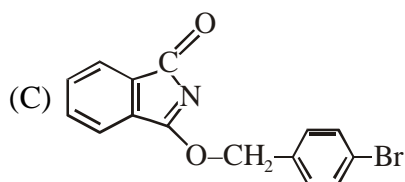
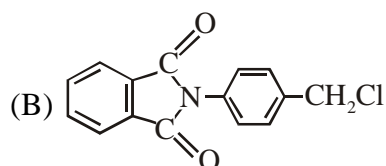
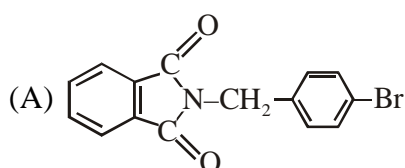
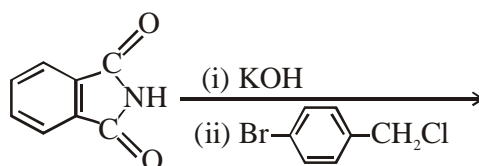
- (P) Reduction with  $\text{Pd-C} / \text{H}_2$   
 (Q) Reduction with  $\text{SnCl}_2 / \text{HCl}$   
 (R) Development of foul smell on treatment with chloroform and alcoholic  $\text{KOH}$   
 (S) Reduction with diisobutylaluminium hydride (DIBAL-H)  
 (T) Alkaline hydrolysis

[IIT 2009]

CA0107

11. The major product of the following reaction is

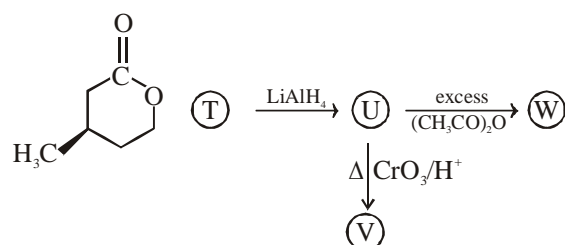
[IIT 2011]



CA0108

12. With reference the scheme given, which of the given statement(s) about T, U, V & W is/are correct

[IIT 2012]



(A) 'T' is soluble in hot aq  $\text{NaOH}$

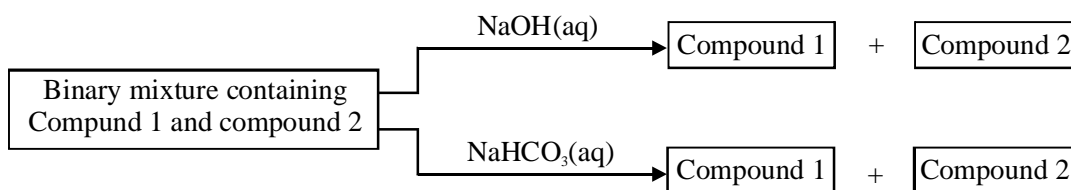
(B) 'U' is optically active

(C) mol formula of W is  $\text{C}_{10}\text{H}_{18}\text{O}_4$

(D) V gives effervescence with aq  $\text{NaHCO}_3$

CA0109

13. Identify the binary mixtures (s) that can be separated into the individual compounds, by differential extraction, as shown in the given scheme - [IIT 2012]

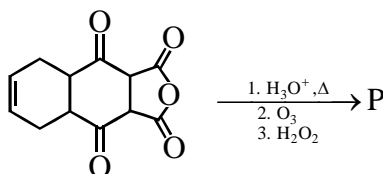


- (A) C<sub>6</sub>H<sub>5</sub>OH and C<sub>6</sub>H<sub>5</sub>COOH                      (B) C<sub>6</sub>H<sub>5</sub>COOH and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH
- (C) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH and C<sub>6</sub>H<sub>5</sub>OH                      (D) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>COOH

CA0110

14. The total number of carboxylic acid groups in the product P is

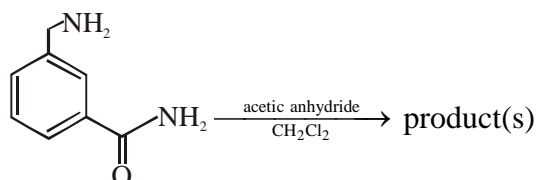
[IIT 2013]



CA0111

15. In the reaction shown below, the major product(s) formed is / are :

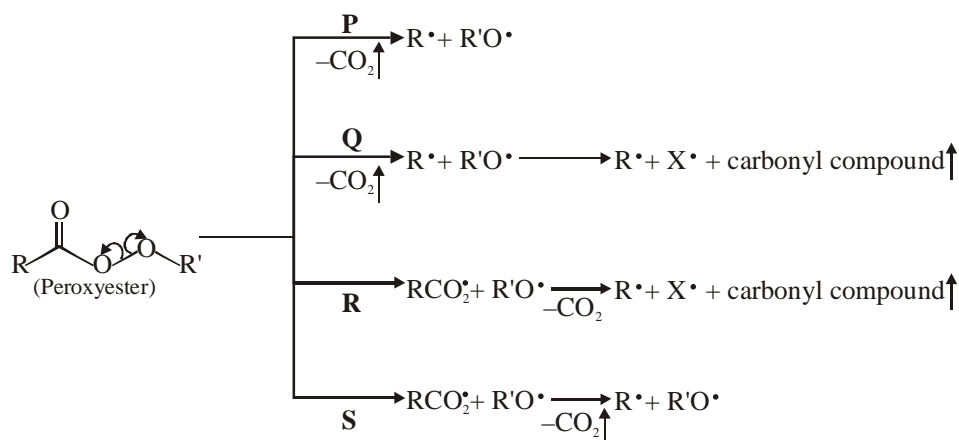
[IIT 2014]



- (A) + CH<sub>3</sub>COOH
- (B) + CH<sub>3</sub>COOH
- (C) + H<sub>2</sub>O
- (D) + CH<sub>3</sub>COOH

CA0112

16. Different possible **thermal** decomposition pathways for peroxyesters are shown below. Match each pathway from List-I with an appropriate structure from List-II and select the correct answer using the code given below the lists. [IIT 2014]



## List-I

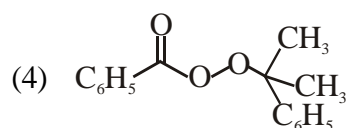
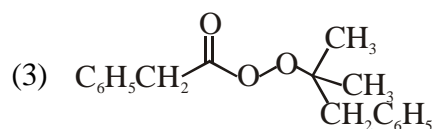
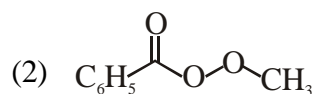
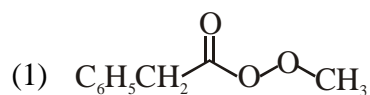
(P) Pathway P

(Q) Pathway Q

(R) Pathway R

(S) Pathway S

## List-II

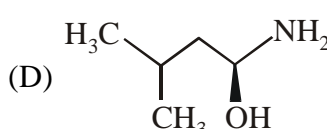
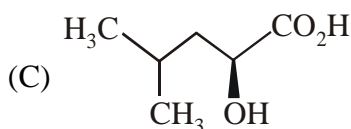
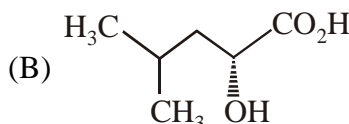
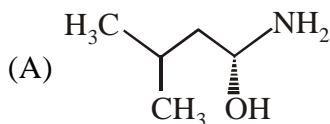
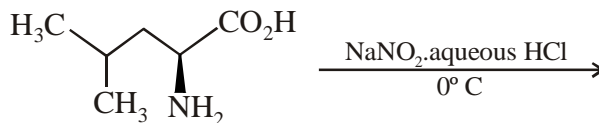


Code :

	P	Q	R	S
(A)	1	3	4	2
(B)	2	4	3	1
(C)	4	1	2	3
(D)	3	2	1	4

17. The major product of the reaction is :

[IIT 2015]

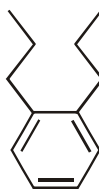


CA0114

PARAGRAPH FOR NO. 18 & 19

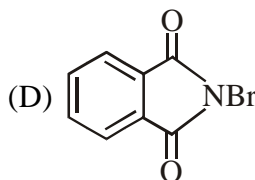
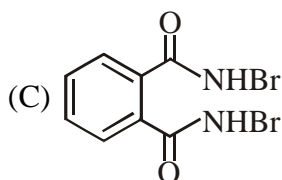
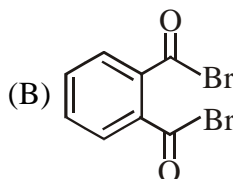
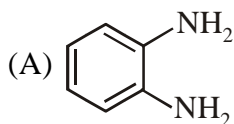
Treatment of compound **O** with  $\text{KMnO}_4 / \text{H}^+$  gave **P**, which on heating with ammonia gave **Q**. The compound **Q** on treatment with  $\text{Br}_2 / \text{NaOH}$  produced **R**. On strong heating, **Q** gave **S**, which on further treatment with ethyl 2-bromopropanoate in the presence of  $\text{KOH}$  following by acidification, gave a compound **T**.

[IIT-JEE-2016]



(O)

18. The compound **R** is :



CA0115

19. The compound **T** is :

(A) Glycine

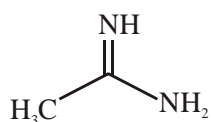
(B) Alanine

(C) Valine

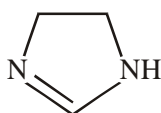
(D) Serine

CA0119

20. The order of basicity among the following compounds is [IIT-JEE(Adv.)-2017]



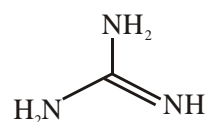
I



II



III



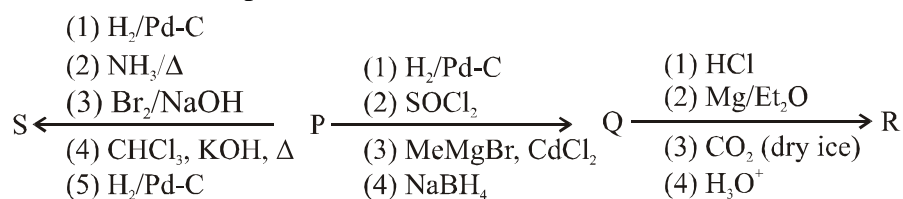
IV

- (A) II > I > IV > III  
 (B) IV > II > III > I  
 (C) I > IV > III > II  
 (D) IV > I > II > III

CA0117

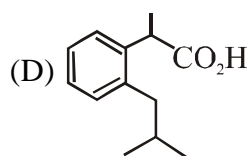
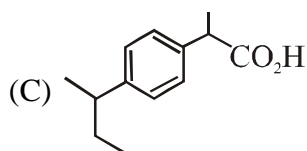
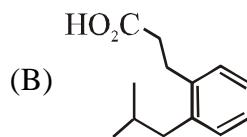
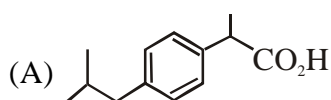
**PARAGRAPH FOR NO. 21 & 22**

An organic acid P ( $C_{11}H_{12}O_2$ ) can easily be oxidized to a dibasic acid which reacts with ethyleneglycol to produce a polymer dacron. Upon ozonolysis, P gives an aliphatic ketone as one of the products. P undergoes the following reaction sequences to furnish R via Q. The compound P also undergoes another set of reactions to produce S. [IIT-JEE(Adv.)-2018]



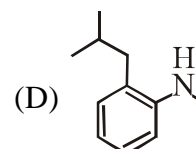
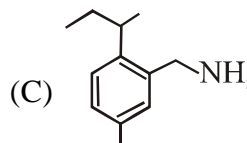
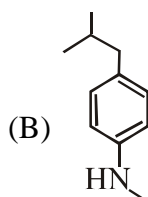
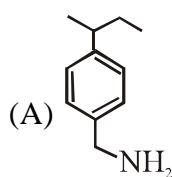
(There are two questions based on PARAGRAPH "A", the question given below is one of them)

21. The compound R is



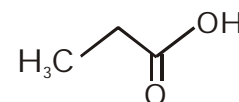
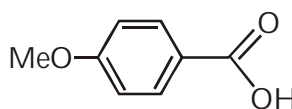
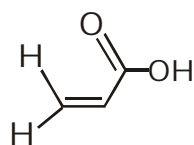
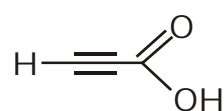
CA0118

22. The compound S is



CA0119

23. The correct order of acid strength of the following carboxylic acids is -



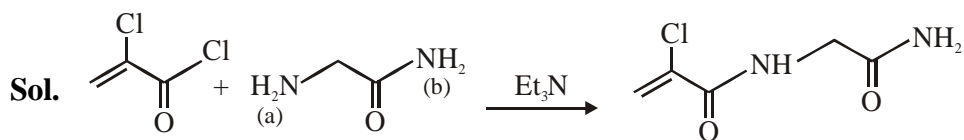
- (A) I > III > II > IV  
 (B) III > II > I > IV  
 (C) II > I > IV > III  
 (D) I > II > III > IV

[IIT-JEE(Adv.)-2019]

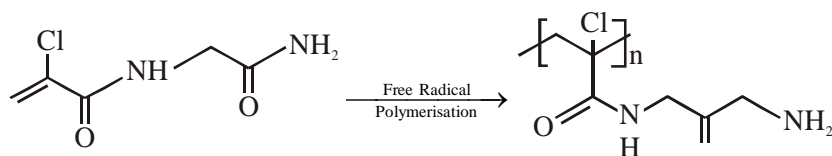
CA0120



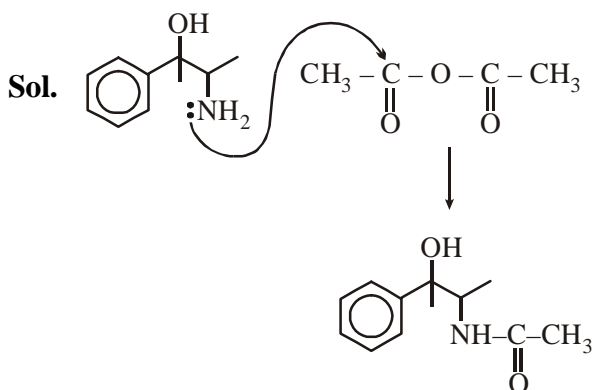
15. Ans. (4)



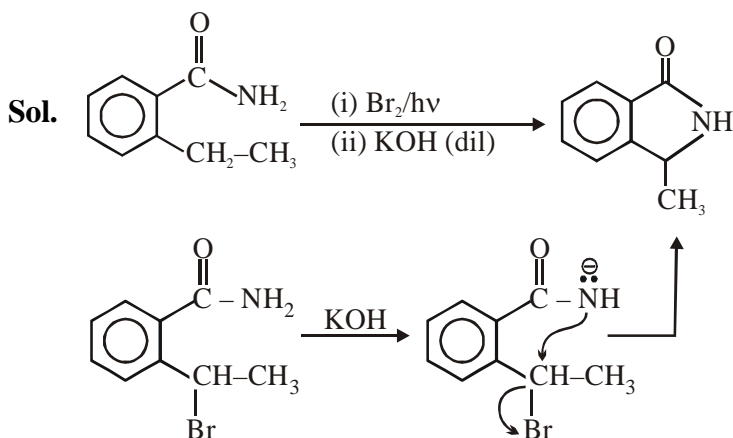
$\text{NH}_2(\text{a})$  will react as nucleophile as (b) is having delocalised lonepair.



16. Ans. (3)



17. Ans. (3)



18. Ans. (4)

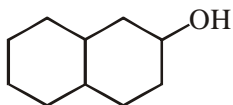
Sol. Adipic acid  $\text{CO}_2\text{H}-(\text{CH}_2)_4-\text{CO}_2\text{H} \xrightarrow[\text{agent}]{\text{dehydrating}}$  7 membered cyclic anhydride (Very unstable)



19. Ans. (2)

Sol. More is the electrophilic character of carbonyl group of ester faster is the alkaline hydrolysis.

20. Ans. (Bonus)

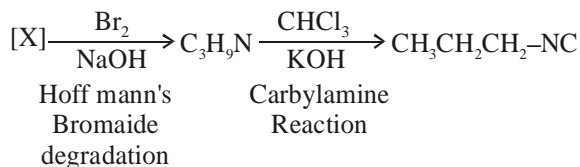
Sol. Answer should be 

21. Ans. (2)

22. Ans. (3)

23. Ans. (3)

Sol.

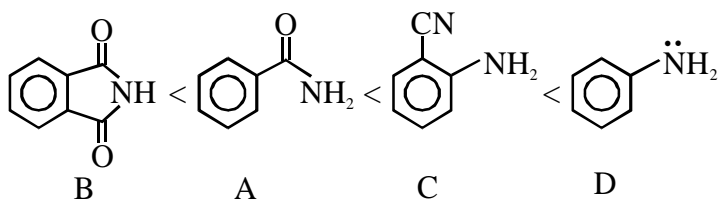


Thus [X] must be aride with oen carbon more than is amine.

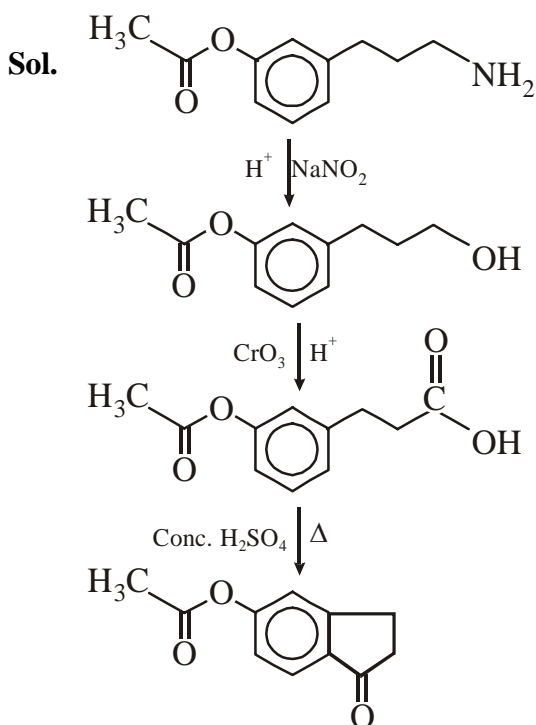
Thus [X] is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$

24. Ans. (2)

Sol. Nucleophilicity order

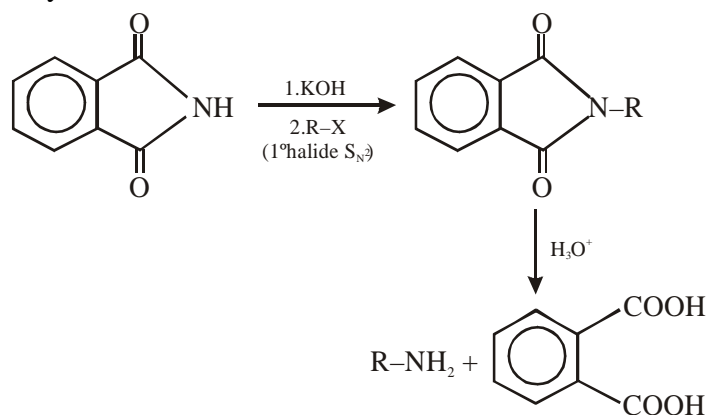


25. Ans. (4)

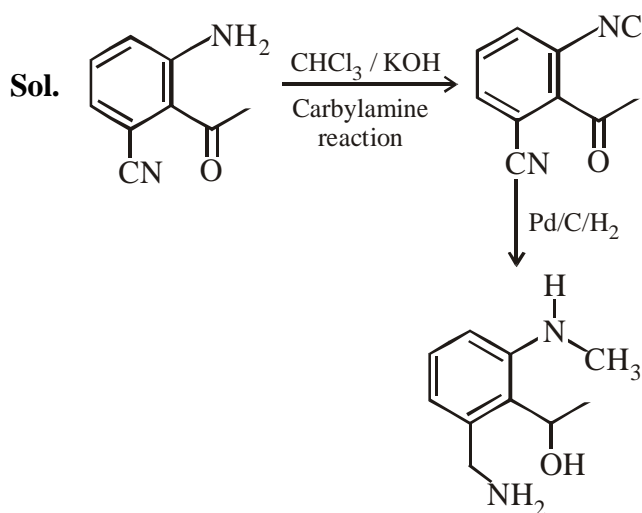


26. Ans. (2)

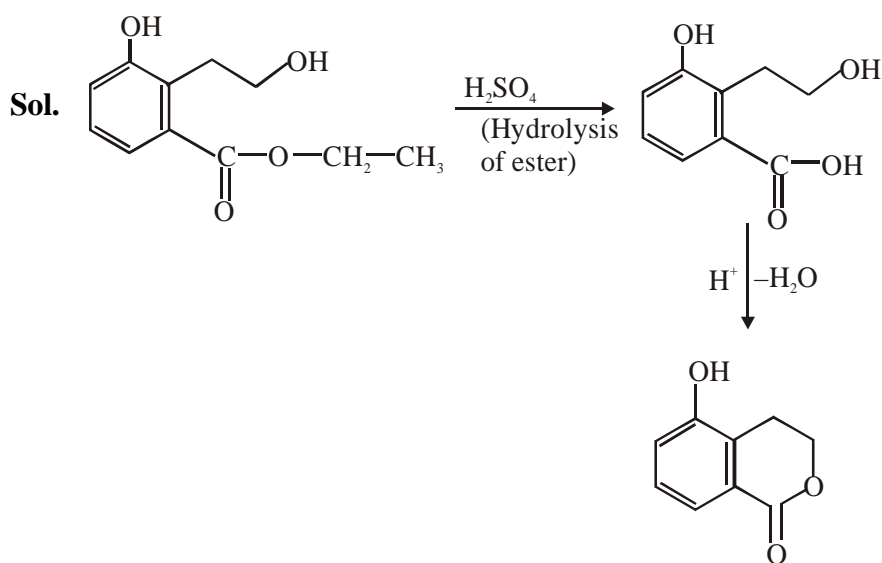
Sol. Gabriel phthalimide synthesis :



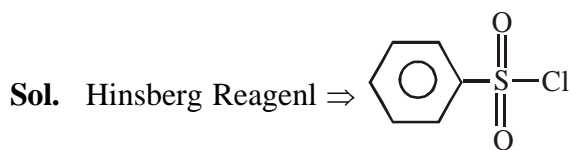
27. Ans. (1)



28. Ans. (3)

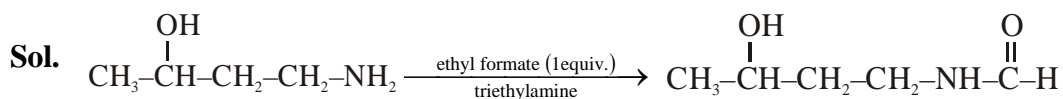


29. Ans.(1)

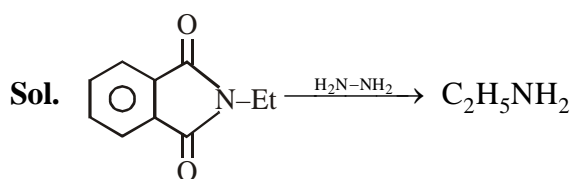
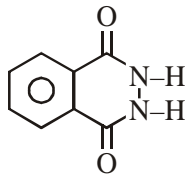


[Benzene Sulphonyl chloride]

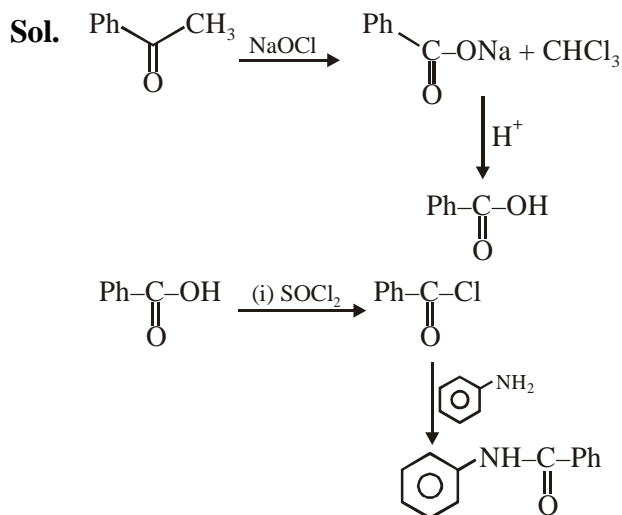
30. Ans. (1)

as  $\text{NH}_2$  is a better nucleophile than  $\text{OH}$ .

31. Ans. (4)

reagent is  $\text{NH}_2-\text{NH}_2$  byproduct will be

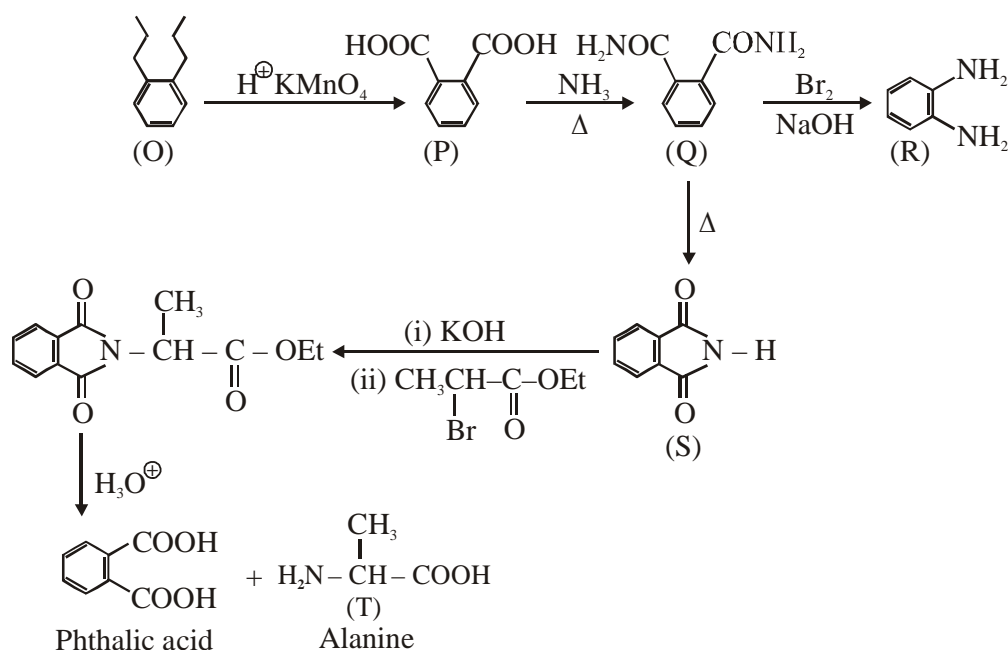
32. Ans. (1)



## EXERCISE # JEE ADVANCED

1. Ans. (A)      2. Ans. (B)      3. Ans. (D)  
 4. Ans. (C)      5. Ans. (C)      6. Ans. (A)      7. Ans. (A)  
 8. Ans. (C)      9. Ans. (A)→R, S ; (B)→P, Q ; (C)→P, Q, R ; (D)→P,S  
 10. Ans. (A)→P, Q, S, T ; (B)→P, S, T ; (C)→P ; (D)→R      11. Ans. (A)  
 12. Ans. (A,C,D)      13. Ans. (B,D)      14. Ans. (2)      15. Ans. (A)  
 16. Ans. (A)      17. Ans. (C)  
 18. Ans. (A)  
 19. Ans. (B)

Solution 18 &amp; 19.



Q to R is Hoffmann's bromamide degradation reaction

S to T is Gabriel's phthalimide synthesis

20. Ans. (D) IV > I > II > III

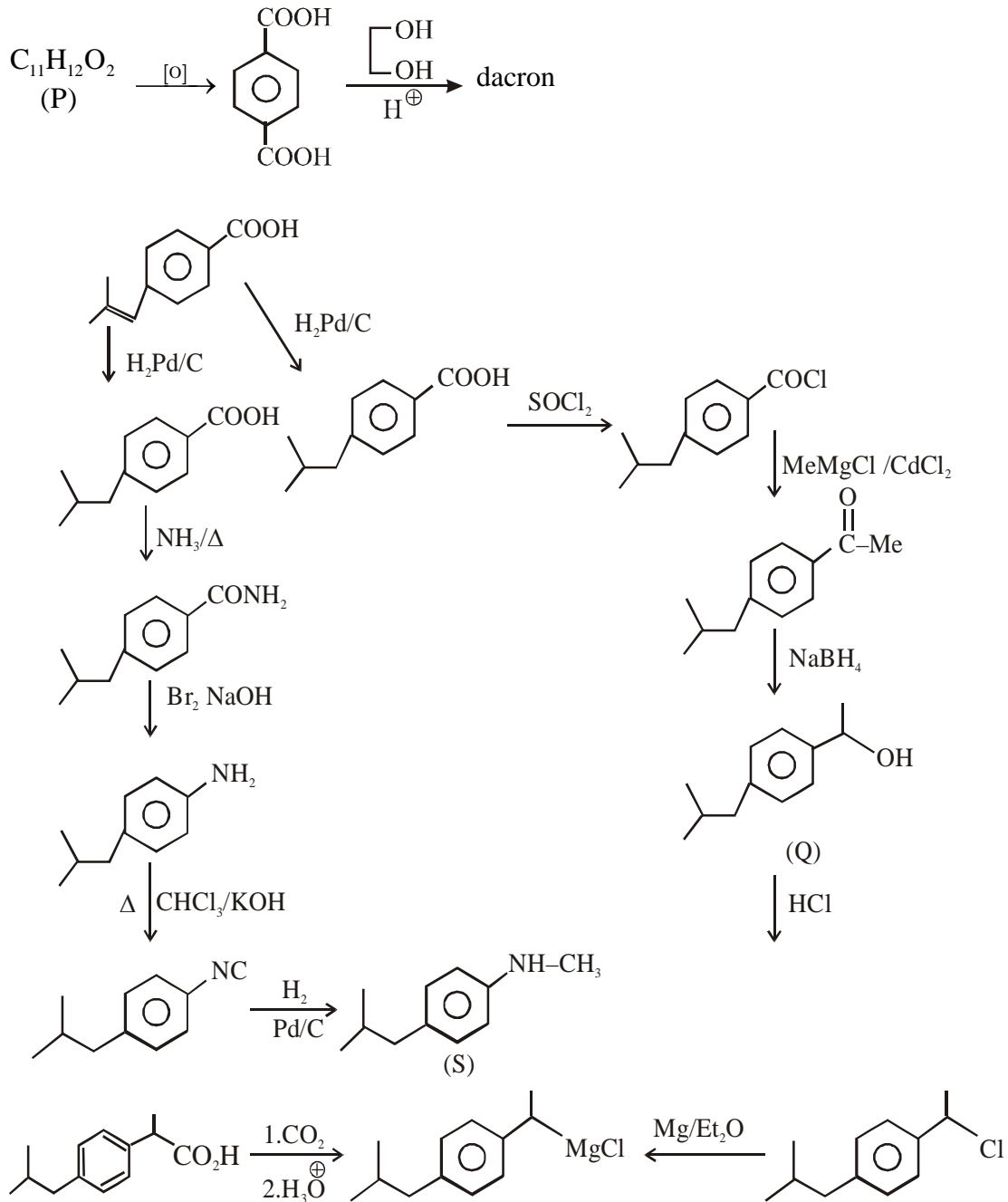
Sol. Basic strength  $\propto$  stability of conjugated acid.

$$\propto +M / +H / +I$$

21. Ans. (A)

22. Ans. (B)

Solution 21 & 22.



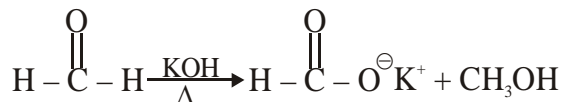
23. Ans. (D)



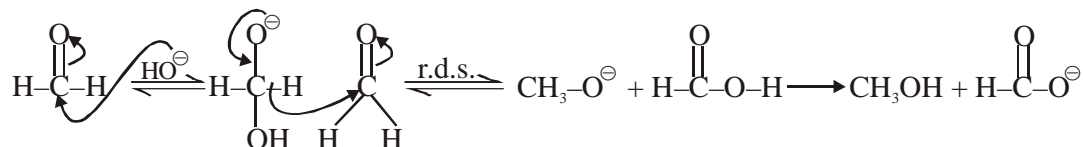
## ALDOL & SIMILAR NAME REACTIONS

### (1) CANNIZARO REACTION

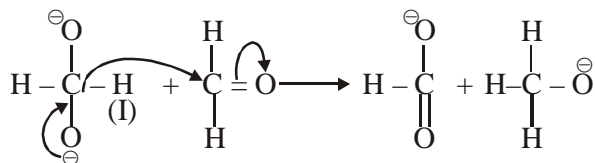
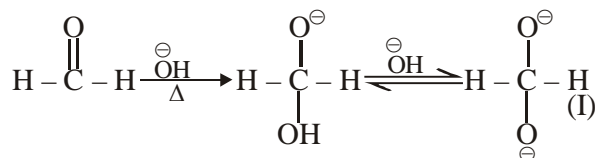
This reaction is given by aldehyde having no  $\alpha$ -hydrogen in the presence of conc.  $\text{NaOH}/\Delta$  or  $\text{KOH}/\Delta$ .



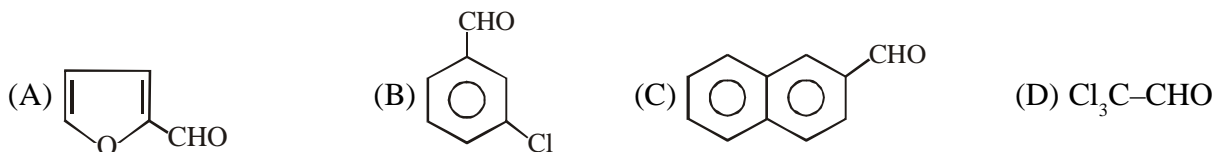
**Mechanism :**



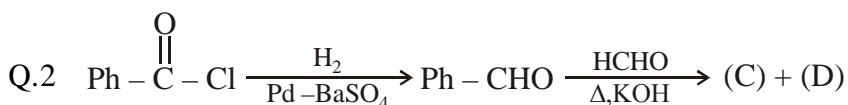
In the presence of a very strong concentration of alkali, aldehyde first forms a doubly charged anion (I) from which a hydride anion is transferred to the second molecule of the aldehyde to form acid and an alkoxide ion. Subsequently, the alkoxide ion acquires a proton from the solvent.



Q.1 Which of following will not undergo Cannizzaro reaction



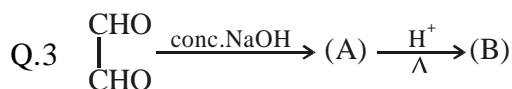
AR0001



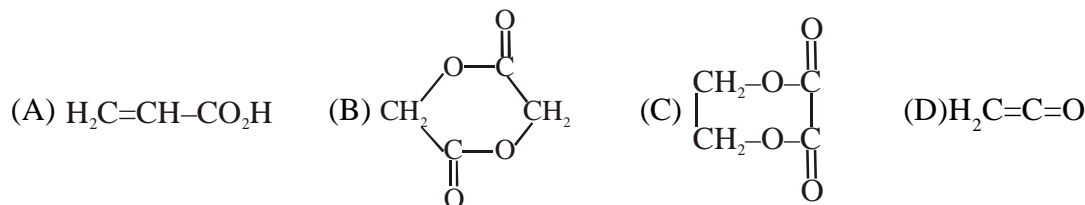
Product (C) & (D) are :

- (A)  $\text{Ph}-\text{CO}_2\text{H}$ ,  $\text{Ph}-\text{OH}$  (B)  $\text{Ph}-\text{CO}_2^-$ ,  $\text{HCO}_2^-$   
 (C)  $\text{Ph}-\text{CH}_2\text{OH}$ ,  $\text{H}-\text{CO}_2^-$  (D)  $\text{Ph}-\text{CO}_2^-$ ,  $\text{CH}_3\text{OH}$

AR0002



Product (B) is :



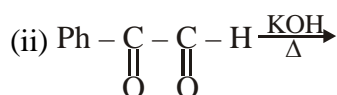
AR0003



AR0004



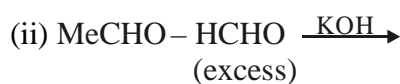
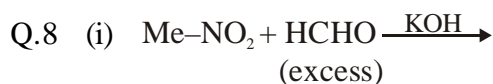
AR0005



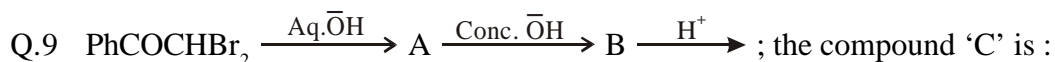
AR0006



AR0007



AR0008



(A)  $\text{PhCH}(\text{OH})\text{CHO}$

(B)  $\text{PhCH}(\text{OH})\text{COOH}$

(C)  $\text{PhCOOH}$

(D) None of these

AR0009

Q.10 Match the column :

**Column - I**

(A)  $\text{HCHO} + \text{NaOD}$  (conc.)

(B)  $\text{DCHO} + \text{NaOH}$  (conc.)

(C)  $\text{DCDO} + \text{NaOH}$  (conc.)

(D)  $\text{DCHO} + \text{NaOD}$  (conc.)

**Column - II**

(P)  $\text{DCOO}^- + \text{CDH}_2\text{OH}$

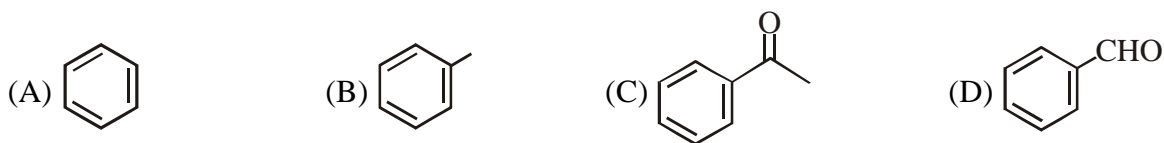
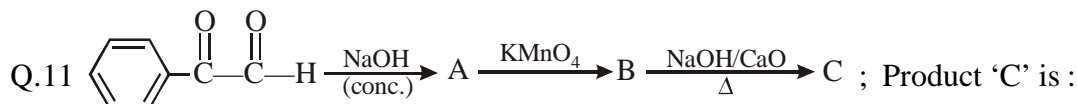
(Q)  $\text{DCOO}^- + \text{CD}_3\text{OH}$

(R)  $\text{DCOO}^- + \text{CDH}_2\text{OD}$

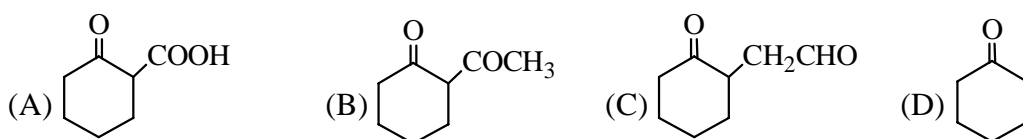
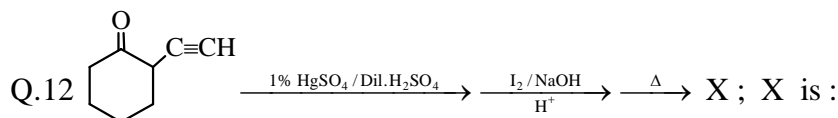
(S)  $\text{HCOO}^- + \text{CH}_3\text{OD}$

AR0010





AR0011

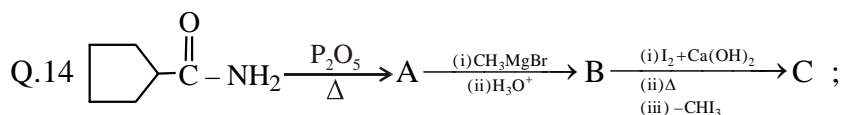


AR0012

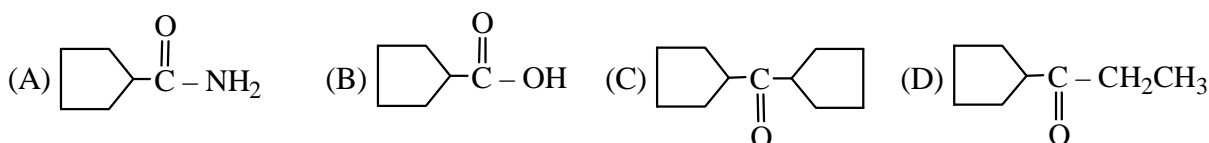
Q.13 The cannizaro reaction of Ph COCHO forms the product(s)

- (A) PhCOCH\_2OH + PhCOCO\_2^- (B) PhCH(OH)CO\_2^-  
 (C) PhCO\_2^- + PhCOCH\_2OH (D) Both (A) and (C)

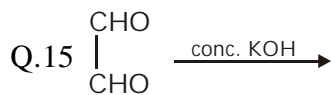
AR0013



Product is:



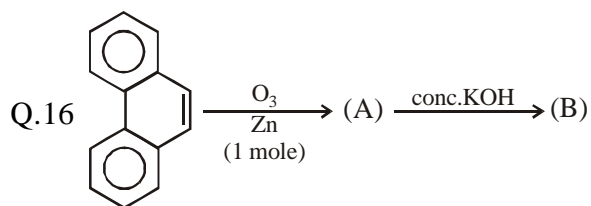
AR0014



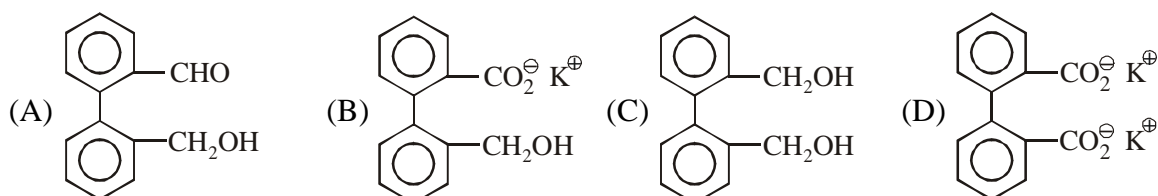
True about this reaction is / are

- (A) Cannizaro name is associated with this reaction  
 (B) It is a disproportion reaction  
 (C) It is a bimolecular reaction in r.d.s.  
 (D) All of these

AR0015

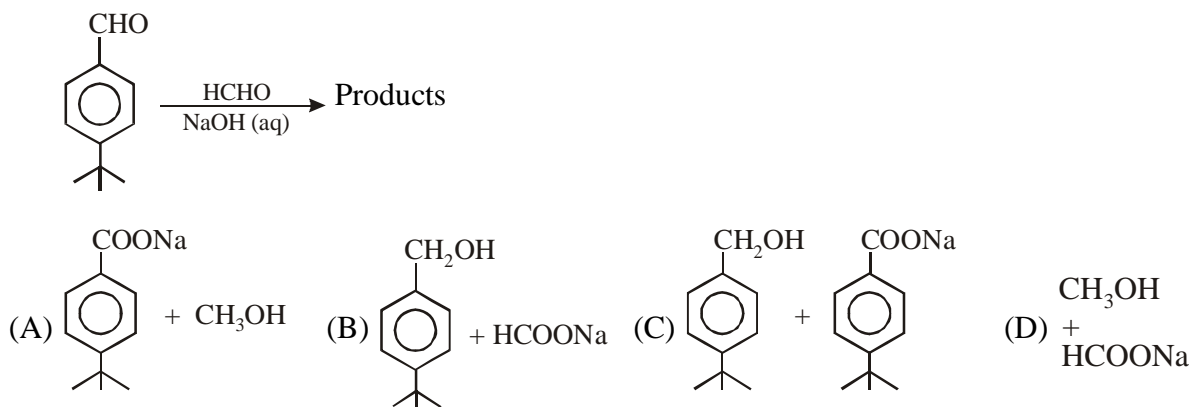


End product (B) of above reaction is :



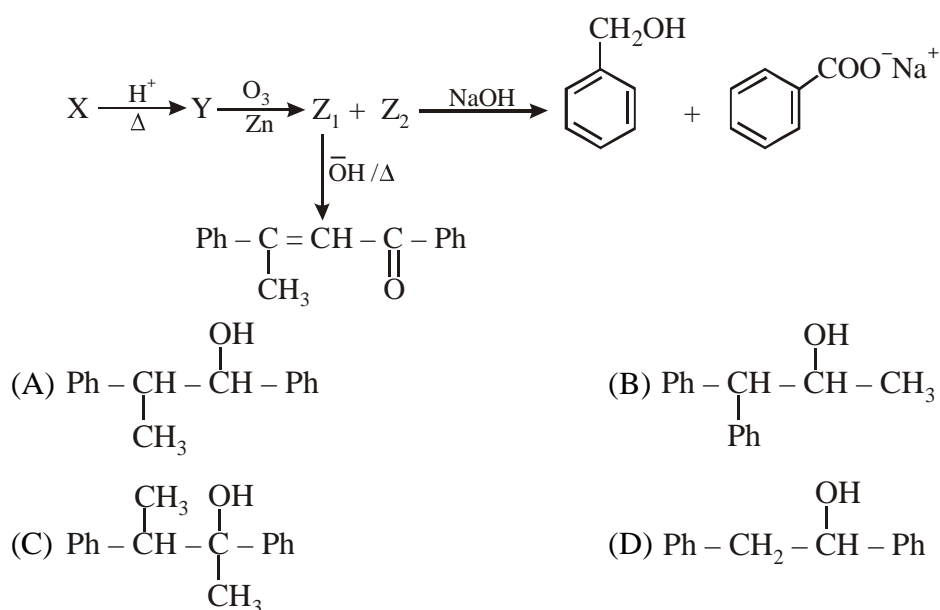
AR0016

Q.17 The major product pair of the following reaction will be :



AR0017

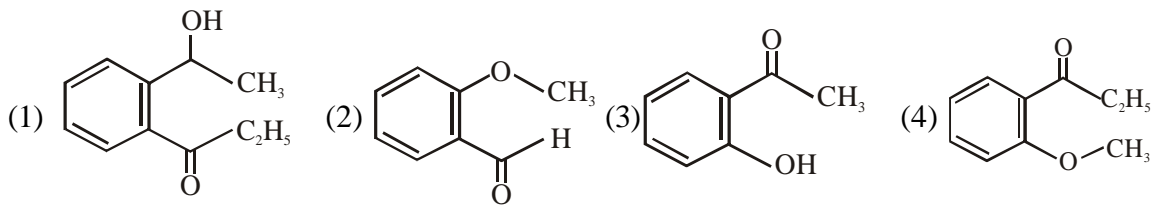
Q.18 Reactant 'X' will be :



AR0018

Q.19 An organic compound neither reacts with neutral ferric chloride solution nor with Fehling solution, It however, reacts with Grignard reagent and gives positive iodoform test. The compound is -

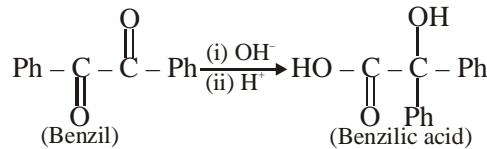
[JEE-MAIN (APRIL)-2019]



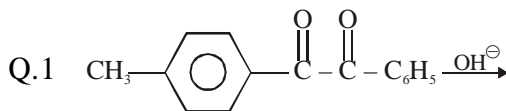
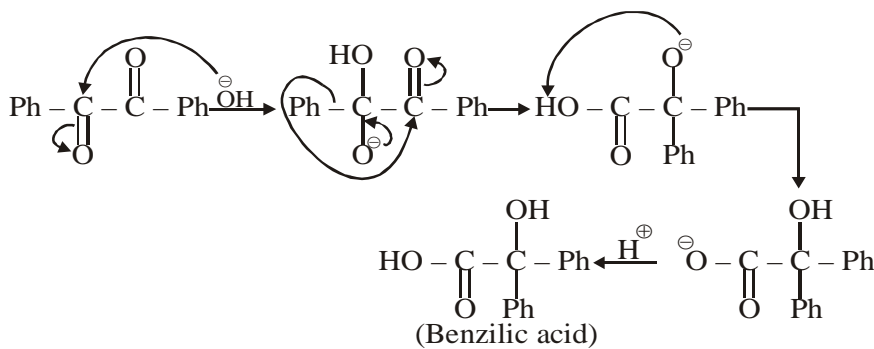
AR0019

**(2) BENZIL-BENZILIC REARRANGEMENT OR BENZILIC ACID REARRANGEMENT**

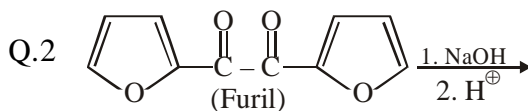
The base catalysed reaction of 1,2-diketones to a salt of -2- hydroxy carboxylic acid is known as Benzilic acid rearrangement, this reaction is mainly applicable when aryl group is present on both carbonyl carbons.



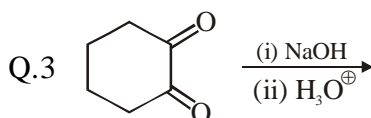
**Mechanism :**



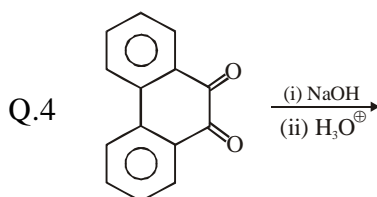
AR0020



AR0021



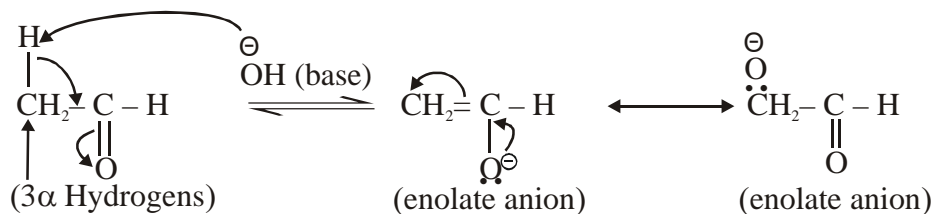
AR0022



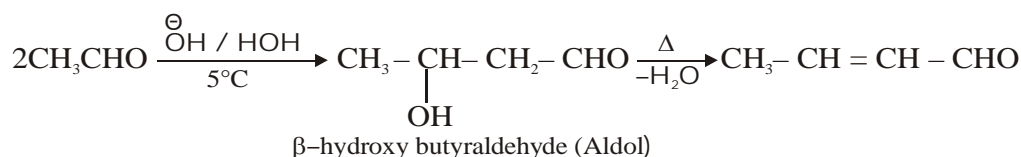
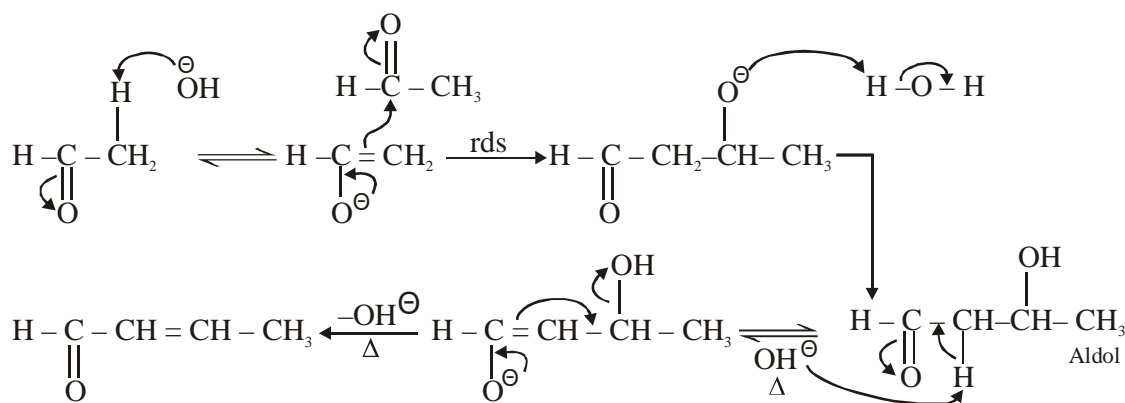
AR0023

**(3) ALDOL CONDENSATION**

The  $\alpha$ -hydrogen of carbonyl compounds are acidic due to the fact that the anion (enolate ion) is stabilized by resonance.

**Base catalysed Aldol**

In aqueous base, two acetaldehyde molecules react to form  $\beta$ -hydroxy aldehyde called aldol. The reaction is called Aldol condensation. The enolate ion is the intermediate in the aldol condensation of aldehyde and ketone. Acetaldehyde for instance, forms a dimeric product aldol in presence of a dilute base ( $\approx 10\%$  NaOH)

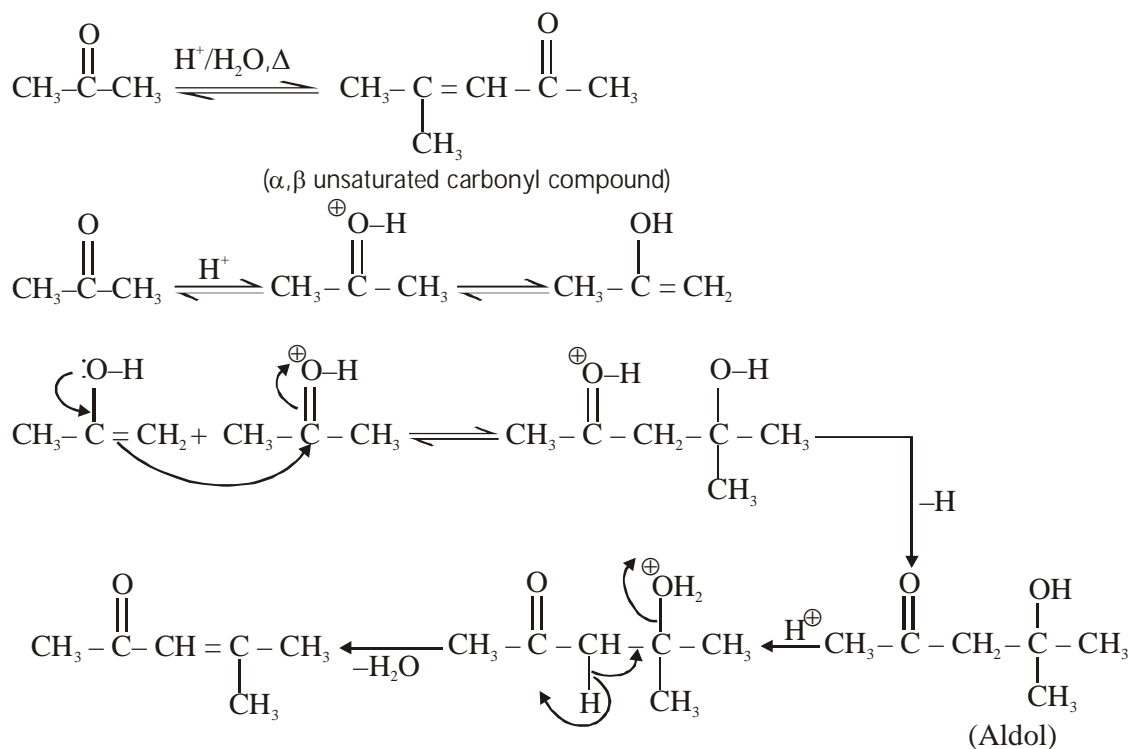
**Mechanism :**

Aldols are stable and may be isolated. They, however can be dehydrated easily by heating the basic reaction mixture or by a separate acid catalyzed reaction. Thus if the above reaction is heated the product is dehydrated to 2-butenal (crotonaldehyde).

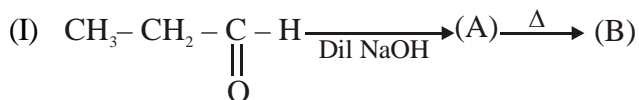
**Acid catalysed Aldol**

In acid catalysed aldol condensation enol form of carbonyl is the nucleophile in place of enolate.

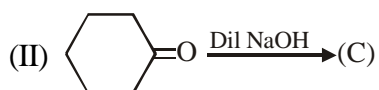
**Mechanism :**



Q.1 Write the product and mechanism for given reactions.



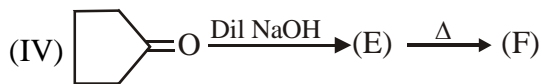
AR0024



AR0025



AR0026



AR0027

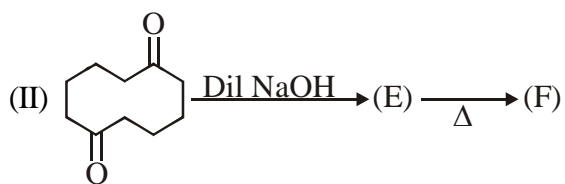


AR0028

Q.2 Identify the intramolecular aldol product ?

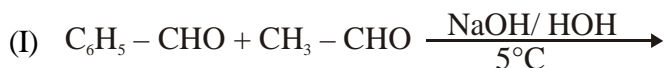


AR0029

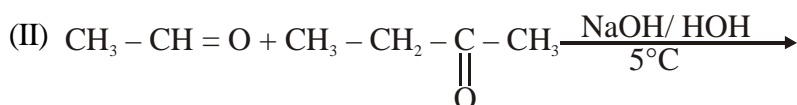


AR0030

Q.3 Find out the total number of possible aldol products (including and excluding stereo products).

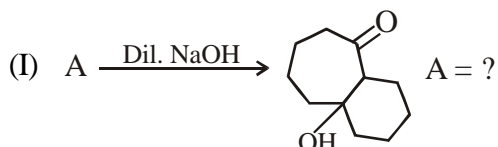


AR0031

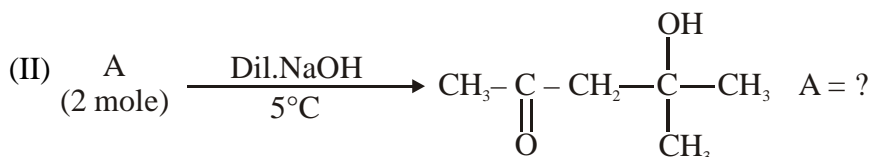


AR0032

Q.4 Identify the structure of substrate ?

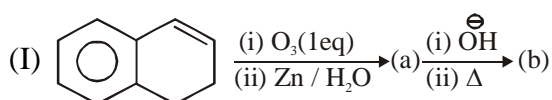


AR0033

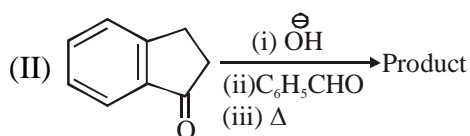


AR0034

Q.5 Complete reaction sequence :

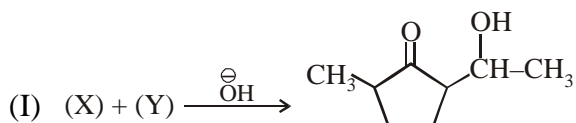


AR0035

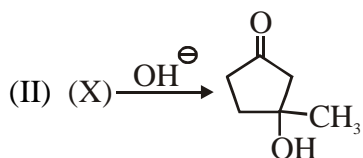


AR0036

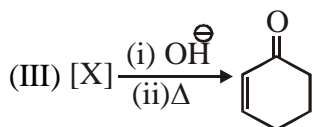
Q.6 Complete the following reactions :



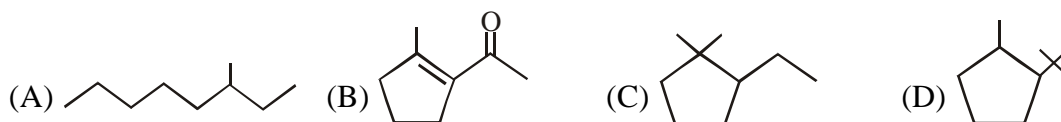
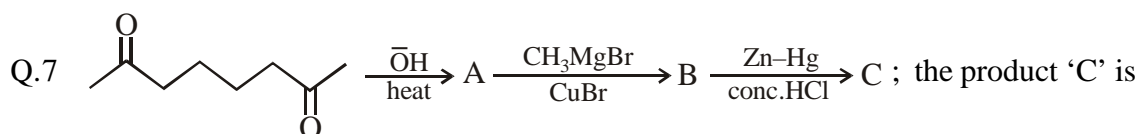
AR0037



AR0038

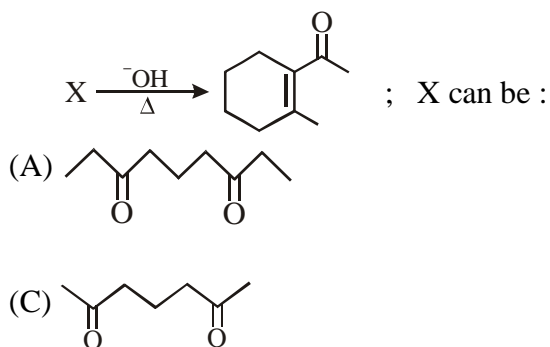


AR0039



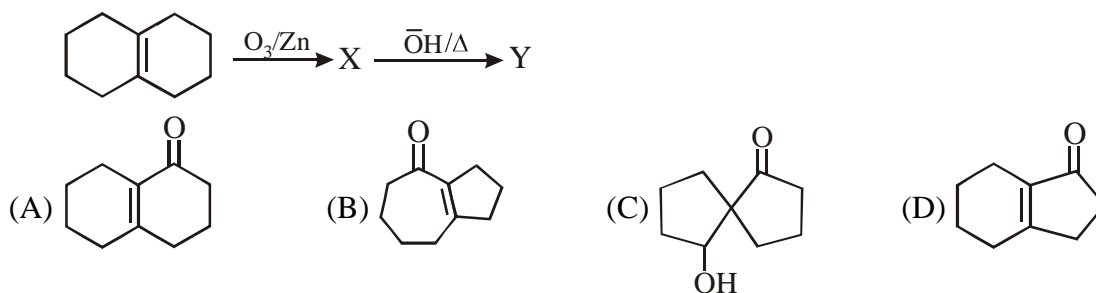
AR0040

Q.8 Consider following intramolecular aldol condensation reaction :



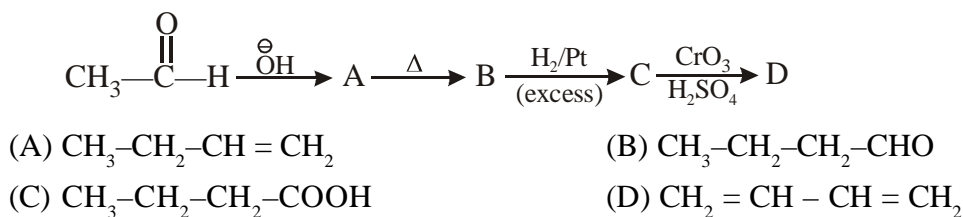
AR0041

Q.9 Product 'Y' formed in the given reaction is :



AR0042

Q.10 Product 'D' is :



AR0043

Q.11  $\text{CH}_3\text{CH}=\text{CHCHO} \xrightarrow[\text{aldol}]{\text{OH}^-} \xrightarrow{\Delta} \text{A}$ , A is :

- (A)  $\text{CH}_3(\text{CH}=\text{CH})_3\text{CHO}$  (B)  $\text{CH}_3\text{CH}_2\text{CH}_2(\text{CH}=\text{CH})_2\text{CHO}$   
 (C)  $\text{CH}_3(\text{CH}_2\text{CH}_2)_3\text{CH}=\text{CH}-\text{CHO}$  (D) None is correct

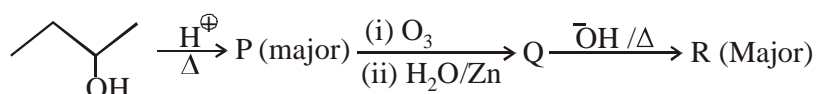
AR0044

Q.12  $\text{MeCHO} \xrightarrow{\text{NaOH}, \Delta} \text{A} \xrightarrow{\text{NaOH}, \Delta} \text{B}$  ; B is :

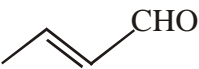

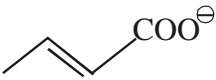
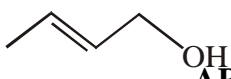
- (A)  $\text{Me}(\text{CH}=\text{CH})_3\text{CHO}$  (B)  $\text{MeCH}=\text{CHCHO}$   
 (C)  $\text{Me}(\text{CH}=\text{CH})_2-\text{CHO}$  (D)  $\text{Me}-(\text{CH}=\text{CH})_4\text{CHO}$

AR0045

Q.13 For the given reaction :

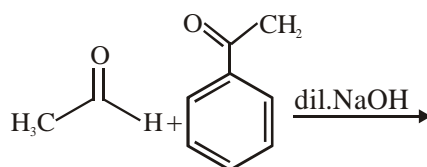


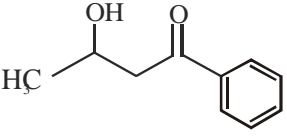
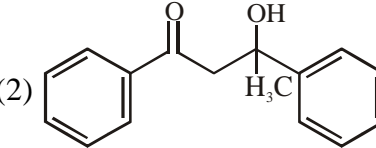
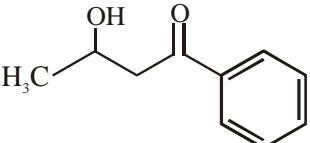
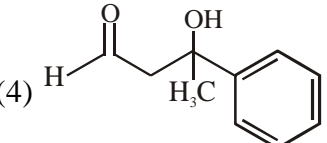
The (R) is :

- (A)  (B)  (C)  (D) 

AR0046

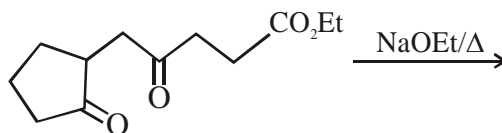
Q.14 The major product formed in the following reaction is: [JEE-MAIN (JANUARY)-2019]

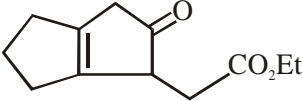
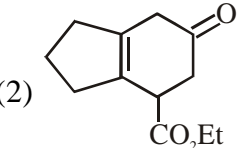
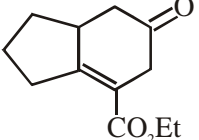
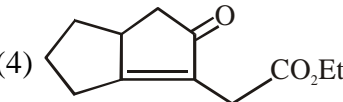


- (1)  (2)   
 (3)  (4) 

AR0047

Q.15 The major product obtained in the following reaction is: [JEE-MAIN (JANUARY)-2019]



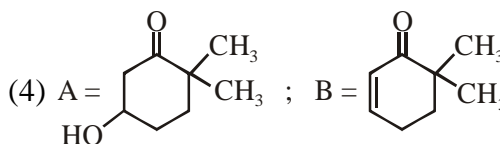
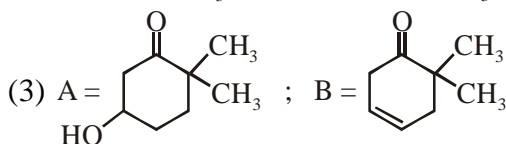
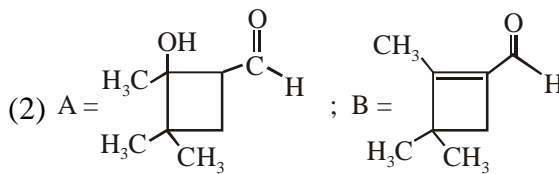
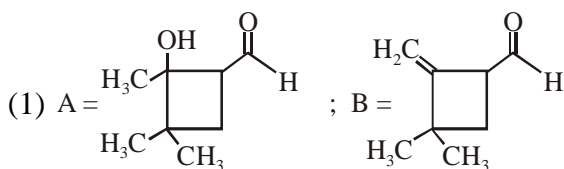
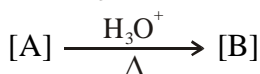
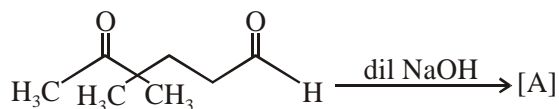
- (1)  (2)   
 (3)  (4) 

AR0048



Q.16 In the following reactions, products A and B are :

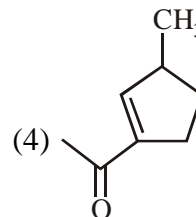
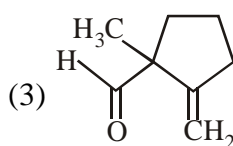
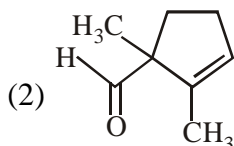
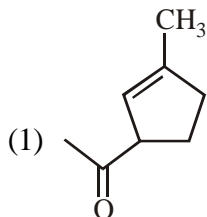
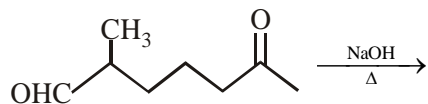
[JEE-MAIN (JANUARY)-2019]



AR0049

Q.17 The major product obtained in the following reaction is

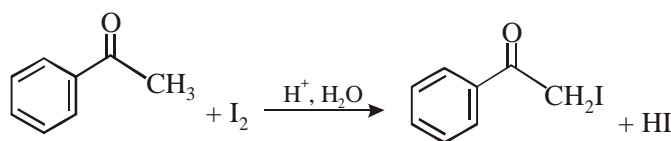
[JEE-MAIN (APRIL)-2019]



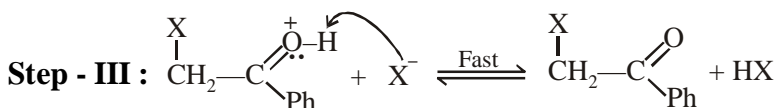
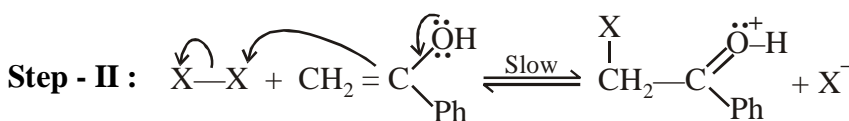
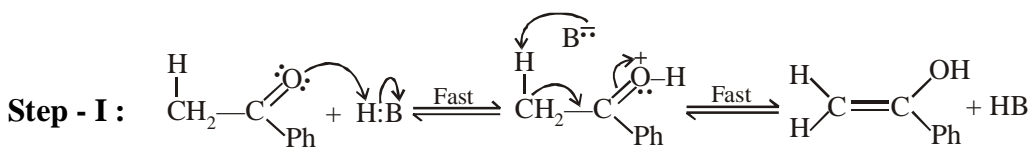
AR0050

**(4) HALOGENATION OF THE  $\alpha$ -CARBON OF ALDEHYDES AND KETONES**

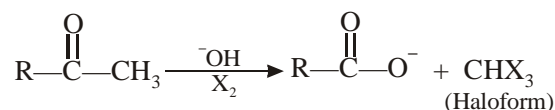
**1<sup>st</sup> Acid-Catalyzed halogenation :** - When  $\text{Br}_2$ ,  $\text{Cl}_2$  and  $\text{I}_2$  is added to an acidic solution of an aldehyde or a ketone, a halogen replaces one of the  $\alpha$ -hydrogens of the carbonyl compound. Halogenation takes place through the slow formation of an enol followed by rapid reaction of the enol with the halogen.



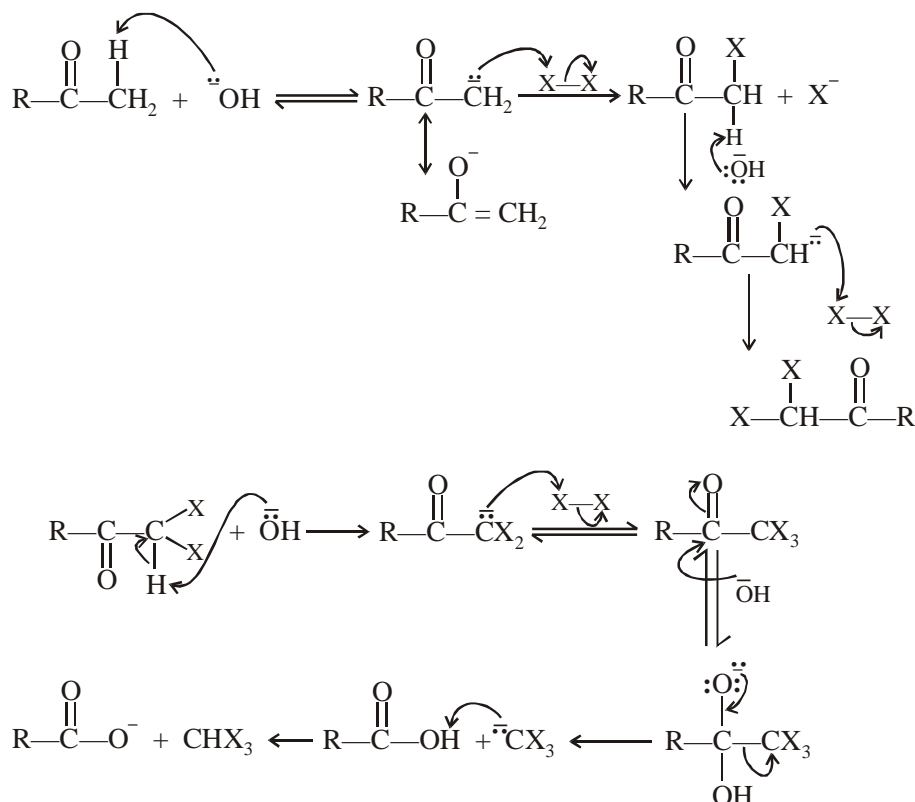
**Mechanism :**



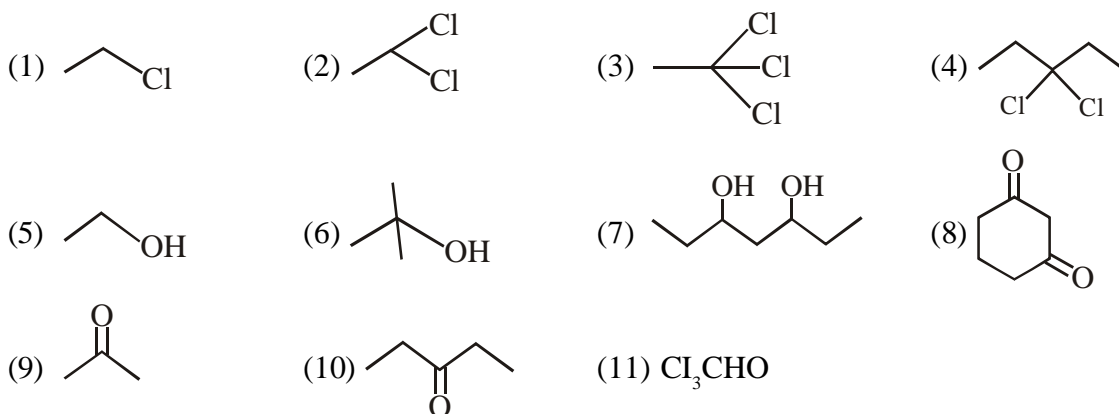
**II<sup>nd</sup> Base-Catalyzed halogenation :** - In the presence of excess base and excess halogen, a methyl ketone is converted first into a trihalo-substituted ketone and then into a carboxylic acid.



**Mechanism :**

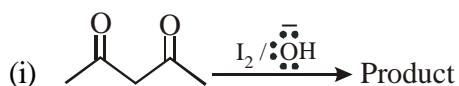


Q.1 Identify the compounds which can show iodoform test and complete the reaction ?

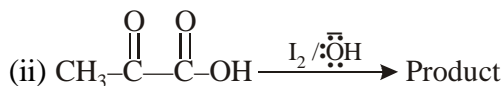


AR0051

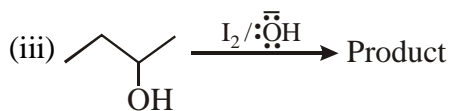
Q.2 Complete the following given reaction :



AR0052

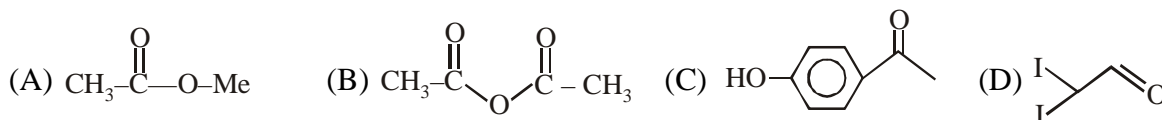


AR0053



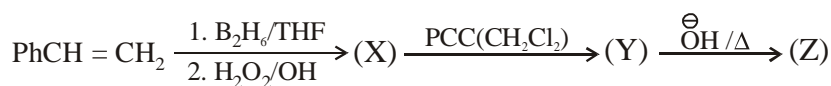
AR0054

Q.3 Select the compound which does not show haloform reaction is/are :

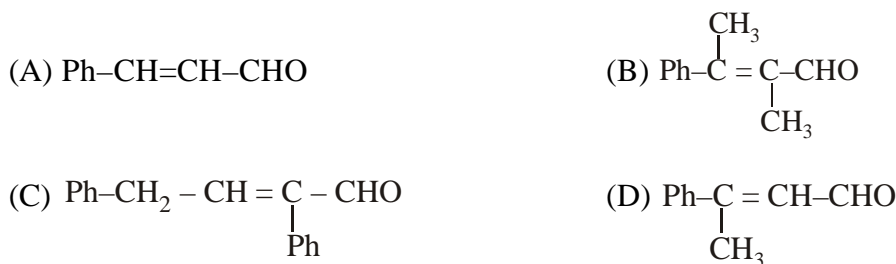


AR0055

Q.4 For the reaction



(Z) is :



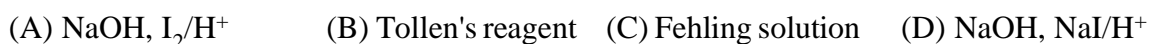
AR0056

Q.5 Two isomeric ketones, 3-pentanone and 2-pentanone can be distinguished by :



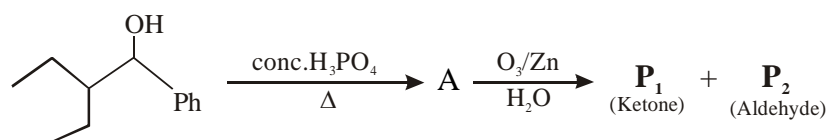
AR0057

Q.6 Which of the reagent is used to convert 2-Butanone into propanoic acid -

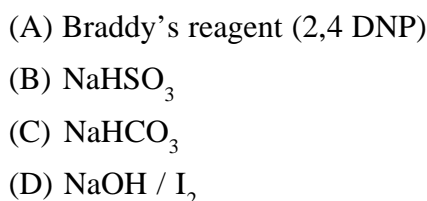


AR0058

Paragraph for Q.07 to Q.09



Q.7 Which one of the following reagent is best suitable for distinction between  $\text{P}_1$  and  $\text{P}_2$  -



AR0059

Q.8 Select the correct statement among the following -

- (A)  $P_1$  will show aldol reaction &  $P_2$  will show cannizaro reaction  
 (B)  $P_1$  will show cannizaro reaction &  $P_2$  will show aldol reaction  
 (C) Both  $P_1$  &  $P_2$  will show cannizaro reaction  
 (D) Both  $P_1$  &  $P_2$  will show aldol reaction

AR0060

Q.9  $P_2 \xrightarrow[\text{(ii) } H^+]{\text{conc. NaOH}}$  products

Select incorrect statement for the above reaction -

- (A) It is a redox reaction  
 (B) It is a disproportionation reaction  
 (C) Two products formed are alcohol & carboxylic acid  
 (D) It is an intramolecular reaction

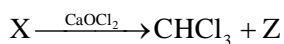
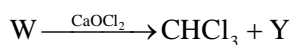
AR0061

Q.10 Which of the following will give yellow precipitate with NaOH /  $I_2$

- (A)  $\text{Ph}-\underset{\text{OH}}{\text{CH}}-\text{Me}$       (B)  $\text{Cl}_3\text{CHO}$       (C)  $\text{Me}-\underset{\text{O}}{\text{C}}-\underset{\text{O}}{\text{C}}-\text{OH}$       (D) EtOH

AR0062

Q.11 Ethylmethanoate  $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) MeMgBr(2eq)}}$   $\frac{W+X}{\text{organic product}}$

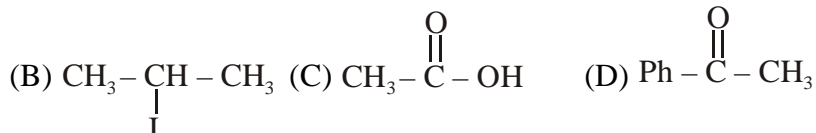
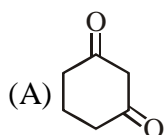


Which of the following organic product can be formed on dry distillation reaction

- (I)  $\text{CH}_3-\text{CHO}$       (II)  $\text{CH}_3-\text{CO}-\text{CH}_3$       (III)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$       (IV) HCHO  
 (A) I and II only      (B) II and III only      (C) I, II and IV only      (D) II and IV only

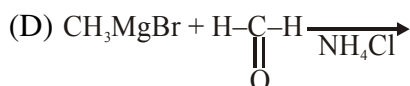
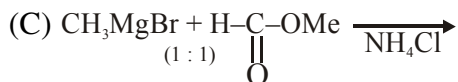
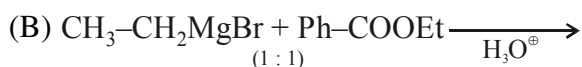
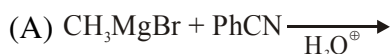
AR0063

Q.12 Which of the following compounds(s) give a sweet smelling product having anesthetic use in presence of  $\text{Cl}_2$ , NaOH,  $\Delta$ .



AR0064

Q.13 Reaction in which product can show positive haloform test :-



AR0065

Q.14 In which reaction haloform is obtained as one product :-

- (A) Electrolysis of ethanolic aqueous solution of NaCl  
 (B) Isopropanol with bleaching powder  
 (C) Chlorination of methane in sun light  
 (D) Chloral is treated with NaOH

AR0066

Q.15. Fructose and glucose can be distinguished by : [JEE-MAIN (APRIL)-2019]

- (1) Fehling's test  
 (2) Barfoed's test  
 (3) Benedict's test  
 (4) Seliwanoff's test

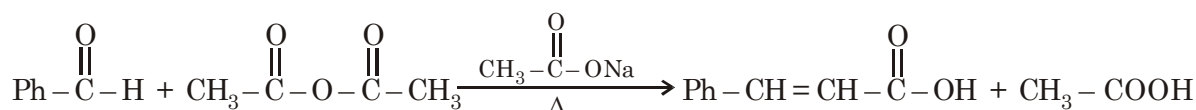
AR0067

### (5) PERKIN CONDENSATION

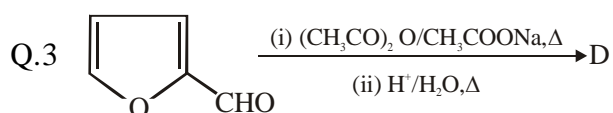
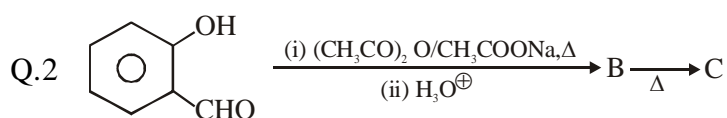
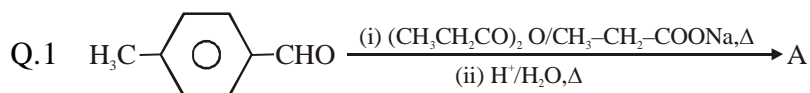
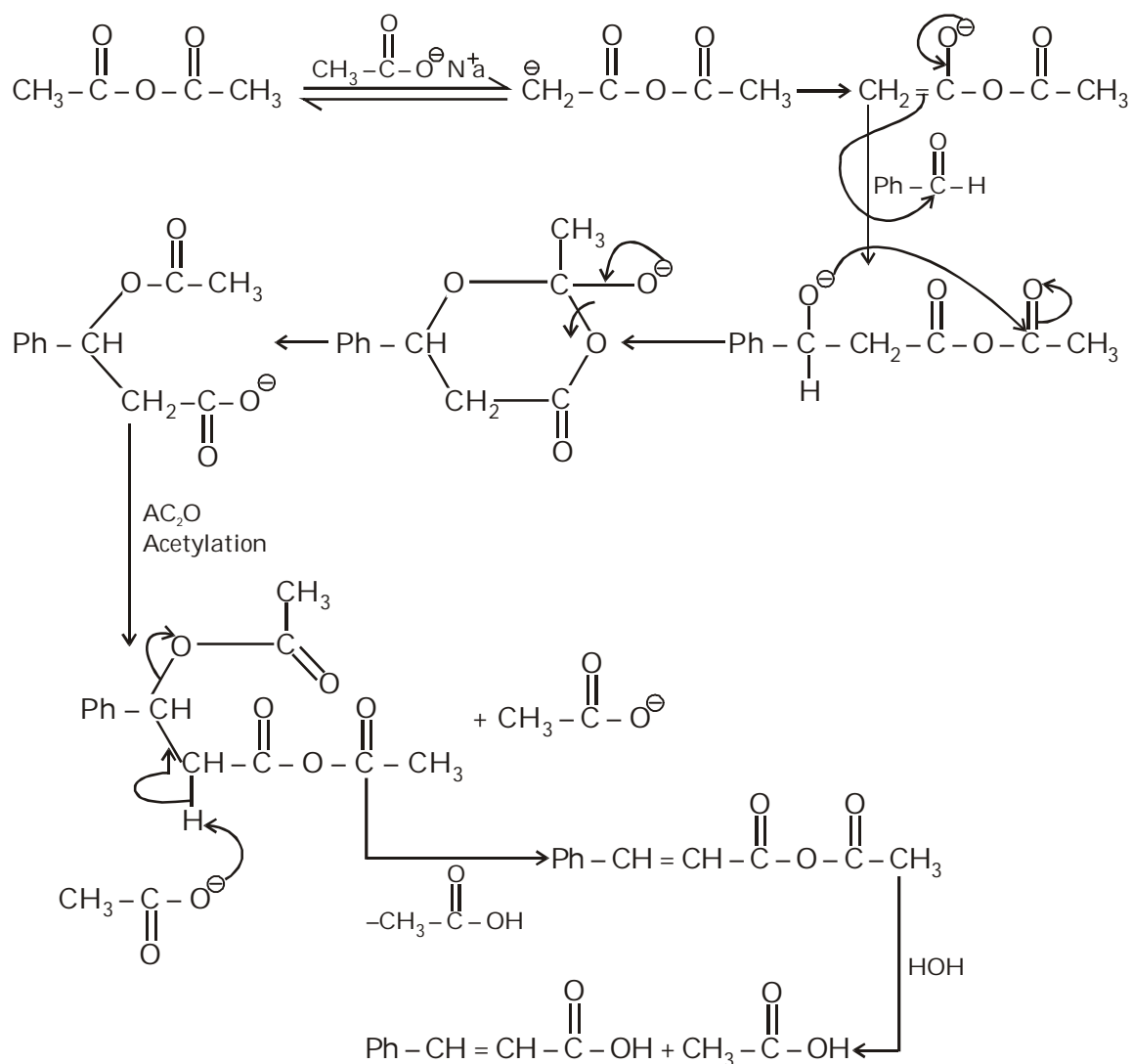
#### Perkin Reaction :

Condensation reaction between aromatic aldehyde and aliphatic acid anhydride having at least two alpha hydrogen in the presence of a base is known as **Perkin reaction**.

In this reaction, the anion of an acid anhydride adds to an aromatic aldehyde to produce an  $\beta$  aryl  $\alpha,\beta$ , unsaturated acid. In order to prevent side reactions, the base that is used to make the anion of the anhydride is usually the sodium salt of the acid corresponding to the anhydride.



## Mechanism :

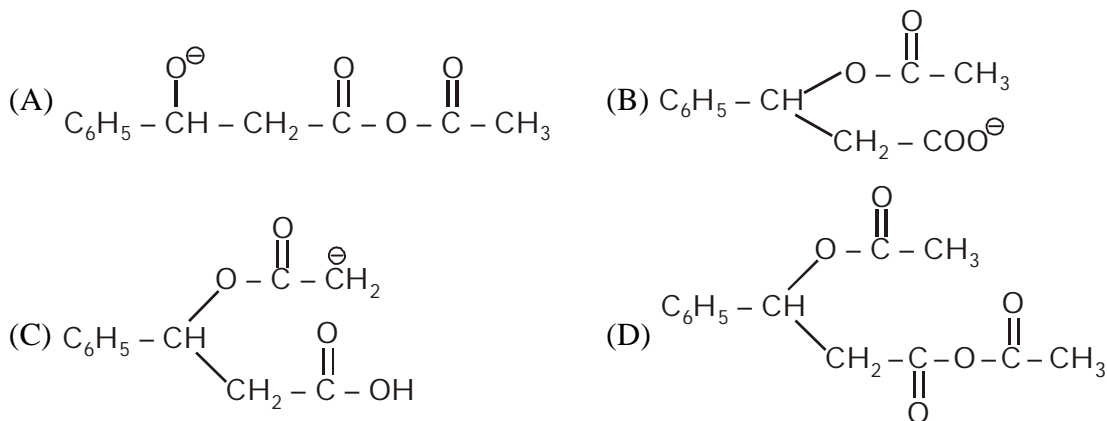
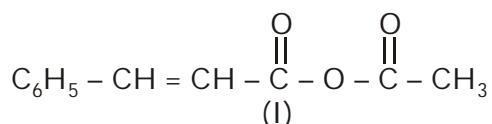


AR0068

AR0069

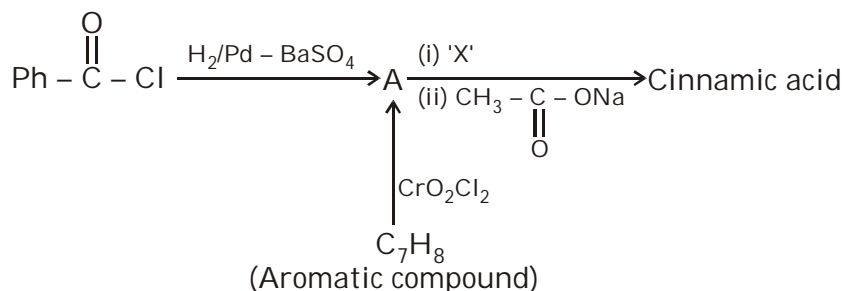
AR0070

4. In the perkin reaction which one of the following intermediates gives compound (I)



AR0071

Paragraph for Q.no. 5-6

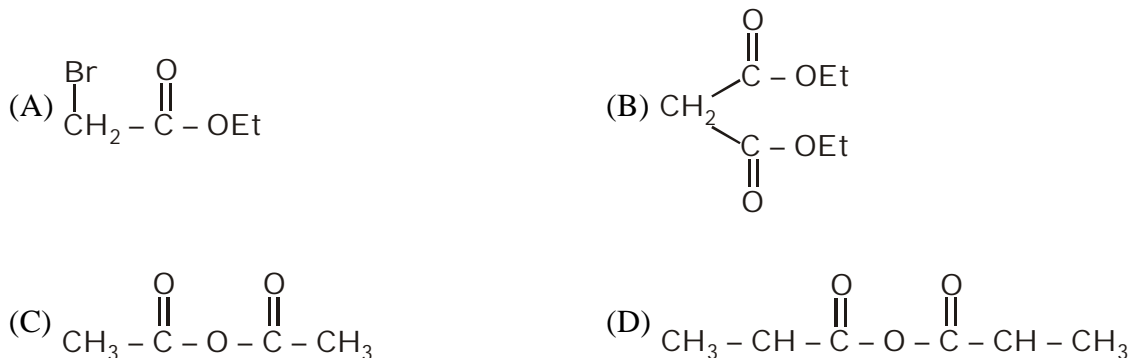


5. Compound 'A' on treatment with conc. NaOH followed by acidification can give :

- (A)  $\text{Ph} - \text{CH}_2 - \text{COOH}$  (B)  $\text{Ph} - \text{OH}$   
 (C)  $\text{Ph} - \text{COOH}$  (D)  $\text{Ph} - \text{CH}_2 - \text{OH}$

AR0072

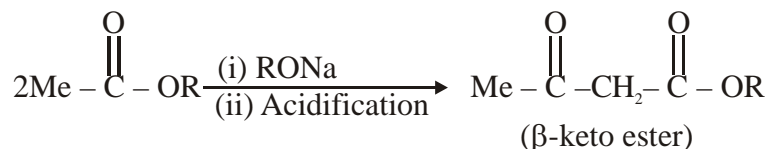
6. In the above reaction the reagent "X" can be :



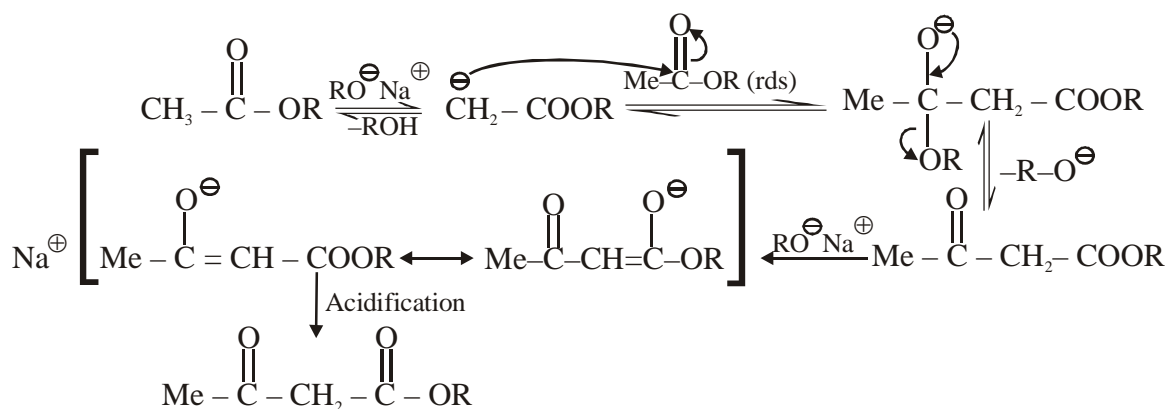
AR0073

**(6) CLAISEN CONDENSATION**

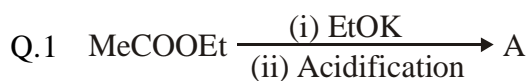
Esters undergo  $S_NAE$  Reaction, when attacked by a  $Nu^-$  generated by the interaction of a base (usually base related to the Alkoxy anion of ester) with one of the molecule of ester and this  $Nu^-$  attacks on another molecule. The reaction over all is considered as condensation of ester known as claisen ester condensation.



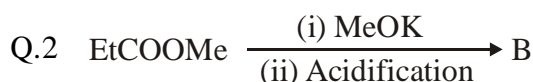
**Mechanism :**



Some times, when two ester group are present within the molecule then the condensation occurs intramolecular then cyclization caused thus is known as Dieckmann cyclization or Dieckmann's condensation.



AR0074



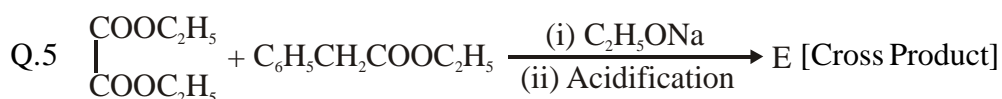
AR0075



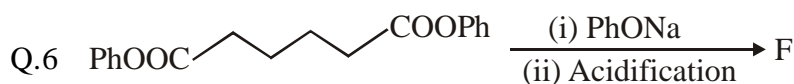
AR0076



AR0077

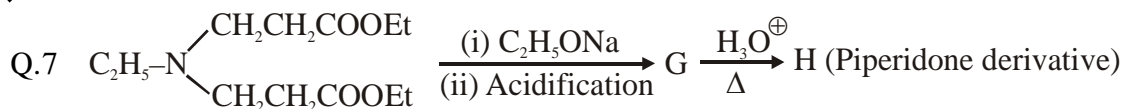


AR0078



AR0079



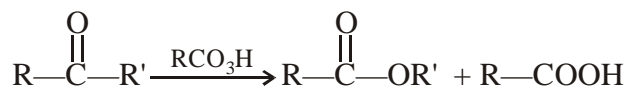


AR0080

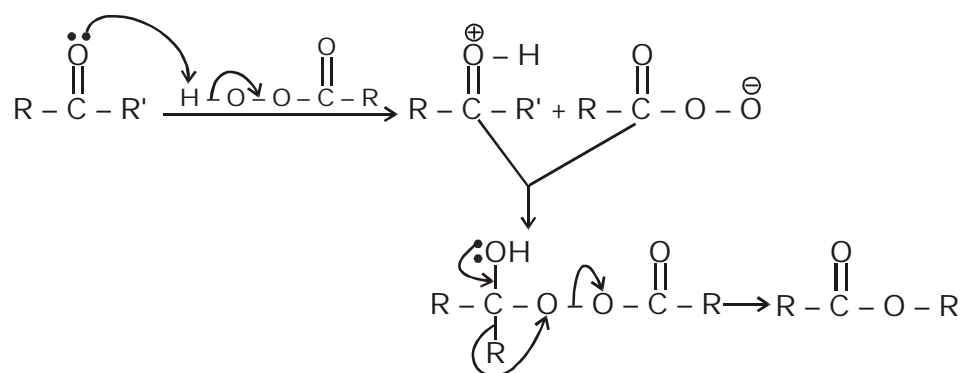
(7) Beayer villiger oxidation

Reaction involve the oxidation of ketone to ester by treatment with per acid such as per acetic acid, MCPBA, per trifluoroacetic acid etc.

- It is a redox reaction
- Cyclic ketones are converted to lactone with ring expansion.



Mechanism



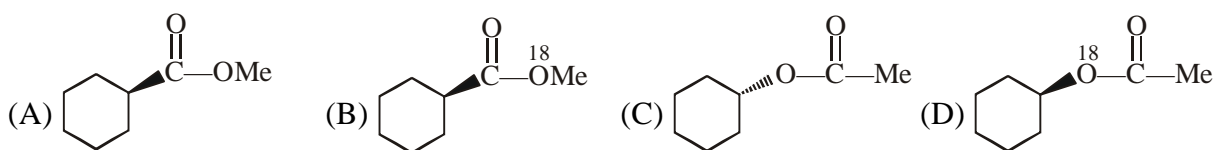
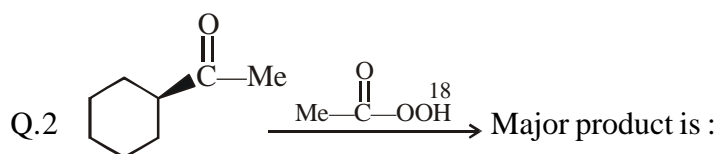
**Note :** In above reaction for shifting of groups migratory aptitude is applicable

Migratory order for above reaction

$-\text{H} > 3^\circ > 2^\circ > -\text{Ph} > 1^\circ > -\text{Me}$



AR0081



AR0082

## ANSWER-KEY

## (1) CANNIZZARO REACTION

Q.1 Ans. (D)

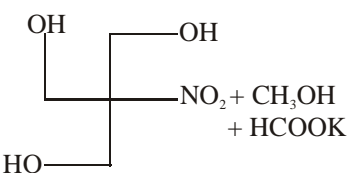
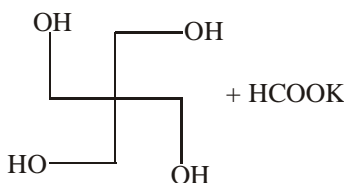
As  $\text{Cl}_3\text{C}-\text{CHO}$  given chloroform

Q.2 Ans. (C)

In crum cannizzaro reaction more reactive carbonyl compound is oxidised &amp; less in reduced.

Q.3 Ans. (B)

Intramolecular cannizzaro followed by heating effect

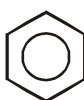
Q.4 Ans. (i)  $\text{CH}_3\text{OD} + \text{HCOONa}$ (ii)  $\text{DCH}_2\text{OD} + \text{DCOONa}$ Q.5 Ans. (i)  $\text{PhCH}_2\text{OD} + \text{PhCOONa}$ (ii)  $\text{Ph}-\text{CH}_2\text{OH} + \text{PhCOONa}^{18}$ Q.6 Ans. (i)  $\text{Ph}-\text{CH}_2\text{OH} + \text{HCOOK}$ (ii)  $\text{Ph}-\underset{\text{OH}}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OK}$ Q.7 Ans. (i)  $\text{MeCH}_2-\text{CH}=\underset{\text{Me}}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ (ii)  $\text{Me}_2\text{CH}-\text{CH}_2\text{OH} + \text{Me}_2\text{CHCOOK}$ Q.8 Ans. (i) (ii) 

Q.9 Ans. (B)

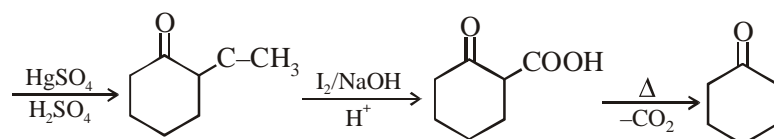
A :  $\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{O}$ B :  $\text{Ph}-\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}-\text{COO}^\ominus$ C :  $\text{Ph}-\underset{\text{OH}}{\text{CH}}-\text{COOH}$ 

Q.10 Ans. (A)→S ; (B)→P ; (C)→Q ; (D)→R

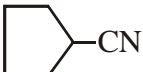
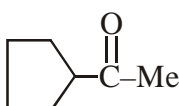
Q.11 Ans. (A)

A :  $\text{Ph}-\underset{\text{OH}}{\text{CH}}-\text{COONa}$ B :  $\text{PhCOOH}$ C : 

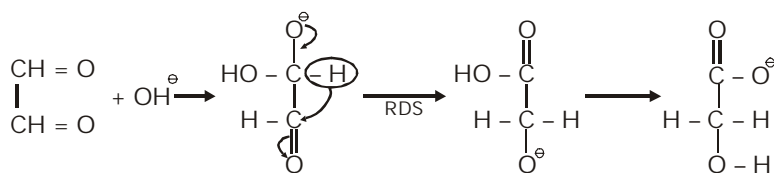
Q.12 Ans. (D)



Q.13 Ans. (B)

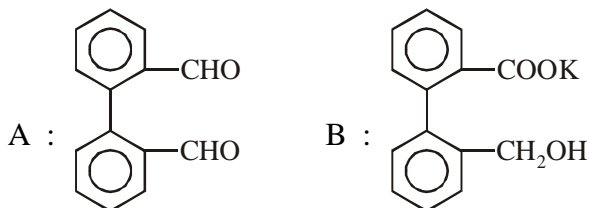
Q.14 Ans. (C) A : B : 

Q.15 Ans. (A)



option A is correct.

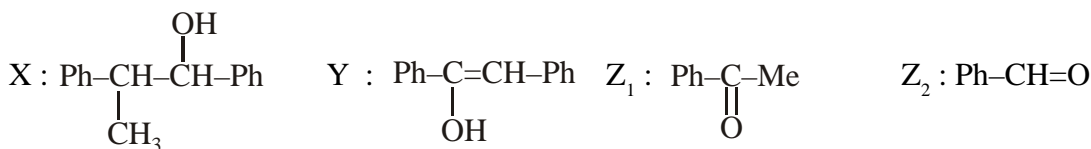
Q.16 Ans. (B)



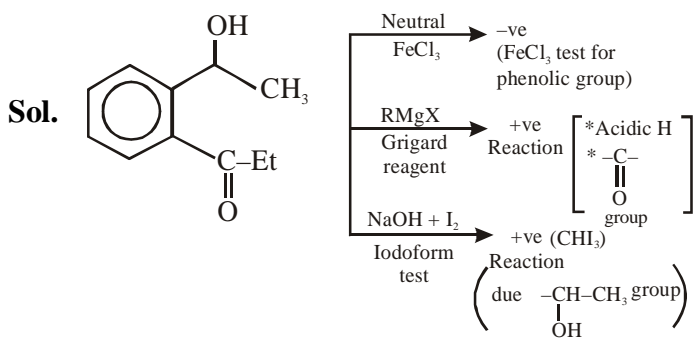
Q.17 Ans. (B)

Cron cannizaro reaction

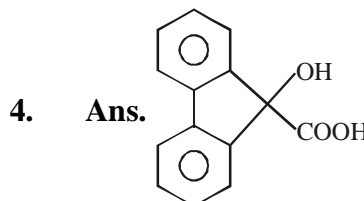
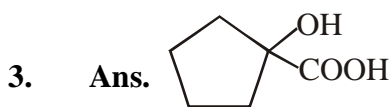
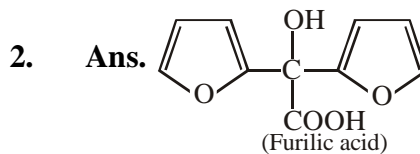
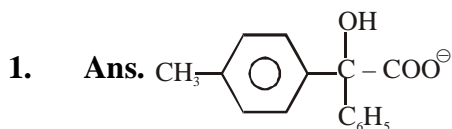
Q.18 Ans. (A)



Q.19 Ans. (1)

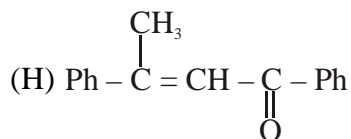
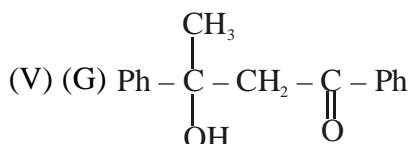
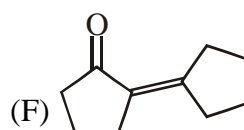
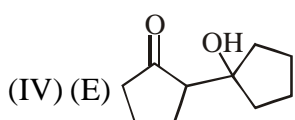
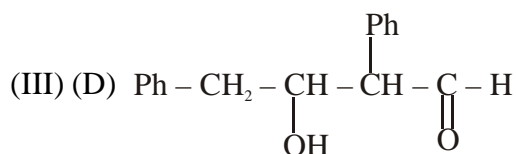
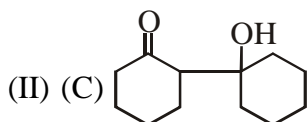
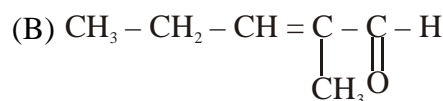
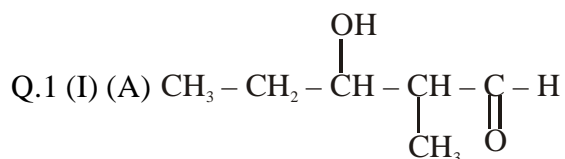


**(2) BENZIL-BENZILIC REARRANGEMENT OR BENZILIC ACID REARRANGEMENT**

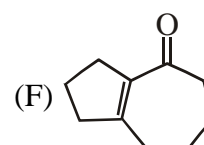
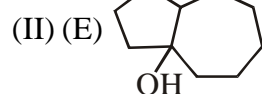
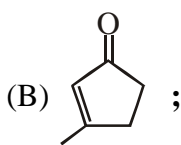
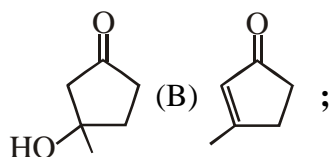


## (3) ALDOL CONDENSATION

Q.1 Ans.



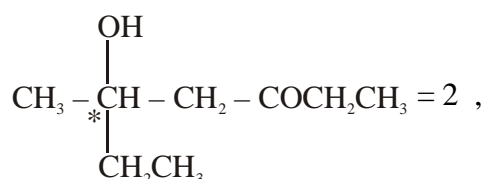
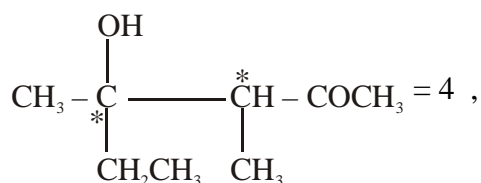
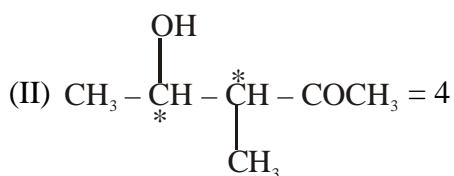
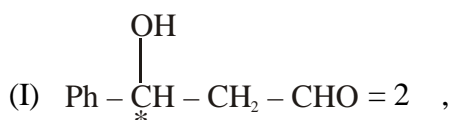
Q.2 Ans. (I) (A)



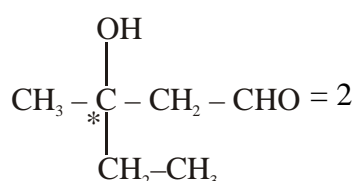
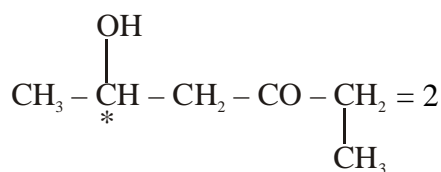
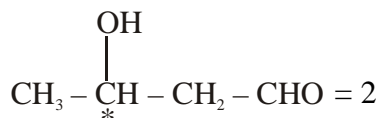
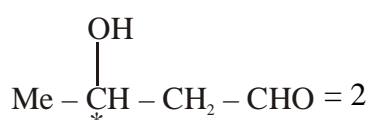
Q.3

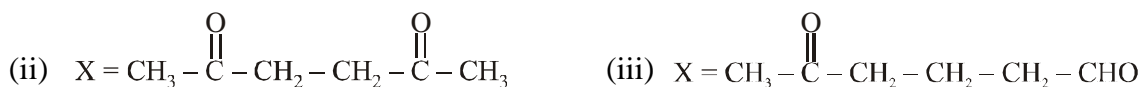
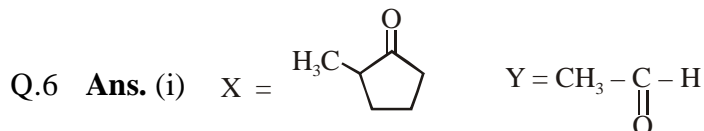
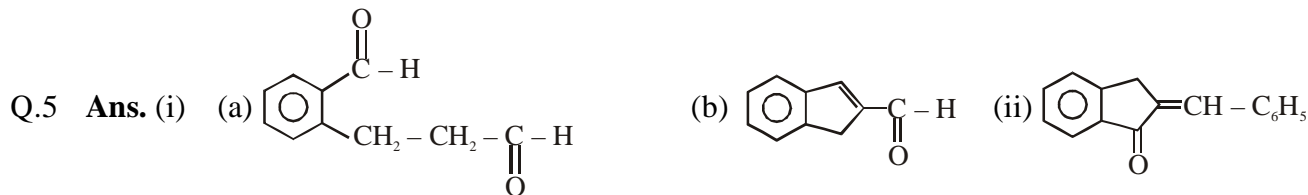
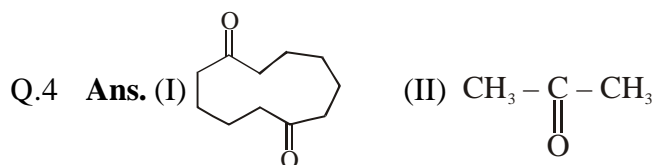
Ans.

Excluding Stereo



Including Stereo





Q.7 Ans. (C)

Intramolecular aldol condensation the 1,4-addition and finally clemmeson reduction.

Q.8 Ans. (D)

Q.9 Ans. (B)

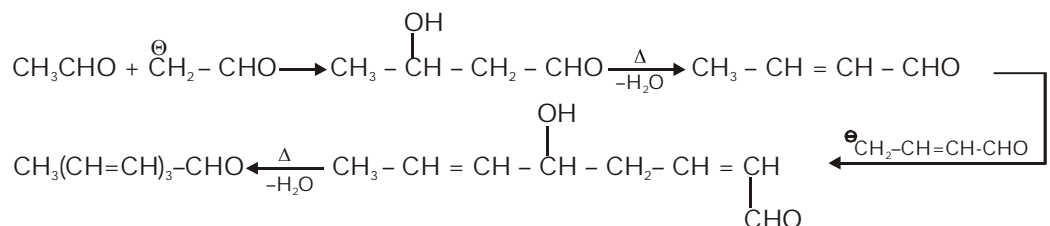
Ozonolysis followed by intramolecular aldol.

Q.10 Ans. (C)

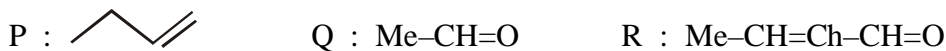


Q.11 Ans. (A)

Q.12 Ans. (A)



Q.13 Ans. (A)



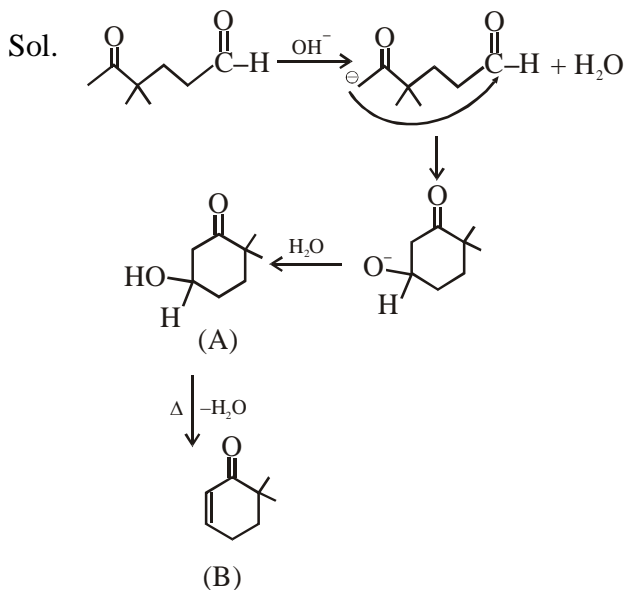
Q.14 Ans. (1)

Sol. Aldehyde reacts at a faster rate than ketone during aldol and sterically less hindered anion will be

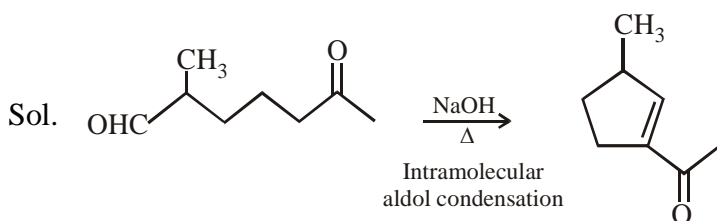
a better nucleophile so self aldol at  $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{H}$  will be the major product.

Q.15 Ans. (4)

Q.16 Ans. (4)



Q.17 Ans. (4)

**(4) HALOGENATION OF THE  $\alpha$ -CARBON OF ALDEHYDES AND KETONES**

Q.1 Ans. (1, 2, 5, 7, 8, 9, 11)

Q.2 Ans. (i)  $\text{CH}_3\text{-COO}^- + \text{CHI}_3$ ; (ii)  $\text{O}=\text{C}-\text{C}(=\text{O})-\text{O}^- + \text{CHI}_3$ ; (iii)  $\text{CH}_2\text{CH}_2\text{COO}^- + \text{CHI}_3$ 

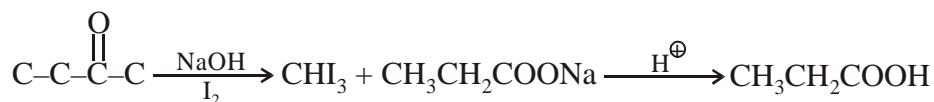
Q.3 Ans. (A,B,C)

Q.4 Ans. (C)

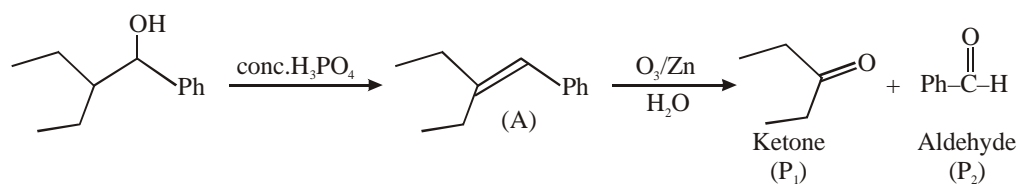


Q.5 Ans. (A)

Q.6 Ans. (A)

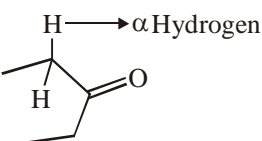


Q.7 Ans. (B)

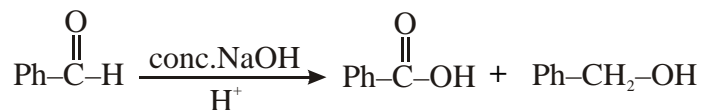


- (A) Both ketone & aldehyde react with braddy's reagent  $\text{H}_2\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$ , 2,4 dinitrophenyl hydrazine.
- (B) With  $\text{NaHSO}_3$  only aldehyde give crystalline bisulphite adduct whereas hindered ketone is unable react.
- (C)  $\text{NaHCO}_3$  will not react any of them.
- (D) Both  $\text{P}_1$  &  $\text{P}_2$  are unable to form idoform with  $\text{NaOH}/\text{I}_2$

Q.8 Ans. (A)

For aldol  $\alpha\text{H}$  should be present i.e.   $\text{P}_1$  where as  $\text{P}_2$   $\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  will give cannizaro's as there is no.  $\alpha\text{H}$  in  $\text{P}_2$ .

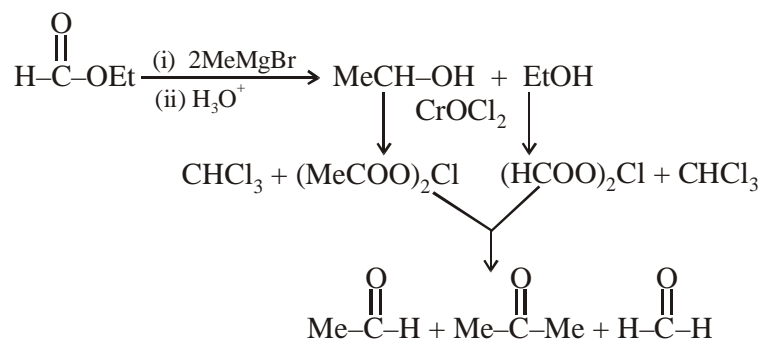
Q.9 Ans. (D)



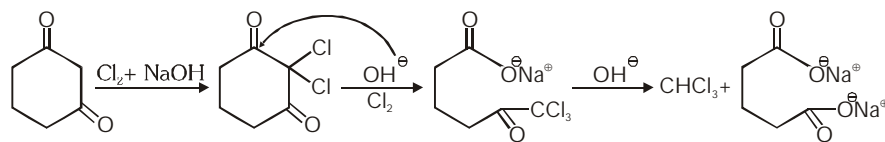
The above reaction is intermolecular redox reaction. In which desprotonation is taking place as a result of which 2 different products are formed from singlet reactant.

Q.10 Ans. (A,B,C,D)

Q.11 Ans. (C)



Q.12 Ans. (A,B,D)

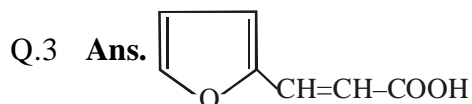
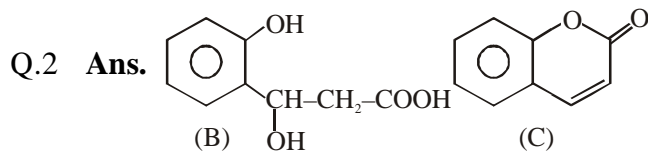
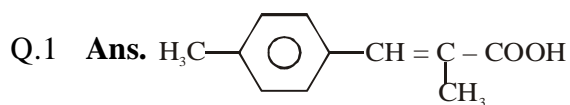


Q.13 Ans. (A,B,C,D)

Q.14 Ans. (A,B,C,D)

Q.15. Ans. (4)

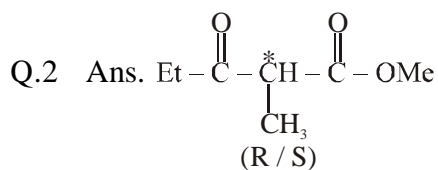
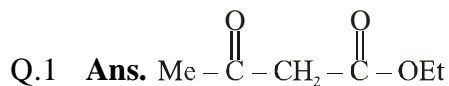
Sol. Seliwanoff's test is used to distinguished aldose and ketose group.

**(5) PERKIN CONDENSATION**

Q.4 Ans. (A)

Q.5 Ans. (C, D)

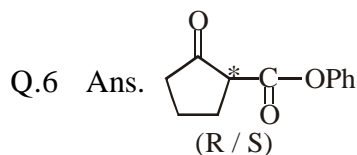
Q.6 Ans. (C)

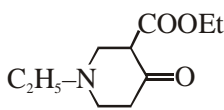
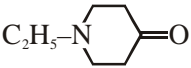
**(6) CLAISEN CONDENSATION**

Q.3 Ans. 4 products

Q.4 Ans.  $\text{C}_6\text{H}_5\text{COCH}_2\text{COOC}_2\text{H}_5$ ,  $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$   
Ethyl benzoylacetate

Q.5 Ans.  $\text{C}_6\text{H}_5-\underset{\text{COCOOC}_2\text{H}_5}{\text{CH}}\text{COOC}_2\text{H}_5$   
Diethyl- $\alpha$ -oxalylphenyl acetate



Q.7 Ans. (G) , (H)   
1-Ethyl-4-piperidone

**(7) Beayer villiger oxidation**

Q.1 Ans.(B)

Q.2. Ans.(D)



## CARBONYL COMPOUND

### EXERCISE # O-I

Q.1 Arrange these compounds in decreasing order of reactivity for the nucleophilic attack :

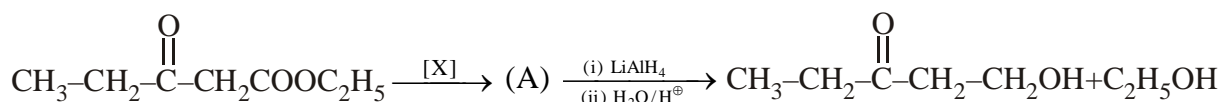
- (I) Acid chloride      (II) Aldehyde      (III) Ketone      (IV) Ester

Select the correct answer from the codes given below :

- (A) I > II > III > IV      (B) IV > III > II > I      (C) III > II > I > IV      (D) I > IV > II > III

CL0001

Q.2 In the given reaction

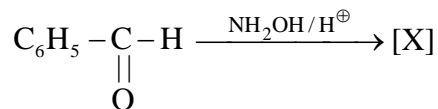


[X] will be :

- (A) HCHO      (B)  $\begin{array}{c} \text{CH}_2\text{-OH} \\ | \\ \text{CH}_2\text{-OH} \end{array} + \text{H}^{\oplus}$       (C)  $\begin{array}{c} \text{CH}_2\text{-OH} \\ | \\ \text{CH}_2\text{-OH} \end{array} + \overset{\ominus}{\text{O}}\text{H} \quad \text{(D) HCN}$

CL0002

Q.3 In the given reaction:



[X] will be:

- (A) Only syn oxime      (B) Only anti oxime  
(C) Mixture of syn and anti oxime      (D) Secondary amide

CL0003

Q.4 Acetophenone can be obtained by the distillation of :

- (A)  $(\text{C}_6\text{H}_5\text{COO})_2\text{Ca}$       (B)  $(\text{CH}_3\text{COO})_2\text{Ca}$   
(C)  $(\text{C}_6\text{H}_5\text{COO})_2\text{Ca}$  and  $(\text{CH}_3\text{COO})_2\text{Ca}$       (D)  $(\text{C}_6\text{H}_5\text{COO})_2\text{Ca}$  and  $(\text{HCOO})_2\text{Ca}$

CL0004

Q.5 Gem dihalide on hydrolysis gives :

- (A) Vic diol      (B) Gem diol  
(C) Carbonyl compound      (D) Carboxylic acid

CL0005

Q.6 Acetal or ketal is:

- (A) Vic dialkoxy compound      (B)  $\alpha$ ,  $\omega$ -dialkoxy compound  
(C)  $\alpha$ -alkoxy alcohol      (D) Gem dialkoxy compound

CL0006

Q.7 Cross cannizzaro reaction is example of :

- (A) Redox reaction      (B) Disproportionation  
(C) Both (A) and (B)      (D) Only oxidation

CL0007

Q.8 Acetaldehyde can be converted into  $\text{HOCH}_2 - \underset{\text{CH}_2\text{OH}}{\overset{\text{CH}_2\text{OH}}{\text{C}}} - \text{CH}_2\text{OH}$  by which reagent ?

- (A) KOH  
(B) KOH followed by LAH  
(C) excess of HCHO and KOH  
(D) KCN followed by SBH

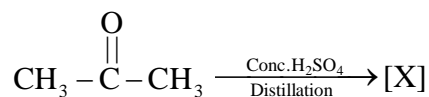
CL0008

Q.9 Which one of the combinations will give propanaldehyde on dry distillation ?

- (A)  $(\text{C}_6\text{H}_5\text{COO})_2\text{Ca}$  and  $(\text{HCOO})_2\text{Ca}$   
(B)  $(\text{CH}_3\text{COO})_2\text{Ca}$  and  $(\text{CH}_3\text{CH}_2\text{-COO})_2\text{Ca}$   
(C)  $(\text{CH}_3\text{-CH}_2\text{-COO})_2\text{Ca}$  and  $(\text{HCOO})_2\text{Ca}$   
(D)  $(\text{CH}_3\text{COO})_2\text{Ca}$  and  $(\text{CH}_3\text{COO})_2\text{Ca}$

CL0009

Q.10 In the given reaction :



[X] will be :

- (A) Methyl oxide  
(B) Phorone  
(C) 1, 3, 5-Trimethylbenzene  
(D) 2-Butyne

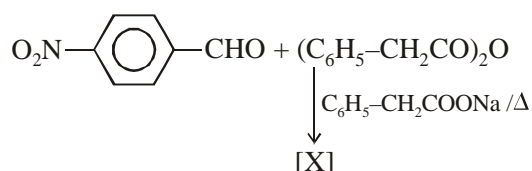
CL0010

Q.11 Grignard reagents can not give carbonyl compounds with :

- (A)  $\text{CO}_2$   
(B)  $\text{RCOCl}$   
(C)  $\text{RCN}$   
(D)  $\text{RCOOR}$

CL0011

Q.12 The product of the reaction :



will be :

- (A)  $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{COOH}$   
(B)  $\text{NO}_2-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{COOH}$   
(C)  $\text{C}_6\text{H}_5-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{COOH}$   
(D)  $\text{NO}_2-\text{C}_6\text{H}_4-\text{CH}=\underset{\text{C}_6\text{H}_5}{\text{C}}-\text{COOH}$

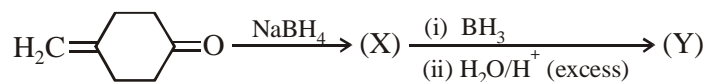
CL0012

Q.13 Cyanohydrin of which compound on hydrolysis will give lactic acid ?

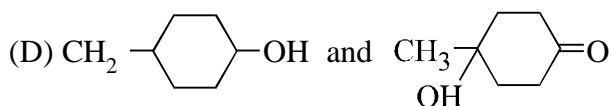
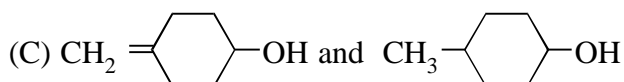
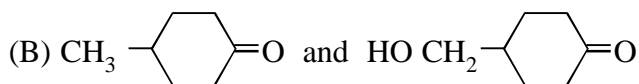
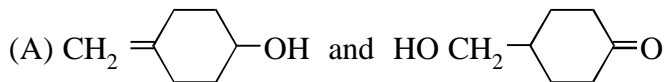
- (A)  $\text{C}_6\text{H}_5\text{CHO}$   
(B)  $\text{HCHO}$   
(C)  $\text{CH}_3\text{CHO}$   
(D)  $\text{CH}_3-\text{CH}_2-\text{CHO}$

CL0013

Q.14 In the given reaction :



(X) and (Y) are :

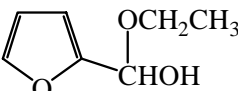
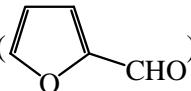


CL0014

Q.15 Acetaldehyde cannot give :

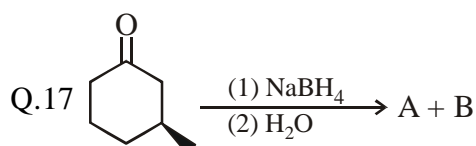
- (A) Iodoform test      (B) Lucas test      (C) Benedict test      (D) Tollens test

CL0015

Q.16 Compound  formed by the reaction of furfural () with ethanol is :

- (A) an aldol      (B) an acetal      (C) a ketal      (D) a hemiacetal

CL0016

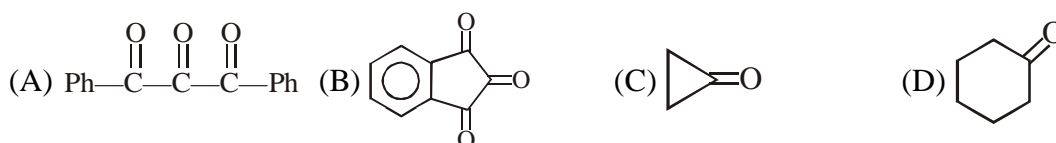


Identify relationship between A & B products ?

- (A) Diastereoisomers      (B) Enantiomers      (C) Positional isomer      (D) Identical

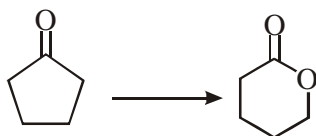
CL0017

Q.18 Which of the following does not form a stable hydrate by the addition of  $\text{H}_2\text{O}$ ?



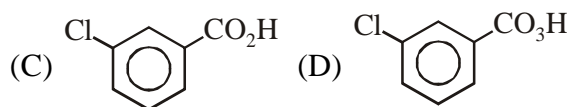
CL0018

Q.19 The conversion

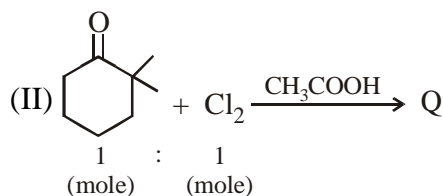
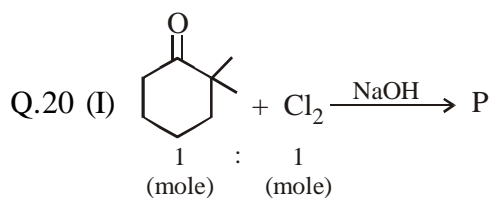


can be effected by using the reagent

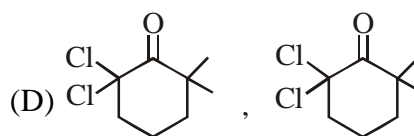
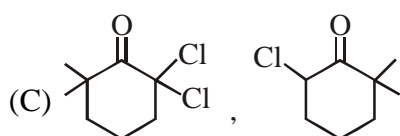
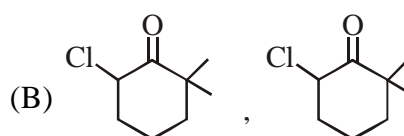
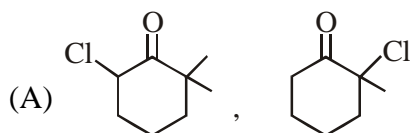
(A) Tollen's reagent      (B)  $O_3$



CL0019



Organic product P & Q are respectively -



CL0020

Q.21 Total number of stereoisomers of major product (Q) are :



(A) 0

(B) 4

(C) 8

(D) 2

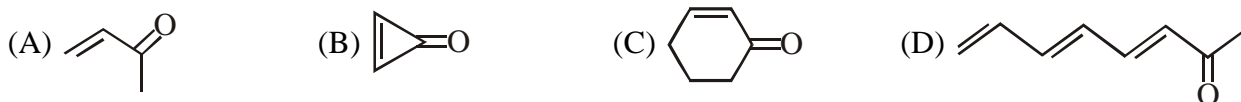
CL0021

Q.22 An organic compound (A),  $C_5H_{10}O$ , reacts with hydrazine to form a hydrazone derivative (B). The hydrazone (B) on being heated with KOH at about  $180^\circ C$ , gives n-pentane. The compound (A) does not respond positively to Tollen's reagent and to the iodoform test. The compound (A) is

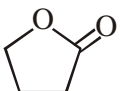


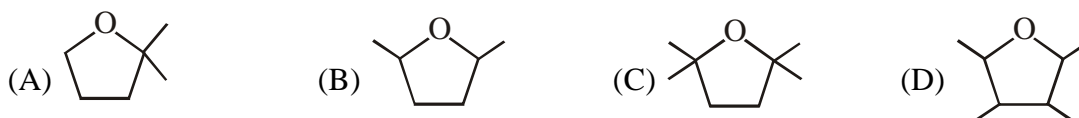
CL0022

Q.23 The compound having the highest dipole moment is :



CL0023

Q.24   $\xrightarrow[(2) H_2O]{(1) \text{ Excess MeMgCl}}$  (A)  $\xrightarrow[H_2SO_4]{\text{conc.}}$  'B' Identify 'B' product ?



CL0024

**Question No. 25 to 27 (3 questions)**

An alkene (A)  $C_{16}H_{16}$  on ozonolysis gives only product (B)  $C_8H_8O$ . (B) also can be obtained by hydrolysis of the product obtained by reaction between cyano benzene and  $CH_3MgBr$ . (A) can show geometrical isomerism and it can decolourise  $Br_2$  water. (B) on treatment with  $SeO_2$  produces (C)

Q.25 Which is not correct about (A) ?

- (A) A is optically inactive  
 (B) On catalytic hydrogenation 'trans' form of A produces racemic mixture  
 (C) A can be prepared by Wittig reaction on acetophenone with  $Ph_3P = C(CH_3)Ph$ .  
 (D) On treatment with per acid followed by hydrolysis 'trans' form of A produces racemic mixture

CL0025

Q.26 Which is not correct about B ?

- (A) It gives iodoform test  
 (B) On treatment with  $LiAlH_4$ ,  $H_2O$  it produces a compound which also responds to iodoform test.  
 (C) It gives Tollen's test  
 (D) On treatment with  $NH_2NH_2$  followed by alc. KOH at high temperature, it produces ethyl benzene

CL0026

Q.27 Which is not correct about C?

- (A) On treatment with  $NaBH_4$  it will produce a diol.  
 (B) On treatment with  $OH^-$  (conc.) followed by acidification racemic mixture of a carboxylic acid is obtained  
 (C) It gives Tollen's test  
 (D) It can take part in aldol condensation

CL0027

*(Question No. 28 & 29)*

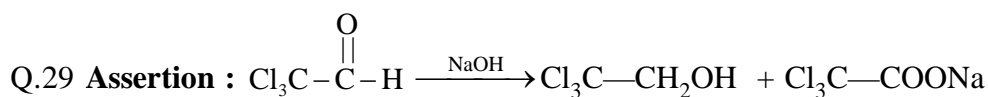
Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

- (A) If both (A) and (R) are true and (R) is the correct explanation of (A)
- (B) If both (A) and (R) are true but (R) is not correct explanation of (A)
- (C) If (A) is true but (R) is false
- (D) If (A) is false and (R) is true

Q.28 **Assertion** : Benzaldehyde with HCN gives two isomeric compounds

**Reason** : Both nitrile and isonitrile compounds are possible when HCN reacts with carbonyl group.

CL0028



**Reason** : There are no  $\alpha$ -H in this compound, so it can't give aldol.

CL0029

EXERCISE # O-II

Q.1 Two isomeric ketones, 3-pentanone and 2-pentanone can be distinguished by :

- (A)  $I_2 / NaOH$                       (B)  $NaSO_3H$                       (C)  $NaCN / HCl$                       (D) 2,4-DNP

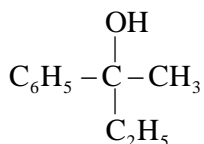
CL0030

Q.2 An optically inactive alcohol (A)  $C_6H_{12}O$  is oxidized by  $MnO_2$  to produce optically inactive carbonyl compound while reduction of (A) by  $H_2/Ni$  produces optically active compound. Possible structure(s) of alcohol is/are

- (A) Hex-2-ene-1-ol                      (B) Hex-3-ene-2-ol  
(C) 2-Methyl pent-2-ene-1-ol                      (D) 3-Methyl pent-2-ene-1-ol

CL0031

Q.3 Consider the structure of given alcohol:



This alcohol can be prepared from:

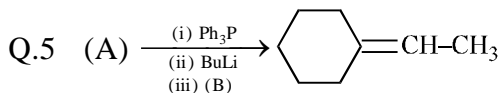
- (A)  $C_6H_5 - \overset{O}{\parallel} C - CH_3$  and  $C_2H_5MgBr$                       (B)  $CH_3 - CH_2 - \overset{O}{\parallel} C - CH_3$  and  $C_6H_5MgBr$   
(C)  $C_6H_5 - \overset{O}{\parallel} C - C_2H_5$  and  $CH_3MgBr$                       (D)  $C_6H_5 - \overset{O}{\parallel} C - Cl$  and  $C_2H_5MgCl$

CL0032

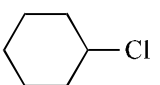
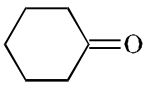
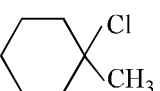
Q.4 Which of the following compounds will not give aldol condensation :

- (A) Acetaldehyde                      (B) Formaldehyde                      (C) Pivaldehyde                      (D) Crotonaldehyde

CL0033



In above reaction (A) and (B) will respectively be

- (A)  &  $CH_3CHO$                       (B)  $CH_3CH_2Cl$  &   
(C)  &  $HCHO$                       (D)  $Cl - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - Cl$  &  $CH_3CHO$

CL0034

Q.6 Stability of hydrates of carbonyl compounds depends on:

- (A) Steric hindrance (B) Presence of -I group on gemdiol carbon  
(C) Intramolecular hydrogen bonding (D) angle strain in carbonyl compound

CL0035

Q.7 Which of the following can be used for protection of carbonyl group

- (A)  $\text{CH}_2\text{OH}-\text{CH}_2\text{OH} / \text{H}^{\oplus}$  (B)  $\text{CH}_2\text{OH}-\text{CH}_2-\text{CH}_2\text{OH} / \text{H}^{\oplus}$   
(C)  $\text{HS}-(\text{CH}_2)_3-\text{SH}$  (D)  $\text{CH}_2\text{OH}-\text{CH}_2-\text{CHO}$

CL0036

Q.8 Which of the following(s) will form stable hemiketal :

- (A)  $\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ph}$  (B)  $\text{HO}-(\text{CH}_2)_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$   
(C)  $\text{CH}_2\text{OH}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CHOH})_3-\text{CH}_2-\text{OH}$  (D)  $\text{H}_3\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$

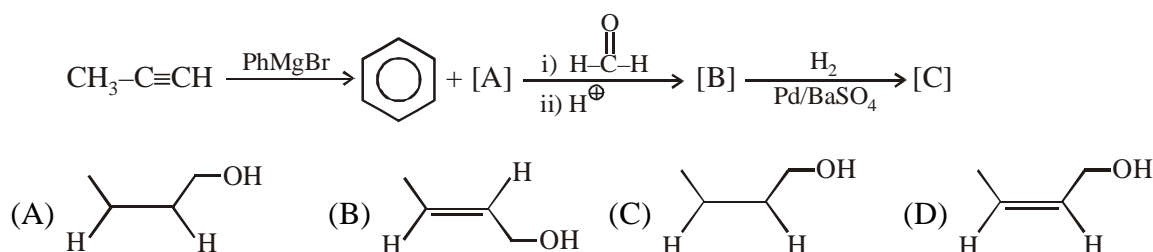
CL0037

Q.9 Mixture of  $\text{Ph}-\text{CHO}$  &  $\text{HCHO}$  is treated with  $\text{NaOH}$  then Cannizzaro reaction involves:

- (A) Oxidation of  $\text{HCHO}$  (B) Reduction of  $\text{HCHO}$   
(C) Oxidation of  $\text{Ph}-\text{CHO}$  (D) Reduction of  $\text{Ph}-\text{CHO}$

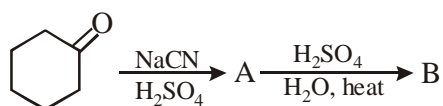
CL0038

Q.10 Final product in the given reaction sequence is :

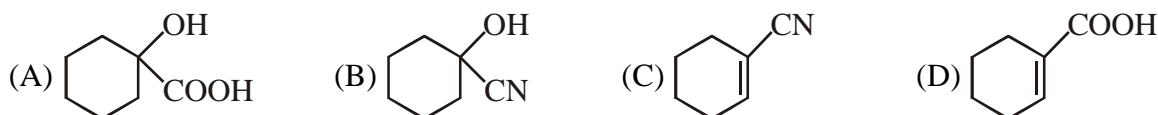


CL0039

Q.11 Consider the following sequence of reactions.

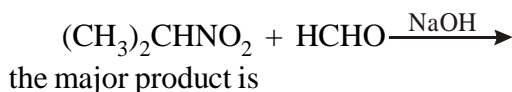


The major product (B) is :

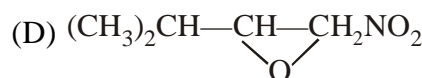
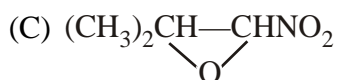
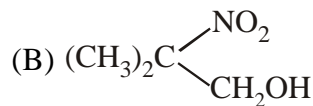


CL0040

Q.12 In the reaction

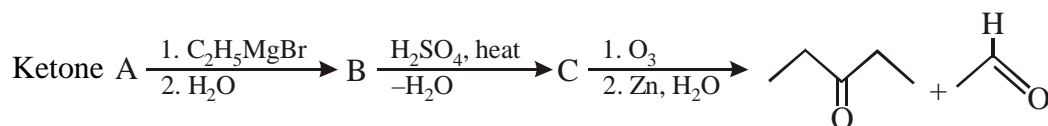




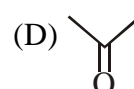
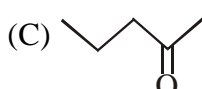
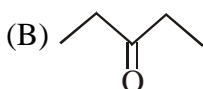
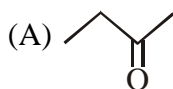


CL0041

Q.13 Consider the following sequence of reactions.

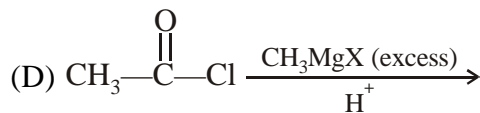
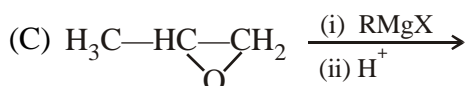
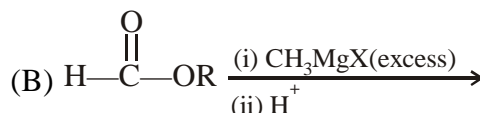
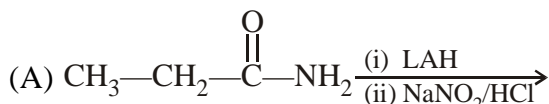


The ketone (A) is :



CL0042

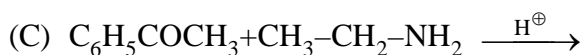
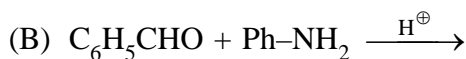
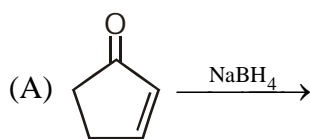
Q.14 Which of the following reactions will give(s) 2° alcohol as a major product :



CL0043

Q.15 Match list-I with list-II :

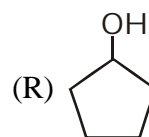
List - I



List - II

(P) Acetal

(Q) Schiff's base



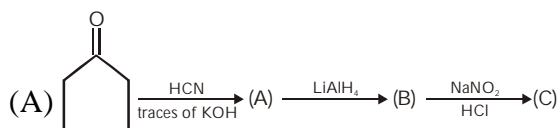
(S) Imine

CL0044

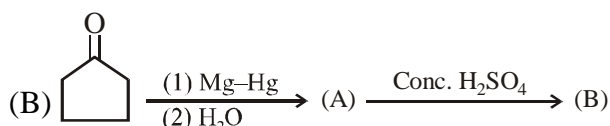
## EXERCISE # S-I

## Q.1 Column - I

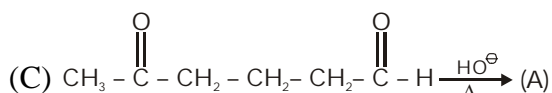
## Column - II



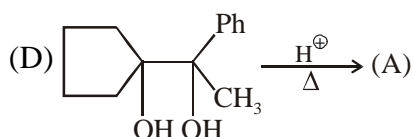
(P) Formation of six member ring takes place



(Q) Final product is Ketone

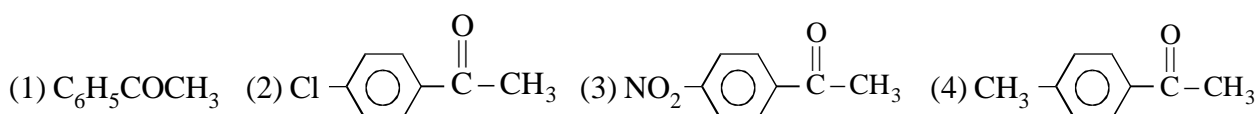


(R) Final product formed will give positive Iodoform test



(S) Final product formed will react with 2,4-DNP. (2,4-Di-nitrophenyl hydrazine)

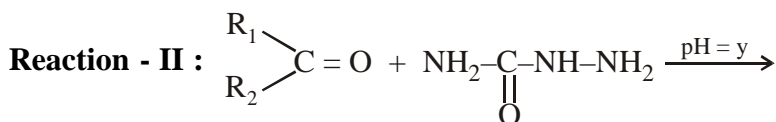
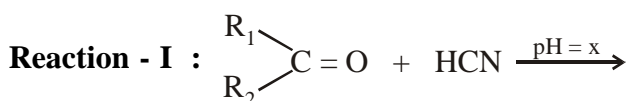
CL0045

Q.2 Arrange the following compounds in decreasing order of  $K_{\text{eq}}$  for hydrate formation.

CL0046

## Paragraph for Q. 03 to 04

Two reactions which are example of nucleophilic attack are given as below .



Q.3 Value of x is :

(A)  $x \leq 4.5$ (B)  $x = 6$ (C)  $x > 7$ 

(D) Can't decide

CL0047

Q.4 Value of y is :

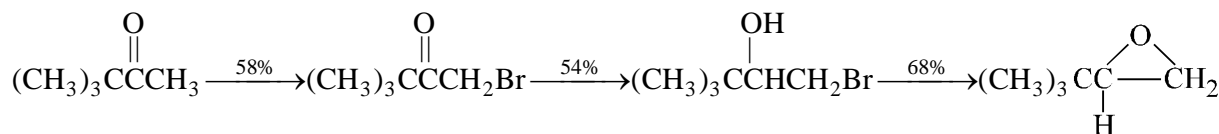
(A)  $x = 4.5$ (B)  $x = 1.5$ (C)  $x = 7$ (D)  $x = 9$ 

CL0048

Q.5 Some Grignard reagents react with ethyl orthoformate, followed by acidic hydrolysis, to give aldehydes. Propose mechanisms for the two steps in this synthesis.

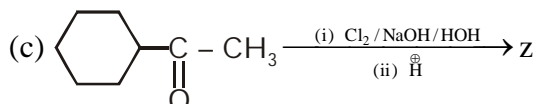
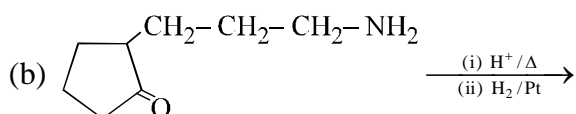
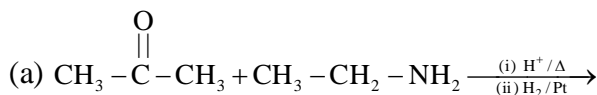
CL0048

Q.6 A synthesis that begins with 3,3-dimethyl-2-butanone gives the epoxide shown. Suggest reagents appropriate for each step in the synthesis.



CL0049

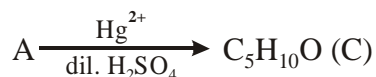
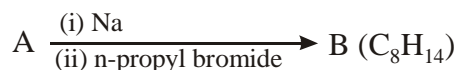
Q.7 Predict the organic products :



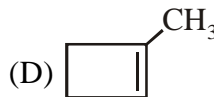
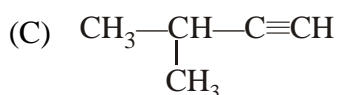
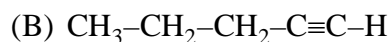
CL0050

Paragraph for Q.No.8 to 9

A (Hydrocarbon) (C ⇒ 88.24%) [Molecular weight of A = 68]



Q.8 'A' can be :



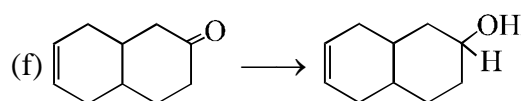
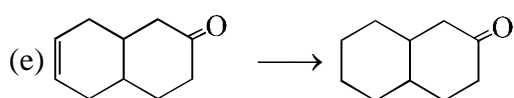
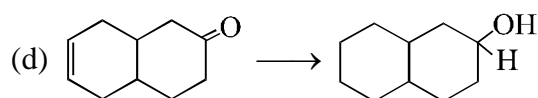
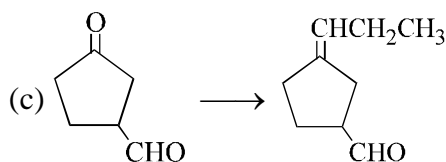
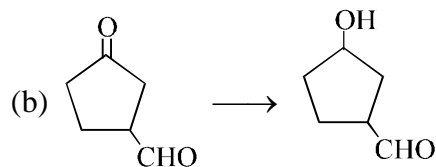
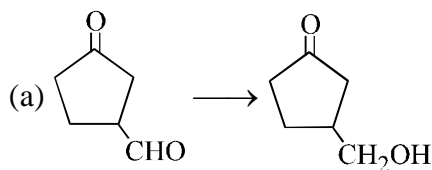
CL0051

Q.9 Correct statement regarding C is.

- (A) C reacts with fehling solution to give red ppt.
- (B) C gives +ve iodoform test
- (C) C give -ve 2, 4, D.N.P test
- (D) C is aldehyde

CL0051

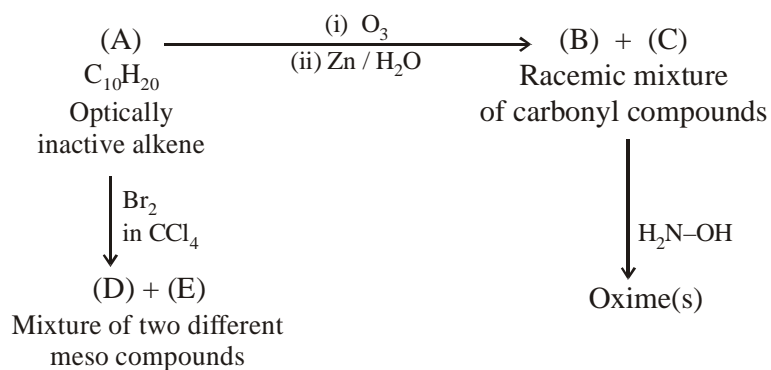
Q.10 Show how you would accomplish the following syntheses efficiently and in good yield. You may use any necessary reagents.



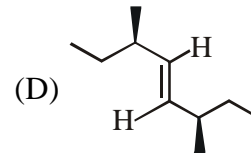
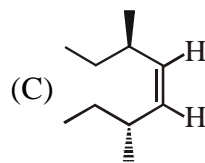
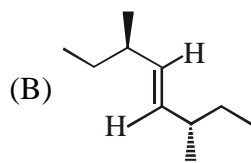
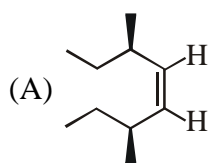
CL0052

### Paragraph for Q.No. 11 to 12

In given reaction sequence



11. Alkene A is :



CL0053

12. How many total oxime(s) is/are obtained

(A) 1

(B) 2

(C) 3

(D) 4

CL0053

## EXERCISE # (MAINS)

1. When  $\text{CH}_2 = \text{CH}-\text{COOH}$  is reduced with  $\text{LiAlH}_4$ , the compound obtained will be -  
 (1)  $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH}$  (2)  $\text{CH}_3-\text{CH}_2-\text{CHO}$  [AIEEE-2003]  
 (3)  $\text{CH}_3-\text{CH}_2-\text{COOH}$  (4)  $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$

CL0054

2. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ? [AIEEE-2004]  
 (1) Phenol (2) Benzaldehyde (3) Butanal (4) Benzoic acid

CL0055

3. Which one of the following is reduced with  $\text{Zn-Hg/HCl}$  to give the corresponding hydrocarbon [AIEEE-2004]  
 (1) Butan-2-one (2) Acetic acid (3) Acetamide (4) Ethyl acetate

CL0056

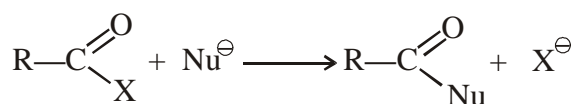
4. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is  
 (1)  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaCl}$  (2)  $\text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$  [AIEEE-2004]  
 (3)  $\text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{OH} + \text{NaOH}$  (4)  $\text{CH}_3\text{Cl} + \text{C}_2\text{H}_5\text{COONa}$

CL0057

5. The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is - [AIEEE-2005]  
 (1) Acidic dichromate (2) Acidic permanganate  
 (3) Pyridinium chloro-chromate (4) Chromic anhydride in glacial acetic acid

CL0058

6. Rate of the reaction- [AIEEE-2005]

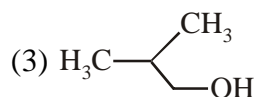


is fastest when X is -

- (1)  $\text{NH}_2$  (2)  $\text{Cl}$  (3)  $\text{OCOR}$  (4)  $\text{OC}_2\text{H}_5$

CL0059

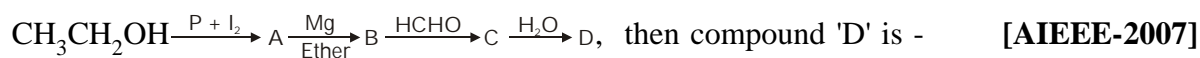
7. Among the following the one that gives positive iodoform test upon reaction with  $\text{I}_2$  and  $\text{NaOH}$  is - [AIEEE-2006]  
 (1)  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$  (2)  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$



- (4)  $\text{PhCHOHCH}_3$

CL0060

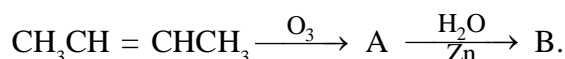
8. In the following sequence of reactions



- (1) Butanal (2) n-Butyl alcohol  
 (3) n-Propyl alcohol (4) Propanal

CL0061

9. In the following sequence of reactions, the alkene affords the compound 'B' :- [AIEEE-2008]



The compound B is

- (1)  $\text{CH}_3\text{CH}_2\text{CHO}$       (2)  $\text{CH}_3\text{COCH}_3$       (3)  $\text{CH}_3\text{CH}_2\text{COCH}_3$       (4)  $\text{CH}_3\text{CHO}$

CL0062

10. Bakelite is obtained from phenol by reacting with [AIEEE-2008]

- (1)  $(\text{CH}_2\text{OH})_2$       (2)  $\text{CH}_3\text{CHO}$       (3)  $\text{CH}_3\text{COCH}_3$       (4)  $\text{HCHO}$

CL0063

11. Which of the following on heating with aqueous KOH, produces acetaldehyde ? [AIEEE-2009]

- (1)  $\text{CH}_2\text{ClCH}_2\text{Cl}$       (2)  $\text{CH}_3\text{CHCl}_2$       (3)  $\text{CH}_3\text{COCl}$       (4)  $\text{CH}_3\text{CH}_2\text{Cl}$

CL0064

12. In Cannizzaro reaction given below :- [AIEEE-2009]



the slowest step is :-

- (1) The abstraction of proton from the carboxylic group  
 (2) The deprotonation of  $\text{PhCH}_2\text{OH}$   
 (3) The attack of  $:\ddot{\text{O}}\text{H}^-$  at the carboxyl group  
 (4) The transfer of hydride to the carbonyl group

CL0065

13. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is :- [AIEEE-2010]

- (1) Ethene      (2) Propene      (3) 1-Butene      (4) 2-Butene

CL0066

14. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of :- [AIEEE-2011]

- (1) An isopropyl group      (2) An acetylenic triple bond  
 (3) Two ethylenic double bonds      (4) A vinyl group

CL0067

15. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds :- [AIEEE-2011]

- (1) 2-Methyl - 1- pentene      (2) 1-Pentene  
 (3) 2-Pentene      (4) 2-Methyl-2-pentene

CL0068

16. Trichloroacetaldehyde was subjected to assumed Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate and another compound. The other compound is :-  
[AIEEE-2011]

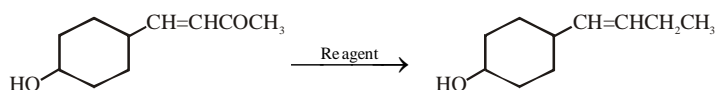
- (1) 2,2,2-Trichloropropanol (2) Chloroform  
(3) 2,2,2-Trichloroethanol (4) Trichloromethanol

CL0069

17. Silver Mirror test is given by which one of the following compounds? [AIEEE-2011]  
(1) Formaldehyde (2) Benzophenone (3) Acetaldehyde (4) Acetone

CL0070

18. In the given transformation, which of the following is the most appropriate reagent ? [AIEEE-2012]



- (1)  $\text{NaBH}_4$  (2)  $\text{NH}_2\text{NH}_2, \text{OH}^-$  (3)  $\text{Zn} - \text{Hg} / \text{HCl}$  (4)  $\text{Na}, \text{Liq. NH}_3$

CL0071

19. Iodoform can be prepared from all except :- [AIEEE-2012]

- (1) Isobutyl alcohol (2) Ethyl methyl ketone  
(3) Isopropyl alcohol (4) 3-Methyl-2-butanone

CL0072

20. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is :- [JEE(Main)-2014]

- (1) 2-Butyne (2) 2-Butene (3) Acetylen (4) Ethene

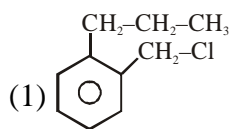
CL0073

21. The most suitable reagent for the conversion of  $\text{R} - \text{CH}_2 - \text{OH} \rightarrow \text{R} - \text{CHO}$  is :- [JEE(Main)-2014]

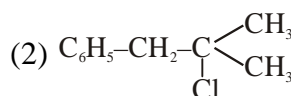
- (1)  $\text{CrO}_3$  (2) PCC (Pyridinium chlorochromate)  
(3)  $\text{KMNO}_4$  (4)  $\text{K}_2\text{Cr}_2\text{O}_7$

CL0074

22. A compound A with molecular formula  $\text{C}_{10}\text{H}_{13}\text{Cl}$  gives a white precipitate on adding silver nitrate solution. A on reacting with alcoholic KOH gives compound B as the main product. B on ozonolysis gives C and D. C gives Cannizaro reaction but not aldol condensation. D gives aldol condensation but not Cannizaro reaction. A is : [JEE(Main)-2015]



- (3)  $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$

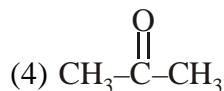
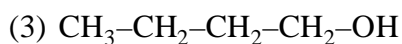
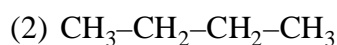
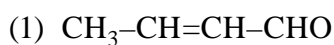
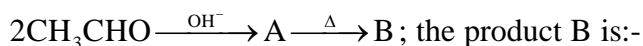


- (4)

CL0075

23. In the reaction sequence

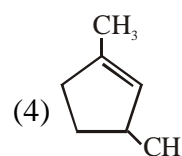
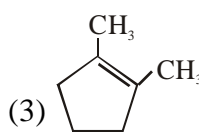
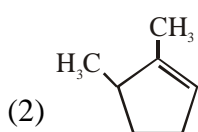
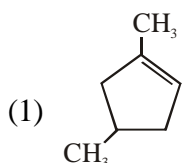
[JEE(Main)-2015]



CL0076

24. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis?

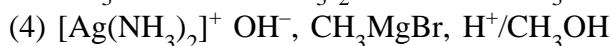
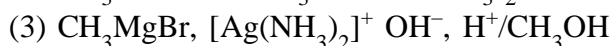
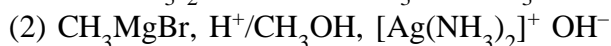
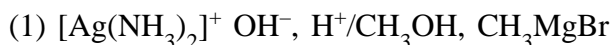
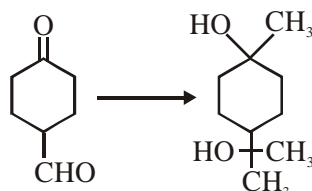
[JEE(Main) 2015]



CL0077

25. The correct sequence of reagents for the following conversion will be :-

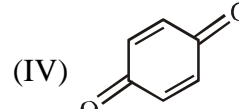
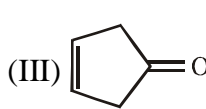
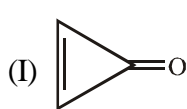
[JEE(Main)-2017]



CL0078

26. Which of the following compounds will show highest dipole moment ?

[JEE(Main-on-line)-2017]



(1) (II)

(2) (III)

(3) (I)

(4) (IV)

CL0079

27. Glucose on prolonged heating with HI gives :

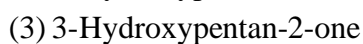
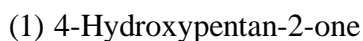
[JEE(Main)-2018]



CL0080

28. Which of the following compounds will most readily be dehydrated to give alkene under acidic condition?

[JEE(Main-on-line)-2018]

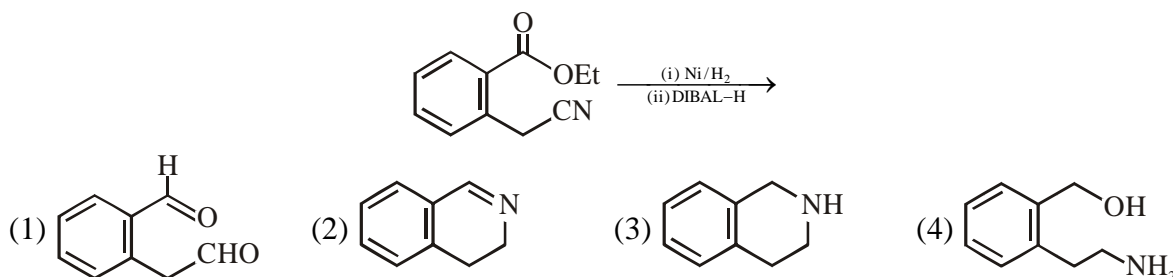


CL0081



29. The major product of the following reaction is:

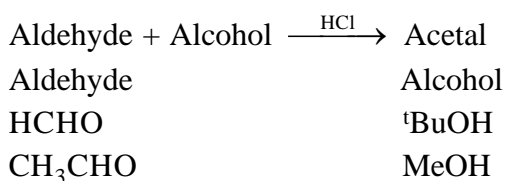
[JEE-Main(January)-2019]



CL0082

30. In the following reaction

[JEE-Main(January)-2019]



The best combinations is :

- |                                  |   |
|----------------------------------|---|
| (1) HCHO and MeOH                | (2) HCHO and <sup>t</sup> BuOH                |
| (3) CH <sub>3</sub> CHO and MeOH | (4) CH <sub>3</sub> CHO and <sup>t</sup> BuOH |

CL0083

31. The aldehydes which will not form Grignard product with one equivalent Grignard reagents are :

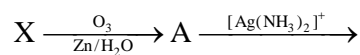
[JEE-Main(January)-2019]



CL0084

32. An unsaturated hydrocarbon X absorbs two hydrogen molecules on catalytic hydrogenation, and also gives following reaction :

[JEE-Main(Jan)-2020]



B (3-oxo-hexanedicarboxylic acid)

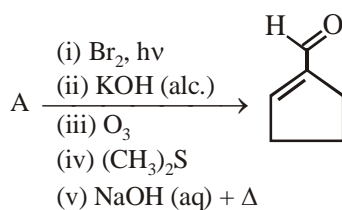
X will be :-



CL0085

33. In the following reaction A is :

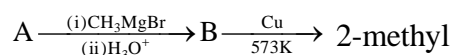
[JEE-Main(Jan)-2020]



CL0086

34. Consider the following reactions

[JEE-Main(Jan)-2020]



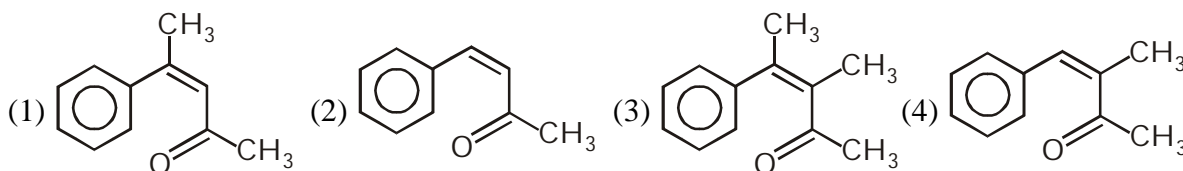
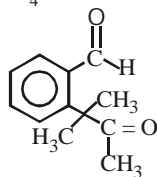
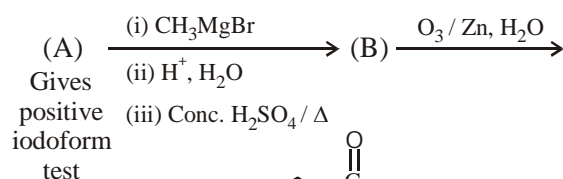
2-butene

The mass percentage of carbon in A is \_\_\_\_\_.

CL0087

35. Identify (A) in the following reaction sequence :

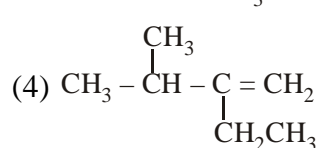
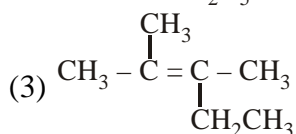
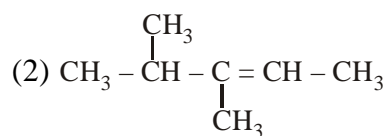
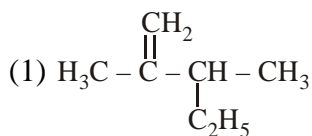
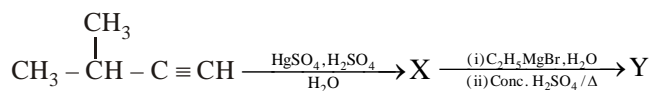
[JEE-Main(Jan)-2020]



CL0088

36. The major product (Y) in the following reactions is :

[JEE-Main(Jan)-2020]



CL0089

## EXERCISE-(IIT QUESTIONS)

Q.1 Which of the following has the most acidic hydrogen: [IIT 2000]

- (A) 3-hexanone  
 (B) 2,4-hexanedione  
 (C) 2,5-hexanedione  
 (D) 2,3-hexandione

CL0090

Q.2 A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives:

- (A) benzyl alcohol and sodium formate  
 (B) sodium benzoate and methyl alcohol  
 (C) sodium benzoate and sodium formate  
 (D) benzyl alcohol and methyl alcohol [IIT 2001]

CL0091

Q.3 1-propanol & 2-propanol can be best distinguished by : [IIT 2001]

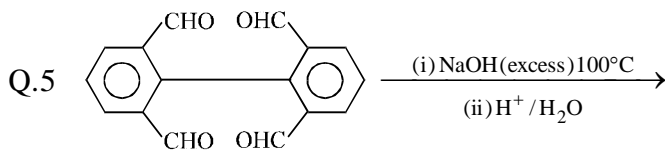
- (A) Oxidation with alkaline  $\text{KMnO}_4$  followed by reaction with Fehling solution  
 (B) Oxidation with acidic dichromate followed by reaction with Fehling solution  
 (C) Oxidation by heating with copper followed by reaction with Fehling solution  
 (D) Oxidation with concentrated  $\text{H}_2\text{SO}_4$  followed by reaction with Fehling solution

CL0092

Q.4 Compound A (molecular formula  $\text{C}_3\text{H}_8\text{O}$ ) is treated with acidified potassium dichromate to form a product B (molecular formula  $\text{C}_3\text{H}_6\text{O}$ ). B forms a shining silver mirror on warming with ammonical silver nitrate. B when treated with an aqueous solution of  $\text{H}_2\text{NCONHNH}_2$ , HCl and sodium acetate gives a product C. Identify the structure of C. [IIT 2002]

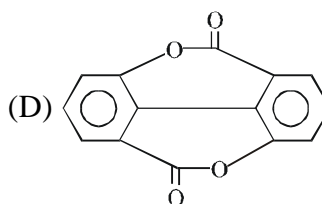
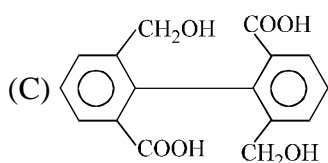
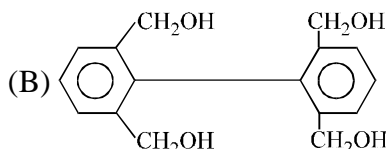
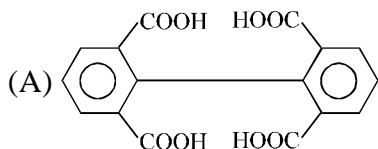
- (A)  $\text{CH}_3\text{CH}_2\text{CH} = \text{NNHCONH}_2$   
 (B)  $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} = \text{NNHCONH}_2$   
 (C)  $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} = \text{NCONHNH}_2$   
 (D)  $\text{CH}_3\text{CH}_2\text{CH} = \text{NCONHNH}_2$

CL0093

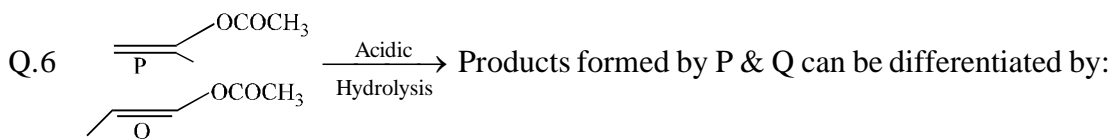


[IIT 2003]

any one of the products formed is :



CL0094



[IIT 2003]

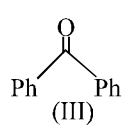
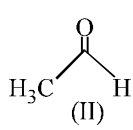
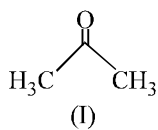
(A) 2, 4 DNP

(B) Lucas reagent ( $\text{ZnCl}_2$ ) conc. HCl(C)  $\text{NaHSO}_3$ 

(D) Fehlings solution

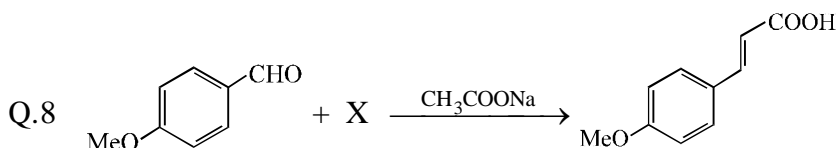
CL0095

Q.7 The order of reactivity of phenyl Magnesium Bromide with the following compounds is [IIT 2004]

(A)  $\text{II} > \text{III} > \text{I}$ (B)  $\text{I} > \text{III} > \text{II}$ (C)  $\text{II} > \text{I} > \text{III}$ 

(D) All react with the same rate

CL0096



[IIT 2005]

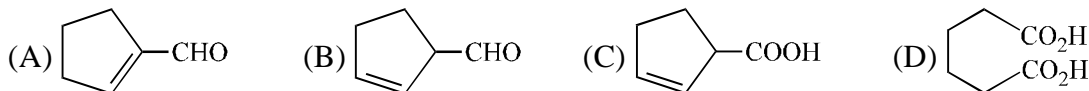
What is X?

(A)  $\text{CH}_3\text{COOH}$ (B)  $\text{BrCH}_2$ ,  $\text{COOH}$ (C)  $(\text{CH}_3\text{CO})_2\text{O}$ (D)  $\text{CHO}-\text{COOH}$ 

CL0097

- Q.9 The smallest ketone and its next homologue are reacted with  $\text{NH}_2\text{OH}$  to form oxime.  
 (A) Two different oximes are formed (B) Three different oximes are formed  
 (C) Two oximes are optically active (D) All oximes are optically active [IIT 2006]  
**CL0098**

- Q.10 Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is  
 [IIT-JEE(ADV.)- 2007]

**CL0099**

- Q.11 **Statement-1** : Glucose gives a reddish-brown precipitate with Fehling's solution.

*because***Statement-2** : Reaction of glucose with Fehling's solution gives  $\text{CuO}$  and gluconic acid.

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True. [IIT-JEE(ADV.)- 2007]  
**CL0100**

- Q.12 Match the compounds/ion in column I with their properties/ reaction in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

[IIT-JEE(ADV.)- 2007]

**Column I**

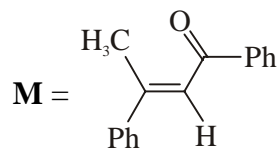
- (A)  $\text{C}_6\text{H}_5\text{CHO}$   
 (B)  $\text{CH}_3\text{C}\equiv\text{CH}$   
 (C)  $\text{CN}^-$   
 (D)  $\text{I}^-$

**Column II**

- (P) gives precipitate with 2,4-dinitrophenylhydrazine  
 (Q) gives precipitate with  $\text{AgNO}_3$   
 (R) is a nucleophile  
 (S) is involved in cyanohydrin formation

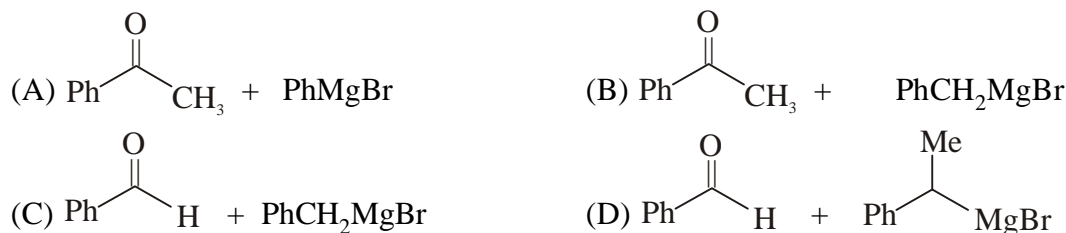
**CL0101****Paragraph for Question No. 13 to 15**

A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I**. Ozonolysis of **I** leads to compounds **J** and **K**. Compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**.

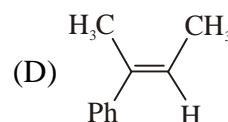
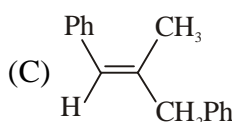
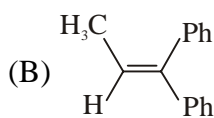
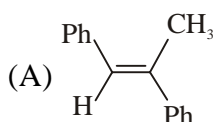


- Q.13 Compound **H** is formed by the reaction of

[IIT-JEE(ADV.)- 2008]

**CL0102**

Q.14 The structure of compound **I** is



[IIT-JEE(ADV.)- 2008]

CL1012

Q.15 The structures of compounds **J**, **K** and **L**, respectively, are

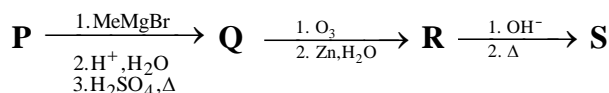


[IIT-JEE(ADV.)- 2008]

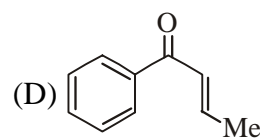
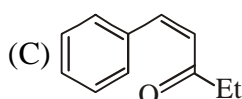
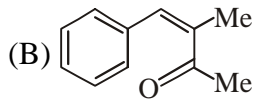
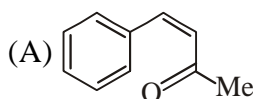
CL1012

### Paragraph for Question Nos. 16 to 38

A carbonyl compound **P**, which gives positive iodoform test, undergoes reaction with  $\text{MeMgBr}$  followed by dehydration to give an olefin **Q**. Ozonolysis of **Q** leads to a dicarbonyl compound **R**, which undergoes intramolecular aldol reaction to give predominantly **S**.



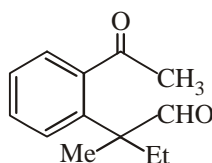
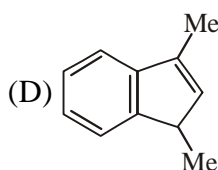
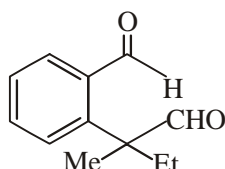
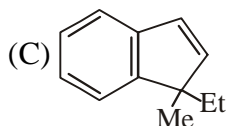
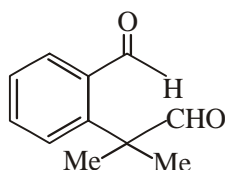
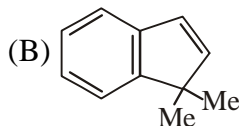
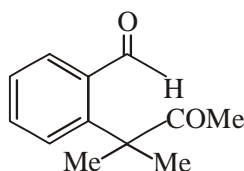
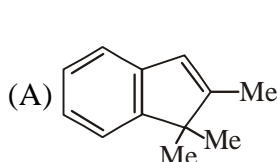
Q.16 The structure of the carbonyl compound **P** is



[IIT-JEE(ADV.)- 2009]

CL1013

Q.17 The structure of the products **Q** and **R**, respectively, are

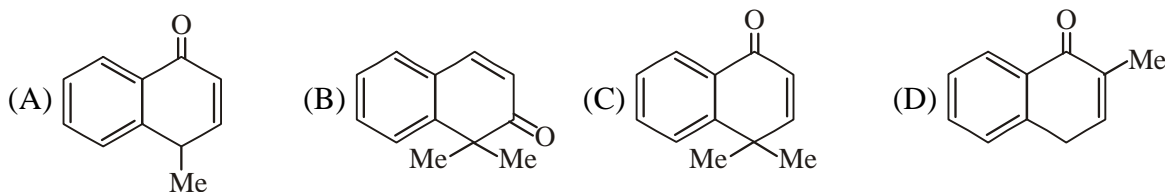


[IIT-JEE(ADV.)- 2009]

CL1013

Q.18 The structure of the product S is

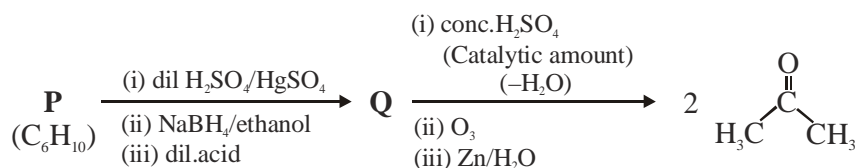
[IIT-JEE(ADV.)- 2009]



CL1013

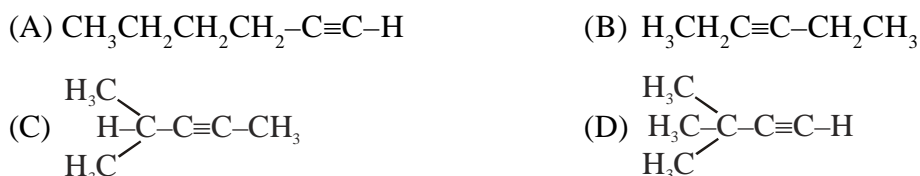
Paragraph for Questions Nos. 19 to 20

An acyclic hydrocarbon P, having molecular formula  $C_6H_{10}$ , gave acetone as the only organic product through the following sequence of reactions, in the which Q is an intermediate organic compound.



Q.19 The structure of compound P is -

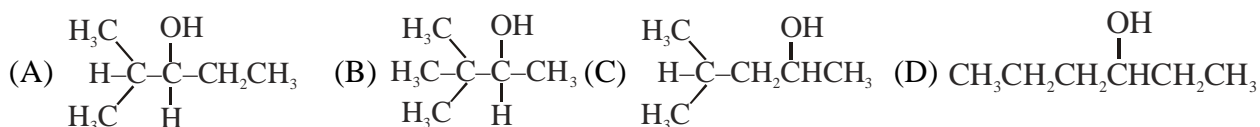
[IIT-JEE(ADV.)- 2011]



CL1014

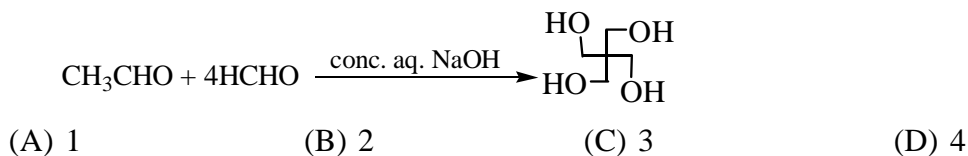
Q.20 The structure of the compound Q is -

[IIT-JEE(ADV.)- 2011]



CL1014

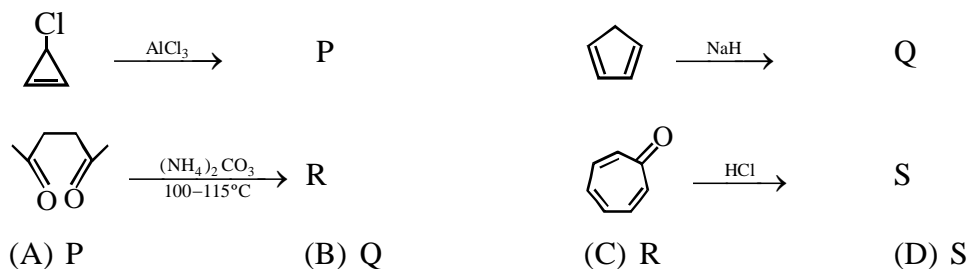
Q.21 The number of aldol reaction(s) that occurs in the given transformation is [IIT-JEE(ADV.)- 2012]



CL1015

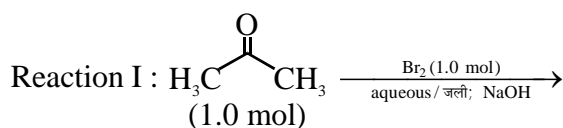
Q.22 Among P, Q, R and S, the aromatic compound(s) is / are :

[IIT-JEE(ADV.)- 2013]

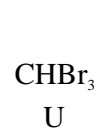
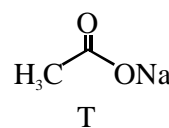
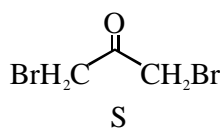
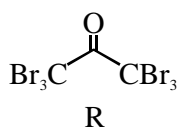
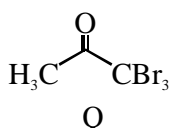
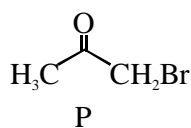
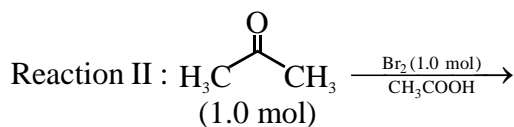


CL1016

Q.23 After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)



[IIT-JEE(ADV.)- 2013]

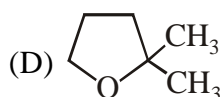
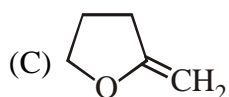
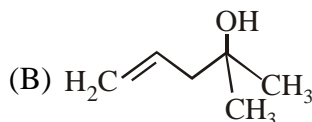
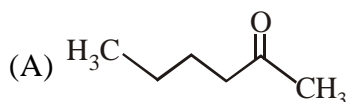
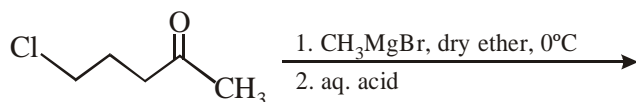


- (A) Reaction I : P and Reaction II : P  
 (B) Reaction I : U, acetone and Reaction II : Q acetone  
 (C) Reaction I : T, U, acetone and Reaction II : P  
 (D) Reaction I : R, acetone and Reaction II : S acetone

CL0107

Q.24 The major product in the following reaction is

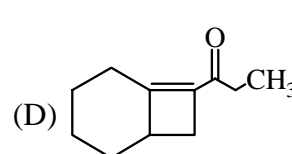
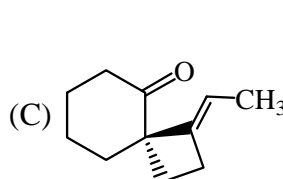
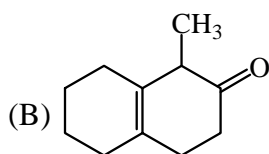
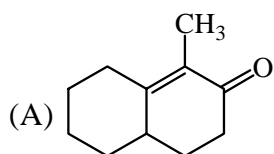
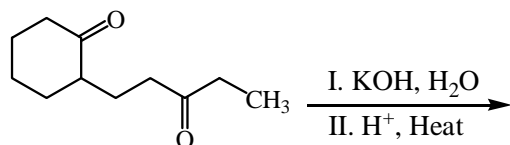
[IIT-JEE(ADV.)- 2014]



CL0108

Q.25 The major product of the following reaction is -

[IIT-JEE(ADV.)- 2015]

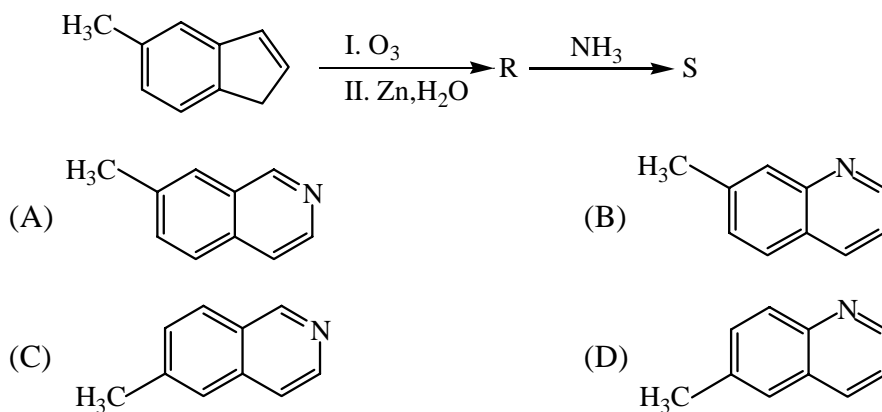


CL0109



Q.26 In the following reactions, the product S is -

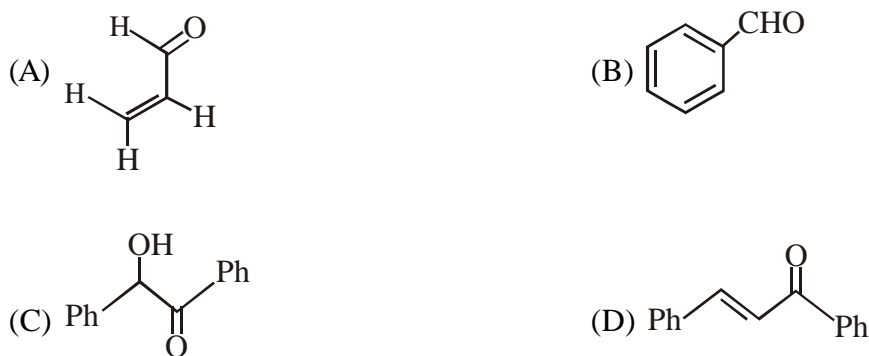
[IIT-JEE(ADV.)- 2015]



CL0110

Q.27 Positive Tollen's test is observed for :

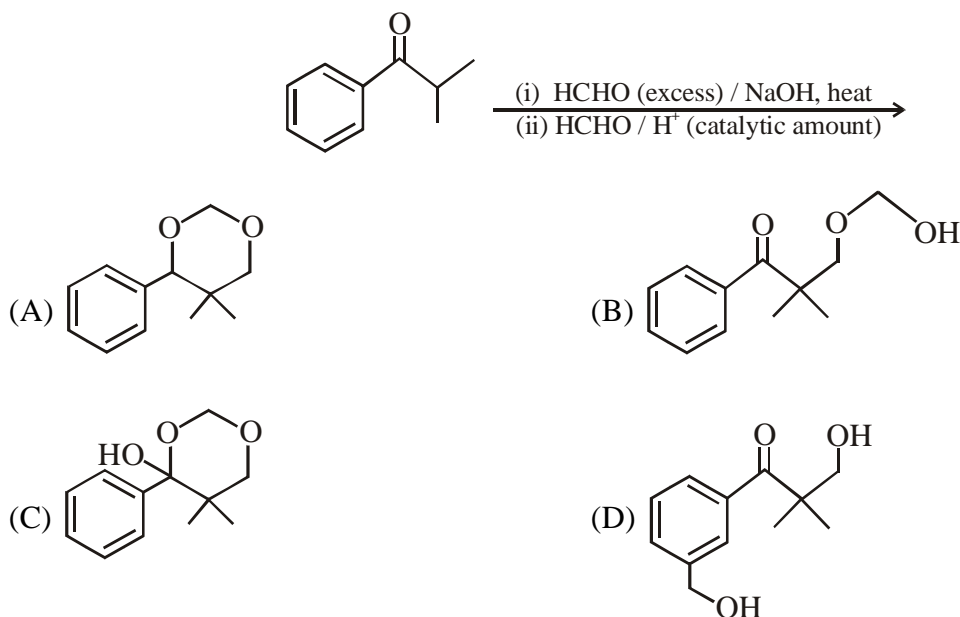
[IIT-JEE(ADV.)- 2016]



CL0111

Q.28 The major product of the following reaction sequence is :

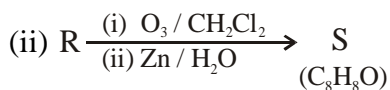
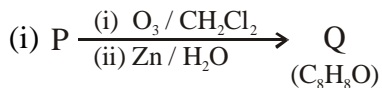
[IITJEE(ADV.)-2016]



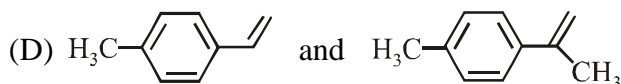
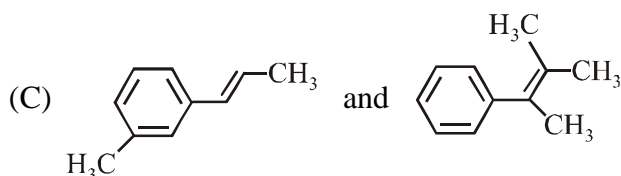
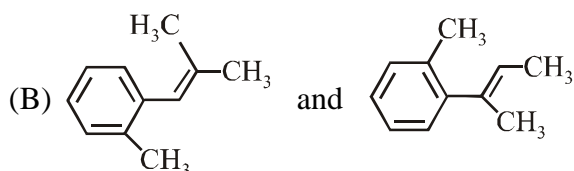
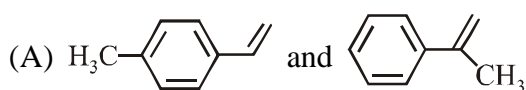
CL0112

Q.29 Compound **P** and **R** upon ozonolysis produce **Q** and **S**, respectively. The molecular formula of **Q** and **S** is  $C_8H_8O$ . **Q** undergoes Cannizzaro reaction but not haloform reaction, whereas **S** undergoes haloform reaction but not Cannizzaro reaction :

[IIT-JEE(ADV.)- 2017]



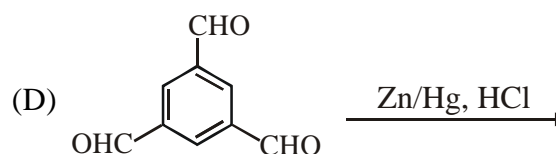
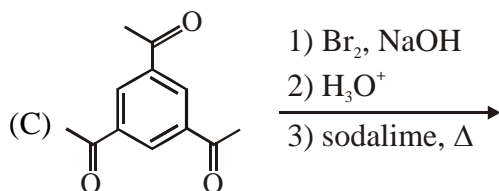
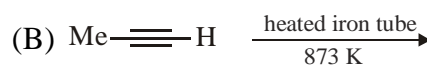
The option(s) with suitable combination of **P** and **R**, respectively, is(are)



CL0113

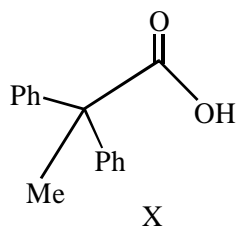
30. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)

[IIT-JEE(ADV.)- 2018]

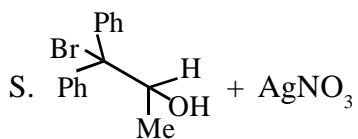
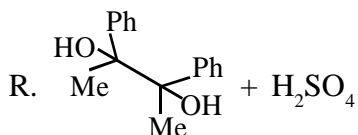
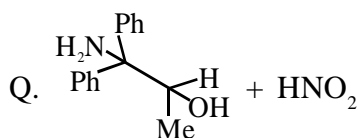
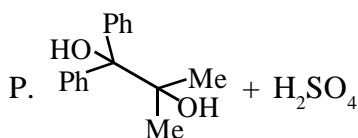


CL0114

31. The desired product X can be prepared by reacting the major product of the reactions in LIST-I with one or more appropriate reagents in LIST-II. [IIT-JEE(Adv.)-2018]  
 (given, order of migratory aptitude: aryl > alkyl > hydrogen)



LIST-I



LIST-II

1. I<sub>2</sub>, NaOH
2. [Ag(NH<sub>3</sub>)<sub>2</sub>]OH
3. Fehling solution
4. HCHO, NaOH
5. NaOBr

The correct option is

- (A) P → 1; Q → 2,3; R → 1,4; S → 2,4      (B) P → 1,5; Q → 3,4; R → 4,5; S → 3  
 (C) P → 1,5; Q → 3,4; R → 5; S → 2,4      (D) P → 1,5; Q → 2,3; R → 1,5; S → 2,3

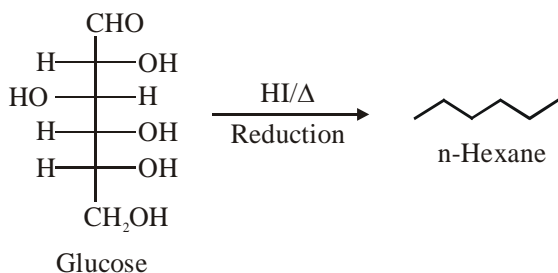
CL0115



EXERCISE # (MAINS)

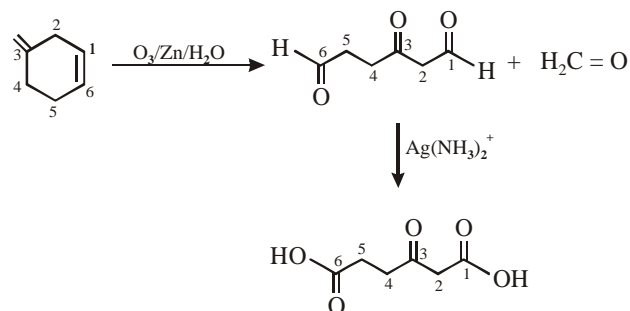
1. Ans. (4)    2. Ans. (2)    3. Ans. (1)    4. Ans. (2)  
 5. Ans. (4)    6. Ans. (2)    7. Ans. (4)    8. Ans. (3)  
 9. Ans. (4)    10. Ans. (4)    11. Ans. (2)    12. Ans. (4)  
 13. Ans. (4)    14. Ans. (4)    15. Ans. (4)    16. Ans. (3)  
 17. Ans. (1, 3)    18. Ans. (2)    19. Ans. (1)    20. Ans. (1)  
 21. Ans. (2)    22. Ans. (2)    23. Ans. (1)    24. Ans. (4)  
 25. Ans. (1)    26. Ans. (3)  
 27. Ans. (4)

Sol.

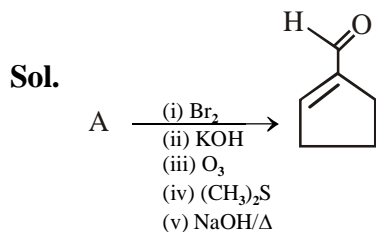


28. Ans. (1)    29. Ans. (2)    30. Ans. (1)    31. Ans. (2)  
 32. Ans. (1)

Sol.

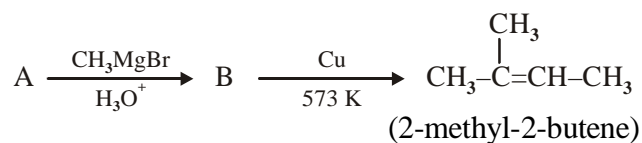


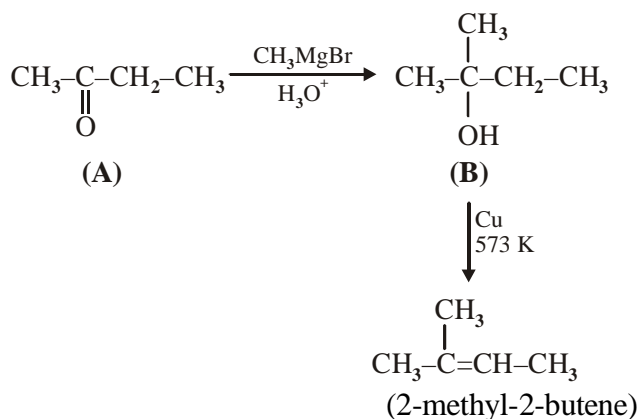
33. Ans. (3)



34. Ans. (66.65 to 66.70)

Sol.





$$\text{C} \Rightarrow 12 \times 4 = 48$$

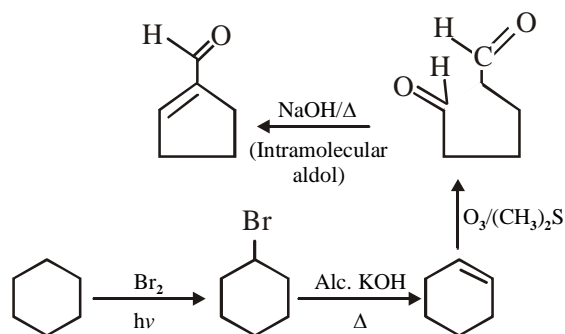
$$\text{H} \Rightarrow 8 \times 1 = 8$$

$$\text{O} \Rightarrow 16 \times 1 = 16$$

---

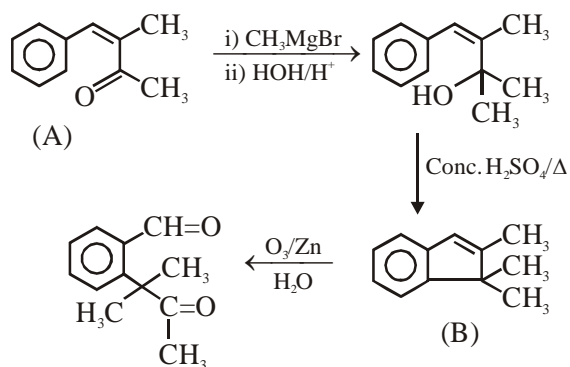

$$\text{Total} \quad 72$$

$$\% \text{ of C} = \frac{48}{72} \times 100 = 66.66\%$$



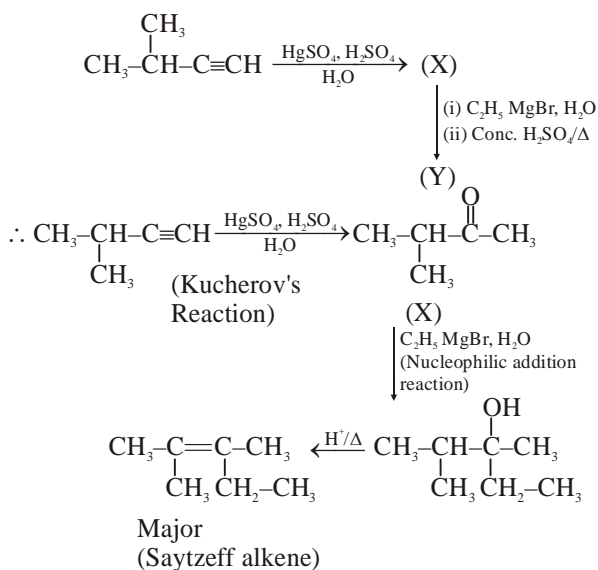
35. Ans. (4)

Sol.



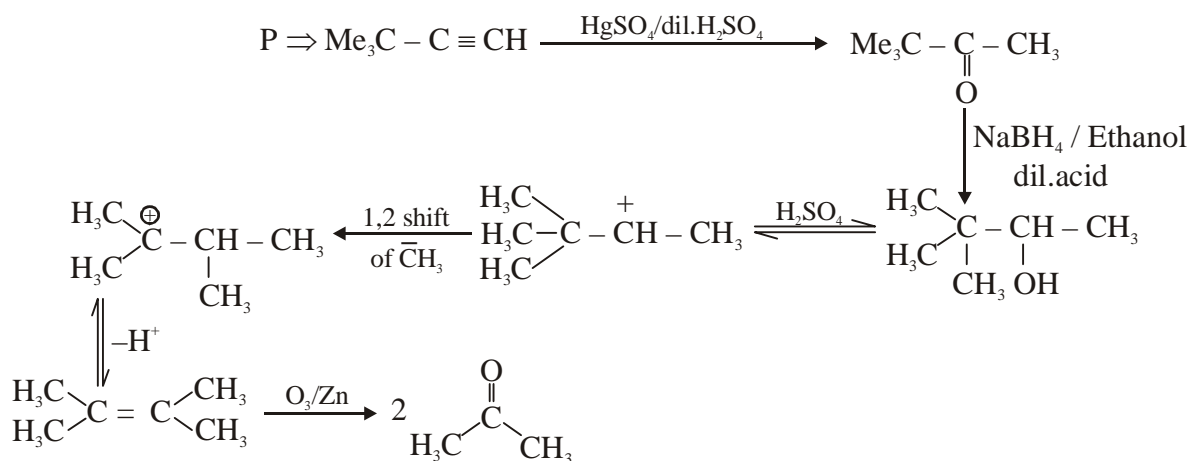
36. Ans. (3)

Sol.

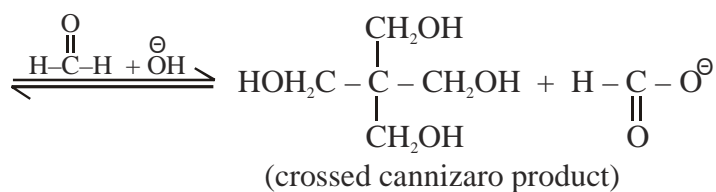
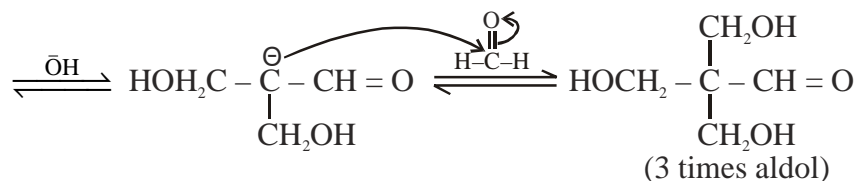
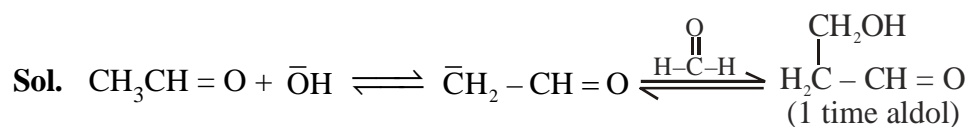


**EXERCISE-#(IIT QUESTIONS)**

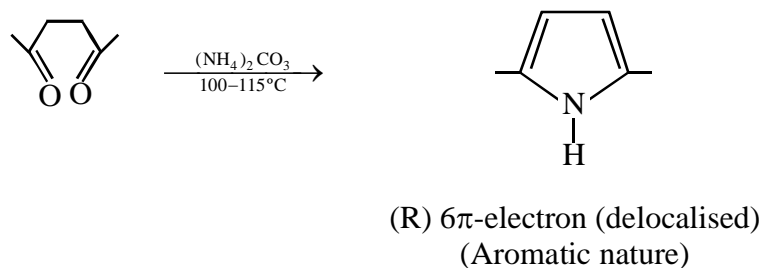
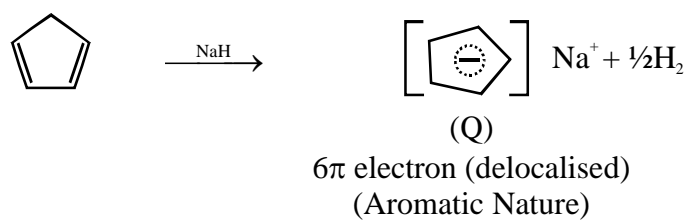
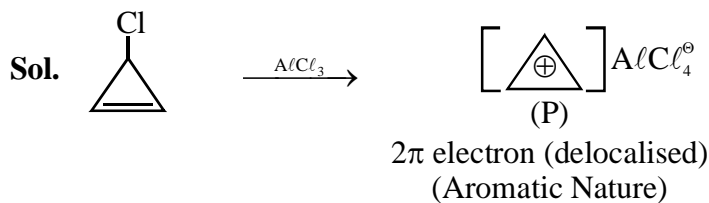
- |   |              |              |              |
|---|--------------|--------------|--------------|
| 1. Ans. (B)                                 | 2. Ans. (A)  | 3. Ans. (C)  | 4. Ans. (A)  |
| 5. Ans. (C)                                 | 6. Ans. (D)  | 7. Ans. (C)  | 8. Ans. (C)  |
| 9. Ans. (B)                                 | 10. Ans. (A) | 11. Ans. (C) |              |
| 12. Ans. (A) P,S; (B) Q; (C) Q,R,S; (D) Q,R | 13. Ans. (B) | 14. Ans. (A) |              |
| 15. Ans. (D)                                | 16. Ans. (B) | 17. Ans. (A) | 18. Ans. (B) |
| 19. Ans. (D)                                |              |              |              |
| 20. Ans.(B)                                 |              |              |              |



21. Ans. (C)

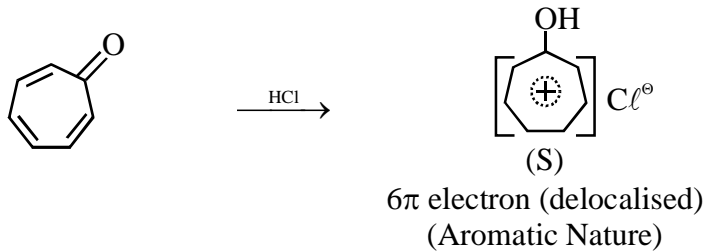
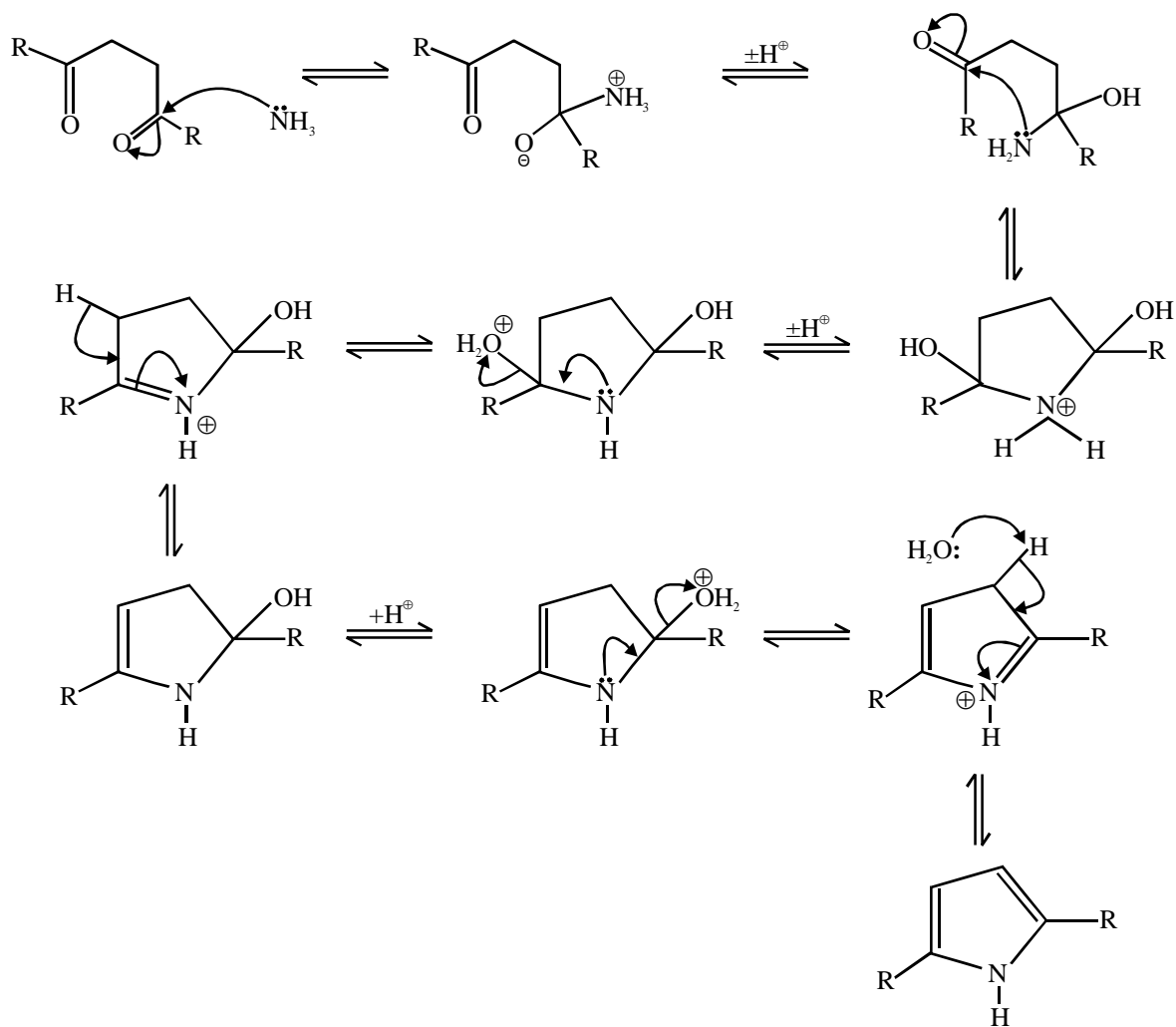


22. Ans. (A,B,C,D)

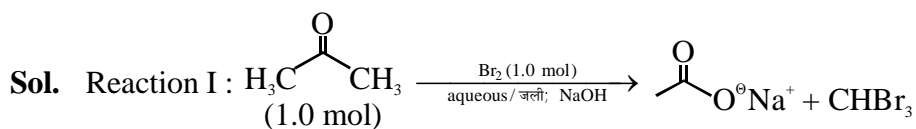


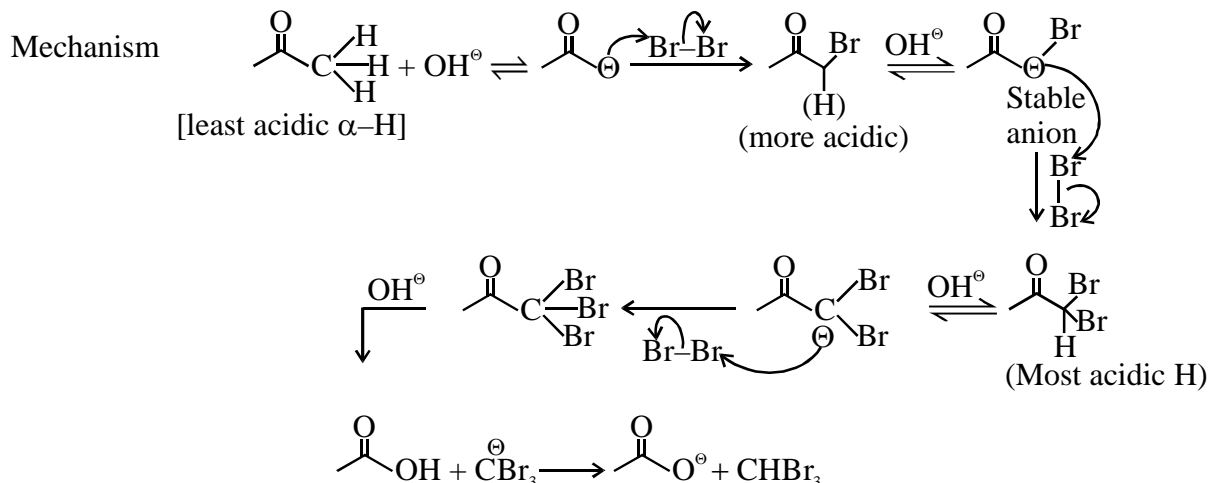


Mechanism :

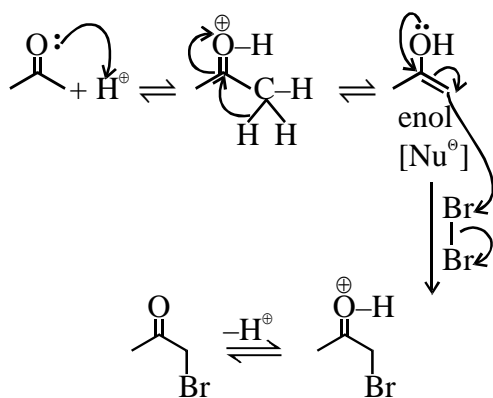
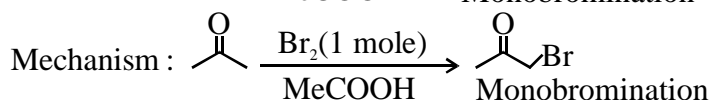
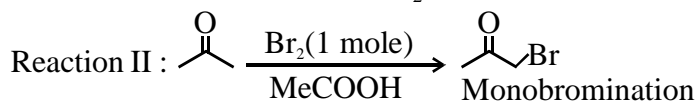


23. Ans. (C)



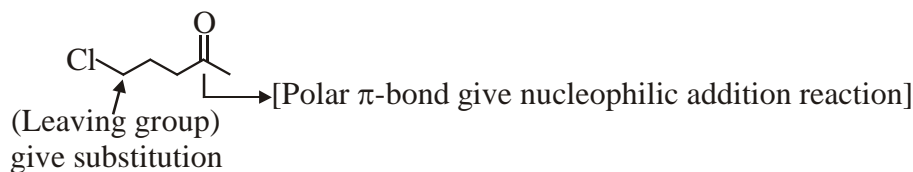


In basic medium halogenation does not stop with replacement of just one hydrogen and poly halogenation takes place because  $\alpha$ -haloketones are more reactive towards base and haloform reaction takes place. In above reaction  $\text{Br}_2$  is limiting agents.



Further bromination is less favourable because of less amount of  $\text{Br}_2$

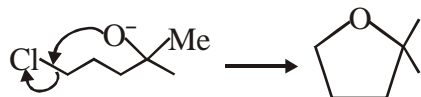
24. Ans. (D)



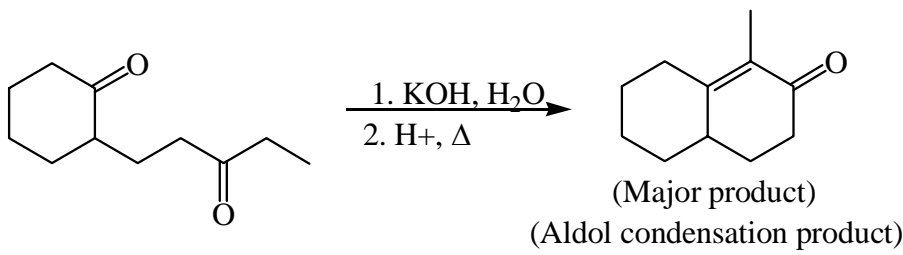
(i) Grignard prefer to give nucleophilic addition on polar  $\pi$ -bond and form anion intermediate.



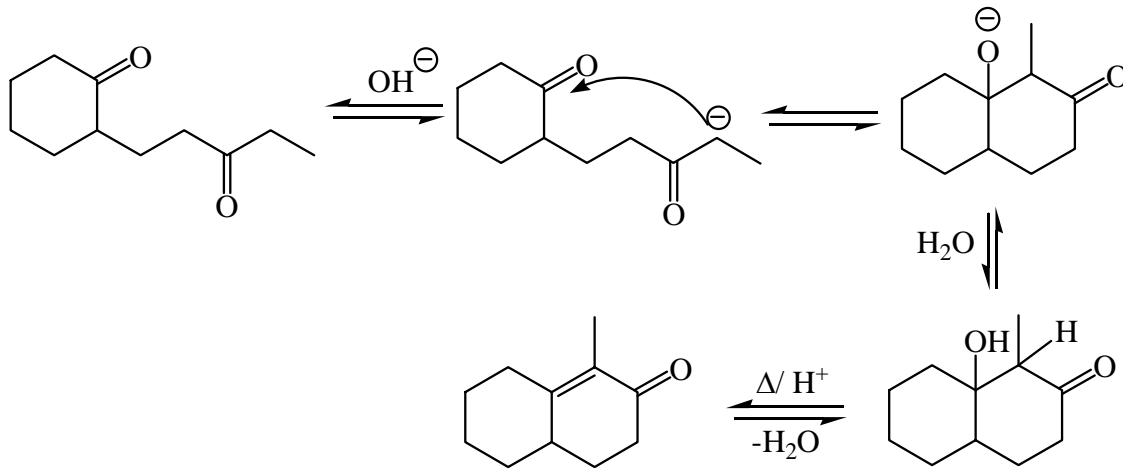
(ii) In next step anion give intramolecular nucleophilic substitution reaction & form 5 membered ring.



25. Ans. (A)

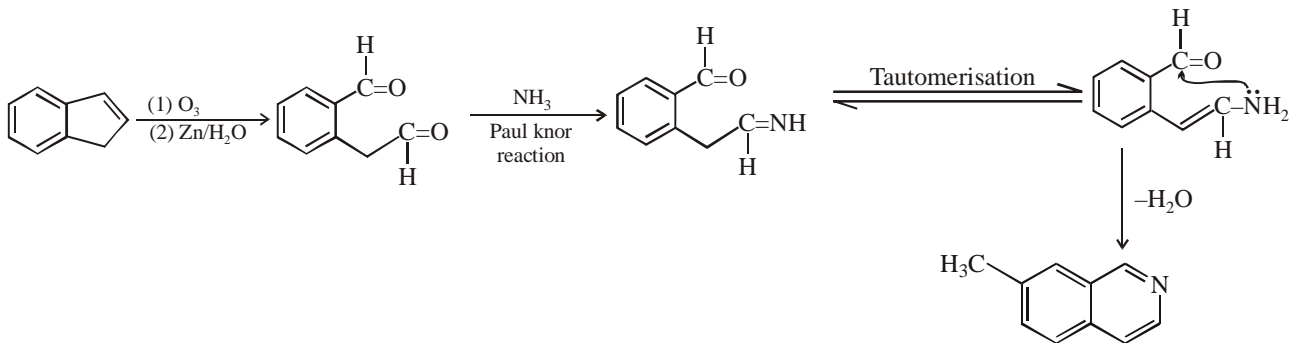


Mechanism :



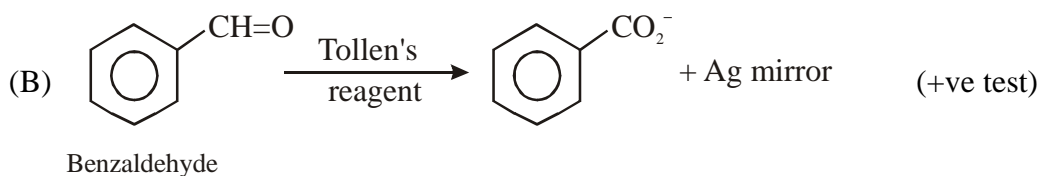
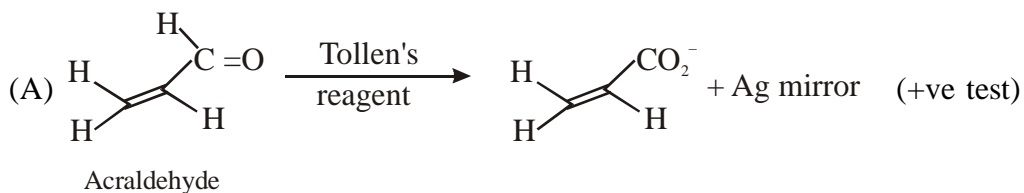
26. Ans.(A)

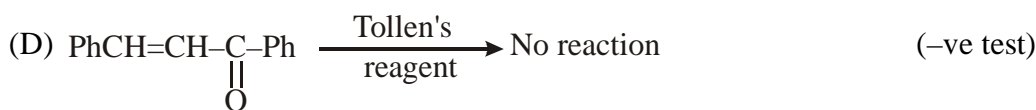
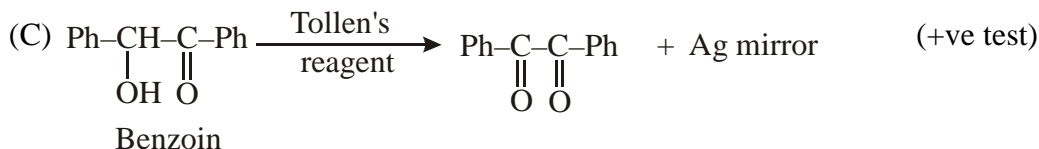
Sol.



27. Ans. (A,B,C)

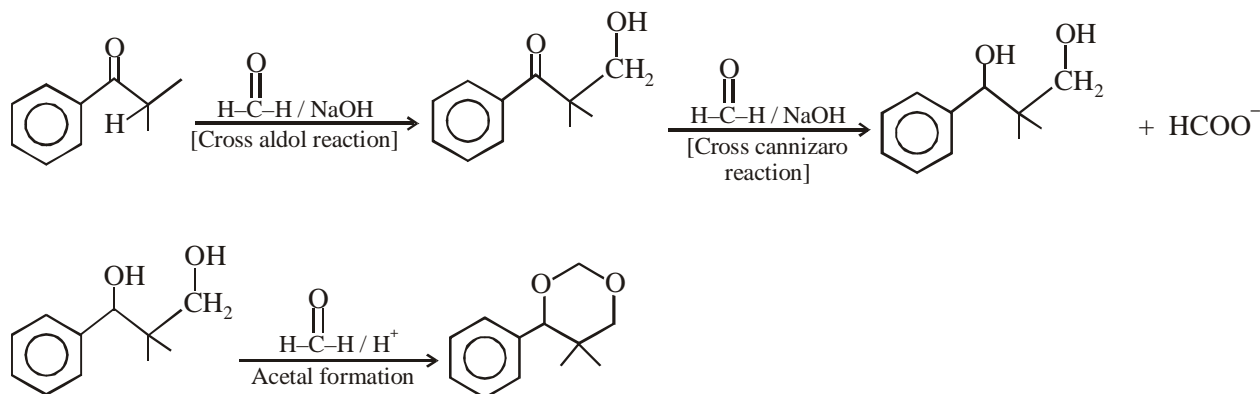
Sol. Tollen's test is given by compounds having aldehyde group. Also  $\alpha$ -hydroxy carbonyl gives positive tollen's test.



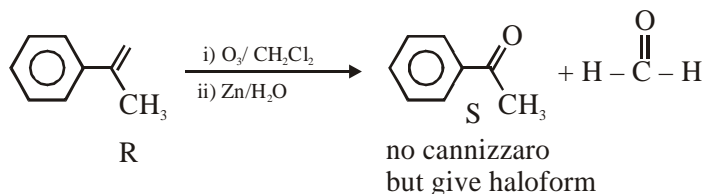
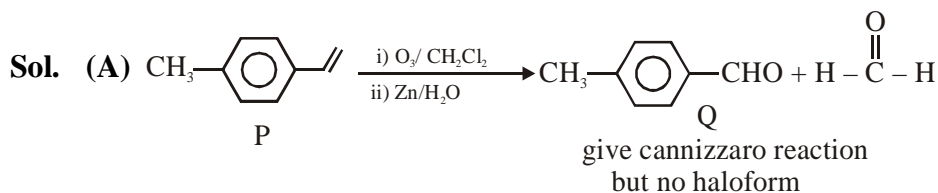


28. Ans. (A)

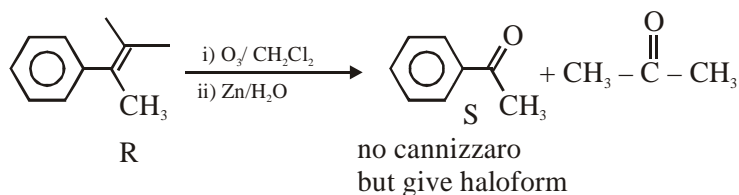
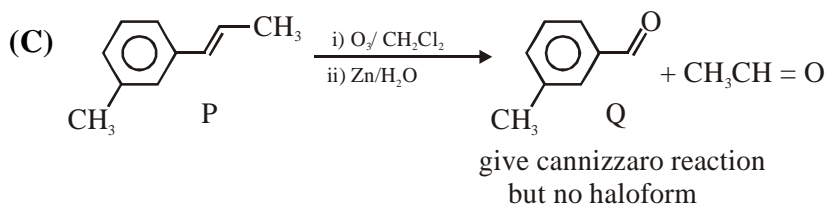
Sol.



29. Ans. (A,C)

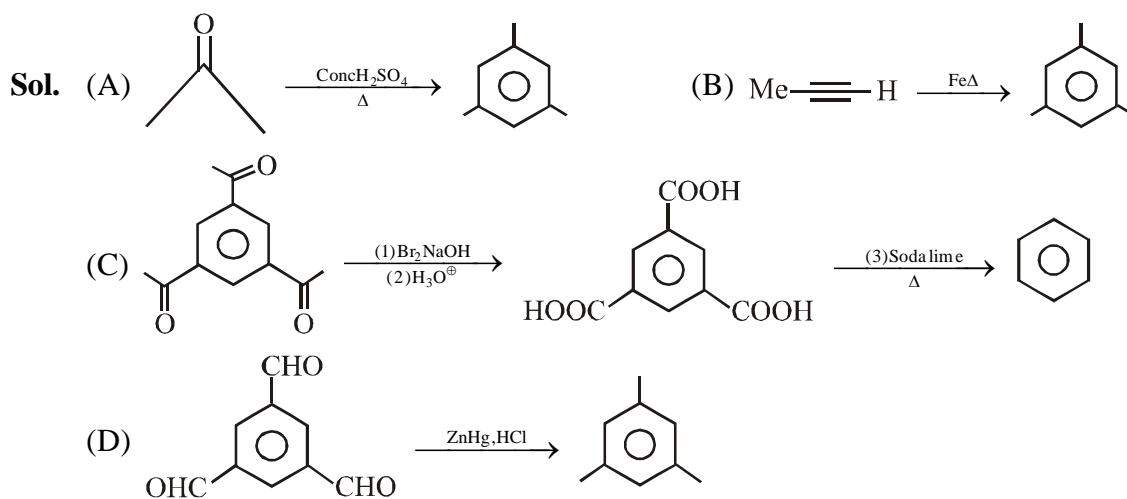


(B) Product of ozonolysis of R is having 9 carbon.



(D) Product of ozonolysis of R is having 9 carbon.

30. Ans. (A,B,D)



31. Ans. (D)



## BIOMOLECULES (AMINO ACIDS AND PROTEINS)

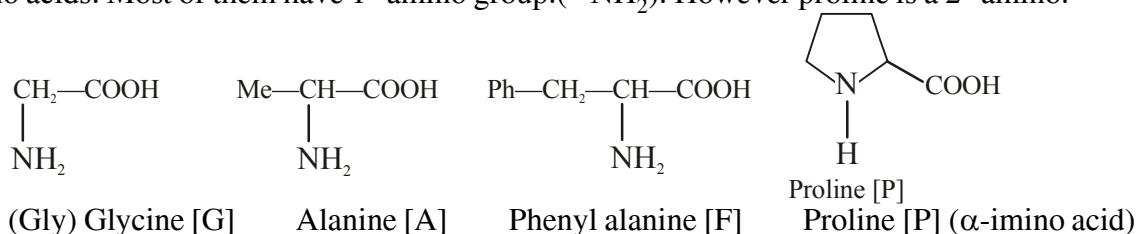
**Proteins:** The name protein is taken from the Greek word "proteios", which means "first". Of all chemical compounds, proteins must almost certainly be ranked first, for they are the substance of life.

Proteins make up a large part of the animal body, they hold it together and they run it. They are found in all living cells.

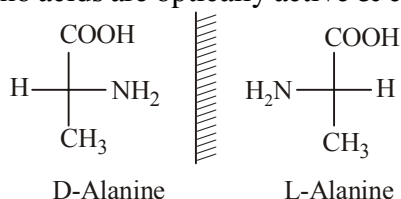
Chemically, proteins are high polymers. They are polyamides and the monomers from which they are derived are the  $\alpha$ -amino carboxylic acids. A single protein molecule contains hundreds or even thousands of amino acid units. These units can be of twenty-odd different kinds. The number of different combinations, i.e., the number of different protein molecules that are possible, is almost infinite.

Bifunctional compounds having an acidic carboxylic group & a basic amino group are known as amino acid.

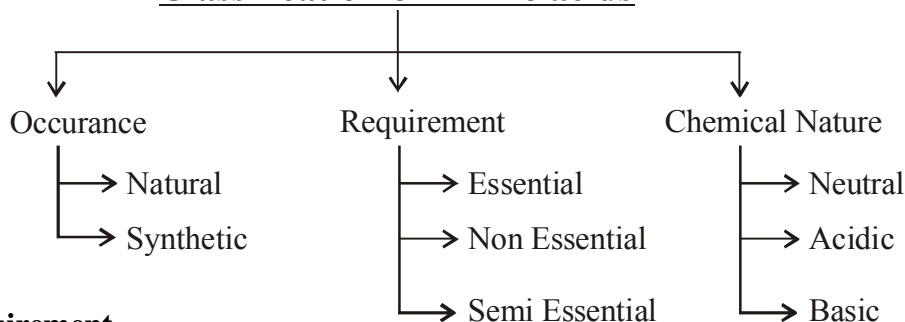
There are 20 amino acids commonly found in proteins and are standard amino acids. All are  $\alpha$  amino acids. Most of them have  $1^\circ$  amino group ( $-\text{NH}_2$ ). However proline is a  $2^\circ$  amino.



All amino acids are chiral molecules with at least one chiral carbon (except glycine,  $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$ ). Except Glycine all other amino acids are optically active & can be assigned D & L configuration.



### Classification of Amino acids



#### Based on requirement.

- Essential amino acids can not be synthesized in human body so dietary intake is required. For any human being 1 gm a day is required.
- Semi essential amino acids can be synthesized in human body but dietary intake is required during growing stages (when more of cell division is required).  
For example : Early childhood, pregnancy and lactating mother.
- Non essential amino acid - Body can synthesize them.

#### Based on chemical nature

**Neutral** - Amino acid having equal number of  $\text{NH}_2$  and  $\text{COOH}$ .

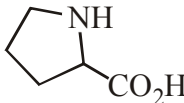
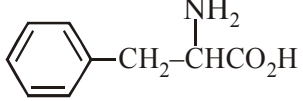
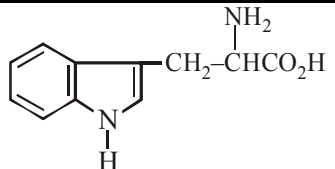
Neutral amino acids are further classified as polar and nonpolar depending on whether their side chains have polar substituents (for example, asparagine with an  $\text{NH}_2\text{CO}$  group) or are completely hydrocarbon in nature (for example alanine, valine etc.).

**Acidic** - Amino acid having more COOH than NH<sub>2</sub> group.

For example : Aspartic acid and glutamic acids, each with a second CO<sub>2</sub>H in their side chain are acidic amino acids.

**Basic** - Amino acid having more NH<sub>2</sub> than COOH group.

For example : Lysine, arginine and histidine)

<i>A-1. Neutral amino acids (with nonpolar side chains)</i>			
NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT [pI]
@Glycine**	Gly(G)	$\begin{array}{c} \text{NH}_2 \\   \\ \text{H}_2\text{C} \\   \\ \text{C}=\text{O} \\   \\ \text{OH} \end{array}$	6.0
Alanine**	Ala(A)	$\begin{array}{c} \text{NH}_2 \\   \\ \text{H}_3\text{C}-\text{CH} \\   \\ \text{C}=\text{O} \\   \\ \text{OH} \end{array}$	6.0
Valine*	Val(V)	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{C}-\text{NH}_2 \\   \quad   \\ \text{CH}_3 \quad \text{C}=\text{O} \\ \quad \quad   \\ \quad \quad \text{OH} \end{array}$	6.0
Leucine*	Leu(L)	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{C}-\text{NH}_2 \\   \quad \quad   \\ \text{CH}_3 \quad \quad \text{C}=\text{O} \\ \quad \quad \quad   \\ \quad \quad \quad \text{OH} \end{array}$	6.0
Isoleucine*	Ile(I)	$\begin{array}{c} \text{CH}_3 \quad \text{NH}_2 \\   \quad   \\ \text{CH}_3\text{CH}_2\text{CH}-\text{CHCO}_2\text{H} \end{array}$	6.0
Methionine*	Met(M)	$\begin{array}{c} \text{NH}_2 \\   \\ \text{CH}_3\text{SCH}_2\text{CH}-\text{CHCO}_2\text{H} \end{array}$	5.7
@@Proline	Pro(P)		6.3
Phenylalanine*	Phe(F)		5.5
Tryptophan*	Trp(W)		5.9



*A -2. Neutral amino acids (with polar, but nonionized side chains)*

NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT [pI]
Asparagine**	Asn(N)	$\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\text{C}=\overset{\text{O}}{\parallel}{\text{OH}}}{\overset{\text{NH}_2}{\text{CH}}}$	5.4
Glutamine**	Gln(Q)	$\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\underset{\text{C}=\overset{\text{O}}{\parallel}{\text{OH}}}{\overset{\text{NH}_2}{\text{CH}}}$	5.7
Serine**	Ser(S)	$\text{HO}-\text{CH}_2-\underset{\text{C}=\overset{\text{O}}{\parallel}{\text{OH}}}{\overset{\text{NH}_2}{\text{CH}}}$	5.7

*A -3. Neutral amino acids (with polar, but nonionized side chains)*

NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT [pI]
Threonine*	Thr	$\begin{array}{c} \text{OH} \quad \text{NH}_2 \\   \quad   \\ \text{CH}_3\text{CH}-\text{CHCO}_2\text{H} \end{array}$	5.6
Tyrosine**	Tyr(Y)	$\text{HO}-\text{C}_6\text{H}_4-\text{CH}_2-\underset{\text{C}=\overset{\text{O}}{\parallel}{\text{OH}}}{\overset{\text{NH}_2}{\text{CH}}}$	5.7
Cysteine	Cys	$\text{HSCH}_2-\underset{\text{C}=\overset{\text{O}}{\parallel}{\text{OH}}}{\overset{\text{NH}_2}{\text{CH}}}$	5.1
‡ Cystine	Cys-Cys	$\begin{array}{c} \text{NH}_2 \quad \quad \quad \text{NH}_2 \\   \quad \quad \quad   \\ \text{HOOCCHCH}_2\text{S}-\text{SCH}_2\text{CHCOOH} \end{array}$	

*B - Acidic amino acids (side chain with carboxylic acid group)*

NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT [pI]
Aspartic acid**	Asp(D)	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\text{C}=\overset{\text{O}}{\parallel}{\text{OH}}}{\overset{\text{NH}_2}{\text{CH}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	2.8
Glutamic Acid	Glu(E)	$\text{O}=\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\underset{\text{C}=\overset{\text{O}}{\parallel}{\text{OH}}}{\overset{\text{NH}_2}{\text{CH}}}$	3.2

<i>C - Basic amino acids (side chain with nitrogenous basic group)</i>			
NAME	ABBREVIATIONS	STRUCTURAL FORMULAE	ISOELECTRIC POINT [pI]
Lysine*	Lys(K)	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{C}=\text{O} \\ \quad \quad \text{OH} \end{array}$	9.7
Arginine*	Arg(R)	$\text{H}_2\text{N}-\overset{\text{NH}}{\underset{\text{H}}{\text{C}}}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{C}=\text{O} \\ \quad \quad \text{OH} \end{array}$	10.8
Histidine*	His(H)		7.6

**Note:**

\* Amino acids with an asterisk are essential amino acids.

\*\* Amino acids with an asterisk are non essential amino acids.

† At pH = 7, Asp and Glu have a net negative charge and exist as anions. At pH = 7, Lys and Arg have a net positive charge and exist as cations. Rest of the amino acids at this pH exist in the neutral form.

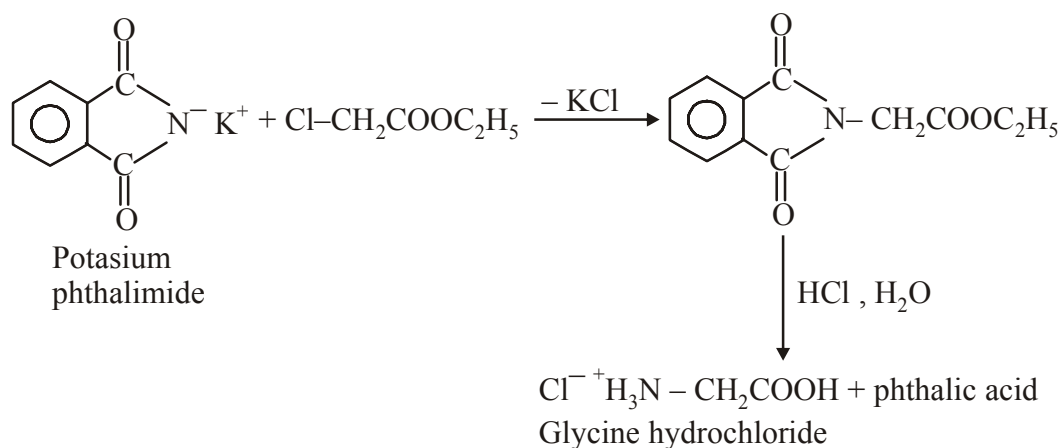
‡ Structurally, in cystine, the two cysteine molecules are joined through sulfur (disulfide linkage).

@@ Proline is an  $\alpha$ -imino acid, all amino acids are primary amines except proline and 4-hydroxyproline, which are 2° amines.

@ Except Glycine all other amino acids are optically active.

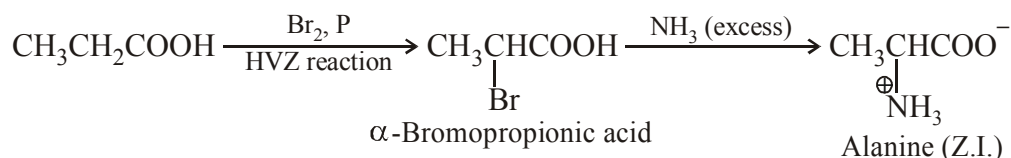
**Preparation of amino acids****(a) Gabriel Phthalimide synthesis**

Good yields of amino acids are generally obtained by the Gabriel phthalimide synthesis ; In this method  $\alpha$  - halo esters are used instead of  $\alpha$  - halo acids .

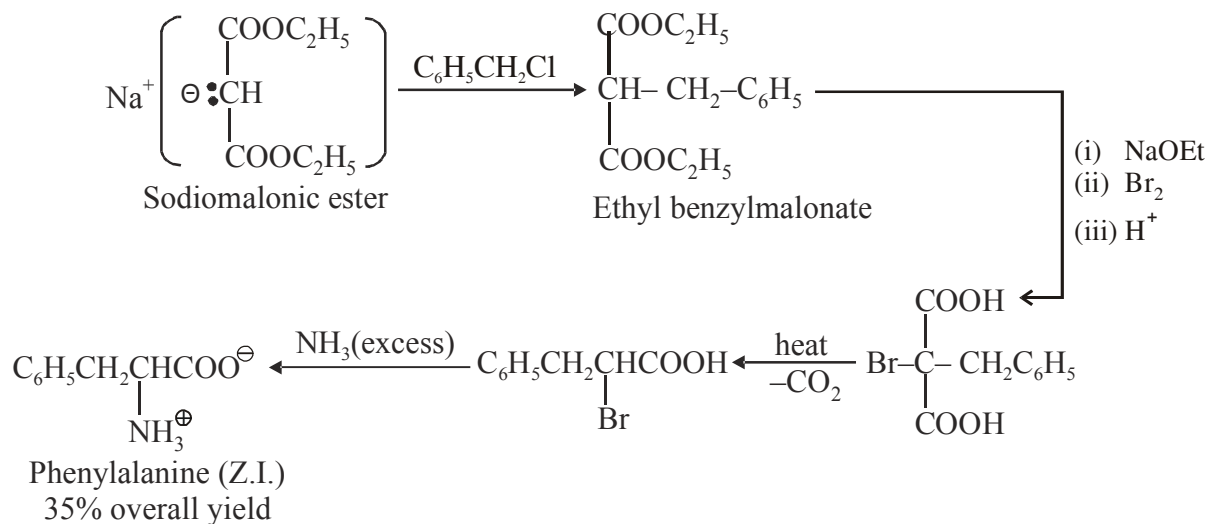


(b) **Amination of  $\alpha$  - Halo acids**

Sometimes an  $\alpha$  - chloro or  $\alpha$  - bromo acid is subjected to direct ammonolysis with excess of concentrated ammonia.

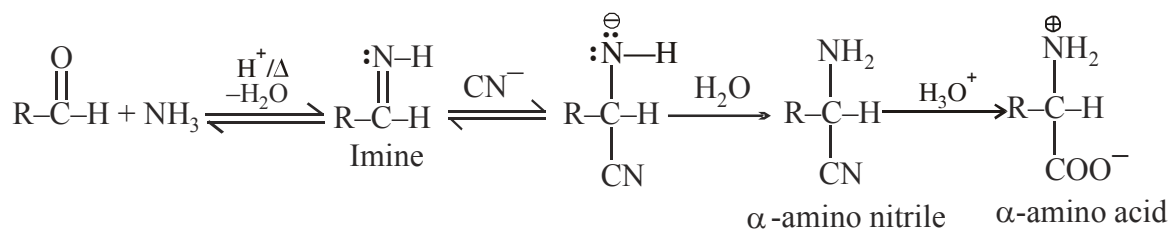


(c) **From diethyl malonate**

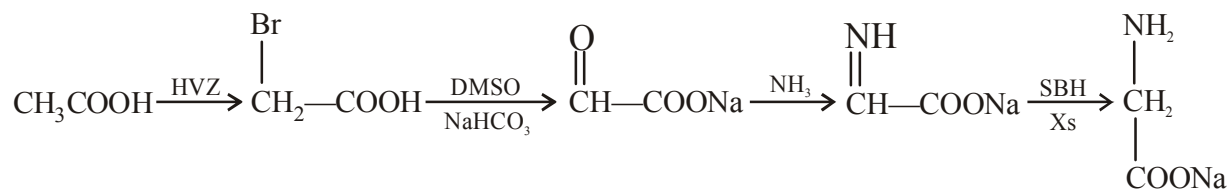


(d) **Strecker's synthesis**

Strecker's synthesis is also used for preparing  $\alpha$  - amino acids



(e) **Using KOOP synthesis**



**Properties of Amino acids**

Although the amino acids are commonly shown as containing an amino group and a carboxyl group, H<sub>2</sub>NCHR<sup>+</sup>COOH, certain properties, (both physical and chemical) are not consistent with this structure

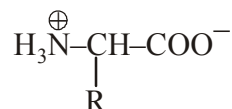
**I. Physical properties**

In contrast to amines and carboxylic acids, the amino acids are nonvolatile crystalline solids, which melt with decomposition at fairly high temperatures. They are insoluble in non-polar solvents like petroleum ether, benzene or ether and are appreciably soluble in water. Their aqueous solutions behave like solutions of substances of high dipole moment due to existence.

**Amino acids as dipolar ions as zwitter ion**

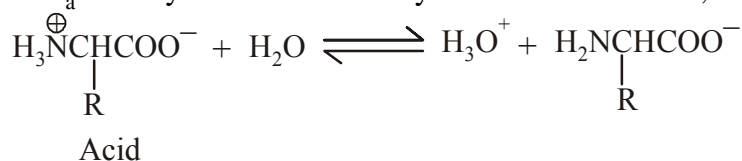
Acidity and basicity constant are ridiculously low for  $-\text{COOH}$  and  $-\text{NH}_2$  groups. Glycine, for example, has  $K_a = 1.6 \times 10^{-10}$  and  $K_b = 2.5 \times 10^{-12}$ , whereas most carboxylic acids have  $K_a$  values of about  $10^{-5}$  and most aliphatic amines have  $K_b$  values of about  $10^{-4}$ .

All these properties are quite consistent with a dipolar ion structure for the amino acids (I)



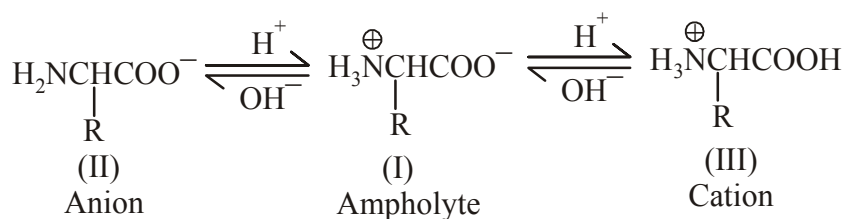
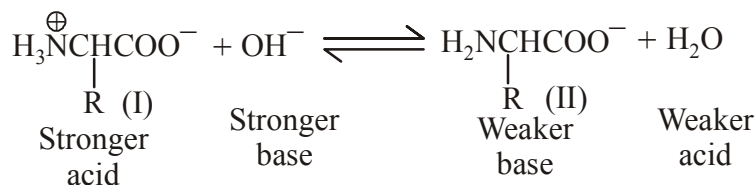
Amino acids : dipolar ions (Zwitter ion)

Physical properties - melting point, solubility, high dipole moment - are just what would be expected of such a salt. The acid-base properties also become understandable when it is realized that the measured  $K_a$  actually refers to the acidity of an ammonium ion,  $\text{RNH}_3^+$ ,



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{NCHRCOO}^-]}{[\text{H}_3\text{NCHRCOO}^+]}$$

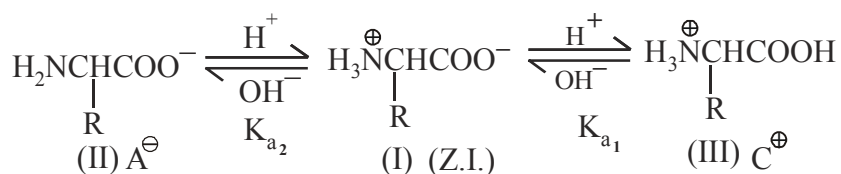
When the solution of an amino acid is made alkaline, the dipolar ion (I) is converted into the anion(II). The stronger base, hydroxide ion, removes a proton from the ammonium ion and displaces the weaker base, the amine.



Wherever feasible, we can speed up a desired reaction by adjusting the acidity or basicity of the solution in such a way as to increase the concentration of the reactive species.

**Isoelectric point of amino acids**

What happens when a solution of an amino acid is placed in an electric field depends upon the of the solution.



In quite alkaline solution, anions (II) exceed cations (III), and there is a net migration of amino acid toward the anode. In quite acidic solution, cations (III) are in excess, and there is a net migration of amino acid toward the cathode. If (II) and (III) are exactly balanced, there is no net migration; under such conditions any one molecule exists as a positive ion and as a negative ion for exactly the same amount of time, and any small movement in the direction of one electrode is subsequently cancelled by an equal movement back towards the other electrode. **The hydrogen ion concentration of the solution in which a particular amino acid does not migrate under the influence of an electric field is called the isoelectric point (pI) of that amino acid. The isoelectric point (pI) is the pH at which the amino acid exists only as a dipolar ion with net charge zero.**

For glycine, for example, the isoelectric point is at pH 6.1.

An amino acid usually shows its lower solubility in a solution at the isoelectric point, since here there is the highest concentration of the dipolar ion. As the solution is made more alkaline or more acidic, the concentration of one of the more soluble ions, (II) or (III) increases.

$$K_{a_1} = \frac{[Z.I.] [H^{\oplus}]}{[C^{\oplus}]} \quad K_{a_2} = \frac{[A^{-}] [H^{\oplus}]}{[DI]} \quad \text{at pI } [A^{\ominus}] = [C^{\oplus}]$$

$$\frac{[Z.I.] [H^{\oplus}]}{K_{a_1}} = \frac{K_{a_2} [DI]}{[H^{\oplus}]} \quad [H^{\oplus}]^2 = K_{a_1} \& K_{a_2}$$

$$\text{on taking antilog pI} = \frac{p^{K_{a_1}} + p^{K_{a_2}}}{2}$$

An amino acid having  $-\text{COOH}$  group more than  $\text{NH}_2$  group or such amino acid have pI less than 7.

An amino acid having more  $-\text{NH}_2$  more than  $\text{COOH}$  group such amino acid have pI more than 7.

Q. Write the structure of alanine at pH 2.5, 10.5 and 6.

### Electrophoresis

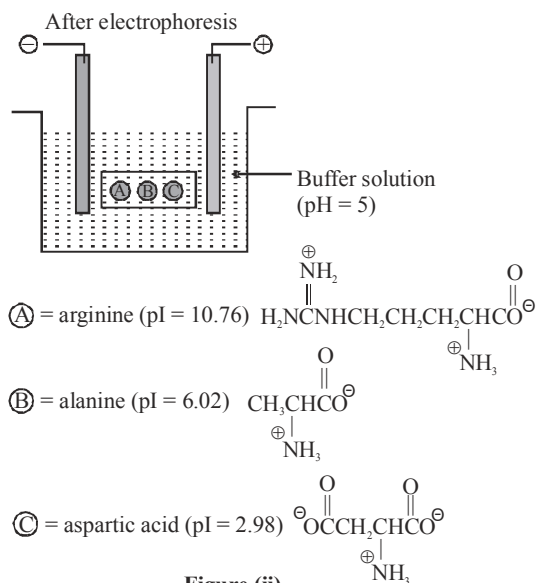
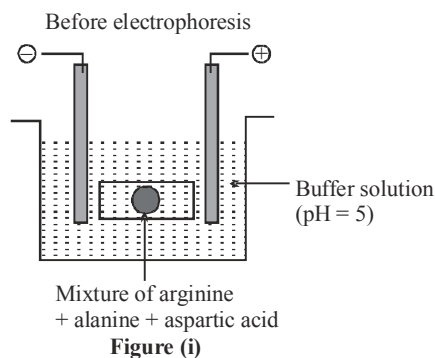
The movement of charged molecules (like amino acid) under the influence of an electric field is called electrophoresis. Electrophoresis separates amino acids on the basis of their pI values.

Amino acid is positively charged (moves towards cathode) if pH of the solution  $<$  pI

Amino acid is negatively charged (moves towards anode) if pH of the solution  $>$  pI

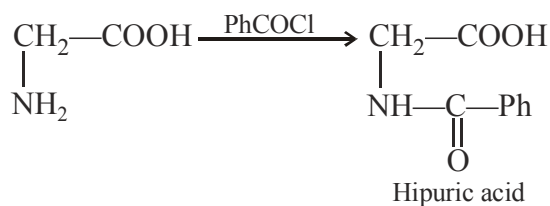
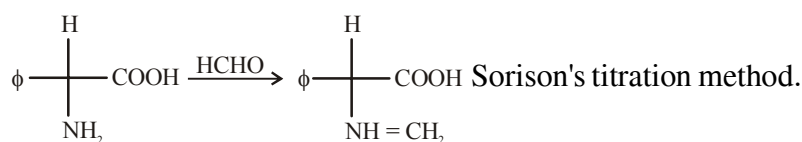
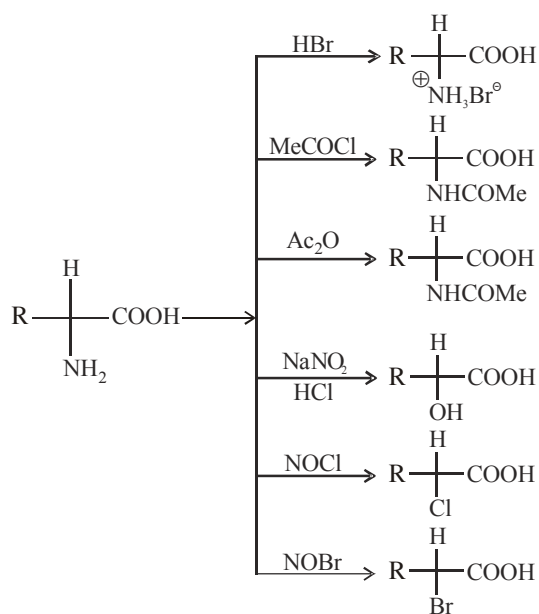
Q. How will you separate a ternary mixture of arginine, alanine & aspartic acid?

Ans. A few drops of a solution of an amino acid mixture are applied to the middle of a piece of filter paper. When the paper is placed in a buffer solution (pH = 5) between the two electrodes and an electric field is applied then arginine & alanine with pI  $>$  pH move towards the cathode and aspartic acid with pI  $<$  pH moves towards the anode. Out of arginine & alanine, alanine will move slowly towards the cathode due to lesser positive charge.



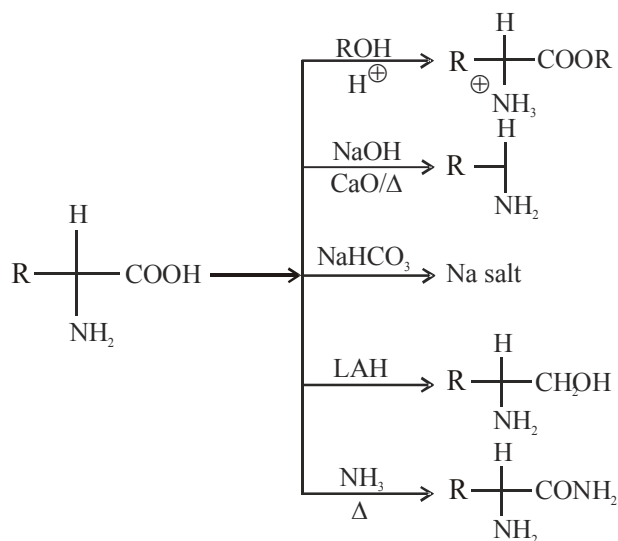
## General reactions of amino acids

### (1) Reactions due to $-\text{NH}_2$ group



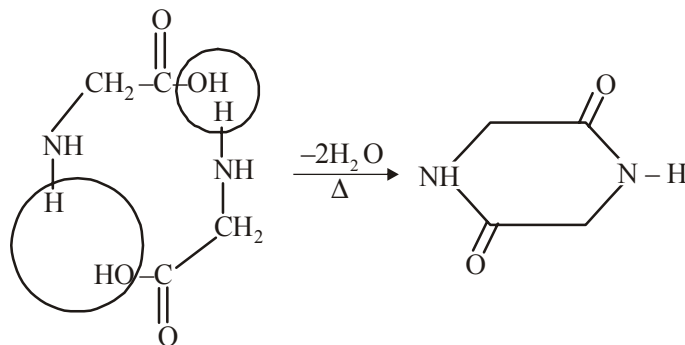
Reactions is used to block  $-\text{NH}_2$  group during volumetric analysis in.

(2) Reactions due to -COOH group.

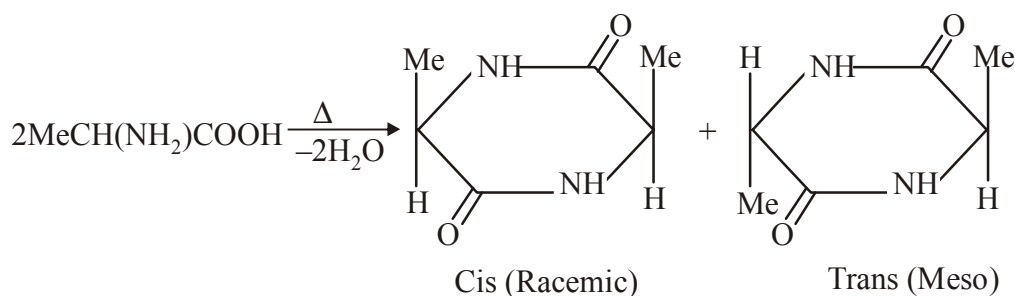


(3) Heating Effect

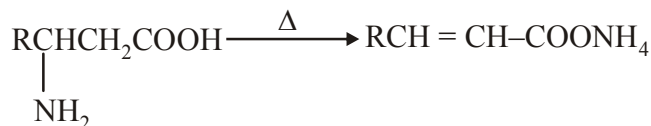
(i) Heating of amino acids leads to intermolecular dehydration to form cyclic diamides.



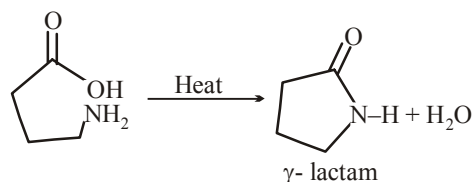
(ii) When alanine is heated, then two diastereomers are obtained. One of them (trans) is not resolvable.

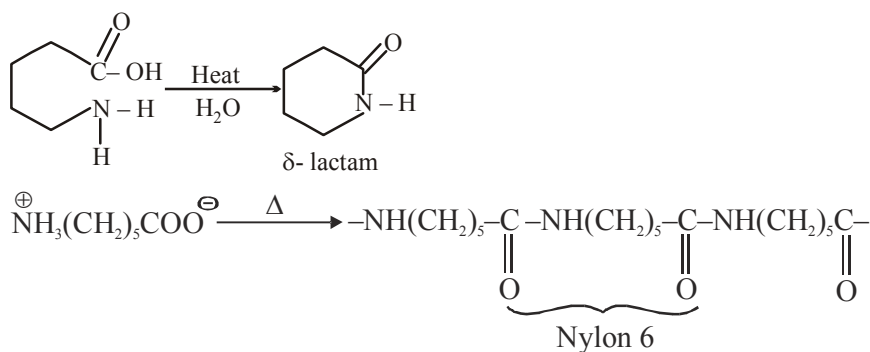


(iii) When β - amino acids are heated, α, β - unsaturated salt are formed.



(iv) γ,δ,ε - amino acids when heated alone gives γ, δ - lactam and polymer respectively. The reason for the formation of polymer is that when ε - amino cyclises intramolecularly, it leads to large angle strain within the compound



(4) **Peptide**

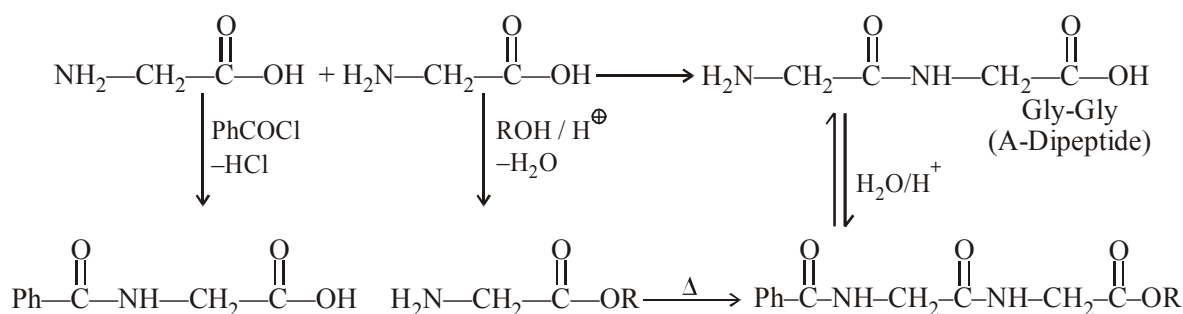
A peptide is a kind of amide formed by intermolecular reaction of the amino group of one amino acid and the carboxyl group of a second amino acid. Dipeptides are made from two amino acids, tripeptides from three amino acids, etc, which may be the same or different. If there are three to ten amino acid residues, the peptide is also called an oligopeptide.

If they give 3 to 10 amino acid they are oligopeptide

If they give 11 to 100 amino acid they are Polypeptide

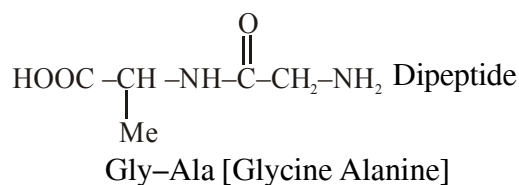
For more than 100 it is Macropeptide

- Peptides can be prepared by blocking technique

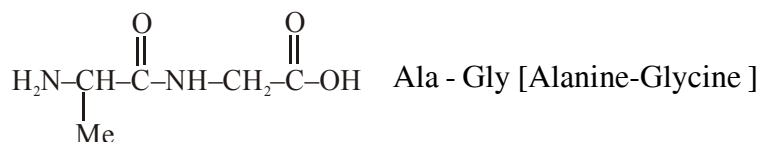


Firstly, the amino and carboxyl groups that are not to be linked in peptide bonds must be blocked to make unreactive.

Abbreviated name of amino acid with free  $\text{NH}_2$  is written first.



By convention, the amino acid with the free amino group (N-terminal) is written at the left end and the one with the unreacted carboxyl group (C-terminal) at the right end.



- When different amino acids are involved in peptide formation.

Then total number of polypeptide possible =  $X^n$

[X = type of amino acid interacting,

n = number of amino acid molecule are interacting.]



- Q. Glycine can form how many Dipeptide ? [Ans. One]  
 Q. Glycine can form how many Tripeptide ? [Ans. One]  
 Q. Glycine and Ala can form how many Dipeptide ? [Ans. Four]  
 Q. Gly, Ala, and Phenyl Ala can form how many Dipeptide ? [Ans. Nine]  
 Q. Gly, Ala, can form how many Tripeptide ? [Ans. Eight]

A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 is called a protein. However, the distinction between a polypeptide and a protein is not very sharp. Polypeptides with fewer amino acids are likely to be called proteins they ordinarily have a well defined conformation of a protein such as insulin which contains 51 amino acids.

### Structure of Proteins

Proteins can be classified into two types on the basis of their molecular shape.

(a) **Fibrous proteins**

When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre-like structure is formed. Such proteins are generally insoluble in water. Some common examples are keratin (present in hair, wool, silk) and myosin (present in muscles), etc.

(b) **Globular proteins**

This structure results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins. Structure and shape of proteins can be studied at four different levels, .i.e., primary, secondary, tertiary and quaternary, each level being more complex than the previous one.

(i) **Primary structure of proteins :** Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of the protein. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.

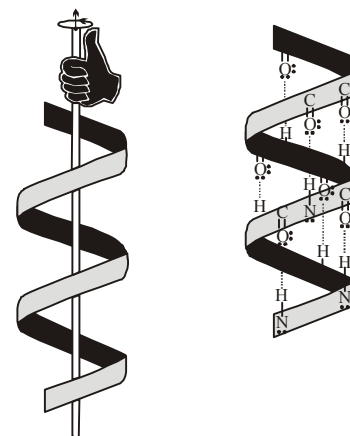
(ii) **Secondary structure of proteins :** The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures viz.  $\alpha$ -helix and  $\beta$ -pleated sheet structure. These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between

$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$  and  $\text{—NH—}$  groups of the peptide bond.

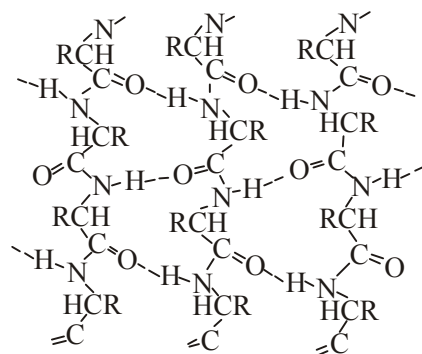
$\alpha$ -Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the  $\text{—NH}$  group of each amino acid residue hydrogen bonded to the

$\text{>C=O}$  of an adjacent turn of the helix as shown in figure.

In  $\beta$ -structure all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together, by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as  $\beta$ -pleated sheet.



$\alpha$ -Helix structure of proteins



$\beta$ -Pleated sheet structure of proteins

- (i) Ionic bonding : between  $\text{COO}^-$  and  $\text{NH}_3^+$  at different sites.
- (ii) H-bonding : mainly between side-chain  $\text{NH}_2$  and  $\text{COOH}$ , also involving OH's (Of serine, for example) and the N-H of tryptophan.
- (iii) Weakly hydrophobic Van der Waal's attractive forces engendered by side-chain R groups and
- (iv) Disulfide cross linkages between loops of the polypeptide chain.

The same kind of attractive and repulsive forces responsible for the tertiary structure operate to hold together and stabilize the subunits of the quaternary structure.

- (iii) **Tertiary structure of proteins :** The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilise the  $2^\circ$  and  $3^\circ$  structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.
- (iv) **Quaternary structure of proteins :** Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure. Example : Haemoglobin, Chlorophyll.

According to their biological action, they are classified as enzymes, hormones, antibodies, etc.

Protein found in living system with definite configuration and biological activity is termed as native protein. If a native protein is subjected to physical or chemical treatment, which may disrupt its higher structures (conformations) without affecting its primary structure, the protein is said to be denatured. During denaturation, the protein molecule uncoils from an ordered and specific conformation into a more random conformation leading to precipitation. Thus denaturation leads to increase in entropy and loss of biological activity of the protein. The denaturation may be reversible or irreversible. Thus, the coagulation of egg white on boiling of egg protein is an example of irreversible protein denaturation. However, in certain cases it is found that if the disruptive agent is removed the protein recovers its original physical and chemical properties and biological activity the reverse of denaturation is known as renaturation.

## Test Of Amino acids and Proteins

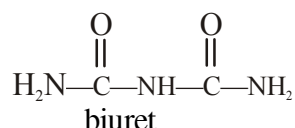
### 1. Biurate Test      2. Nin hydrin Test      3. Xanthoproteic test

### 4. Sakaguchi test      5. Millon's Test

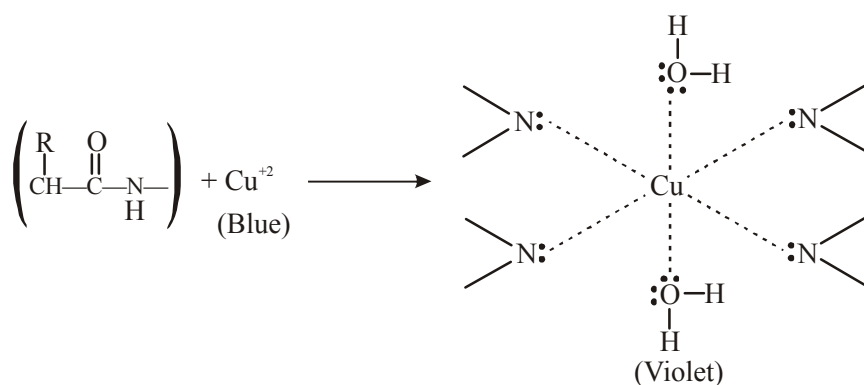
#### 1. Biurate Test

Addition of a very dilute solution of  $\text{CuSO}_4$  to an alkaline solution of a protein is done. A positive test is indicated by the formation of a pink violet to purple violet color.

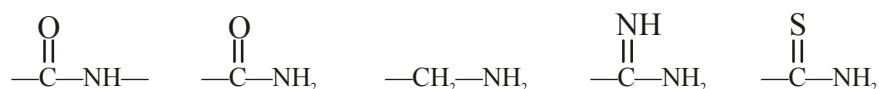
The name of test is derived from a specific compound, biuret, which gives a positive test with this reagent



When a protein reacts with copper (II) sulfate (blue), the positive test is the formation of a violet colored complex.



The biuret test works for any compound containing two or more of the following groups.

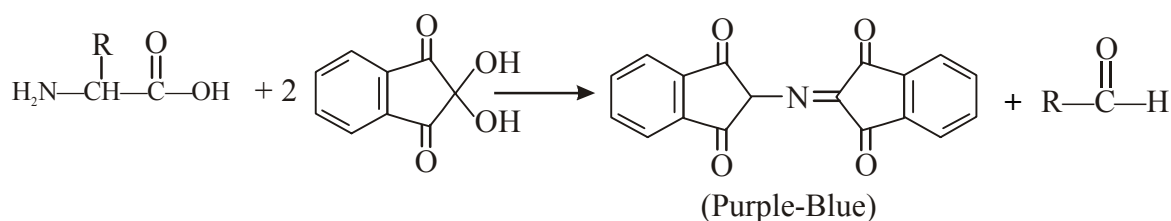


#### 2. Nin hydrin Test

The ninhydrin test is a test for amino acids and proteins with a free  $-\text{NH}_2$  group.

Amino acids are detected by ninhydrin test. All amino acids give violet - coloured product with ninhydrin (triketo hydroindene hydrate) except proline and 4 - hydroxy proline, which gives yellow colour with it.

When such an  $-\text{NH}_2$  group reacts with ninhydrin, a purple-blue complex is formed.



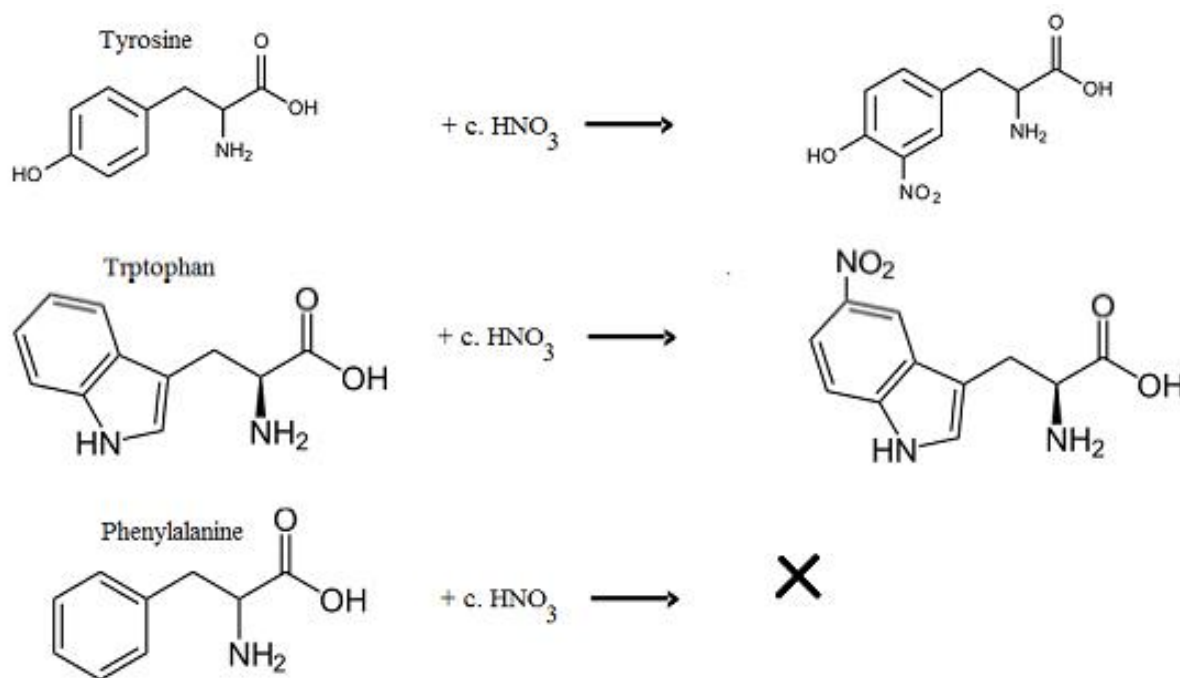
The same violet coloured dye forms from all  $\alpha$  - AA's with  $1^\circ$  amino groups because only their nitrogen is incorporated into it. The  $2^\circ$  amines proline and 4 - hydroxyproline give different adducts that absorb light at a different and thus have a different yellow colour.

#### 3. Xanthoproteic test

This test is used for aromatic amino acids which give positive result from other amino acids. Such as tyrosine, and tryptophan gives Xanthoproteic test, phenyl alanine does not respond with this test.

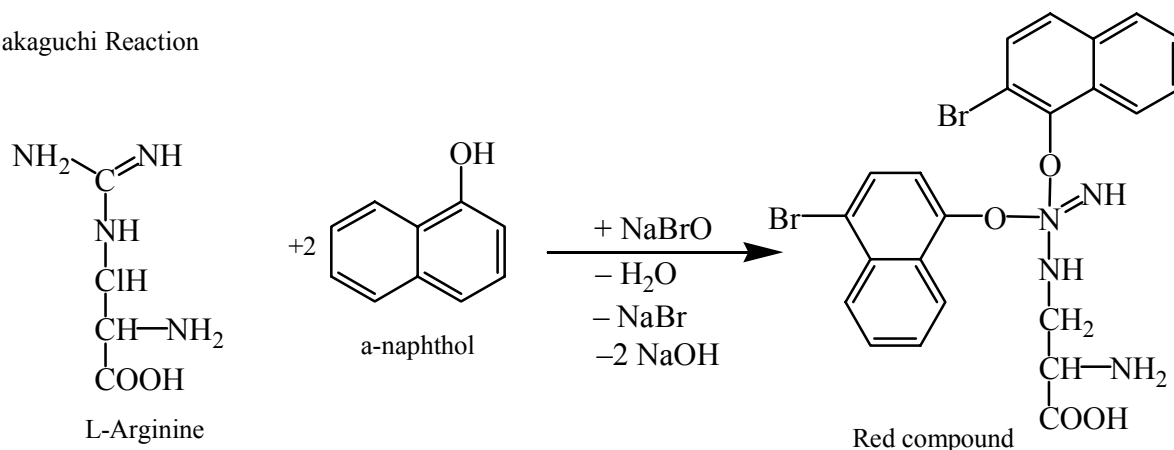
**Principle:**

Xanthoproteic test is used to detect amino acids containing an aromatic nucleus (tyrosine, tryptophan and phenylalanine) in a protein solution which gives yellow color nitro derivatives on heating with conc.  $\text{HNO}_3$ . The aromatic benzene ring undergoes nitration to give yellow colored product. Phenylalanine gives negative or weakly positive reaction though this amino acid contains aromatic nucleus because it is difficult to nitrate under normal condition. On adding alkali to these nitro derivative salts, the color change for yellow to orange.

**4. Sakaguchi test**

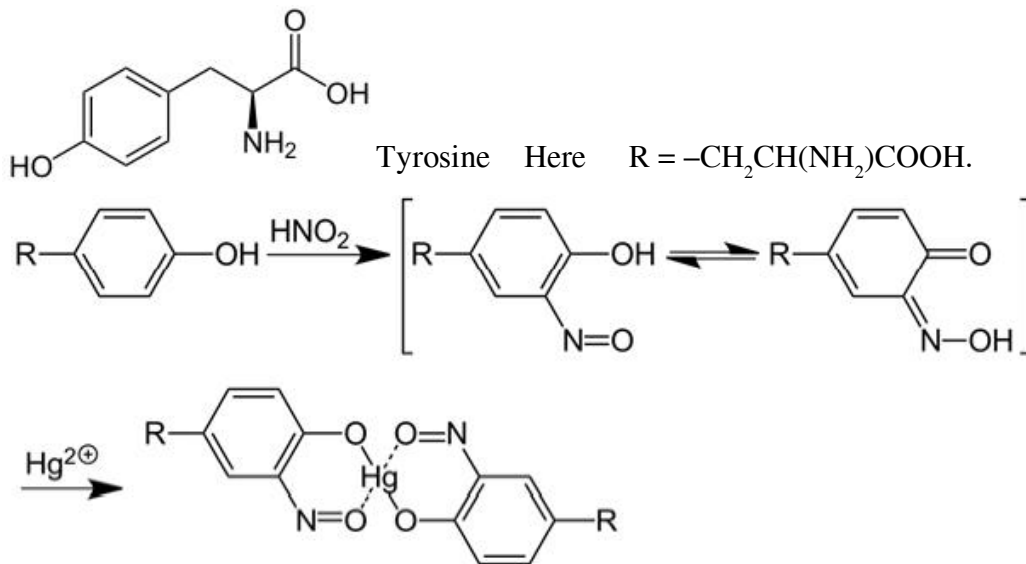
The Sakaguchi test is a chemical test used for detecting the presence of arginine in proteins. Sakaguchi reagent consists of  $\alpha$ -Naphthol and a drop of sodium hypobromite. The guanidine group in arginine reacts with Sakaguchi reagent to form a red-coloured complex.

Sakaguchi Reaction



5. Millon's Test

Millon's reagent is an analytical reagent used to detect the presence of soluble proteins. A few drops of the reagent are added to the test solution, which is then heated gently. A reddish-brown coloration or precipitate indicates the presence of tyrosine residue which occur in nearly all proteins



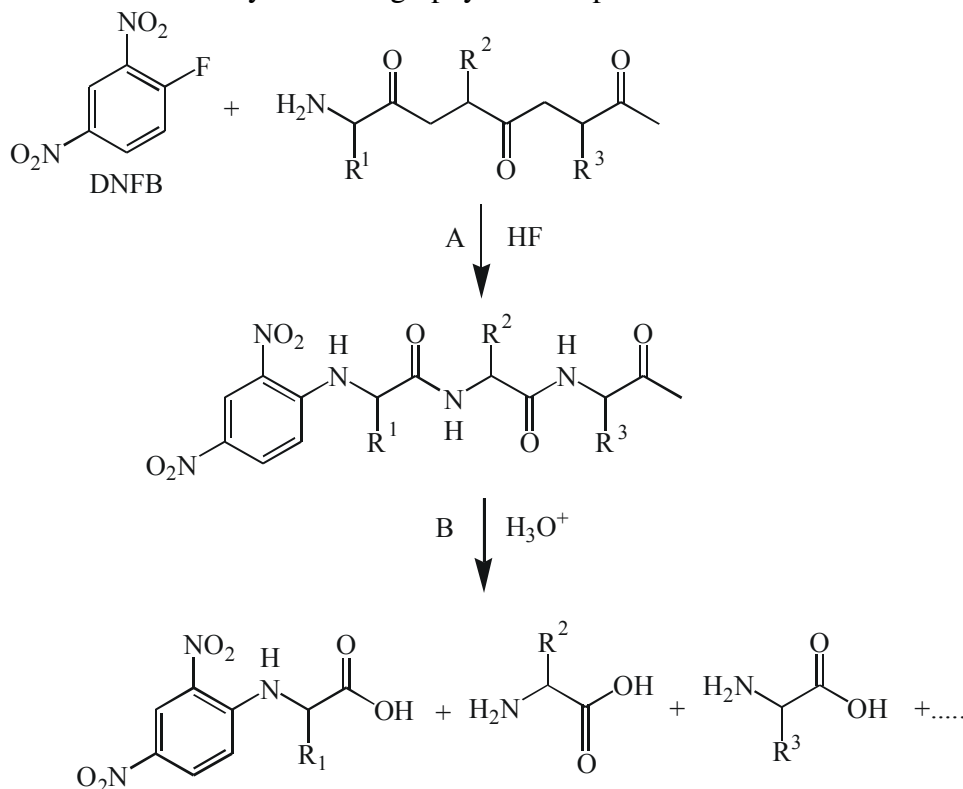
**reddish-brown colored complex**

**Sanger's Method of sequencing of Amino acids of polypeptide chain**

It is N-terminal amino acid analysis

Sanger's reagent (1-fluoro-2,4-dinitrobenzene)

1. React the peptide with a reagent that will selectively label the N-terminal amino acid.
2. Hydrolyse the protein.
3. Determine the amino acid by chromatography and comparison with standards.



## CARBOHYDRATES

Carbohydrates (hydrates of carbon) are naturally occurring compounds having general formula  $C_x(H_2O)_y$ , which are constantly produced in nature & participate in many important bio-chemical reactions.

Ex. - Glucose	$C_6H_{12}O_6$	$C_6(H_2O)_6$
Fructose	$C_6H_{12}O_6$	$C_6(H_2O)_6$
Cellulose and Starch	$(C_6H_{10}O_5)_n$	$(C_6(H_2O)_5)_n$

- Sucrose (Cane sugar) -  $C_{12}H_{22}O_{11}$ , and
- Maltose (Malt Sugar)  $C_{12}(H_2O)_{11}$

But some compounds which have formula according to  $C_x(H_2O)_y$  are not known as carbohydrate

Ex.	$CH_2O$	Formaldehyde
	$C_2(H_2O)_2$	Acetic acid
	$C_3(H_2O)_3$	lactic acid

There are many compounds, which shows chemical behaviour of carbohydrate but do not confirm the general formula  $C_x(H_2O)_y$  such as -  $C_5H_{10}O_4$  (2-deoxyribose),  $C_6H_{12}O_5$  (Rahmnose)  
 $C_7H_{14}O_6$  (Rahmnohexose)

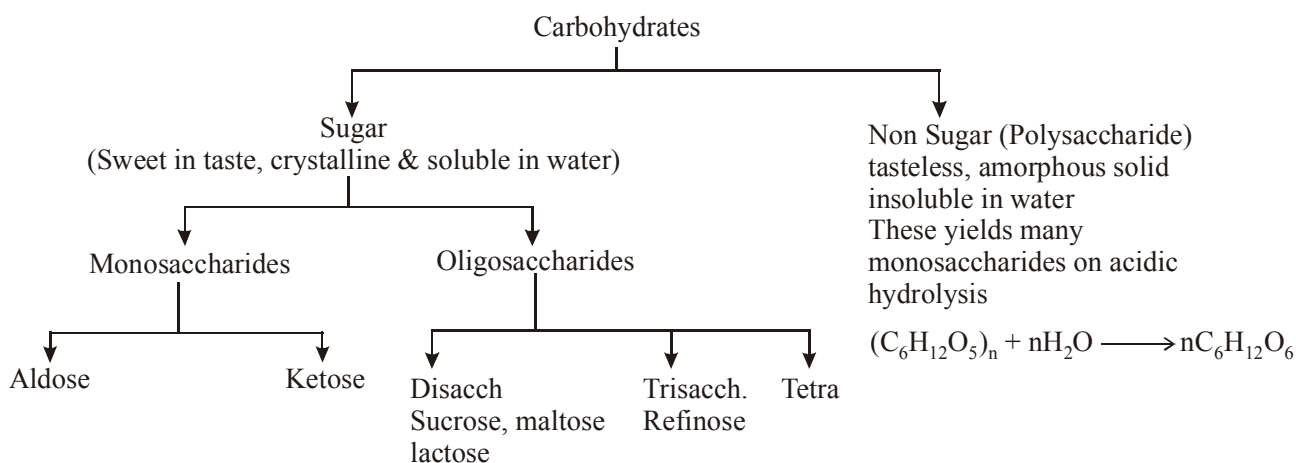
**Modern Concept :** Carbohydrates are polyhydroxy aldehyde or ketone

or

Substances which yield these (polyhydroxy aldehyde or ketone) on hydrolysis

- Carbohydrates  $\xrightarrow{H_2O/H^+}$  Polyhydroxy aldehyde or ketone
- Carbohydrates are also known as Saccharides.
- In plants carbohydrates are synthesised by photosynthesis

**Classification of carbohydrates :**



**Monosaccharides :** (simple sugars)

These are the sugars which cannot be hydrolysed into smaller molecules.

General formula is  $C_nH_{2n}O_n$

Ex. - Glucose, Fructose, Ribose, Deoxyribose

- If aldehyde group is present in monosaccharide, then it is known as aldose.
- If ketone group is present in monosaccharide, then it is known as ketose.

On the basis of C-atom monosaccharides can be farther classified as, Trioses, Tetras, Pentoses, Hexoses.

Table

		<b>Aldoses</b>	<b>Ketoses</b>
3C	Triose or Triose	Aldotriose	Ketotriose
4C	Tetrose	Aldotetrose	Ketotetrose
5C	Pentose	Aldopentose	Ketopentose
5C	Including $-CHO$	Aldopentose (Ribose)	$  \begin{array}{c}  H-C=O \\    \\  H-C-OH \\    \\  H-C-OH \\    \\  H-C-OH \\    \\  CH_2OH  \end{array}  $
5C	Including $-C(=O)-$	Ketopentose	$  \begin{array}{c}  CH_2OH \\    \\  C=O \\    \\  H-C-OH \\    \\  H-C-OH \\    \\  CH_2OH  \end{array}  $ (Ribulose)
6C	Hexose	Aldohexose	Ketohexose
6C	Including $-CHO$	Aldohexose (Glucose)	$  \begin{array}{c}  CHO \\    \\  H-C-OH \\    \\  HO-C-H \\    \\  H-C-OH \\    \\  H-C-OH \\    \\  CH_2OH  \end{array}  $ D-glucose
6C	Including $-C(=O)-$	Ketohexose (Fructose)	$  \begin{array}{c}  CH_2OH \\    \\  C=O \\    \\  HO-C-H \\    \\  H-C-OH \\    \\  H-C-OH \\    \\  CH_2OH  \end{array}  $ D-fructose

**Oligosaccharides :-**

These are the sugars which yields 2–10 monosaccharides units on hydrolysis. such as.

These are of following types

(a) *Disaccharides* :- Gives two monosaccharide unit on hydrolysis (may or may not be same).

Ex. - Sucrose, Maltose, Lactose

(b) *Trisaccharides* :- Gives Three monosaccharide unit on hydrolysis.

**Polysaccharides** :- These are the non sugars which yield a large no of monosaccharide units on hydrolysis General formula -  $(C_6H_{10}O_5)_n$ . Ex.- Starch, Cellulose, Glycogen

**Note** :- A group of polysaccharides which are not so widely used in nature is pentosans  $(C_5H_8O_4)_n$  Monosaccharides, General formula  $C_x(H_2O)_y$   $x = 3 - 8$ . Nomenclature of monosaccharides are given according to the no. of carbons present in them.

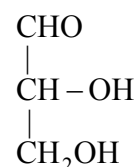
**Stereochemistry of carbohydrates :**

**D & L-Sugars** : The series of aldoses or ketoses in which the configuration of the penultimate C-atom (C-next to  $CH_2-OH$  group) is described as D-sugars if  $-OH$  is towards RHS & L-sugars if it is towards LHS.

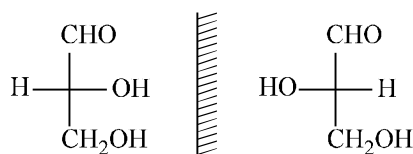
Smallest carbohydrate

\* Aldotriose

\* Glyceraldehyde



Fischer projection



D-Glyceraldehyde (+)

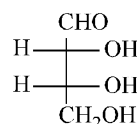
L-Glyceraldehyde (-)

**Classification of Aldotetrose :**

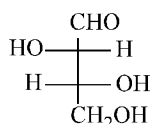
(i) Erythrose

(ii) Threose

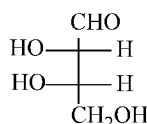
C-4



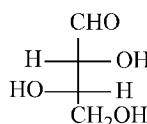
D-Erythrose



D-Threose

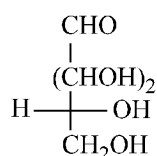


L-Erythrose

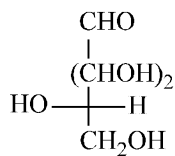


L-Threose

C-5



D-Aldopentose



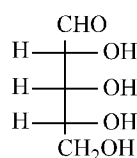
L-Aldopentose

No. of  $C^* = 3$  (in Aldopentose)

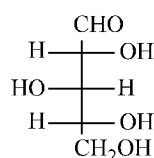
No. of optical isomers  $2^3 = 8$

No. of D Sugars 4

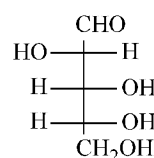
No. of L Sugars 4

**D-Aldopentose :**

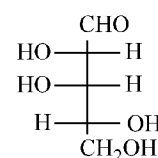
(I)



(II)



(III)



(IV)



All Isomeric D-sugars are diastereomers.

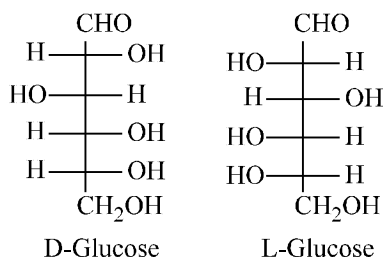
**Aldohexose :**

No. of C\* = 4

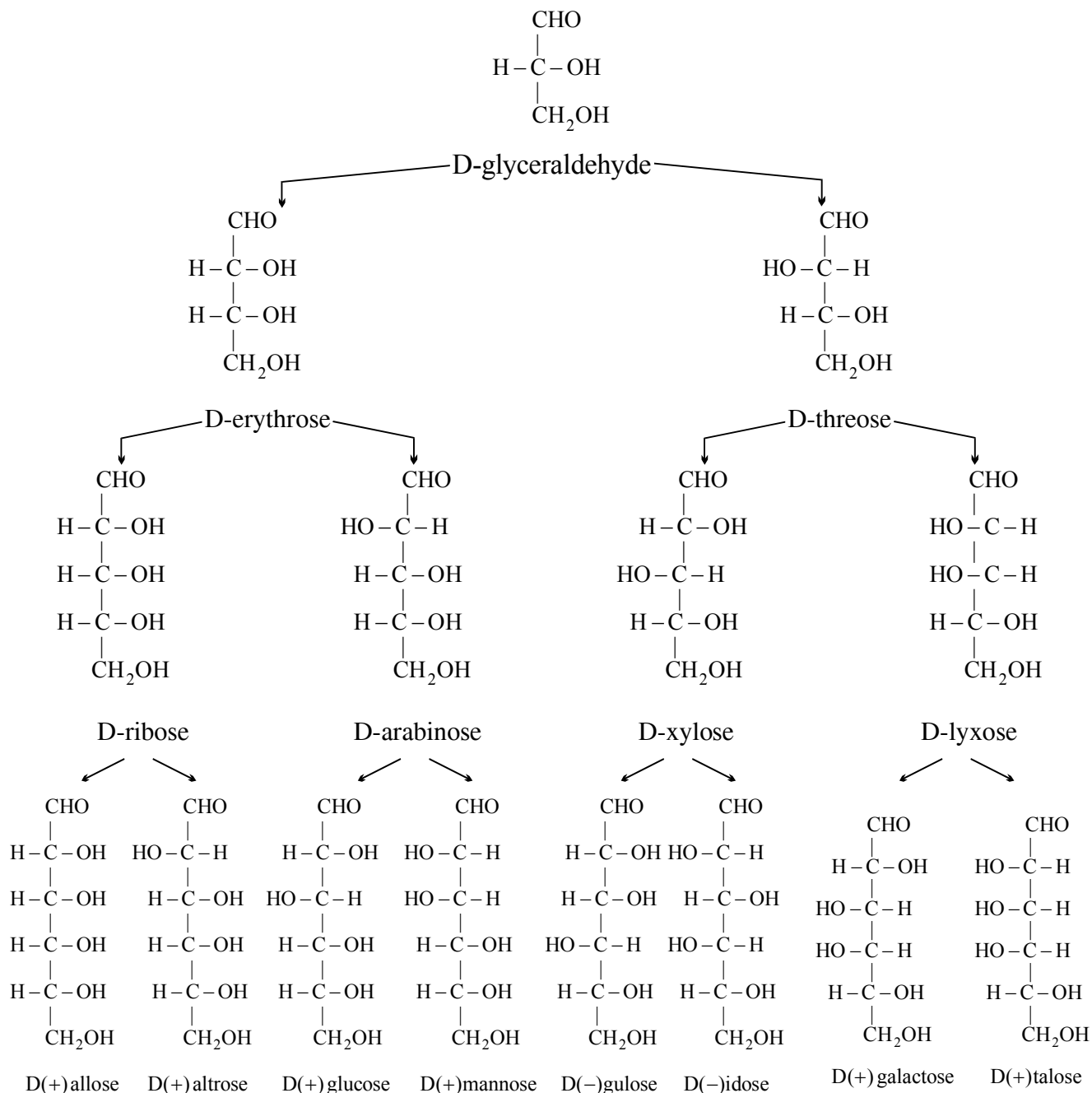
No. of stereoisomers =  $2^4 = 16$

No. of D-sugars = 8

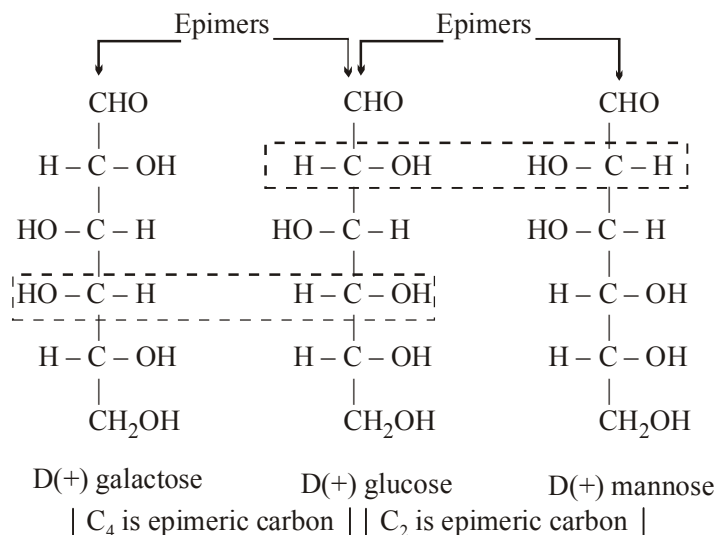
No. of L-sugars = 8



**The D-family aldoses**



**Epimers:** A pair of diastereomers that differ only in the configuration about of a single carbon atom are said to be epimers. D(+)-glucose is epimeric with D(+)- mannose and D(+)-galactose as shown below.




Example with C<sub>2</sub> epimeric carbon is

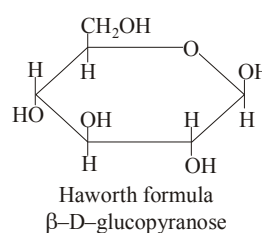
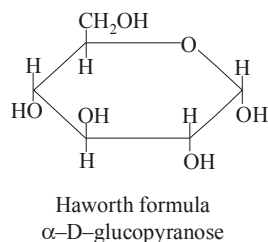
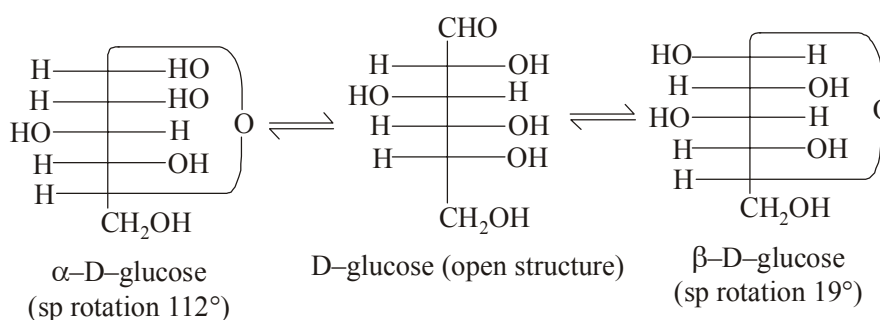


**Anomers:** Anomers are the stereoisomers which differs at a single chiral centre out of many & are ring chain tautomer of the same open chain compound.

The two sugars that differs in configuration only on the carbon that was the carbonyl carbon in the open chain form is called as anomers  $\alpha$  glucose and  $\beta$  glucose are known as anomers their equilibrium mixture contains 36 %  $\alpha$ -D-glucose , 63.8 %  $\beta$ -D-glucose and 0.2 % open chain form.

C<sub>1</sub> Carbon is known as anomeric carbon.

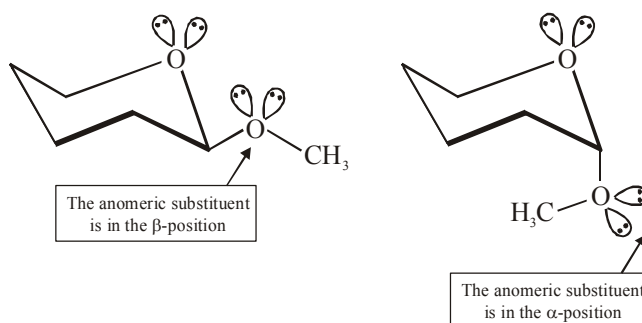
Haworth suggested to write  $\alpha$  glucose and  $\beta$  glucose in pyran structure 



Anomers are epimers but epimers may not be anomers.

**Anomeric effect :**

$\beta$ -D-glucose is more stable than  $\alpha$ -D glucose because there is more room for a substituent in the equatorial position. However when glucose reacts with an alcohol to form a glucoside, the major product is the  $\alpha$ -glucoside. The preference for the axial position by certain substituents bonded to the anomeric carbon is called anomeric effect.



What is responsible for the anomeric effect? One clue is that all the substituents that prefer the axial position have lone pair electrons on the atom bonded to the ring. The lone pair electrons of the anomeric substituent have repulsive interaction with the lone pair electron of the ring oxygen if the anomeric substituent is the  $\beta$ -position, but not if it is the  $\alpha$ -position.

Apparently attractive interaction of the hydrogen of the anomeric OH group of D-glucose with the lone pair electron of the ring oxygen decreases the importance of the anomeric effect making  $\beta$ -D glucose more stable than  $\alpha$ -D glucose. However, when the hydrogen is replaced by an alkyl group, the anomeric effect decreases the stability of the  $\beta$ -position so,  $\alpha$ -glycosides are more stable than  $\beta$ -glycosides.

**Cyclic structures of monosaccharides**

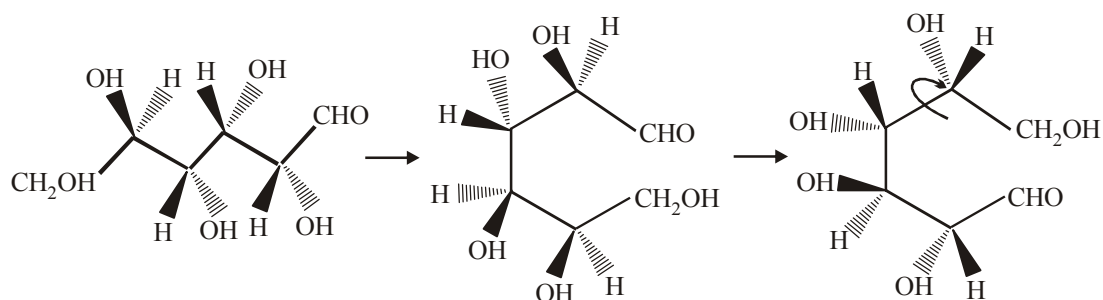
Many five membered and six membered monosaccharides occur in cyclic form. Cyclic structures of monosaccharides are established by many experiments. The cyclic structure is due to intramolecular hemiacetal formation between aldo / keto group and OH of any one carbon. The ring formed are generally six membered (pyranose) or five membered (furanose). Each cyclization results in creation of a new asymmetric centre apart from the existing ones. The isomers resulting from cyclizations are called anomers. example, when D-glucose (open structure) cyclise, it gives  $\alpha$ -D-glucose and  $\beta$ -D-glucose.

**Haworth projection :-**

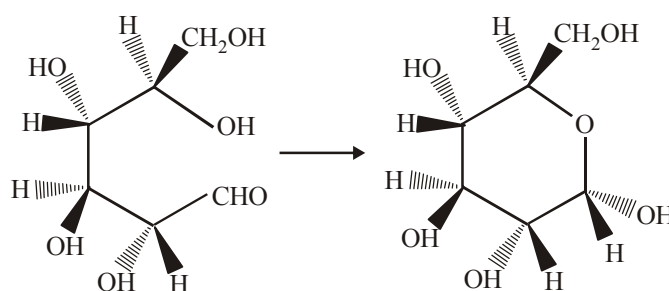
Many of monosaccharides form cyclic structures. The actual structure is almost planar and be represented by Haworth projection, which is a way of depicting three - dimensional cyclic structure.

- Rule -1 :-** In a Haworth projection draw a fisher projection in which ring oxygen is in a down position.
- Rule -2 :-** Imagine that carbon chain of fisher projection is folded around a barrel or drum, which provide a ring lies in a plane  $\perp$  to the page.
- Rule -3 :-** Now plane of ring is turned  $90^\circ$  so that anomeric carbon is on the right and the ring oxygen is in the rear. Obtained projection is a Haworth projection.

**Example :** (D-glucose)

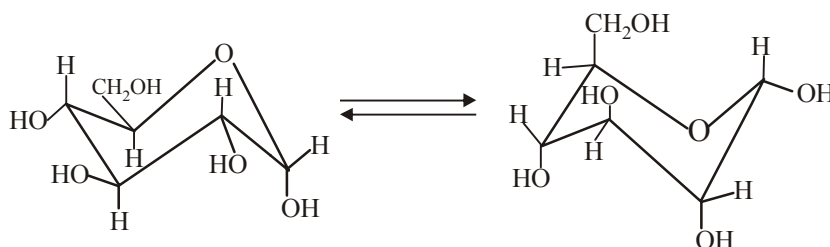


**Projection :**

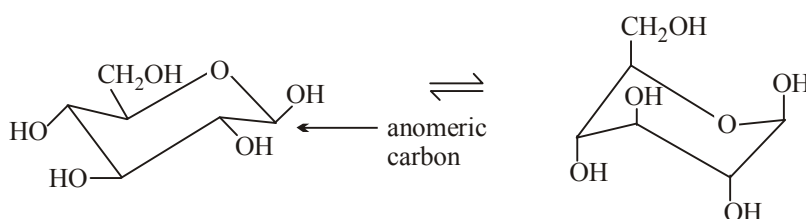


**Hawarth projection**

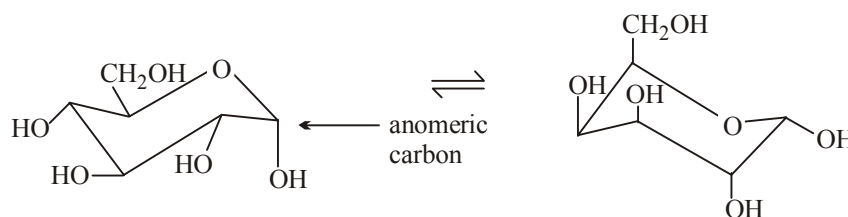
⇒ Chair conformation of D-glucose



**Chair forms of (conformation)  $\alpha$  and  $\beta$  D-Glucose :**

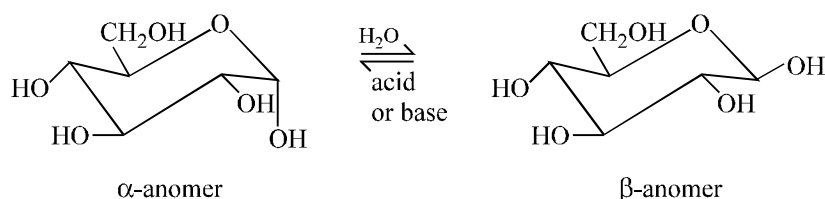


$\beta$ -D-Glucose (most stable glucose form) all groups are equatorial.



$\alpha$ -D-Glucose -OH group at anomeric carbon is axial.

### Mutarotation



Specific rotation of  $\alpha$  glucose + 112°

Specific rotation of  $\beta$  glucose + 19°

Equilibrium mixture  $[\alpha]_D = 52.5$  degree mL g<sup>-1</sup> dm<sup>-1</sup>

**Fresh  $\alpha$ -glucose**  $\longrightarrow$  52.5  $\longleftarrow$  **Fresh  $\beta$ -glucose**

112°

36 %  $\alpha$  glucose

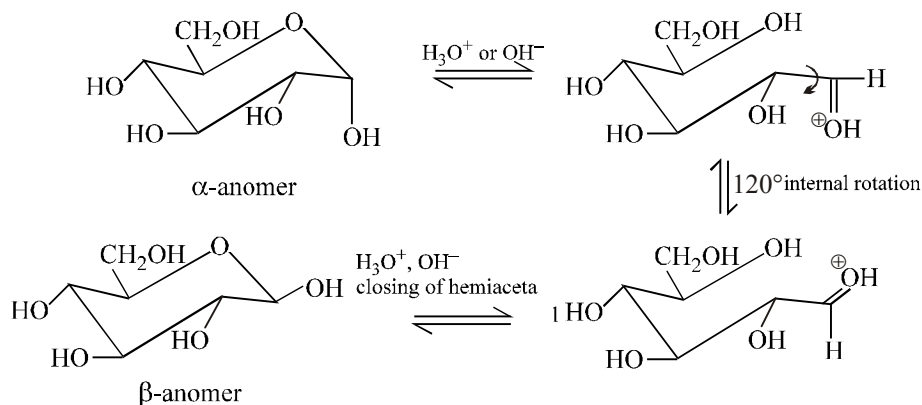
19°

63.8 %  $\beta$  glucose

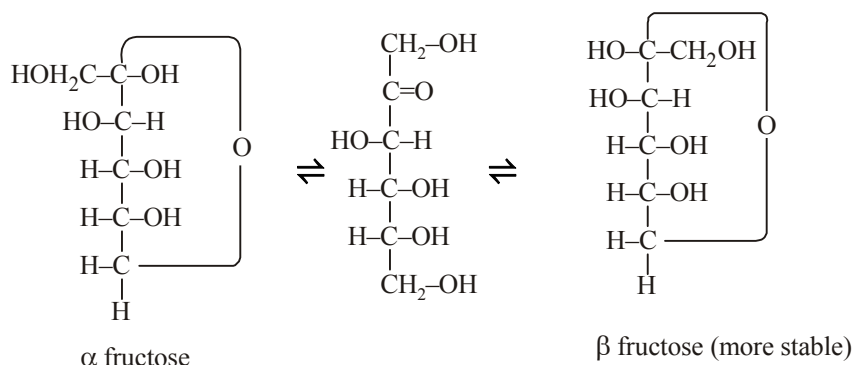
When pure  $\alpha$ -D glucose is dissolved in water its specific rotation is found to be +112° with time, however the specific rotation of the solution decreases ultimately reaches stable value of +52.5°. When  $\beta$  D-glucose is dissolved in water, it has a specific rotation of 19°. The specific rotation of this solution increases with time also to + 52.5°.

This change of optical rotation with time is called mutarotation. It is caused by the conversion of  $\alpha$  and  $\beta$  glucopyranose anomers into an equilibrium mixture of both. Mutarotation is catalyzed by both acid and base, but also occurs is even in pure water. Mutarotation is characteristic of the cyclic hemiacetal form of glucose.

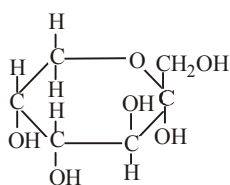
Mutarotation occurs first by opening of the pyranose ring to the free aldehyde form.



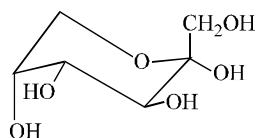
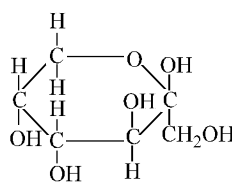
### Structure of fructose



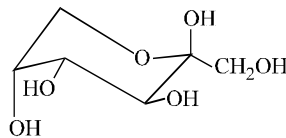
Ring structure of fructose C, Pyranose structures 6 membered ring, C<sub>2</sub> – C<sub>6</sub> linkage



Chair conformations

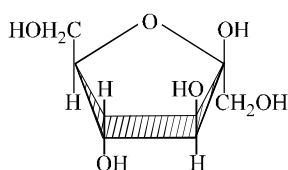


$\alpha$ -D-fructopyranose

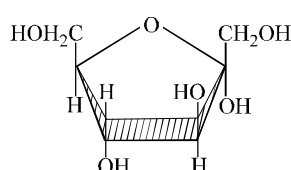


$\beta$ -D-fructopyranose

Furanose structure (5 membered ring)

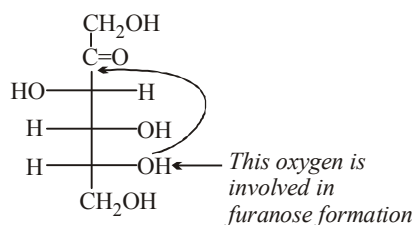
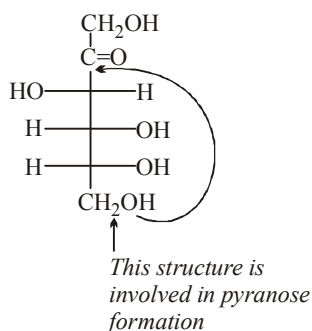


$\beta$ -D-fructofuranose

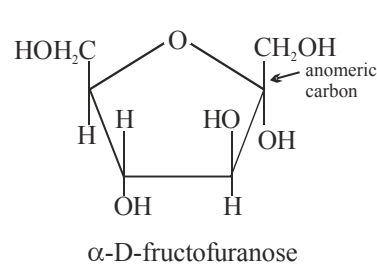
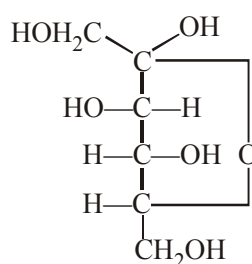
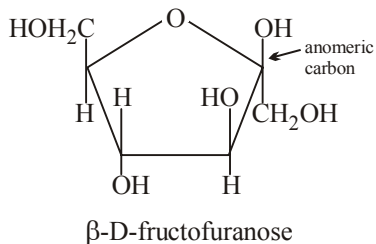
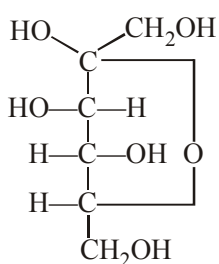
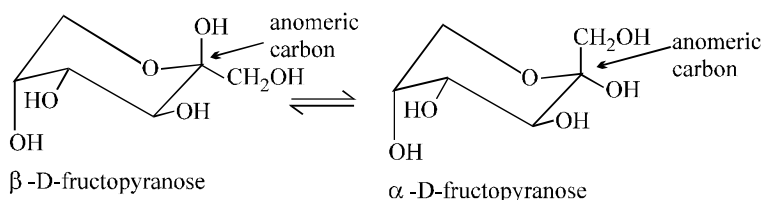


$\alpha$ -D-fructofuranose

**Mutarotation:** Fructose undergo complex mutarotation. The structure of the cyclic hemiacetal form of d-fructose can be derived from its carbonyl (Ketone) form using the methods described as follows.



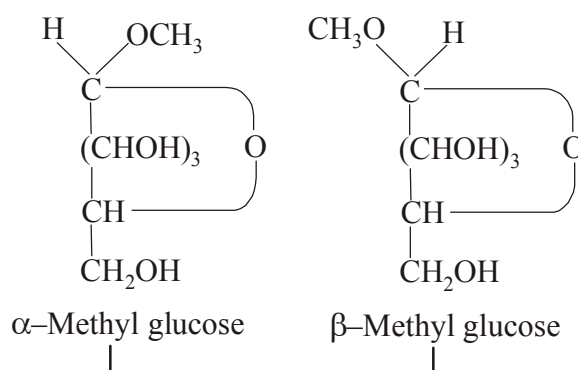
It happens that the crystalline form of D-fructose is  $\beta$ -D-Fructopyranose. When crystals of this form are dissolved in water, it equilibrates to both pyranose & furanose forms.



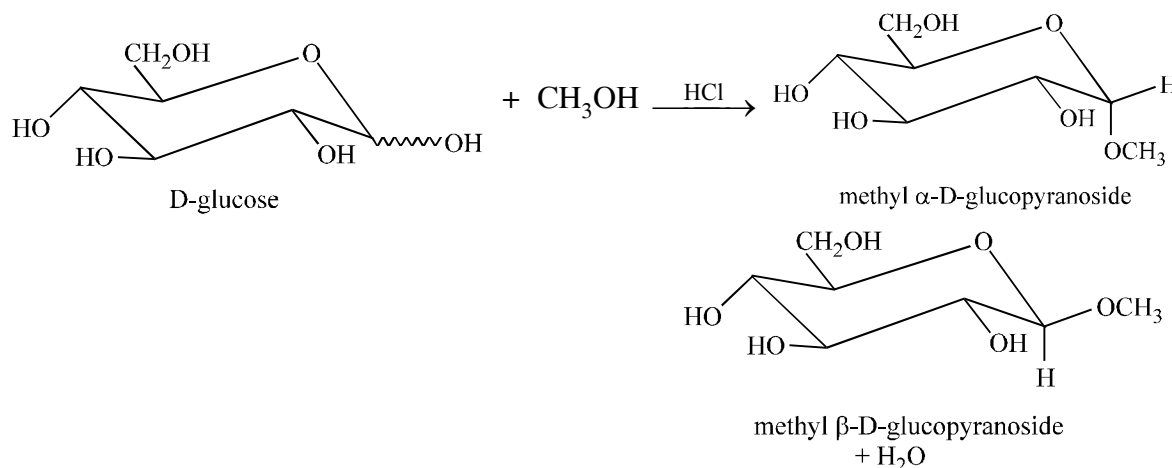
- \* All monosaccharides are reducing sugars and they show mutarotation.
- \* Starch, cellulose are Polymers of Glucose
- \* Lactose and sucrose are disaccharides
- \* Sucrose is a non reducing sugar, gives negative test for Benedict and tollen's reagent, they do not form osazone and do not show mutarotation.
- \* Acetals of carbohydrates are called as GLYCOSIDE

**Formation of Glycosides**

Glucose reacts with methyl alcohol in presence of dry HCl to form  $\alpha$  and  $\beta$ -methyl glycoside of glucose. The reaction takes place only on OH of hemi-acetylic carbon. Other hydroxyl groups are unreactive.



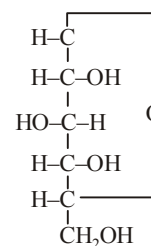
To methylate all the OH groups, methylating agent used is dimethyl sulphate.



Such compounds are called glucoside (cyclic acetals). They are special type of acetals in which one of the oxygen of the acetal linkage is the ring oxygen of the pyranose or furanose.

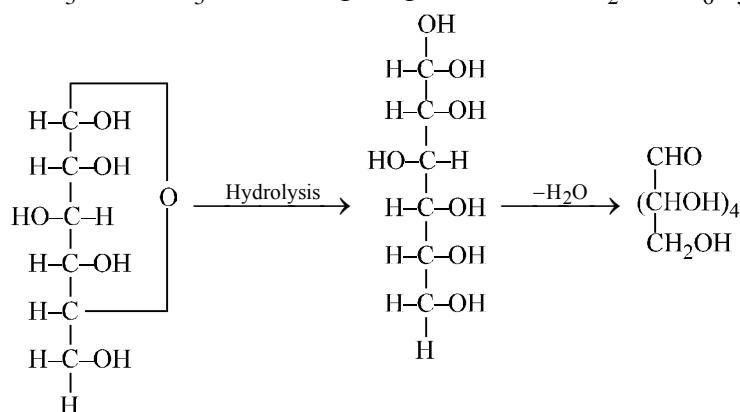
**Ring structure of glucose :**

- (i) Glucose does not give pink colour with schief reagent.
- (ii) Does not form adduct with NaHSO<sub>3</sub>, NH<sub>3</sub>
- (iii) Glucose exist in two isomeric form
- (iv) It show mutarotation

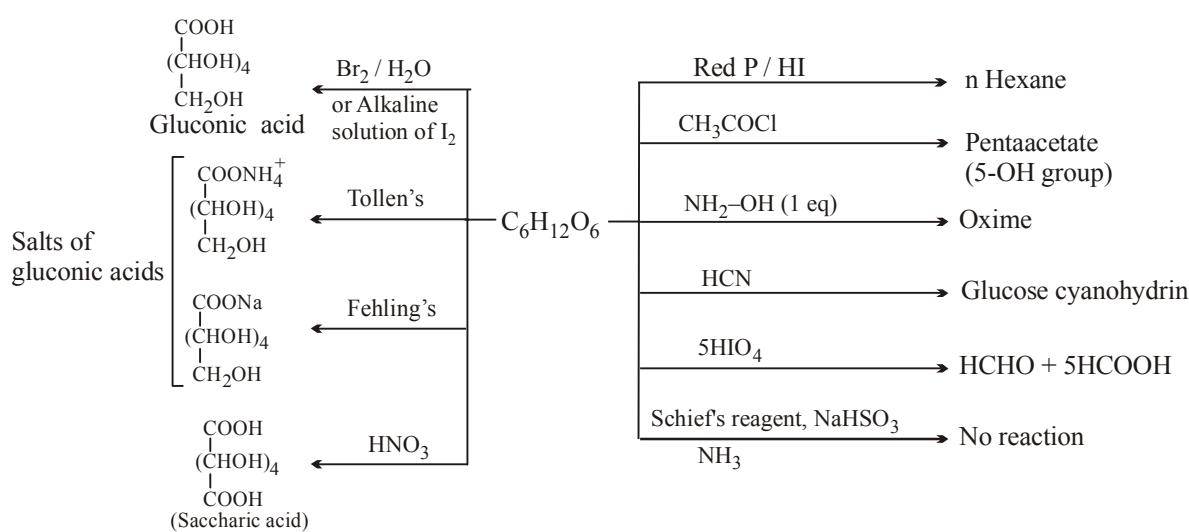


Since there is no free aldehyde group, so it does not react with weak reagent

( $\text{NH}_3$ ,  $\text{NaHSO}_3$ ) but strong reagent ( $\text{HCN}$ ,  $\text{NH}_2\text{OH}$ ,  $\text{C}_6\text{H}_5\text{NH}-\text{NH}_2$ ) break up ring

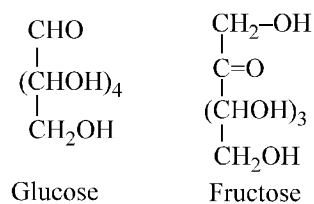


## REACTIONS OF GLUCOSE

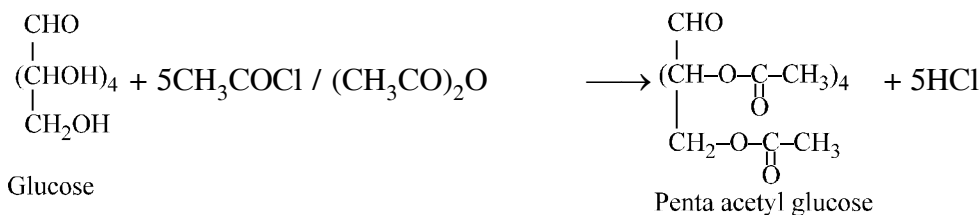


These reactions indicate that glucose has 6-C straight chain with one  $-\text{CHO}$  group & 5-OH group.

### General reactions of monosaccharies



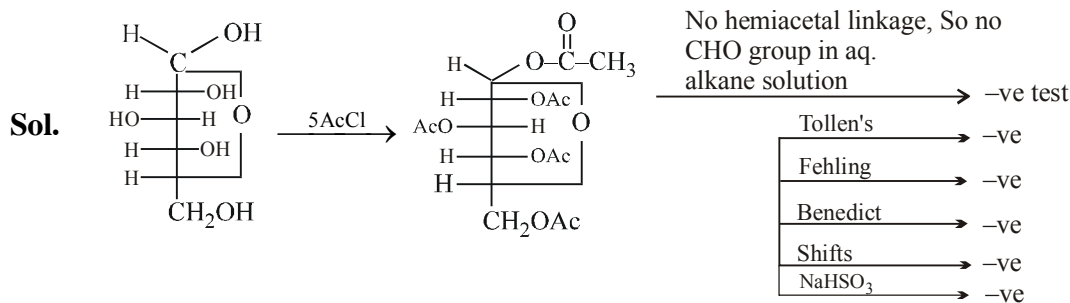
#### 1. Acetylation :



This reaction suggests presence of 5(OH) group.



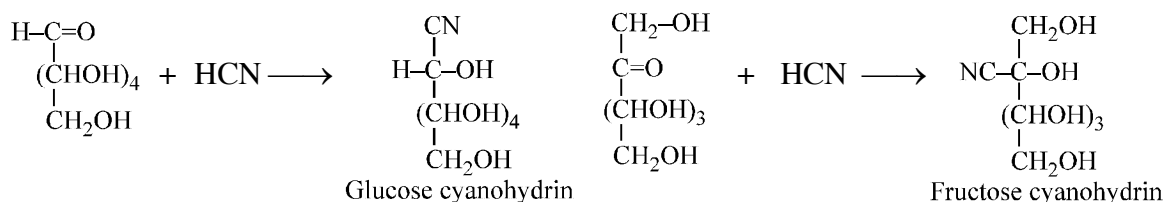
Q. The penta acetate of glucose give -ve test with Tollen's reagent & Fehling solution, explain?



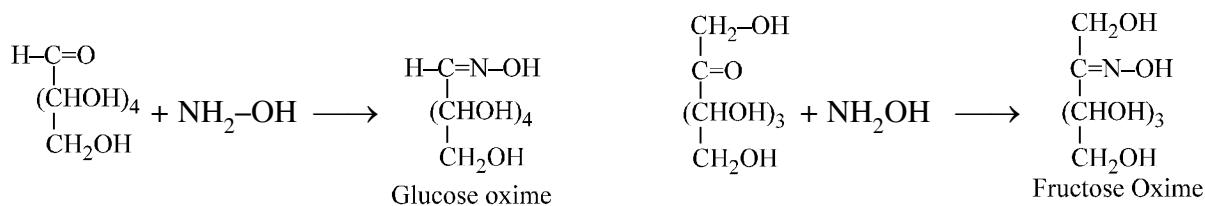
2. Red by HI / Red P :



3. Reaction with HCN:

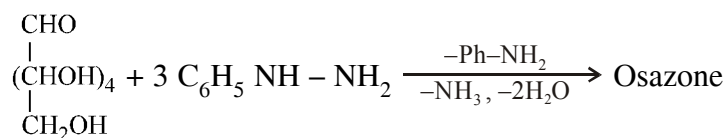


4. Reaction with NH<sub>2</sub>-OH (hydroxyl amine):

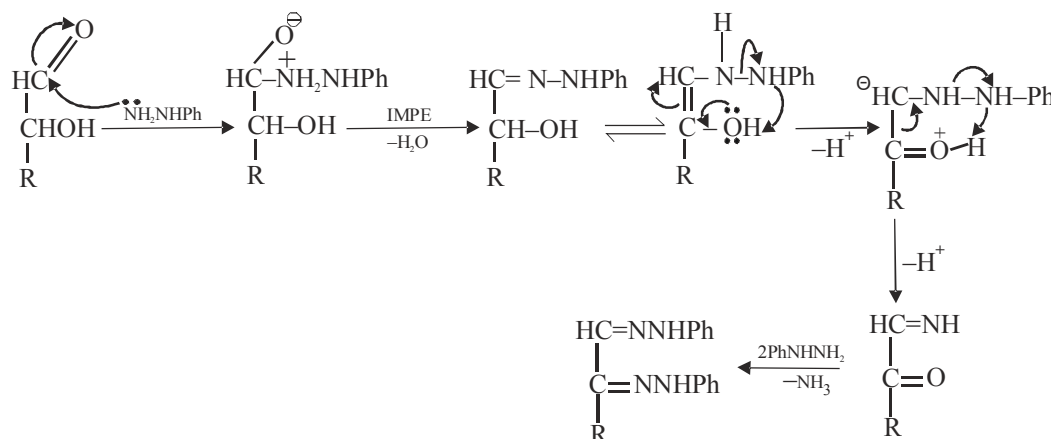


5. Reaction with phenyl hydrazine: Both glucose and fructose give "osazone".

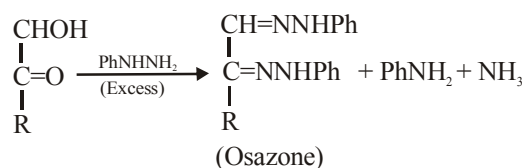
Reaction with glucose :



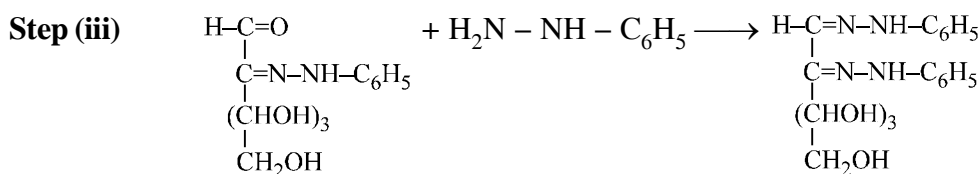
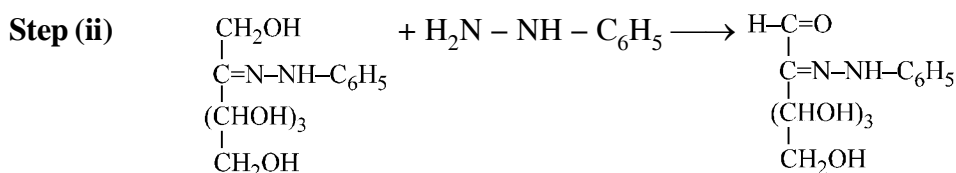
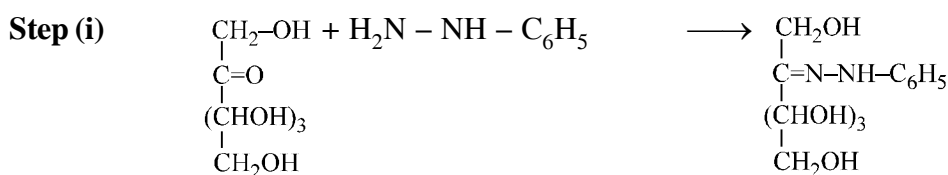
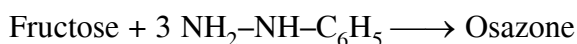
Mechanism :



Propose Mechanism for :



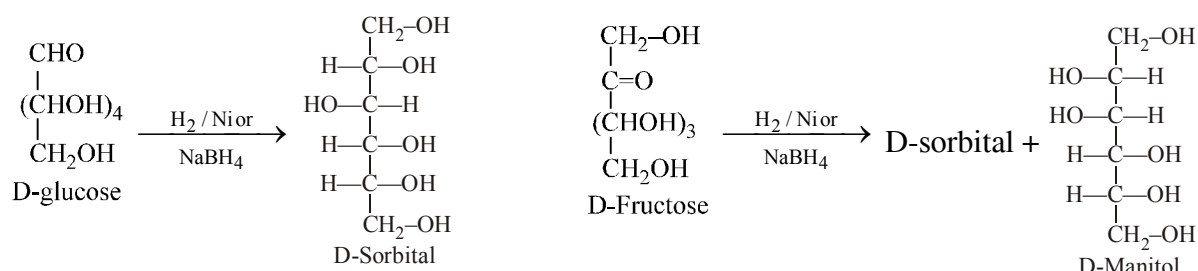
Reaction with fructose :



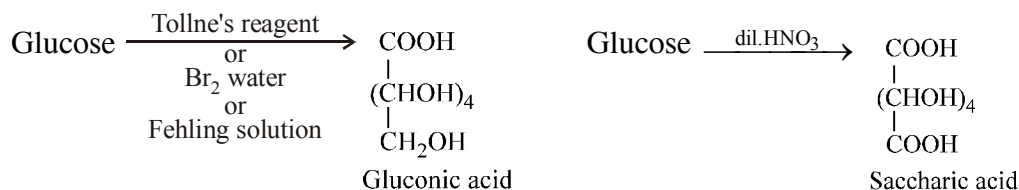
Glucose, Mannose & Fructose give same osazone because structure of last four carbons in these carbohydrates is same.

Only C-1 and C-2 in glucose and fructose are involved in osazone formation addition reaction do not run through out the chain. The failure to undergo further reaction has been explained by stabilization of the osazone by chelation.

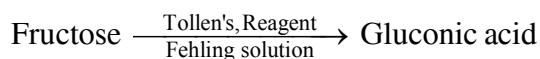
#### 6. Catalytic reduction:



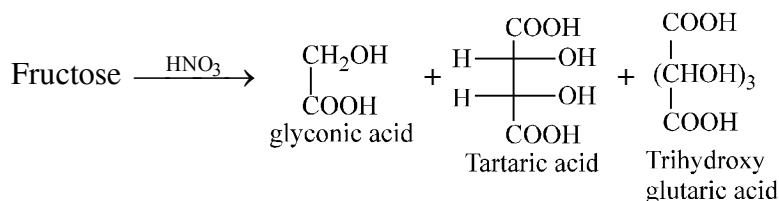
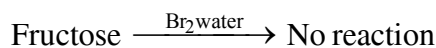
7. Oxidation:



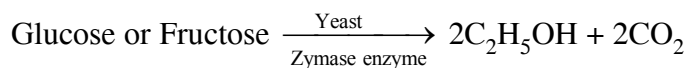
Oxidation of fructose :



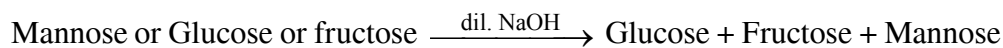
Fructose also reduces tollen's & fehling reagent because in basic medium fructose isomerises to glucose.



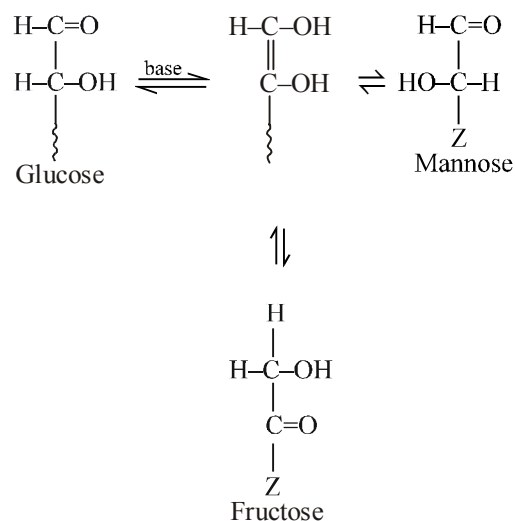
8. Reaction with enzyme:



9. Reaction with dil NaOH / Ca(OH)<sub>2</sub>

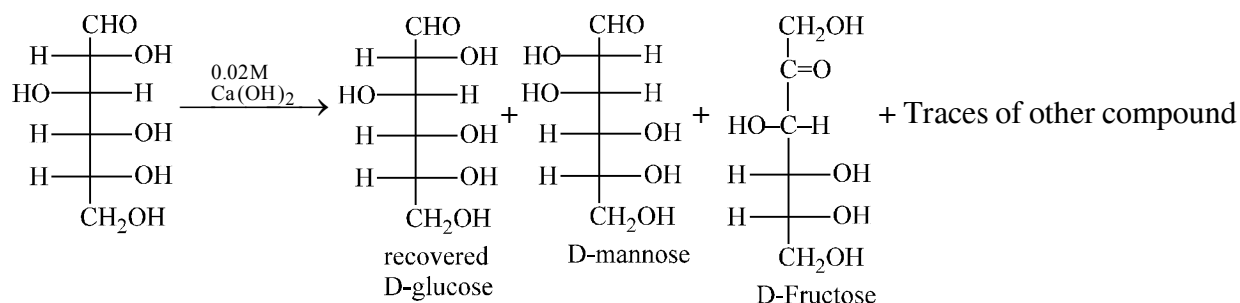


Mechanism :

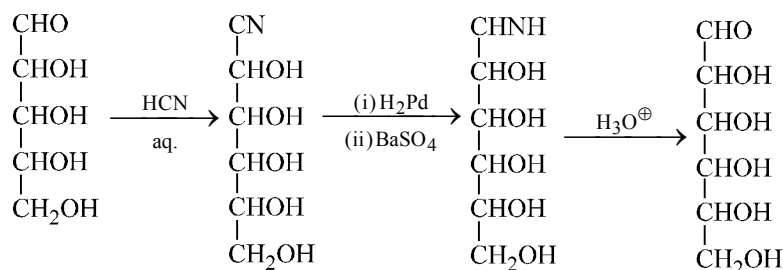


**Base-catalyzed isomerisation of aldoses and Ketoses:**

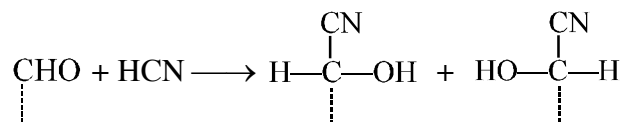
Although glucose in solution exists mostly in its cyclic hemiacetal forms it is also in equilibrium with a small amount of its acyclic aldehyde form.

**Method of ascending the sugar series:**

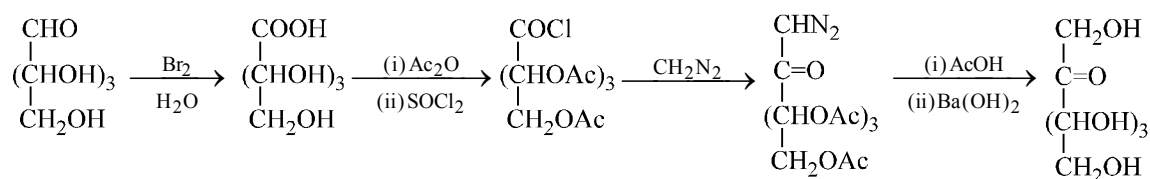
An aldose may be converted into its next higher aldose eg. an aldopentose into an aldohexose.

**By Kiliani Fischer upgradation:**

Theoretically two lactones are possible, since two cyanohydrin may be formed when hydrogen cyanide adds on to the aldopentose (a new asymmetrical carbon is produced)

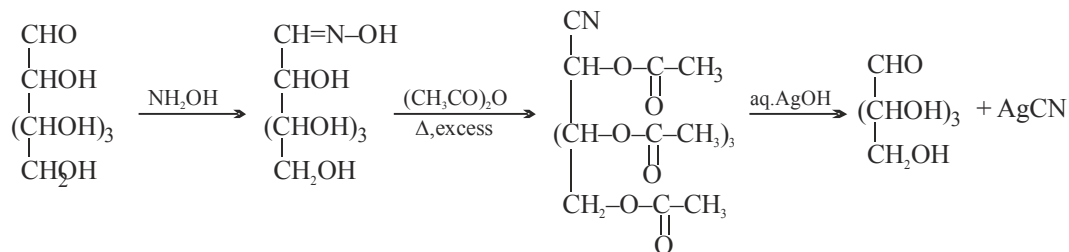


**Wolf from reaction :** Wolf from have stepped up an aldose to a ketose with one more carbon atom by a modified Arndt-Eistere reaction.

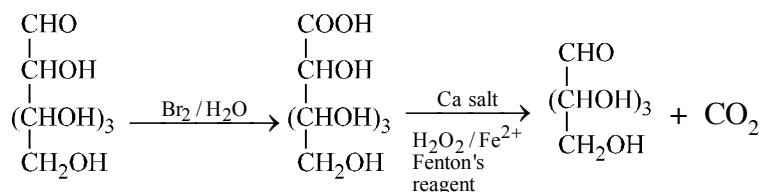


**Method of descending the sugar series :**

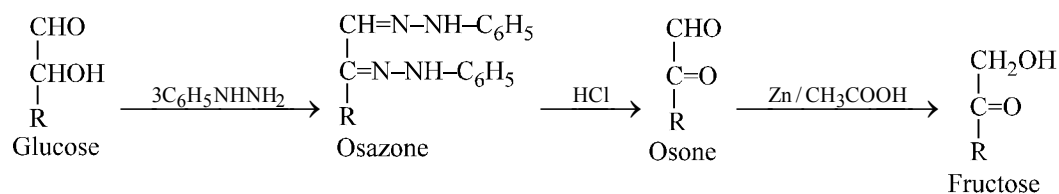
**Wohl's method:**



**Ruff's method:**

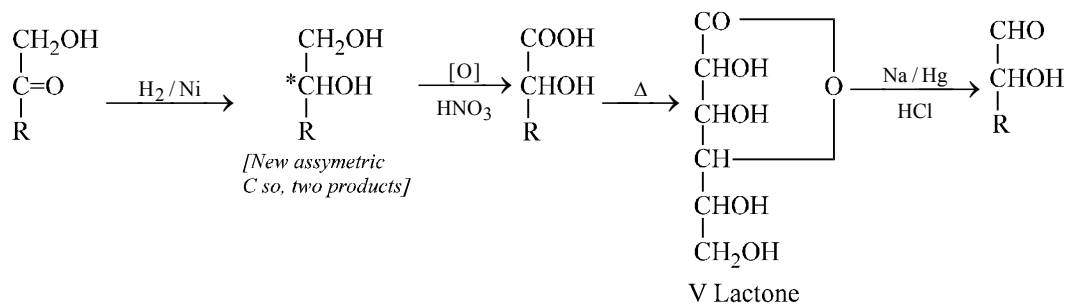


**Conversion of an aldehyde into a ketose :**



An aldehyde group is reduced more readily than a ketonic group.

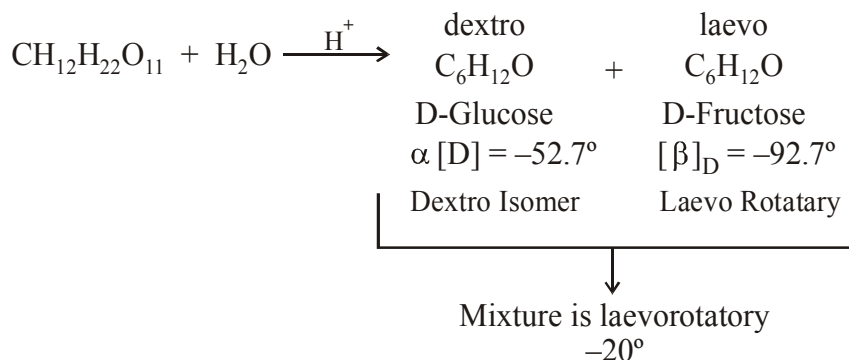
**Conversion of a Ketose into an allose :**



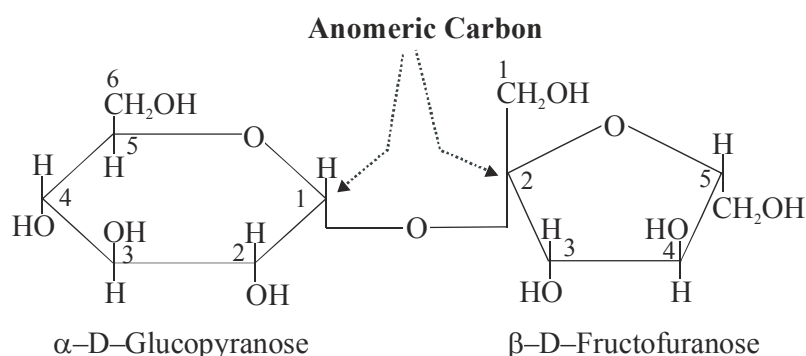
## SOME IMPORTANT CARBOHYDRATES

1. **Sucrose** ( $C_{12}H_{22}O_{11}$ ) : → A dimer of  $\alpha$ -D-Glucose &  $\beta$ -D-Fructose. It is white, crystalline & sweet substance soluble in water obtained from the sugar cane. When heated above its melting point. It forms a brown substance known as caramel.

It's aqueous solution is dextrorotatory  $[\infty]_D = +66.5^\circ$

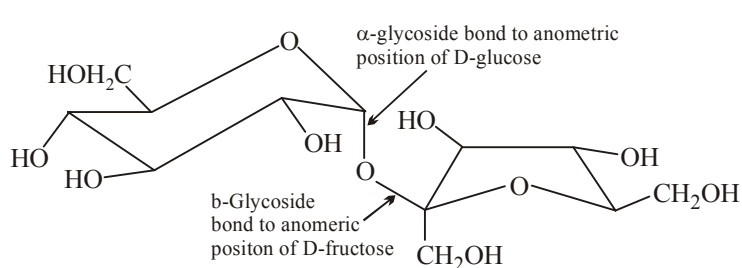


- Thus hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (-) & such a change is known as inversion of sugar and the mixture obtained on acidic hydrolysis is known as *invert sugar*.
- The inversion of cane-sugar may also be done by the enzyme invertase which is found in yeast.
- Sucrose is non-reducing sugar because it has stable acetal linkage & in aq. solution it does not give free carbonyl group and so it does not reduce Tollen's & Fehling's solution.
- This indicates that neither the aldehyde group of glucose nor the ketonic group of fructose is free in sucrose.

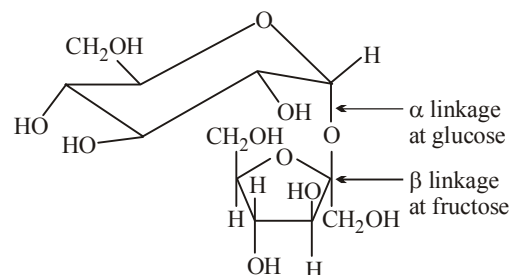


Structure of sucrose  
( $\alpha$ -D-glucopyranosyl- $\beta$ -D-fructofuranoside)

Do not show mutarotation .



**Fig. Showing Sucrose in other structure**

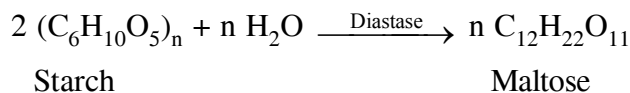


**Fig. Showing Sucrose in other structure**

## 2. Maltose :

- It is dimer of  $\alpha$ -D-Glucose

It is obtained by partial hydrolysis of starch by the enzyme diastase present in malt i.e., sprouted barely seeds.

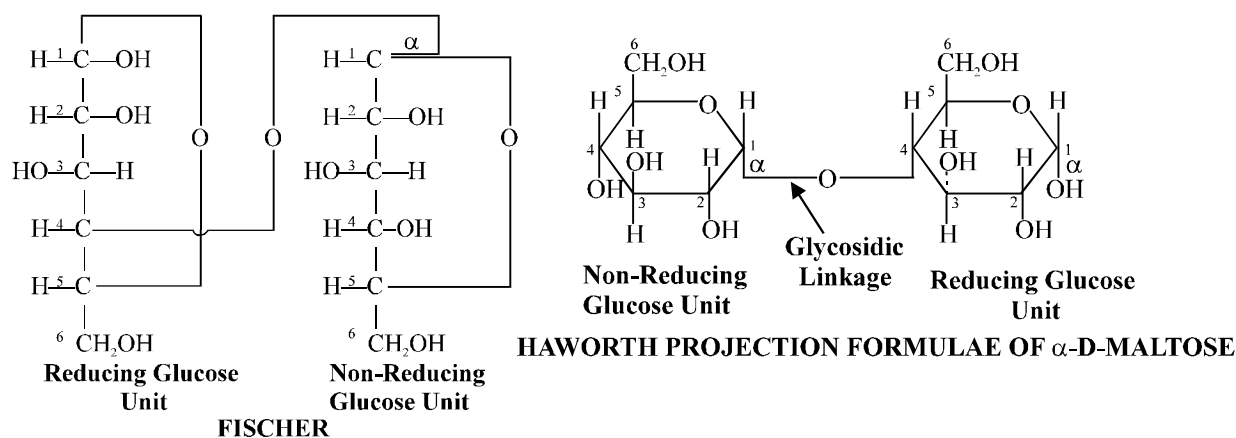


- Hydrolysis of one mole of maltose yields two moles of D-glucose.
- Maltose is a reducing sugar since it forms an osazone, undergoes mutarotation and also reduces Tollen's reagents and Fehling's solutions, Methylation studies have revealed that

(i) Both glucose units are present in the pyranose form.

(ii)  $\text{C}_1$  of one glucose unit is linked to  $\text{C}_4$  of the other

Further since maltose is hydrolysed by the enzyme maltase which specifically hydrolyses  $\alpha$ -glycosidic linkage, therefore, the non-reducing glucose unit in maltose must be present in the  $\alpha$ -form. In other words,  $\text{C}_1 - \alpha$  of non-reducing glucose unit is attached to  $\text{C}_4$  of the reducing glucose unit as shown in the figure on next page.



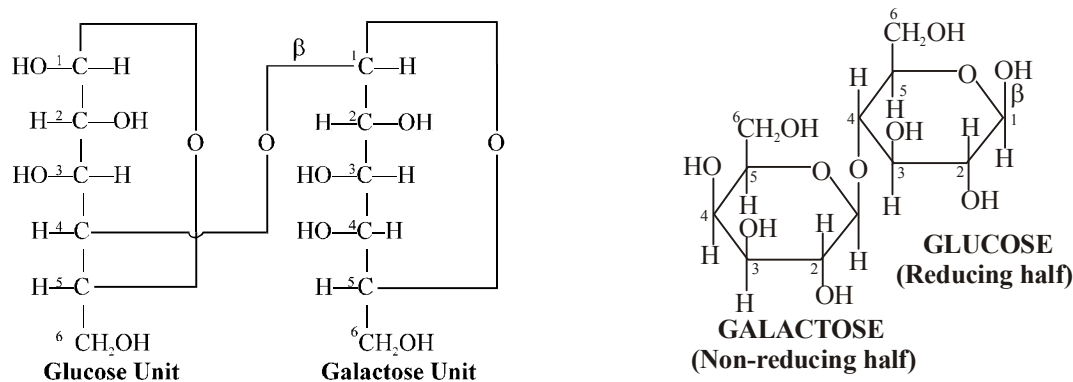
## 3. Lactose (Milk sugar) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

Lactose occurs in milk and that is why it is called milk sugar.

Lactose on hydrolysis with dilute acid or by enzyme lactase, yields an equimolar mixture of D-glucose and D-galactose. It is a reducing sugar it forms an osazone, undergoes mutarotation and also reduces Tollen's or Fehling's solution. Methylation studies have revealed that

- (i) both glucose and galactose are present in the pyranose form.
- (ii) glucose is the reducing half while  $\beta$ -galactose is the non-reducing half.
- (iii)  $\text{C}_1$  of galactose unit is connected to  $\text{C}_4$  of glucose unit.

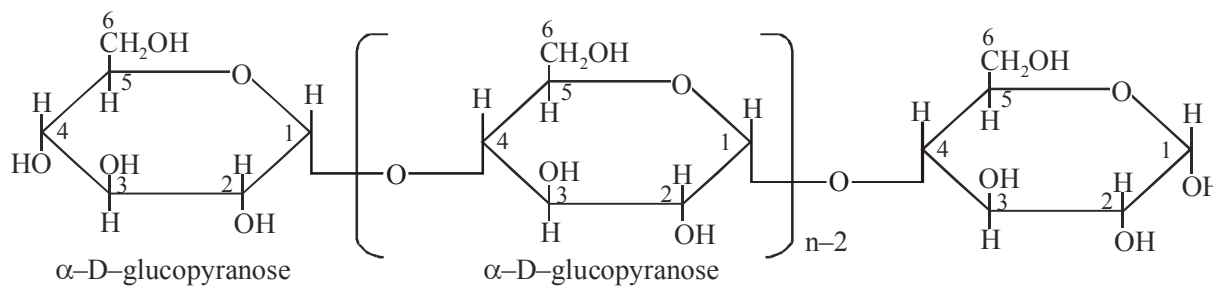
Further since emulsin, as, enzyme which specifically hydrolyses  $\beta$ -glycosidic linkages also hydrolyses lactose, therefore, galactose must be present in the  $\beta$ -form. In other words, in lactose,  $C_1 - \beta$  of galactose is attached to  $C_4$  of glucose as shown in figure.



#### 4. Starch Amylum, $(C_6H_{10}O_5)_n$

**Occurrence :** The value of  $n$  (100 – 3000) generally however it may varies from source to source. It is the chief food reserve material or storage polysaccharide of plants and is found mainly in seeds, roots tubers wheat, maize, rice, potatoes, barley, bananas and sorghum are the main sources of starch. Starch occurs in the form of granules, which vary in shape and size depending upon their plant source.

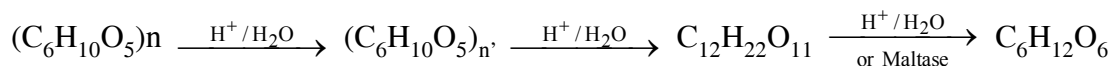
Occurs in all green plants. Starch consists of two fractions, one being known as (amylose), which gives blue colour with iodine. This blue colour is believed to be due to the formation of an inclusion complex. An aqueous solution of  $\alpha$ -amylose slowly forms a precipitate, since  $\alpha$ -amylose has a strong tendency to 'revert' to the insoluble state in solution. Amylopectin is insoluble in water and is stable towards both hydrolysis to maltose by the enzyme diastase and to D(+)-glucose by dilute acids (amylopectin gives about 50 percent of maltose).



$\alpha$ -amylose consists of an unbranched chain, with a molecular weight varying between 10,000 ( $n \approx 60$ ) and 10,00,000 ( $n \approx 6,000$ ), The value of  $n$  depends on the source and treatment of  $\alpha$ -amylose.



**Properties :** (i) Starch is a white amorphous powder sparingly soluble in water. Its aqueous solution gives a blue colour with iodine solution due to the formation of an inclusion complex. The blue pearls on cooling. (ii) On hydrolysis with dilute mineral acids or enzymes, starch breaks down first to smaller molecules ( $n > n'$ ), then to maltose and finally to D-glucose.



Starch

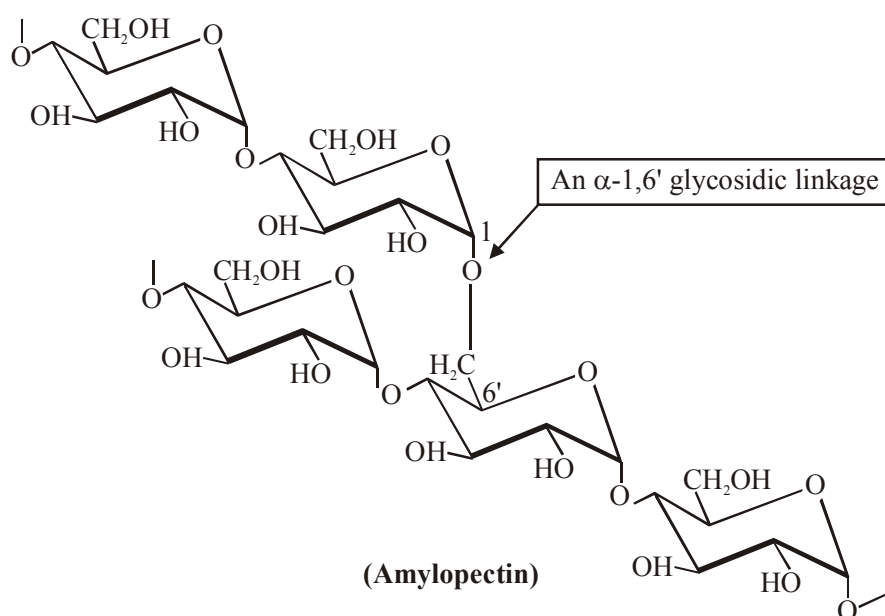
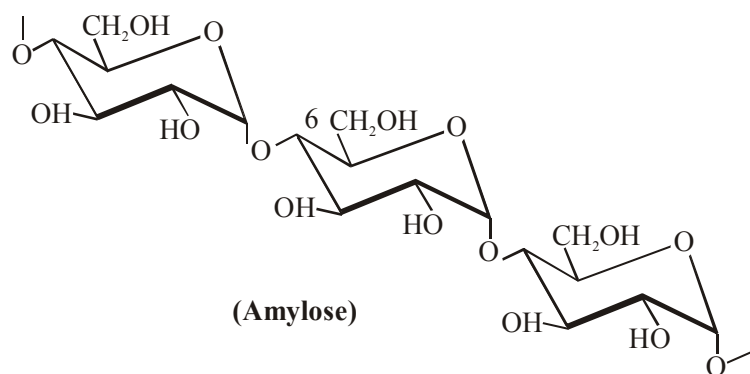
Maltose

D-Glucose

(iii) Starch is a non-reducing saccharide. It neither reduces Tollen's reagent or Fehling's solution nor forms an osazone. This suggests that all hemiacetal OH groups of glucose units at  $C_1$  are not free but are involved in glycosidic linkages.

**Composition :** Starch is not a single compound but is a mixture of two components—a water soluble component called amylose (10-20%) and a water insoluble component called amylopectin (80-90%). Both amylose and amylopectin are polymers of  $\alpha$ -D-glucose.

**Structure of amylose :** Amylose is water soluble and gives blue colour with iodine solution. It may have 100-3000 glucose units, i.e., its molecular mass can vary from 10,000 to 500,000. It is a linear polymer of  $\alpha$ -D-glucose in which  $C_1$  of one glucose unit is attached to  $C_4$  of the other through  $\alpha$ -glycosidic linkage as shown in figure.



**Pectins**

Pectins are found in plant and fruit juices. Their characteristic property is the ability of their solutions to gelate, i.e. form jellies. They have a high molecular weight and are polygalacturonic acid (linked 1,4) with the carboxyl groups partially esterified with methanol.

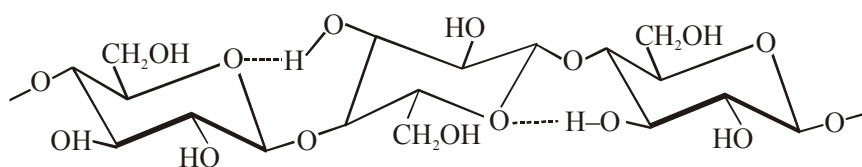
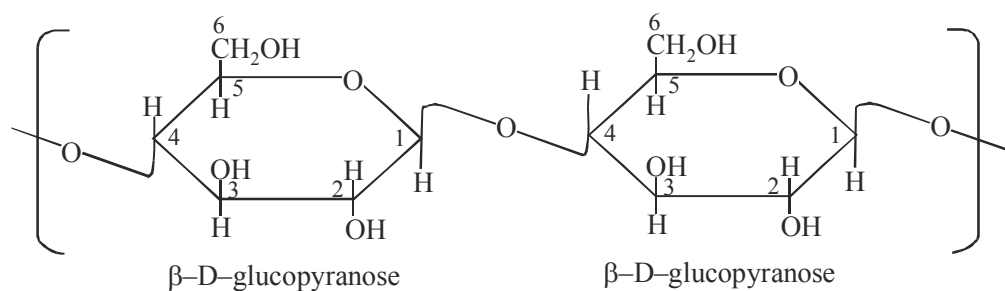
**Glycogen ( $C_6H_{10}O_5$ )<sub>n</sub> :**

Glycogen is found in nearly all animals cells, occurring mainly in liver. It is the reserve carbohydrate of animals and so is often known as 'animal starch'. It has also been isolated from plant sources.

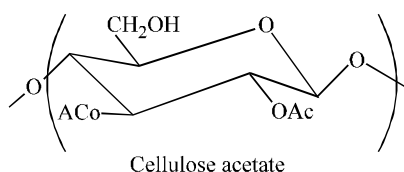
Glycogen is a white powder, soluble in water, the solution giving a purplish-red colour with iodine. On hydrolysis with dilute acid, glycogen gives D(+)-glucose. The molecular weight of glycogen has been given as 10,00,000 to 50,00,000 and glycogen contains highly branched chains. Glycogen has a structure similar to amylopectin, except that it has more cross-linking.

**5. Cellulose:**

Cellulose is colourless, solid which is insoluble in water & organic solvents. But it is soluble in ammonical cupric hydroxide (Schweizer's reagent) or in conc. HCl cellulose is a regular polymer of d-glucopyranose residues connected by  $\beta$ -1,4 glycosidic linkages. It is straight chain polymer.

**Some points about cellulose :**

1. General empirical formula ( $C_6H_{10}O_5$ )
2. Cellulose +  $H_2O \xrightarrow{H^+}$  96% of crystalline D-glucose
3. No. of monomer units in cellulose are 1000 – 1500 in one molecule.
4. Cellulose doesn't show mutarotation (like starch)
5. It is non reducing sugar because there is no hemiacetal linkage.
6. Acetylation, nitration & methylation of cellulose give trisubstituted cellulose which suggest that only three – OH groups are free.



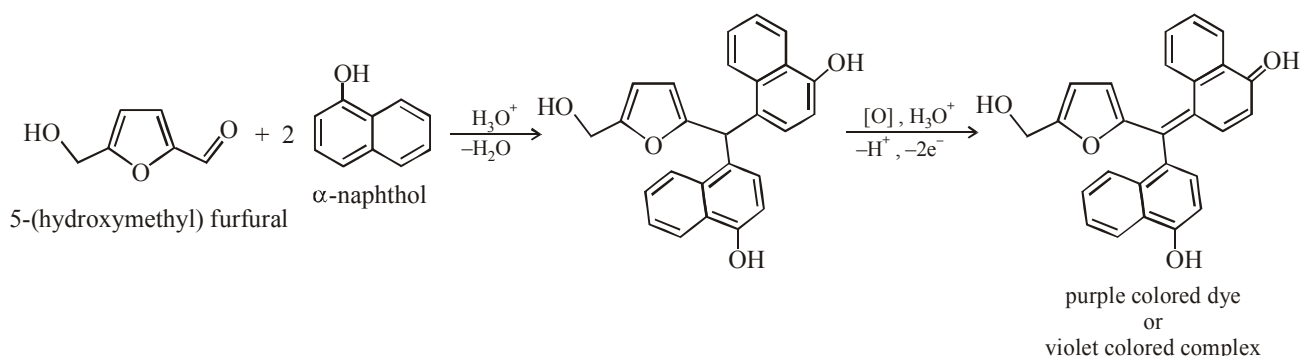
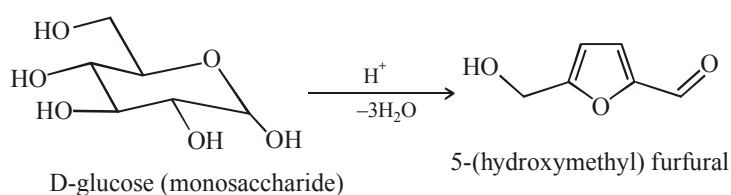
## TEST OF CARBOHYDRATES

- |                 |                  |                       |                  |
|-----------------|------------------|-----------------------|------------------|
| 1. Molish Test  | 2. Barfoed Test  | 3. Salivanoff's Test. | 4. Bial's Test   |
| 5. Osazone Test | 6. Benedict Test | 7. Fehling Test       | 8. Tollen's Test |
| 9. Iodine Test  |                  |                       |                  |

### 1. Molish Test

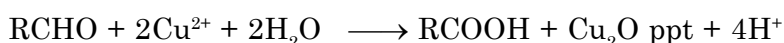
Molish test is the general test for the identification of all carbohydrates (Monosaccharides, Disaccharides and Poly saccharides ) and Glycoprotein, Sulphuric acid is added to hydrolyzes the all glycosidic linkage to yield monosaccharides, which on dehydration form furfural or its derivative in presence of acid. which condensed with  $\alpha$ -naphthol to give a violet colored complex.

Oligosaccharide or poly saccharides +  $H_2SO_4 \xrightarrow{H_3O^+ \text{ (Hydrolysis)}}$  Monosaccharides



### 2. Barfoed Test

This test is used to differentiate reducing monosaccharide from a disaccharide sugar. It is done in mild acidic medium.



It is based on the reduction of copper(II) acetate to copper(I) oxide ( $Cu_2O$ ), which forms a brick-red precipitate.

Reducing monosaccharides react with Barfoed's reagent much faster than disaccharides and produce red precipitate of copper (I) oxide within three minutes.

Disaccharide sugars as they are weaker reducing agents, react at a slower rate, so they do not form red precipitate even for ten minutes.

### 3. Selivanoff's Test

It is test of Ketose sugar (eg Fructose), it is used to differentiate Ketose sugar from aldose sugar.

This test relies on the principle that keto hexose are more rapidly dehydrated than aldoses to form 5-Hydroxy methyl furfural when heated in acidic medium, which on condensation with resorcinol, a cherry red (or Brown red) colored complex is formed rapidly indicating a positive test.



### 5. Osazone Test

Reducing Sugars when heated with Phenyl Hydrazine, Characteristic yellow crystals of Osazone are formed with specific shape.

Glucose, Mannose & Fructose gives same Osazone crystals, like NEEDLE SHAPED.

Maltose gives Maltosazone crystals, like SUNFLOWER SHAPED.

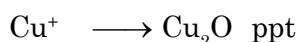
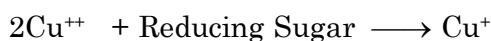
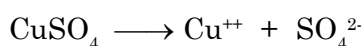
Lactose gives lactosazone crystals,

like TIGHT BALL or POWDER PUFF SHAPED..

### 6. Benedict test

Carbohydrates which has Aldehyde functional group (Not Aromatic Aldehyde) or Having alpha hydroxy ketone gives positive Benedict Test

It is in mild Basic Medium.



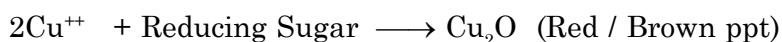
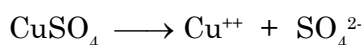
Glucose (Blue Red Solution), Galactose (Orange Red Solution)

Maltose (Dark Brown with Brick Red Solution), Fructose (Dark Brown with Brick Red Solution)

Xylose (Brick Red solution)

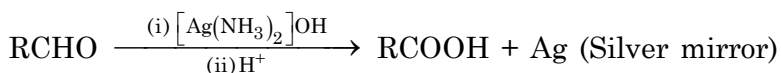
### 7. Fehling's test

All reducing Carbohydrates give Positive Fehling's test with Fehling solution. Carbohydrates which has Aldehyde functional group (Not Aromatic Aldehyde) and alpha hydroxy carbonyl also gives positive Fehling's test (e.g. fuctose). While Ketones give negative fehling test. During this reaction the aldehyde group is oxidised to acid while the copper ions are reduced to red/brown precipitate of  $\text{Cu}_2\text{O}$ . This is a common test used to detect glucose in urine as positive indication of diabetes.



### 8. Tollen's test

This test is also given by reducing sugars. Carbohydrates reacts with Tollens reagent forms a silver mirror on the inner walls of the test tube. This confirms the presence of reducing sugars. Silver ions are reduced to metallic silver.



**Note :** Sucrose, poly sachharides also others non reducing sugar do not give Benedict test, Fehling test and Tollen's Test.

### 9. Iodine Test

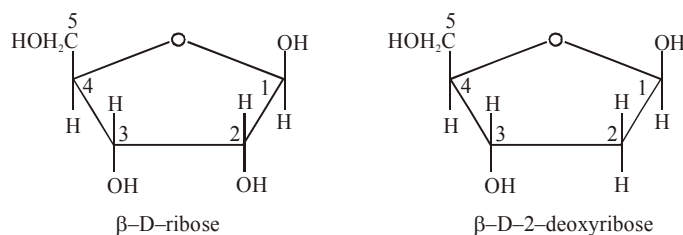
The iodine test is used to test for the presence of starch. Starch turns into an intense 'Deep blue' colour upon addition of aqueous solutions of the triiodide anion.

## NUCLEIC ACIDS

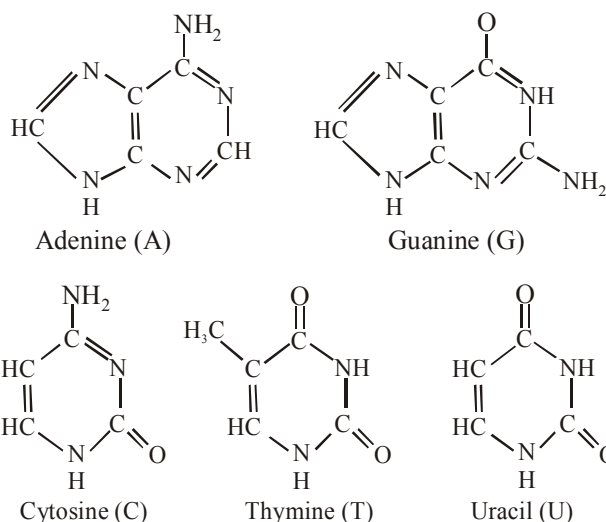
The particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called **nucleic acids**. These are mainly of two types, the **deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)**. Since nucleic acids are long chain polymers of **nucleotides**, so they are also called polynucleotides.

### Chemical Composition of Nucleic Acids

Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases). In DNA molecules, the sugar moiety is  $\beta$ -D-2-deoxyribose whereas in RNA molecule, it is  $\beta$ -D-ribose.

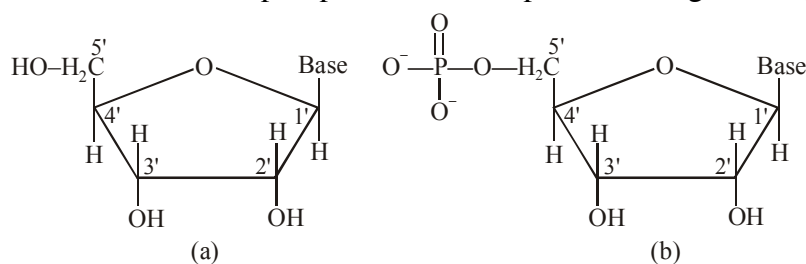


DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T). RNA also contains four bases, the first three bases are same as in DNA but the fourth one is uracil (U).



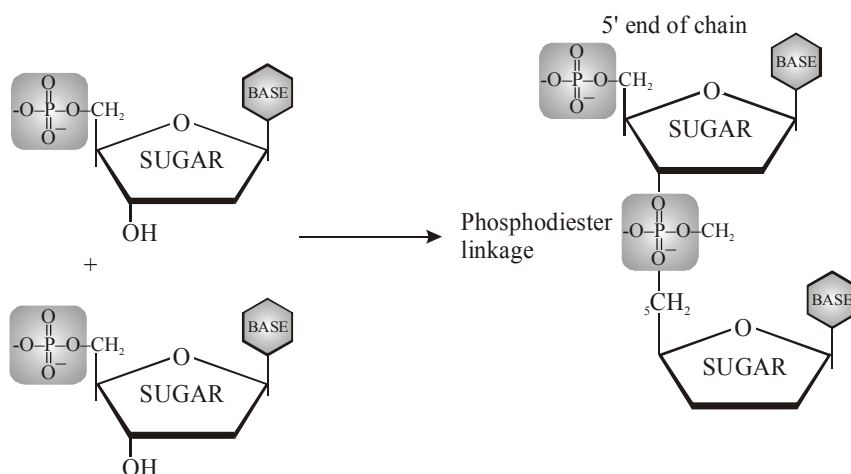
### Structure of Nucleic Acids

A unit formed by the attachment of a base to 1' position of sugar is known as **nucleoside**. In nucleosides, the sugar carbons are numbered as 1', 2', 3', etc. in order to distinguish these from the bases. When nucleoside is linked to phosphoric acid at 5'-position of sugar moiety, we get a nucleotide



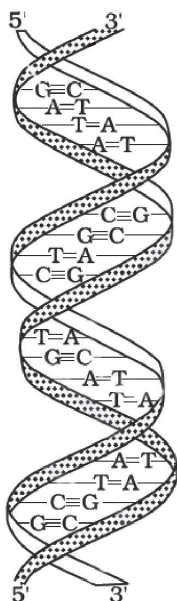
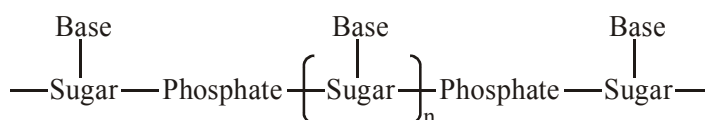
Structure of (a) a nucleoside and (b) a nucleotide

Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of the pentose sugar. The formation of a typical dinucleotide is shown in Fig.



### Formation of dinucleotide

A simplified version of nucleic acid chain is as shown below.

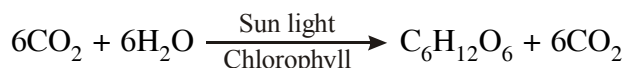


Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure also. James Watson and Francis Crick gave a double strand helix structure for DNA (Fig. 14.7). Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.

In secondary structure of RNA, helices are present which are only single stranded. Sometimes they fold back on themselves to form a double helix structure. RNA molecules are of three types and they perform different functions. They are named as **messenger RNA (m-RNA)**, **ribosomal RNA (r-RNA)** and **transfer RNA (t-RNA)**.

**Fig. : Double strand helix structure for DNA**

### Photosynthesis



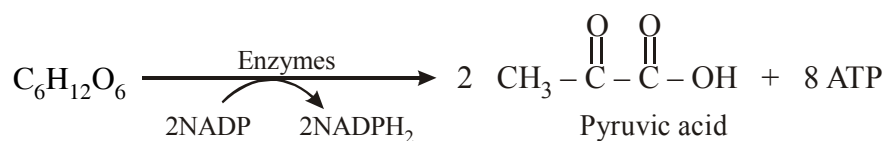
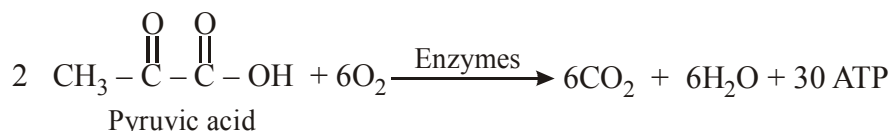
\* 3ATP are required to fix 1 mole of  $\text{CO}_2$ . Therefore 18 ATP are required to fix 6 mole of  $\text{CO}_2$ .

### Cellular Respiration



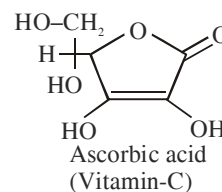
\* 38 ATP are generated by complete oxidation of 1 mole of glucose. But net gain of ATP are 36, because 2 ATP are consumed when pyruvic acid enter in mitochondria.

\* Complete oxidation takes place in two steps

**Step - 1 : Glycolysis or EMP or HMP (Completes in cytoplasm)****Step - 2 : Krebs cycle (Completes in mitochondria)****VITAMINES****Table : Some important Vitamins, their Sources and their Deficiency Diseases**

Sl. No.	Name of Vitamins	Sources	Deficiency diseases
1	Vitamin A	Fish liver oil, carrots, butter and milk	Xerophthamlia (hardening of cornea of eye) Night blindness
2	Vitamin B <sub>1</sub> (Thiamine)	Yeast, milk, green vegetables and cereals	Beri beri (loss of appetite, retarded growth)
3	Vitamin B <sub>3</sub> (Riboflavin)	Milk, eggwhite, liver, kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
4	Vitamin B <sub>3</sub> (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
5	Vitamin B <sub>12</sub>	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
6	Vitamin B <sub>5</sub> (Ascorbic acid)	Citrus fruits, amla and green leafy vegetables	Scurvy (bleeding gums)
7	Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)
8	Vitamin E	Vegatable oils like wheat germ oil, sunflower oil, etc.	Increased fragility of RBCs and muscular weakness
9	Vitamin K	Green leafy vegetables	Increased blood clotting time

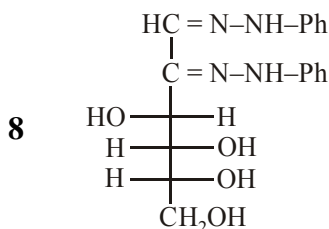
**NOTE :** Vitamin-D , E , K , A are fat soluble vitamins.  
Vitamin-B , C are water soluble vitamins.





## EXERCISE # O-I

- 1 Iso-electric point of alanine is (pH = 6). At which pH, maximum concentration of zwitter ion of alanine will be present ?  
 (A) pH > 6 (B) pH < 6 (C) pH = 6 (D) pH = 7 **BM0001**
- 2 At iso-electric point :  
 (A) Concentration of cation is equal to concentration of anion  
 (B) Net charge is zero  
 (C) Maximum conc. of di-pole ion (Zwitter ion) will be present  
 (D) All of the above **BM0002**
- 3 Which of following amino acid has lowest iso-electric point ?  
 (A) Glycine (B) Alanine (C) Aspartic acid (D) Lysine **BM0003**
- 4  $\text{H}-\text{C}\equiv\text{C}-\text{H} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} (\text{A}) \xrightarrow[\text{(2) H}_3\text{O}^+]{\text{(1) NH}_3+\text{HCN}} (\text{B})$  ; Product (B) of given reaction is :  
 (A) Glycine (B) Alanine (C) Valine (D) Leucine **BM0004**
- 5 Which amino acid does not contain chiral centre ?  
 (A) Valine (B) Leucine (C) Glycine (D) Iso-leucine **BM0005**
- 6 Which of the following is Sanger reagent ?  
 (A) 2,4-Di-nitro flurobenzene (B) Phenyl isocyanane  
 (C) 2,4-Di-nitro chlororbenzene (D) 12,4-Di-nitro-iodobenzene **BM0006**
- 7 A D-carbohydrate is :  
 (A) Always dextrorotatory  
 (B) Always laevorotatory  
 (C) Always the mirror of the corresponding L-carbohydrate  
 (D) None of these **BM0007**



8 The given osazone can be obtained by :

- (A) D-glucose                      (B) D-mannose                      (C) D-Idose                      (D) Both (A) & (B)

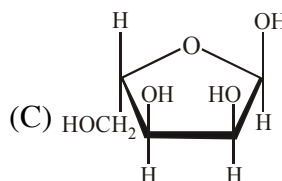
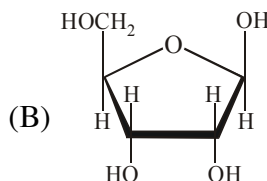
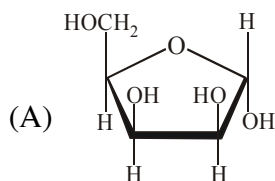
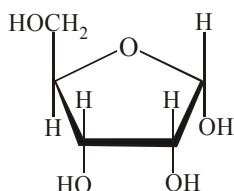
BM0008

9 Which of the following pair gives same phenyl osazone ?

- (A) D-Glucose and D-Allose                      (B) D-Glucose and D-Altrose  
 (C) D-Glucose and D-Mannose                      (D) D-Glucose and D-Talose

BM0009

10 Which of the following represents the anomer of the compound shown ?



(D) None of these

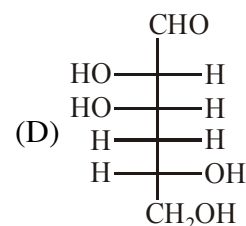
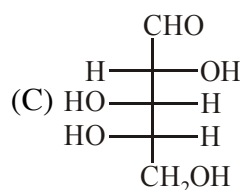
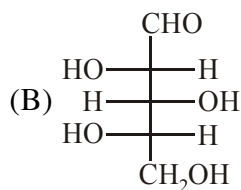
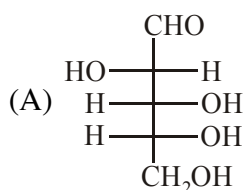
BM0010

11 For the complex conversion of D-glucose into the corresponding osazone, the minimum number of equivalents of phenyl hydrazine required is :

- (A) Two                      (B) Three                      (C) Four                      (D) Five

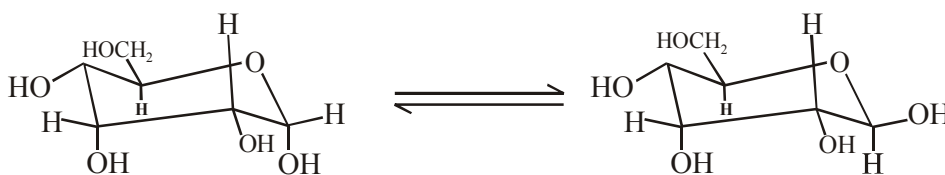
BM0011

12 Which of the following structure is L-arabinose ?



BM0012

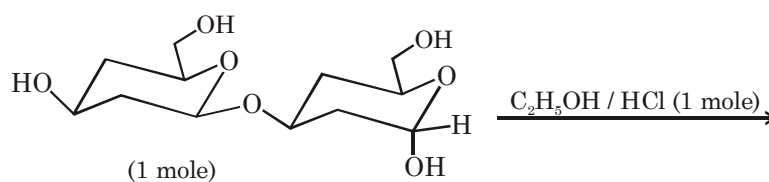
13 Which one of the statements concerning the equilibrium shown is true ?



- (A) The two structures are enantiomers of each other. They have equal but opposite optical rotations and racemize slowly at room temperature
- (B) The two structures are enantiomers of each other. They racemize too rapidly at room temperature for their optical rotations to be measured
- (C) The two structures are diastereomers of each other. Their interconversion is called mutarotation
- (D) The two structures are diastereomers of each other. Their interconversion does not require breaking and making bonds, only a change in conformation

BM0013

14 Major product of following reaction is :



- (A)
- (B)
- (C)
- (D)

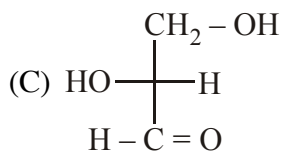
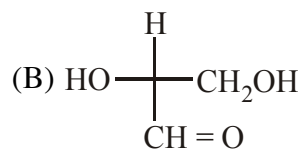
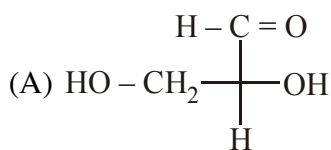
BM0014

15 What is the structure of L-glucose ?

- (A) 
$$\begin{array}{c} \text{CHO} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{CH}_2\text{OH} \end{array}$$
- (B) 
$$\begin{array}{c} \text{CHO} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$$
- (C) 
$$\begin{array}{c} \text{CHO} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{CH}_2\text{OH} \end{array}$$
- (D) None of these

BM0015

16 What is the structure of L-glyceraldehyde ?



(D) Both (A) and (B)

BM0016

17 
$$\begin{array}{c} \text{HC} - \text{OH} \\ || \\ \text{C} - \text{OH} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \quad | \\ \text{H} - \text{C} - \text{OH} \\ | \quad | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$$
, the given is enol form of :

(A) D-glucose                      (B) D-mannose                      (C) D-fructose                      (D) All of these

BM0017

18 D-glucose & D-fructose can be differentiated by :

(A) Fehling solution              (B) Tollen's reagent              (C) Benedict test              (D)  $\text{Br}_2 / \text{H}_2\text{O}$

BM0018

19 D-Glucose exist in x different forms. The value of x (stereoisomer) is :

(A) 2                                      (B) 3                                      (C) 4                                      (D) 5

BM0019

20  $\text{D-Mannose} \xrightleftharpoons{\text{HO}^-} \text{D-Glucose} \xrightleftharpoons{\text{HO}^-} (\text{A}) ;$

Product (A) of above reaction is :

(A) D-glucose                      (B) D-fructose                      (C) D-talose                      (D) D-idose

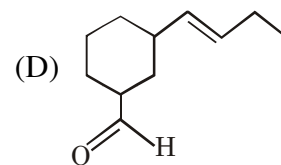
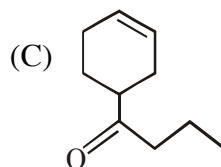
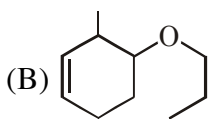
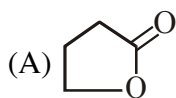
BM0020

21 Which of the following statement is not correct for maltose.

(A) It is a disaccharide                      (B) It undergoes mutarotation  
(C) It is a reducing sugar                      (D) It does not have hemiacetal group.

BM0021

22 A compound which does not react with Brady's reagent but decolourise  $\text{Br}_2 / \text{H}_2\text{O}$  solution is :



BM0022

23 Maltose is made up of two sugars—

(A) Glucose

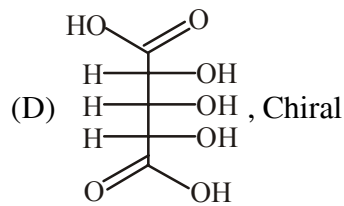
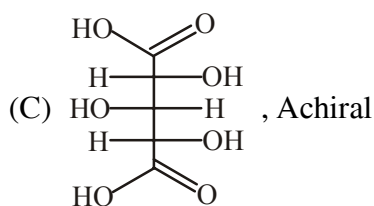
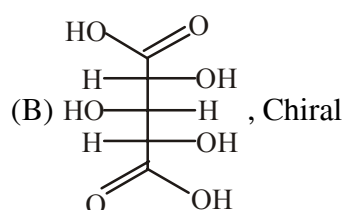
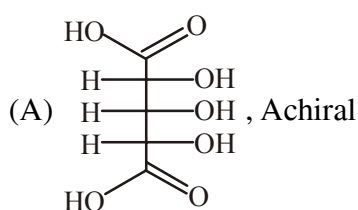
(B) Fructose

(C) Glucose & galactose

(D) Glucose & fructose

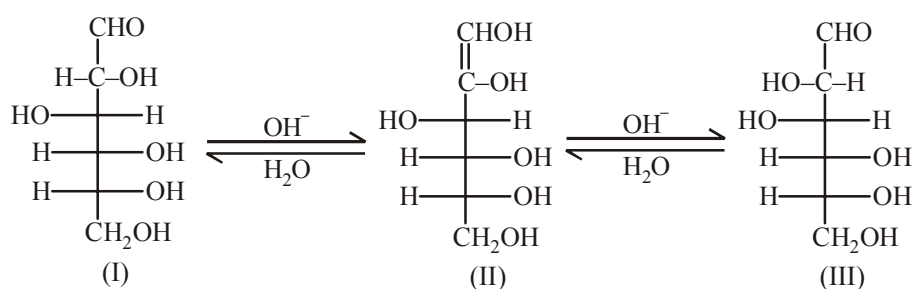
BM0023

24 D-Ribose when treated with dilute  $\text{HNO}_3$  forms.



BM0024

25 Consider the given process



and identify the incorrect statement.

(A) Configuration at C-2 is lost on enolisation

(B) I and III are epimers

(C) Proton transfer from water to C-1 converts ene diol to an aldose.

(D) D-glucose can isomerise to D-fructose through enol intermediate.

BM0025

26 When methyl D-glucopyranoside is treated with  $\text{HIO}_4$  its number of mole consumed per mole of the sugare is -

- (A) 2 (B) 3 (C) 4 (D) 5

BM0026

27  $\alpha$  - amino acid when heated with  $\text{NaOH}/\text{CaO}$  forms -

- (A)  $\alpha,\beta$  - unsaturated acid (B)  $\alpha,\beta$  - unsaturated amine  
(C) Carboxylic acid (D) Amine

BM0027

28 The configuration of the C-2 epimer of D-glucose is-

- (A) 2R, 3S, 4R, 5S (B) 2S, 3S, 4R, 5R  
(C) 2S, 3R, 4S, 5R (D) 2R, 3S, 4R, 5R

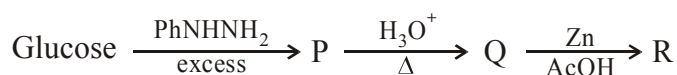
BM0028

29 Mutarotation involve-

- (A) Racemisation (B) Diastereomerisation  
(C) Optical resolution (D) Conformational inversion

BM0029

30 Consider the reaction sequence -

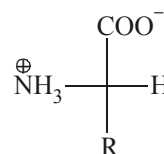


The product R is -

- (A) Arbinose (B) Sorbitol (C) Fructose (D) Mannose

BM0030

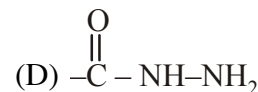
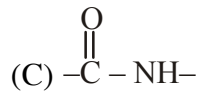
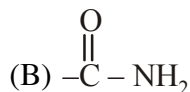
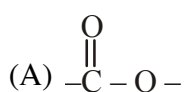
31 The pH of the solution containing following zwitter ion species is



- (A) 4 (B) 5 (C) 7 (D) 9

BM0031

32 Peptide linkage is -



BM0032

33 Same osazone derivative is obtained in case of D-glucose, D-Mannose and D-Fructose due to

(A) The same configuration at C-5

(B) The same constitution.

(C) The same constitution at C-1 and C-2

(D) The same constitution and acid configuration at C-3, C-4, C-5 and C-6 but different constitution and configuration at C-1 and C-2 which becomes identical by osazone formation.

BM0033

34 D(-)-Erythrose  $\xrightarrow{\text{NaBH}_4}$  (P)

D(-)-Threose  $\xrightarrow{\text{NaBH}_4}$  (R)

Which of the following statement is correct about P and R ?

(A) Both are optically active

(B) Both are optically inactive

(C) P is optically inactive and R is optically active

(D) Neither P nor R has asymmetric carbon.

BM0034

35 The monomer of nucleic acids are held together by

(A) Phosphodiester linkage

(B) Amide linkage

(C) Glycosidic linkage

(D) Ester linkage

BM0035

36 Select the incorrect statement about Nylon 2-nylon-6.

(A) It is a copolymer

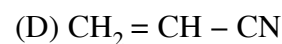
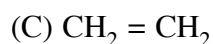
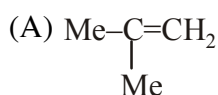
(B) It is biodegradable

(C) It is an alternating polyamide

(D) It is made up of  $\text{CH}_3-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$  and  $\text{H}_2\text{N}(\text{CH}_2)_5\text{COOH}$

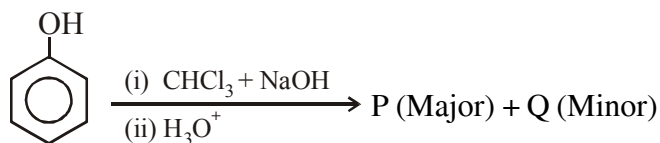
BM0036

37 The monomer that can undergo radical, cationic and anionic polymerisation with equal ease-



BM0037

38 Consider the reaction-



Mixture of A and B can be best separated by -

- (A) Steam distillation (B) Vacuum distillation  
(C) Fractional distillation (D) Crystallisation

BM0038

39 Which of the following statements are incorrect :

- (A) Copolymer of 1,3-butadiene & acrylonitrile is Buna-S  
(B) HDPE is obtained by Ziegler-Natta polymerisation  
(C) Polymer dacron can be polyester fabric  
(D) Phenol & formaldehyde resin is called novolac

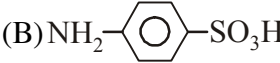
BM0039

40 A segment (X) of cellulose obtained on partial hydrolysis has molecular mass 1476 gm. On complete acidic hydrolysis, mass of the product obtained is 1620 gm. Find out the number of glycosidic linkage(s) present in segment (X) :

- (A) 8 (B) 6 (C) 4 (D) 10

BM0040

41 When solidum extract is treated with  $\text{FeCl}_3$  solution a blood red coloured is obtained due to the presence of -

- (A)  (B)   
(C)  (D) 

BM0041

42 The monomer that undergo radical polymerisation most easily is

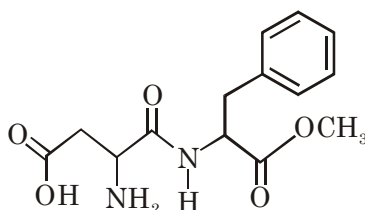
- (A)  $\text{CH}_2=\text{CH}_2$  (B)  $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$  (C)  $\text{CH}_2=\text{C} \begin{array}{l} \text{Me} \\ \text{Me} \end{array}$  (D)  $\text{CH}_3-\text{CH}=\text{CH}_2$

BM0042



## EXERCISE # O-II

- 1 Carbohydrates may be :  
 (A) Sugars  
 (B) Starch  
 (C) Polyhydroxy aldehyde/ ketones  
 (D) Compounds that can be hydrolysed to sugar
- BM0043**
- 2 Select the correct statement :  
 (A) Glycosides do not undergo mutarotation  
 (B) All OH groups of a cyclic monosaccharides are converted to ethers by treatment with base and an alkyl halide  
 (C)  $\alpha$ -D glucose reacts with  $\text{Ag}_2\text{O}$  and excess  $\text{CH}_3\text{I}$  to form tetramethyl ether  
 (D) D-glucose upon treatment with warm  $\text{HNO}_3$  forms D-glucaric acid
- BM0044**
- 3 "Aspartame" is roughly 100 times as sweet as cane sugar. On complete hydrolysis of aspartame, products obtained is/are :



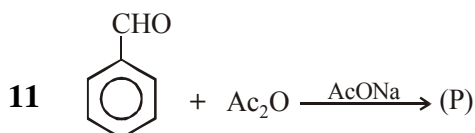
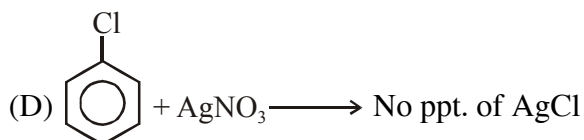
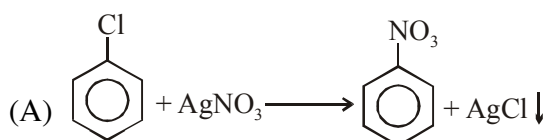
- (A)  $\text{PhCH}_2-\underset{\text{CO}_2\text{H}}{\text{CH}}-\text{NH}_2$     (B)  $\text{H}_2\text{N}-\underset{\text{CH}_2\text{CO}_2\text{H}}{\text{CH}}-\text{CO}_2\text{H}$     (C)  $\text{CH}_3\text{OH}$     (D)  $\text{CH}_3-\underset{\text{CO}_2\text{H}}{\text{CH}}-\text{NH}_2$

**BM0045**

- 4 Starch molecules are polymer with repeating glucose units. Select the correct statement(s).  
 (A) Glucose units are joined through  $\alpha$ -glycosidic linkage  
 (B) The branches of amylopectin are linked to the chain with  $\alpha$ -1,6'-glycosidic linkages  
 (C) The linear linkages of amylopectin are formed by  $\alpha$ -1,6'-glycosidic bond  
 (D) Amylose has an unbranched skeleton of glucose molecules with  $\alpha$ -1,4'-glycosidic linkages
- BM0046**
- 5 Select the correct option.  
 (A) Isoelectric point is the pH at which an amino acid exists primarily in its neutral form.  
 (B) Isoelectric point is the average of  $\text{pK}_a$  values of  $\alpha$ -COOH amino  $\alpha$ -  $\text{NH}_3^+$  groups [ valid only for neutral amino acid ]  
 (C) Glycine is characterised by two  $\text{pK}_a$  values  
 (D) For neutral amino acid the concentration of zwitter ion is maximum at its isoelectric point
- BM0047**

- 6 Amino acids are synthesised from  
 (A)  $\alpha$ -Halo acids by reaction with  $\text{NH}_3$   
 (B) Aldehydes by reaction with  $\text{NH}_3$  and cyanide ion followed by hydrolysis  
 (C) Pyruvic acid is treated with  $\text{NH}_3$  followed by addition of  $\text{H}_2(\text{Ni})$   
 (D) Alcohols by reaction with  $\text{NH}_3$  and  $\text{CN}^-$  ion followed by hydrolysis. BM0048
- 7 Which of the following carbohydrates develops blue colour on treatment with iodine solution ?  
 (A) Glucose (B) Amylose (C) Starch (D) Fructose BM0049
- 8 Select the **correct** statement  
 (A) High density polythene is a linear polymer.  
 (B) Low density polythene is a branched chain polymer.  
 (C) Chain growth polymers are also known as addition polymer.  
 (D) Step growth polymer is also known as condensation polymer. BM0050
- 9 Select the correct statement.  
 (A) Elastomers have the weakest intermolecular forces  
 (B) Buna-N is example of synthetic copolymer  
 (C) Some fibres have crystalline nature  
 (D) Thermoplastic polymers have stronger intermolecular forces than fibres BM0051

- 10 Which of the following options are correct :



Before isolating (P) unreacted Ph-CHO is removed first. Select the correct statement.

- (A) P is cinnamaldehyde (B) P is crotonic acid  
 (C) Removal is done by simple distillation (D) P is cinnamic acid. BM0053

- 12 If on a strand of DNA the base sequence is ATTGACGCAT then the sequence transcription on RNA would be -  
 (A) UAACUGCGUA (B) AUUCUGCGUA  
 (C) UAACTGCGUA (D) TAACTGCGTA

BM0054

- 13 Select the correct statement among following  
 (A) Number of chiral atom in  $\alpha$ -D-glucose is less than D-glucose  
 (B) D-glucose and D-fructose give same product with  $\text{HIO}_4$   
 (C) D-glucose and D-fructose give same product with  $\text{H}_2\text{NOH}$   
 (D) D-glucose and D-fructose form same product with  $\text{H}_2\text{N-NH-Ph}$

BM0055

- 14 The N-base which differentiate DNA with RNA is :  
 (A) Cytosine (B) Uracil (C) Adenine (D) Guanine

BM0056

- 15 Correct statement  
 (A) Nylon-66 is example of addition polymer  
 (B) Alanin having pH 9 at isoelectric point  
 (C) Fructose when reacts with fehling solution reddish brown ppt. formed  
 (D) All of these

BM0057

- 16 Match the column :

**Column I**

- (A) Sucrose  
 (B) Maltose  
 (C) Lactose  
 (D) Cellulose

**Column II**

- (P) Two acetals  
 (Q) No hemiacetal  
 (R)  $\beta$ -1,4'-glycosidic bond  
 (S) One of the hydrolysis product is glucose

BM0058

- 17 Match the column

**Column I****(Component of mixture)**

- (A) Crystalline  $\text{Na}_2\text{CO}_3$  + Sodium citrate +  $\text{CuSO}_4$ (aq. sol.)  
 (B)  $\text{CuSO}_4$  + Rochelle Salt +  $\text{NaOH}$ (Aq. sol.)  
 (C) 10%  $\alpha$  - naphthol in alcohol  
 (D)  $\text{HgCl}$  +  $\text{KI}$  +  $\text{KOH}$  (aq. sol.)

**Column II****(Reagent)**

- (P) Fehling solution  
 (Q) Nessler's Reagent  
 (R) Benedict's solution  
 (S) Molisch's Reagent

BM0059

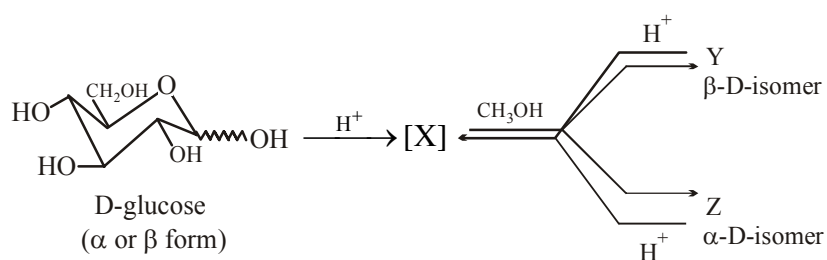
## EXERCISE # S-I

**Assertion Reason**

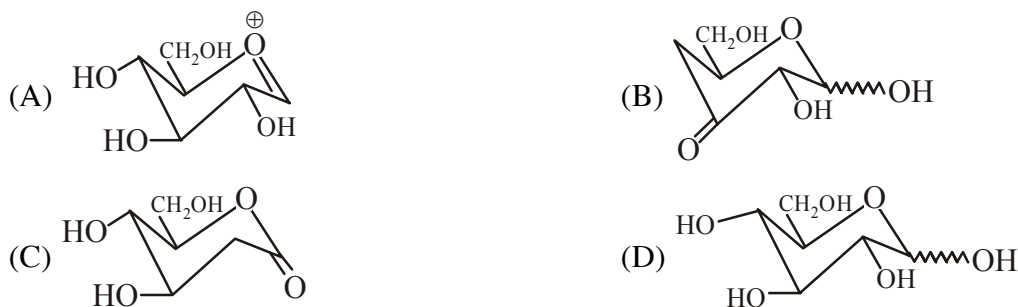
- 1 **Statement 1** : Furanose ring, like pyranose rings are not planar.  
**Statement 2** : The most stable conformation of furanose is envelope form.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- BM0060**
- 2 **Statement 1** : Bromine water changes glucose to gluconic acid.  
**Statement 2** : Bromine water acts as oxidising agent.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- BM0061**
- 3 **Statement 1** : All monosaccharide ketoses are reducing sugars.  
**Statement 2** : Monosaccharide ketose give positive Tollen's and Fehling's test.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- BM0062**

**Comprehension (Q.4 to Q.6)**

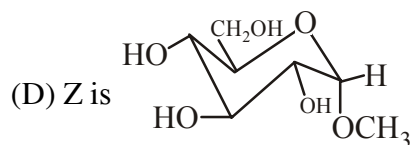
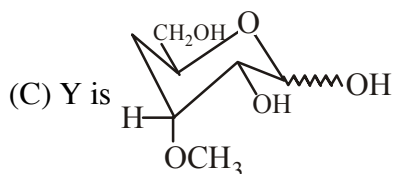
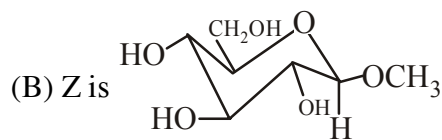
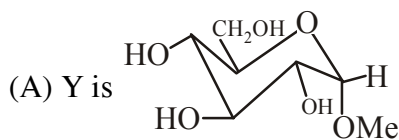
Consider the following reversible process for a reaction of D-glucose.



- 4 The structure of intermediate [X] is

**BM0063**

5 Select the correct option.



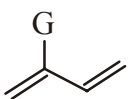
BM0064

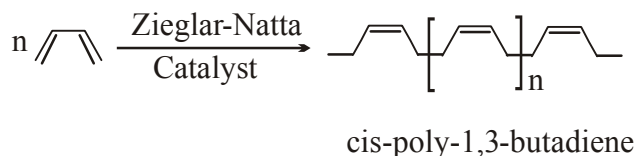
6 Select the correct statement.

- (A) Y is more stable than Z due to H-bond (B) Y is less stable than Z due to anomeric effect.  
 (C) Y is more stable than Z due to anomeric effect (D) Y is less stable than Z due to H-bond.

BM0065

Comprehension (Q.7 to Q.9)

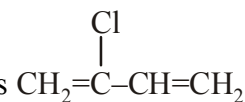
The monomer  (G = Me or Cl) when treated with Ziegler - Natta catalyst undergo polymerisation in the manner given below -



7 The Ziegler-Natta catalyst is

- (A)  $\text{TiCl}_4$  (B)  $\text{R}_3\text{Al}$  (C)  $\text{R}_3\text{Al} / \text{TiCl}_4$  (D)  $\text{R}_3\text{B} / \text{TiCl}_4$

BM0066

8 The polymer obtained when monomeric unit used is 

- (A) Neoprene (B) Stilbene (C) Styrene (D) Chloropicrin

BM0067

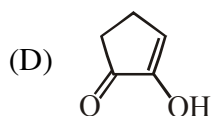
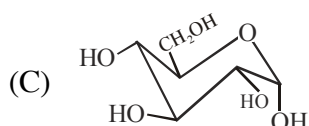
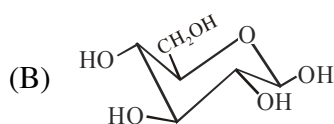
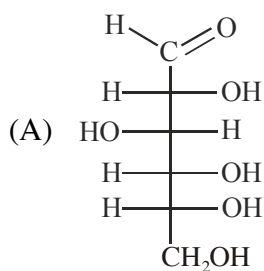
9 Which of the following statement is not true considering the process given above.

- (A) The general class of polymer formed is known as homopolymer  
 (B) The polymer obtained is stereoregular  
 (C) Buna-N can be prepared using above process  
 (D) Synthetic rubber can be formed by above process using 1,3- butadiene.

BM0068

**Match the Column**

- 10 Match the compounds given below existing in equilibrium mixture with their percentage given in the right hand side.

**Column I****Column II**

(P) 36 %

(Q) 63.8 %

(R) 99.9 %

(S) 0.2 %

**BM0069**

- 11 Match the column :

**Column I****(Carbohydrate)**

- (A) Starch  
(B) Sucrose  
(C) Lactose  
(D) Maltose

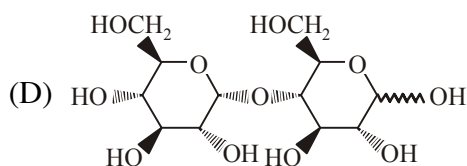
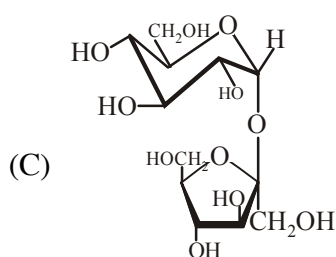
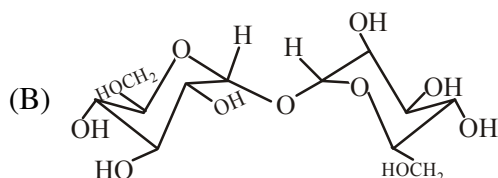
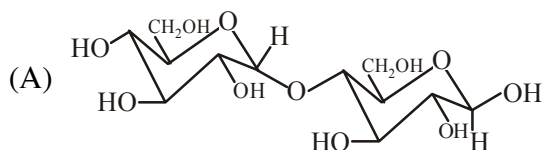
**Column II****(Properties)**

- (P) Mutarotation  
(Q) Non reducing sugar  
(R)  $\beta$ -glycosidic bond  
(S)  $\alpha$ -glycosidic bond  
(T) Reducing sugar  
(U) Hemiacetal

**BM0070**

12 Match the column :

Column I



Column II

(P)  $\alpha$ -glycoside bonds

(Q) Reducing sugar

(R) Forms enediol intermediate

(S)  $\beta$ -glycoside bond

BM0071

13 Match the column

Column I

(Functional group)

(A) Aldehydic

(B) Phenolic

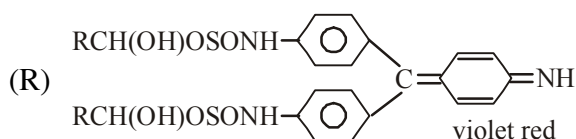
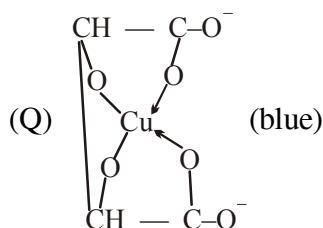
(C) Alcohol

(D)  $\alpha$ -D- Glucopyranose

Column II

(Test used or complex formed during confirmatory test)

(P)  $[(C_6H_5O)_6Fe]^{-3}$  (violet)



(S)  $(ROH)_2Ce(NO_3)_4$  (Red)

(T) Molisch's Test

BM0072

14 Match the column :

**Column I**

- (A) Addition polymer  
 (B) Condensation polymer  
 (C) Homopolymer  
 (D) Copolymers

**Column II**

- (P) Buna-S  
 (Q) Buna-N  
 (R) Polythene  
 (S) Nylon 6,6

BM0073

15 Match the column

**Presence of the element in Na - extract**

- (A) N  
 (B) S  
 (C) N and S together

**Complex formed in one of the test**

- (P)  $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$   
 (Q)  $\text{Fe}(\text{CNS})_3$   
 (R) PbS  
 (S)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]$

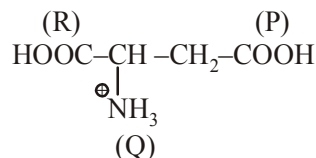
**Colour of the complex**

- (W) Prussian Blue  
 (X) Black  
 (Y) Violet  
 (Z) Blood Red

BM0074

**Subjective Type :**

16 The pKa values for the three acidic group P,Q,R are 4.3, 9.7 and 2.2 respectively



Calculate the isoelectric point of the amino acid ?

BM0075

17 How will you separate?

- (a) Ethane & Ethyne  
 (b) 1-Butyne & 2-Butyne  
 (c) Phenol & Propanol  
 (d) 2-Propanol & Propanone  
 (e)  $\text{CH}_3\text{COOH}$  &  $\text{HCOOCH}_3$   
 (f) PhOH & PhCOOH  
 (g)  $\text{C}_2\text{H}_4$  &  $\text{C}_2\text{H}_2$   
 (h)  $\text{EtNH}_2$  &  $\text{Me}_2\text{NH}$   
 (i) EtOH & Et - O - Et

BM0076

BM0077

BM0078

BM0079

BM0080

BM0081

BM0082

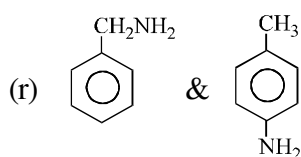
BM0083

BM0084



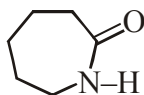
18 How will you differentiate?

- |  |        |
|--|--------|
| (a) Propane & Propene                        | BM0085 |
| (b) 1,1-Dichloroethane & 1,2-Dichloroethane  | BM0086 |
| (c) Chloroethane & Chloroethene              | BM0087 |
| (d) Pure & Oxidized $\text{CHCl}_3$          | BM0088 |
| (e) p-chlorotoluene & benzylchloride         | BM0089 |
| (f) n-propylchloride & isopropylchloride     | BM0090 |
| (g) Methanol & ethanol                       | BM0091 |
| (h) Isobutanol & tert-butanol                | BM0092 |
| (i) 2-Pentanol & 3-pentanol                  | BM0093 |
| (j) O-cresol & benzylalcohol                 | BM0094 |
| (k) Ethanol & Propanol                       | BM0095 |
| (l) Propanone & Ethanol                      | BM0096 |
| (m) HCHO & PhCHO                             | BM0097 |
| (n) Glucose & Fructose                       | BM0098 |
| (o) HCOOH & $\text{CH}_3\text{COOH}$         | BM0099 |
| (p) HCOOH & HCHO                             | BM0100 |
| (q) $\text{MeNH}_2$ & $\text{Me}_2\text{NH}$ | BM0101 |



BM0102

- 19 (a) What is the structure of nylon-6, made by alkaline polymerisation of caprolactum.



BM0103

- (b) Suggest mechanism for the process. Is polymerisation of the chain reaction or step reaction type.

BM0103

- 20 Compound (A)  $C_5H_{10}O_5$  give a tetra-acetate with  $Ac_2O$  & oxidation of A with  $Br_2/H_2O$  gives an acid  $C_5H_{10}O_6$ . Reduction of A with HI & Red P. Give 2-methyl butane. What is structure of 'A'?

BM0104

- 21 (i) Sulphanilic acid although has acidic as well as basic group. It is soluble in alkali but insoluble in mineral acid. Explain.

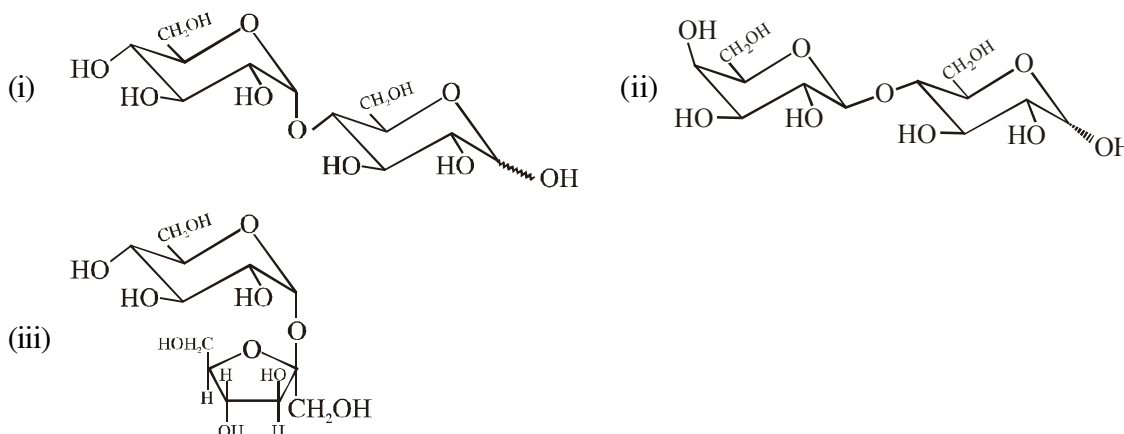
- (ii) Explain why sulphonic acid is not soluble in organic solvents.

BM0105

- 22 Account for the fact that 2-amino ethanoic acid (glucine) exist as a dipolar ion as does p-aminobenzene sulphonic acid but p-amino benzoic acid does not.

BM0106

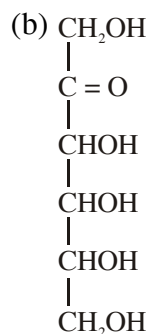
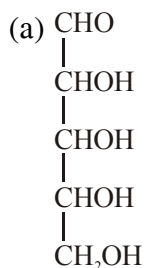
- 23 For given compound



- (a) Which glycosidic linkage is present (b) Name of the compound  
 (c) Products obtained on hydrolysis (d) Is it reducing sugar  
 (e) Number of moles of  $HIO_4$  consumed (f) Is mutarotation possible  
 (g) Number of moles of  $CH_3COCl$  consumed per mole of compound.

BM0107

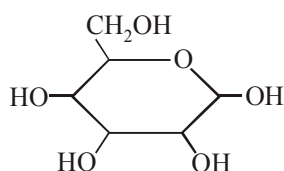
24 For given compound



- (i) Number of possible isomers
- (ii) Number of possible D-configuration isomers
- (iii) Number of possible L-configuration isomers

BM0108

25 Number of possible isomers of  $\alpha$ -D-gluco pyranose configuration.



BM0109

26 Calculate isoelectric point of following amino acid

	pKa <sub>1</sub>	pKa <sub>2</sub>	pKa
	( $\alpha$ -COOH)	( $\alpha$ -COOH)	(side chain)
(a) Glycine $\text{NH}_3^+ - \text{CH}_2 - \text{COOH}$	2.3	9.6	—
(b) Serine $\begin{array}{c} \text{CH}_2 - \text{CH} - \text{COOH} \\   \quad   \\ \text{OH} \quad \text{NH}_3^+ \end{array}$	2.2	9.2	—
(c) Alanine $\begin{array}{c} \text{NH}_3^+ \\   \\ \text{CH}_3 - \text{CH} - \text{COOH} \end{array}$	2.3	9.7	—
(d) Aspartic acid $\text{HOOC} - \text{CH}_2 - \begin{array}{c} \text{CH} - \text{COOH} \\   \\ \text{NH}_3^+ \end{array}$	2.1	9.8	3.9
(e) Lysine $\text{NH}_3^+ - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \begin{array}{c} \text{CH} - \text{COOH} \\   \\ \text{NH}_3^+ \end{array}$	2.2	9.0	10.5

BM0110

## EXERCISE # J-MAIN

1. Which of the following pairs give positive Tollen's test? [J-Main-2004]  
 (1) Glucose, sucrose (2) Glucose, fructose  
 (3) Hexanal, Acetophenone (4) Fructose, sucrose  
 BM0111
2. Two forms of D – glucopyranose, are called. [J-Main-2005]  
 (1) Enantiomers (2) Anomers (3) Epimers (4) Diastereomers  
 BM0112
3. When benzene sulfonic acid and p-nitrophenol are treated with  $\text{NaHCO}_3$ , the gases released respectively are [J-Main-2006]  
 (1)  $\text{SO}_2$ ,  $\text{NO}_2$  (2)  $\text{SO}_2$ , NO (3)  $\text{SO}_2$ ,  $\text{CO}_2$  (4)  $\text{CO}_2$ ,  $\text{CO}_2$   
 BM0113
4. **Statement-1** : Glucose gives a reddish-brown precipitate with Fehling's solution.  
*because* [J-Main-2007]  
**Statement-2** : Reaction of glucose with Fehling's solution gives CuO and gluconic acid.  
 (1) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (2) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (3) Statement-1 is True, Statement-2 is False.  
 (4) Statement-1 is False, Statement-2 is True.  
 BM0114
5. Which one of the following bases is **not present** in DNA ? [J-Main-2014]  
 (1) Cytosine (2) Thymine (3) Quinoline (4) Adenine  
 BM0115
6. Which one is classified as a condensation polymer? [J-Main- 2014]  
 (1) Teflon (2) Acrylonitrile (3) Dacron (4) Neoprene  
 BM0116
7. Which of the vitamins given below is water soluble? [J-Main- 2015]  
 (1) Vitamin E (2) Vitamin K (3) Vitamin C (4) Vitamin D  
 BM0117
8. Thiol group is present in : [J-Main-2016]  
 (1) Methionine (2) Cytosine (3) Cystine (4) Cysteine  
 BM0118

9. The distillation technique most suited for separating glycerol from spent-lye in the soap industry is [J-Main-2016]

- (1) Distillation under reduced pressure
- (2) Simple distillation
- (3) Fractional distillation
- (4) Steam distillation

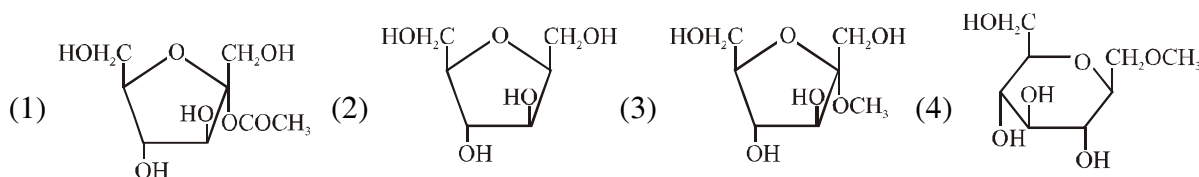
BM0119

10. Which of the following statements about low density polythene is FALSE ? [J-Main-2016]

- (1) It is used in the manufacture of buckets, dust-bins etc
- (2) Its synthesis requires high pressure
- (3) It is a poor conductor of electricity
- (4) Its synthesis requires dioxygen or a peroxide initiator as a catalyst.

BM0120

11. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution [J-Main-2017]



BM0121

12. The formation of which of the following polymers involves hydrolysis reaction ? [J-Main-2017]

- (1) Nylon 6
- (2) Bakelite
- (3) Nylon 6, 6
- (4) Terylene

BM0122

13. Glucose on prolonged heating with HI gives : [J-Main-2018]

- (1) 1-Hexene
- (2) Hexanoic acid
- (3) 6-iodohexanal
- (4) n-Hexane

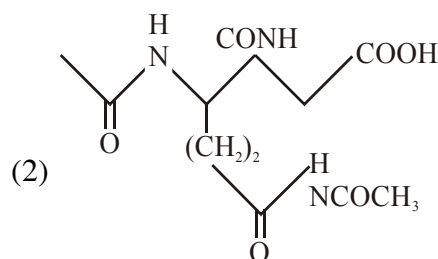
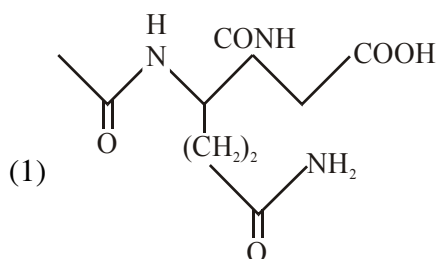
BM0123

14. Which of the following statement is not true :- [J-Main-2018]

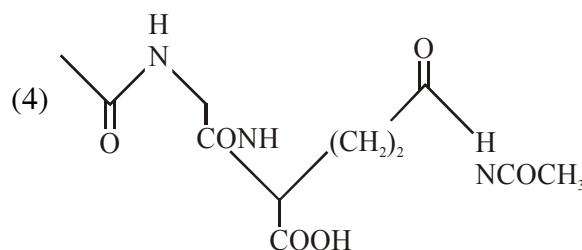
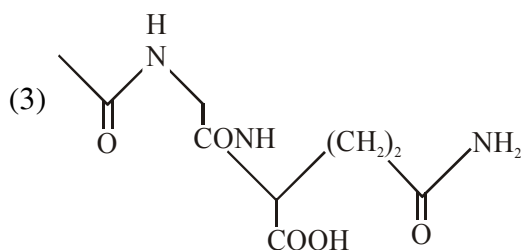
- (1) Nylon 6 is an example of step-growth polymerisation
- (2) Chain growth polymerisation involves homopolymerisation only
- (3) Step growth polymerisation requires a bifunctional monomer
- (4) Chain growth polymerisation includes both homopolymerisation and copolymerisation

BM0124

15. The dipeptide, Gln-Gly, on treatment with  $\text{CH}_3\text{COCl}_3$  followed by aqueous work up gives :-



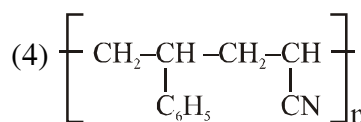
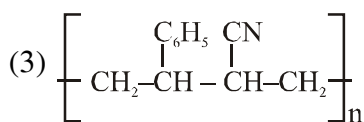
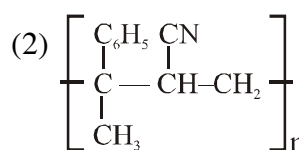
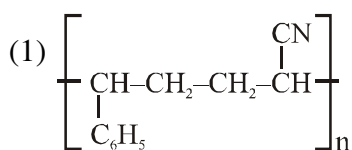
[J-Main-2018]



BM0125

16. The copolymer formed by addition polymerization of styrene and acrylonitrile in the presence of peroxide is :

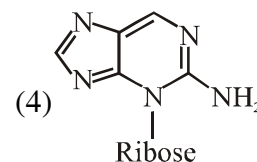
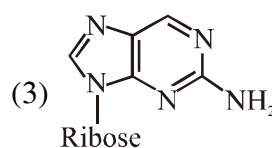
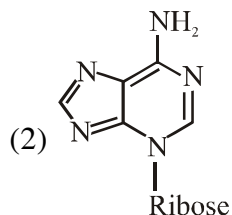
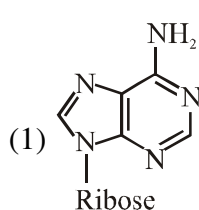
[J-Main-2018]



BM0126

17. Which of the following is the correct structure of Adenosine ?

[J-Main-2018]



BM0127

18. Among the following, the incorrect statement is:-

[J-Main-2018]

- (1) Cellulose and amylose has 1, 4-glycosidic linkage.
- (2) Lactose contains  $\beta$ -D-galactose and  $\beta$ -D-glucose.
- (3) Maltose and lactose has 1, 4-glycosidic linkage.
- (4) Sucrose and amylose has 1, 2-glycosidic linkage.

BM0128

19. The correct match between items of List-I and List-II is :-

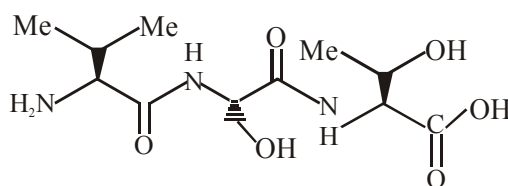
[J-Main-2018]

	List-I		List-II
(A)	Phenelzine	(P)	Pyrimidine
(B)	Chloroxylenol	(Q)	Furan
(C)	Uracil	(R)	Hydrazine
(D)	Ranitidine	(S)	Phenol

- (1) (A)-(S), (B)-(R), (C)-(P), (D)-(Q)      (2) (A)-(R), (B)-(S), (C)-(P), (D)-(Q)  
 (3) (A)-(S), (B)-(R), (C)-(Q), (D)-(P)      (4) (A)-(R), (B)-(S), (C)-(Q), (D)-(P)

BM0129

20. The correct sequence of amino acids present in the tripeptide given below is : [J-Main-(Jan)-2019]

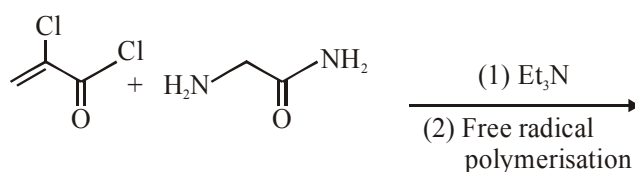


- (1) Leu - Ser - Thr      (2) Thr - Ser - Leu      (3) Thr - Ser - Val      (4) Val - Ser - Thr

BM0130

21. Major product of the following reaction is :

[J-Main-(Jan)-2019]

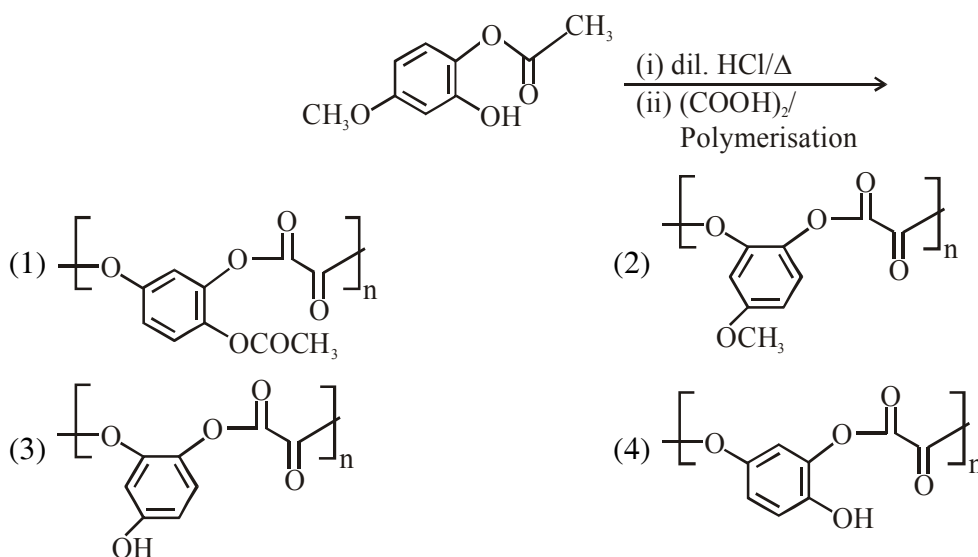


- (1)
- (2)
- (3)
- (4)

BM0131

22. The major product of the following reaction is:

[J-Main-(Jan)-2019]



BM0132

23. Which of the following tests cannot be used for identifying amino acids ?

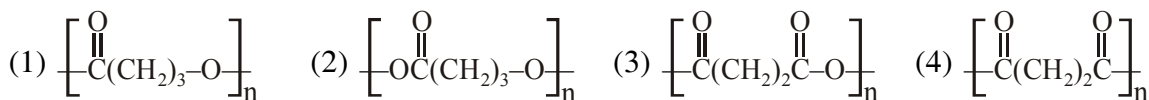
[J-Main-(Jan)-2019]

- (1) Biuret test      (2) Xanthoproteic test      (3) Barfoed test      (4) Ninhydrin test

BM0133

24. The homopolymer formed from 4-hydroxy-butanoic acid is :-

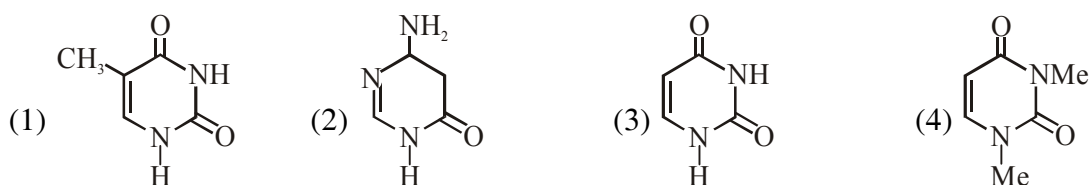
[J-Main-(Jan)-2019]



BM0134

25. Among the following compound which one is found in RNA ?

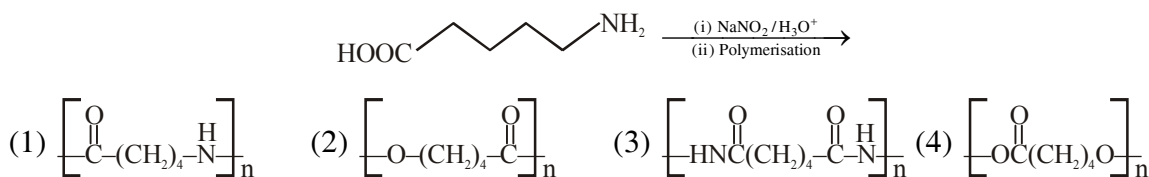
[J-Main-(Jan)-2019]



BM0135

26. The polymer obtained from the following reactions is :

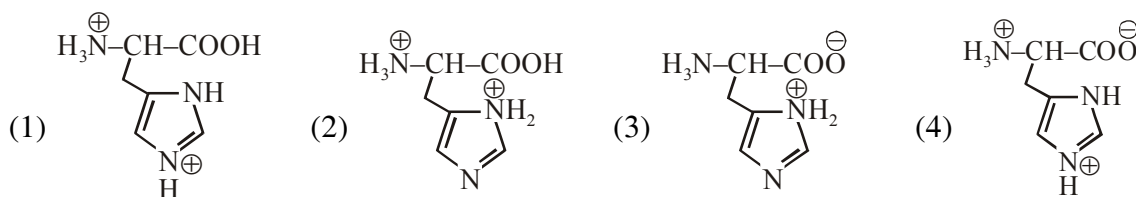
[J-Main-(Jan)-2019]



BM0136

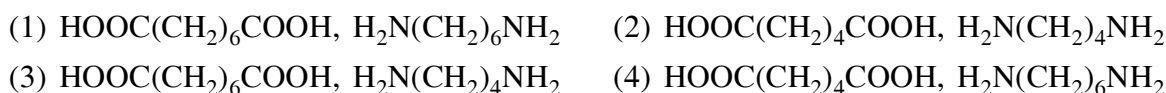


27. The correct structure of histidine in a strongly acidic solution (pH=2) is [J-Main-(Jan)-2019]



BM0137

28. The two monomers for the synthesis of Nylon 6, 6 are : [J-Main-(Jan)-2019]



BM0138

29. Maltose on treatment with dilute HCl gives : [J-Main-(April)-2019]



BM0139

30. Fructose and glucose can be distinguished by : [J-Main-(April)-2019]



BM0140

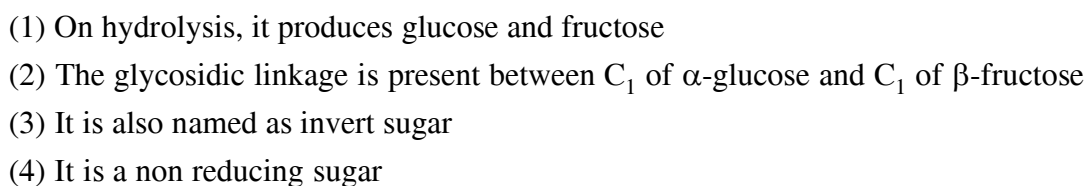
31. The peptide that gives positive ceric ammonium nitrate and carbylamine tests is :

[J-Main-(April)-2019]



BM0141

32. Which of the following statements is not true about sucrose? [J-Main-(April)-2019]



BM0142

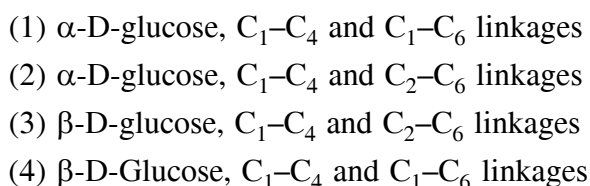
33. Number of stereo centers present in linear and cyclic structures of glucose are respectively :



[J-Main-(April)-2019]

BM0143

34. Amylopectin is composed of : [J-Main-(April)-2019]



BM0144

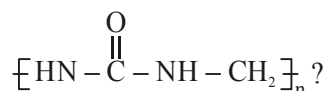
35. Which of the following statements is not true about RNA ?

- (1) It has always double stranded  $\alpha$ -helix structure
- (2) It usually does not replicate
- (3) It is present in the nucleus of the cell
- (4) It controls the synthesis of protein

[J-Main-(April)-2019]

BM0145

36. Which of the following compounds is a constituent of the polymer

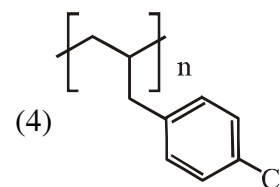
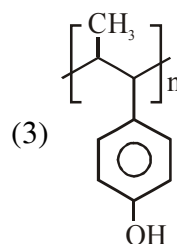
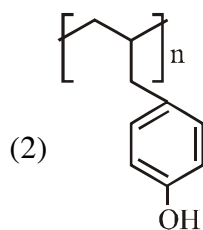
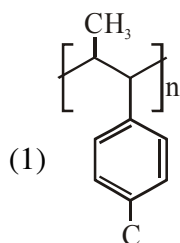
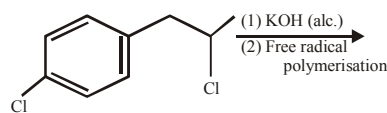


- (1) Formaldehyde
- (2) Ammonia
- (3) Methylamine
- (4) N-Methyl urea

[J-Main-(April)-2019]

BM0146

37. The major product of the following reaction is :



[J-Main-(April)-2019]

BM0147

38. Which of the following is a condensation polymer ?

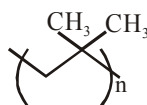
- (1) Buna - S
- (2) Nylon 6, 6
- (3) Teflon

[J-Main-(April)-2019]

- (4) Neoprene

BM0148

39. The correct name of the following polymer is:



- (1) Polyisoprene
- (2) Polytert-butylene
- (3) Polyisobutane

- (4) Polyisobutylene

BM0149

40. Which of the following is a thermosetting polymer?

- (1) Buna-N
- (2) PVC
- (3) Bakelite

[J-Main-(April)-2019]

- (4) Nylon 6

BM0150

41. Which of the following statements is correct-

- (1) Gluconic acid can form cyclic (acetal/ hemiacetal) structure
- (2) Gluconic acid is a partial oxidation product of glucose
- (3) Gluconic acid is obtained by oxidation of glucose with  $\text{HNO}_3$
- (4) Gluconic acid is a dicarboxylic acid

[J-Main-(Jan)-2020]

BM0151

42. Match the following :

[J-Main-(Jan)-2020]

- (i) Riboflavin (a) Beriberi  
 (ii) Thiamine (b) Scurvy  
 (iii) Pyridoxine (c) Cheilosis  
 (iv) Ascorbic acid (d) Convulsions

(1) (i)-(c), (ii)-(a), (iii)-(d), (iv)-(b)

(2) (i)-(c), (ii)-(d), (iii)-(a), (iv)-(b)

(3) (i)-(d), (ii)-(b), (iii)-(a), (iv)-(c)

(4) (i)-(a), (ii)-(d), (iii)-(c), (iv)-(b)

BM0152

43. Two monomers in maltose are :

[J-Main-(Jan)-2020]

(1)  $\alpha$ -D-glucose and  $\beta$ -D-glucose

(2)  $\alpha$ -D-glucose and  $\alpha$ -D-Fructose

(3)  $\alpha$ -D-glucose and  $\alpha$ -D-glucose

(4)  $\alpha$ -D-glucose and  $\alpha$ -D-galactose

BM0153

44. A, B and C are three biomolecules. The results of the tests performed on them are given below:

	Molisch's Test	Barfoed Test	Biuret Test
A	Positive	Negative	Negative
B	Positive	Positive	Negative
C	Negative	Negative	Positive

[J-Main-(Jan)-2020]

A, B and C are respectively :

(1) A = Glucose, B = Fructose, C = Albumin

(2) A = Lactose, B = Fructose, C = Alanine

(3) A = Lactose, B = Glucose, C = Alanine

(4) A = Lactose, B = Glucose, C = Albumin

BM0154

## EXERCISE # J-ADVANCED\_(OBJECTIVE)

1. **Statement-1** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.

*because*

[JEE 2007]

**Statement-2** : o-Hydroxybenzoic acid has intramolecular hydrogen bonding.

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.

BM0155

2. Match the chemical substances in Column I with type of polymers / type of bonds in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

[JEE 2007]

**Column I**

- (A) Cellulose  
 (B) Nylon-6, 6  
 (C) Protein  
 (D) Sucrose

**Column II**

- (P) Natural polymer  
 (Q) Synthetic polymer  
 (R) amide linkage  
 (S) Glycoside linkage

BM0156

3. Match the compounds/ion in column I with their properties/ reaction in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS. [JEE 2007]

**Column I**

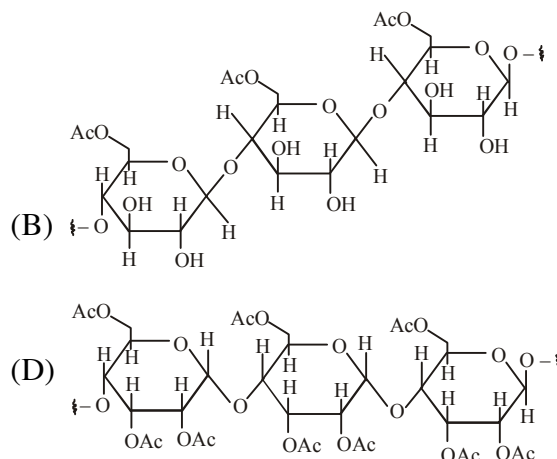
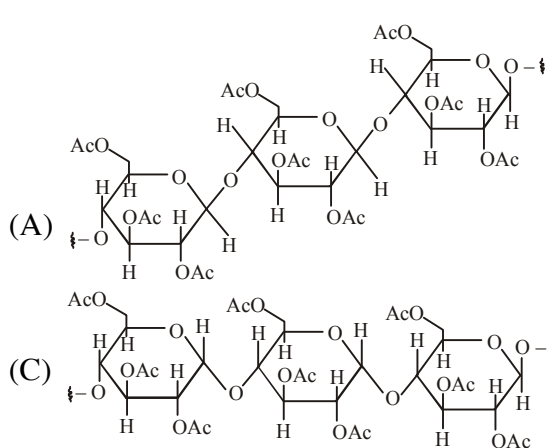
- (A)  $C_6H_5CHO$   
 (B)  $CH_3C \equiv CH$   
 (C)  $CN^-$   
 (D)  $F^-$

**Column II**

- (P) gives precipitate with 2,4-dinitrophenylhydrazine  
 (Q) gives precipitate with  $AgNO_3$   
 (R) is a nucleophile  
 (S) is involved in cyanohydrin formation

BM0157

4. Cellulose upon acetylation with excess acetic anhydride /  $H_2SO_4$  (catalytic) gives cellulose triacetate whose structure is [JEE 2008]

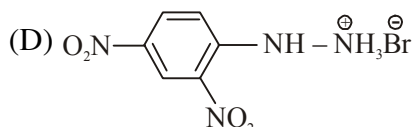
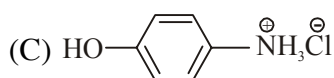
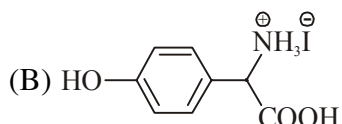
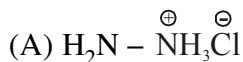


BM0158

5. Match the compounds in **Column I** with their characteristic test(s)/reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

[JEE 2008]

**Column-I**



**Column II**

(P) Sodium fusion extract of the compound gives Prussian blue colour with  $\text{FeSO}_4$

(Q) Gives positive  $\text{FeCl}_3$  test

(R) Gives white precipitate with  $\text{AgNO}_3$

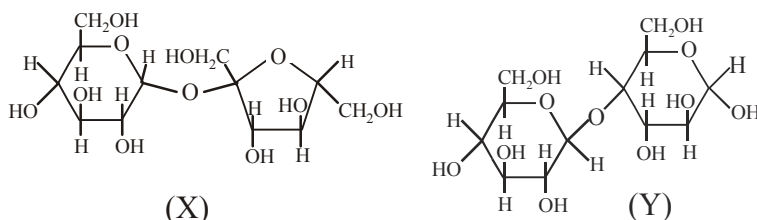
(S) Reacts with aldehydes to form the corresponding

Hydrazone derivative

BM0159

6. The correct statement(s) about the following sugars X and Y is(are)

[JEE 2009]



- (A) X is a reducing sugar and Y is a non-reducing sugar  
 (B) X is a non-reducing sugar and Y is a reducing sugar  
 (C) The glucosidic linkages in X and Y are  $\alpha$  and  $\beta$ , respectively.  
 (D) The glucosidic linkages in X and Y are  $\beta$  and  $\alpha$ , respectively

BM0160

7. Among cellulose, poly(vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is

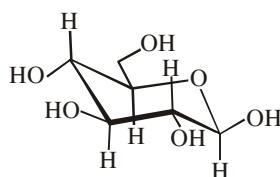
[JEE 2009]

- (A) Nylon (B) Poly (vinyl chloride)  
 (C) Cellulose (D) Natural Rubber

BM0161

8. The following carbohydrate is

[JEE 2011]

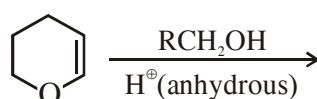


- (A) a ketohexose (B) an aldohexose  
(C) an  $\alpha$ -furanose (D) an  $\alpha$ -pyranose

BM0162

9. The major product of the following reaction is

[JEE 2011]

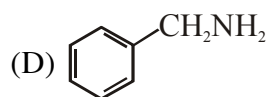
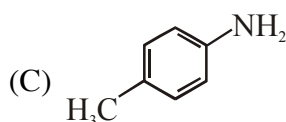
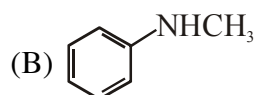
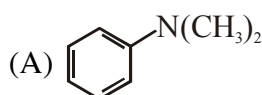


- (A) a hemiacetal (B) an acetal  
(C) an ether (D) an ester

BM0163

10. Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with  $\text{NaNO}_2$  in dil.  $\text{HCl}$  followed by addition to an alkaline solution of  $\beta$ -naphthol is -

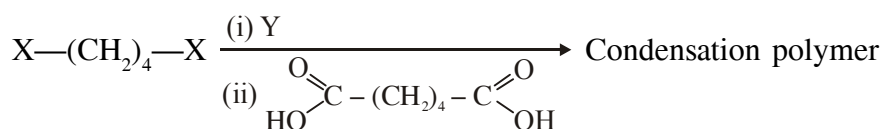
[JEE 2011]



BM0164

11. The correct functional group X and the reagent/reaction conditions Y in the following scheme are

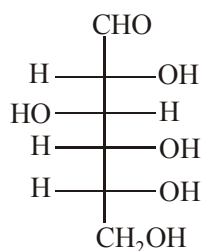
[JEE 2011]



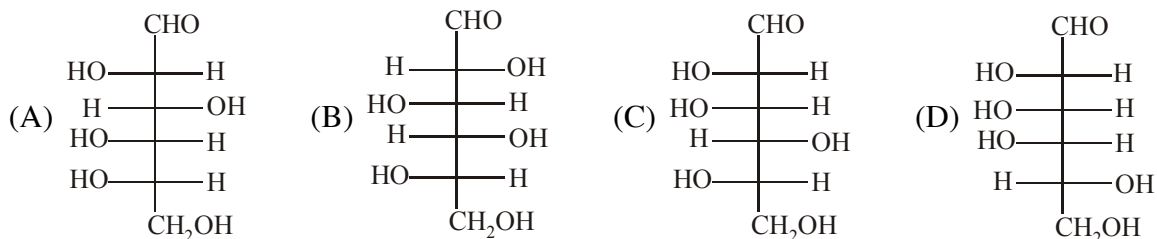
- (A)  $\text{X} = \text{COOCH}_3$ ,  $\text{Y} = \text{H}_2 / \text{Ni} / \text{heat}$   
(B)  $\text{X} = \text{CONH}_2$ ,  $\text{Y} = \text{H}_2 / \text{Ni} / \text{heat}$   
(C)  $\text{X} = \text{CONH}_2$ ,  $\text{Y} = \text{Br}_2 / \text{NaOH}$   
(D)  $\text{X} = \text{CN}$ ,  $\text{Y} = \text{H}_2 / \text{Ni} / \text{heat}$

BM0165

12. The structure of D-(+)-glucose is [IIT 2011]



The structure of L(-)-glucose is



BM0166

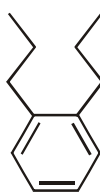
13. For 'invert sugar', the correct statement(s) is (are) : [JEE 2016]  
 (Given : specific rotations of (+)-sucrose, (+)-maltose, L(-)-glucose and L-(+)-fructose in aqueous solution are  $+66^\circ$ ,  $+140^\circ$ ,  $-52^\circ$  and  $+92^\circ$ , respectively)

- (A) 'invert sugar' is prepared by acid catalyzed hydrolysis of maltose  
 (B) 'invert sugar' is an equimolar mixture of D-(+) glucose and D-(-)-fructose  
 (C) specific rotation of 'invert sugar' is  $-20^\circ$   
 (D) on reaction with  $\text{Br}_2$  water, 'invert sugar' forms saccharic acid as one of the products

BM0167

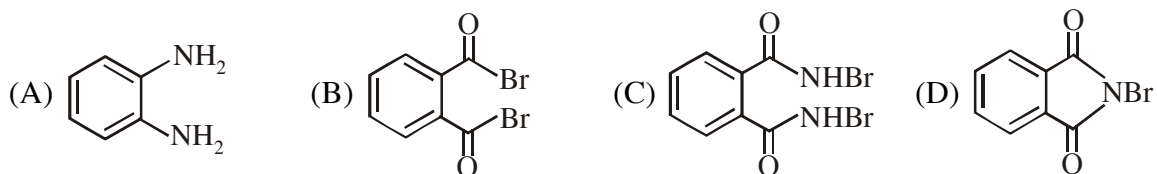
**Comprehension : Q.No. 14 to 15**

Treatment of compound **O** with  $\text{KMnO}_4 / \text{H}^+$  gave **P**, which on heating with ammonia gave **Q**. The compound **Q** on treatment with  $\text{Br}_2 / \text{NaOH}$  produced **R**. On strong heating, **Q** gave **S**, which on further treatment with ethyl 2-bromopropanoate in the presence of  $\text{KOH}$  following by acidification, gave a compound **T**.



(O)

14. The compound **R** is : [JEE 2016]



BM0168

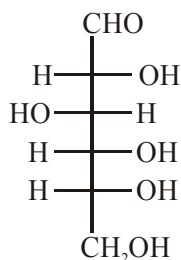
15. The compound **T** is : [JEE 2016]

- (A) Glycine                      (B) Alanine                      (C) Valine                      (D) Serine

BM0169

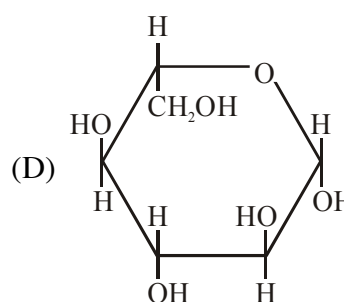
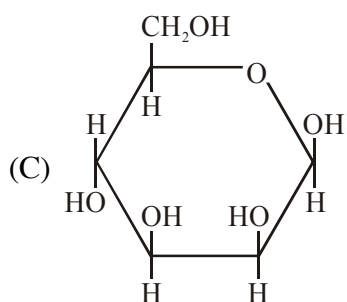
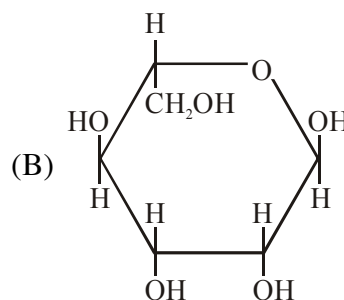
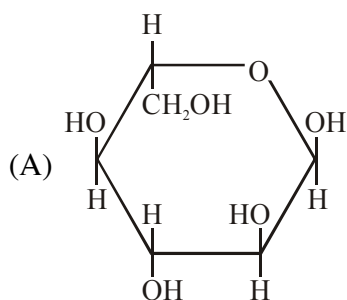
16. The Fischer presentation of D-glucose is given below.

[JEE 2018]



D-glucose

The correct structure(s) of  $\beta$ -L-glucopyranose is (are) :-



BM0170

17. Which of the following statement(s) is(are) true ?

[JEE 2019]

- (A) Oxidation of glucose with bromine water gives glutamic acid  
 (B) The two six-membered cyclic hemiacetal forms of D-(+)-glucose are called anomers  
 (C) Hydrolysis of sucrose gives dextrorotatory glucose and laevorotatory fructose  
 (D) Monosaccharides **cannot** be hydrolysed to give polyhydroxy aldehydes and ketones

BM0171

18. Choose the correct option(s) from the following

[JEE 2019]

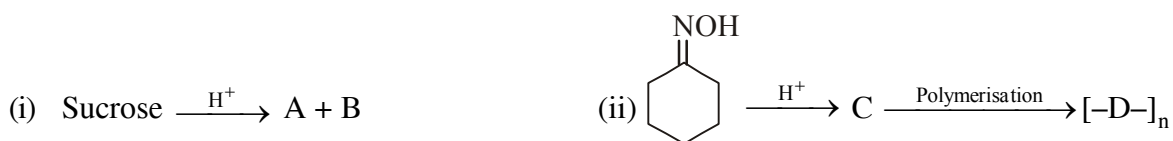
- (A) Natural rubber is polyisoprene containing *trans* alkene units  
 (B) Nylon-6 has amide linkages  
 (C) Cellulose has only  $\alpha$ -D-glucose units that are joined by glycosidic linkages  
 (D) Teflon prepared by heating tetrafluoroethene in presence of a persulphate catalyst at high pressure

BM0172



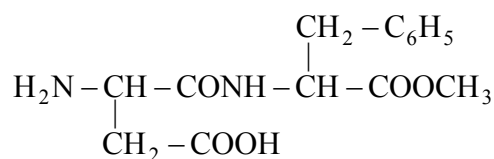
EXERCISE # J-ADVANCED\_(SUBJECTIVE)

1. Give the structures of the products in each of the following reactions. [JEE 2000]



BM0173

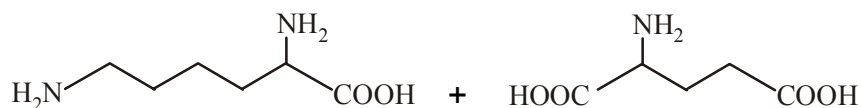
2. Aspartame, an artificial sweetener, is a peptide and has the following structure: [JEE 2001]



- (i) Identify the four functional groups  
 (ii) Write the zwitterionic structure  
 (iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame  
 (iv) Which of the two amino acids is more hydrophobic ?

BM0174

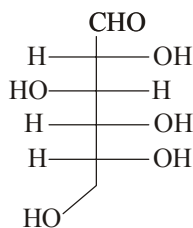
3. Following two amino acids lysine and glutamine form dipeptide linkage. What are two possible dipeptides ? [JEE 2003]



BM0175

4. The structure of D-Glucose is as follows- [JEE 2004]

- (a) Draw the structure of L -Glucose  
 (b) Give the reaction of L - Glucose with Tollens reagent.



BM0176

5. Monomer A of a polymer on ozonolysis yields two moles of HCHO and one mole of  $\text{CH}_3\text{COCHO}$ .

(a) Deduce the structure of A.

[JEE 2005]

(b) Write the structure of “all cis” – form of polymer of compound A.

BM0177

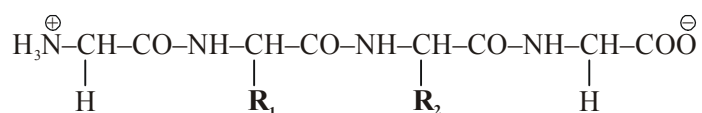
6. A decapeptide (Mol. Wt. 796) on complete hydrolysis gives glycine (Mol. Wt. 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is

[JEE 2011]

BM0178

7. The substitutes  $\mathbf{R}_1$  and  $\mathbf{R}_2$  for nine peptides are listed in the table given below. How many of these peptides are positively charged at  $\text{pH} = 7.0$  ?

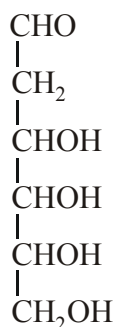
[JEE 2012]



Peptide	$\mathbf{R}_1$	$\mathbf{R}_2$
I	H	H
II	H	$\text{CH}_3$
III	$\text{CH}_2\text{COOH}$	H
IV	$\text{CH}_2\text{CONH}_2$	$(\text{CH}_2)_4\text{NH}_2$
V	$\text{CH}_2\text{CONH}_2$	$\text{CH}_2\text{CONH}_2$
VI	$(\text{CH}_2)_4\text{NH}_2$	$(\text{CH}_2)_4\text{NH}_2$
VII	$\text{CH}_2\text{COOH}$	$\text{CH}_2\text{CONH}_2$
VIII	$\text{CH}_2\text{OH}$	$(\text{CH}_2)_4\text{NH}_2$
IX	$(\text{CH}_2)_4\text{NH}_2$	$\text{CH}_3$

BM0179

8. When the following aldohexose exists in its d-configuration, the total number of stereoisomers in its pyranose form is - [JEE 2012]



BM0180

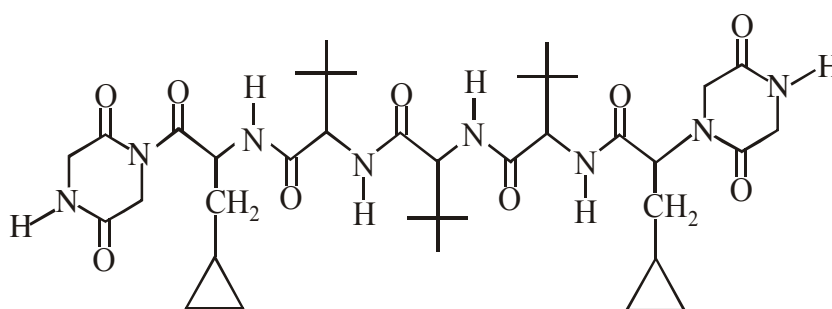
9. A tetrapeptide has  $-\text{COOH}$  group on alanine. This produces glycine (Gly), valine (Val), phenyl alanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (Primary structures) with  $-\text{NH}_2$  group attached to a chiral center is [JEE 2013]

BM0181

10. The total number of lone-pairs of electrons in melamine is : [JEE 2013]

BM0182

11. The total number of *distinct naturally occurring amino acids* obtained by complete acidic hydrolysis of the peptide shown below is : [JEE 2014]



BM0183

**ANSWER KEY****EXERCISE # O-I**

- |              |              |              |              |              |
|--------------|--------------|--------------|--------------|--------------|
| 1. Ans. (C)  | 2. Ans. (D)  | 3. Ans. (C)  | 4. Ans. (B)  | 5. Ans. (C)  |
| 6. Ans. (A)  | 7. Ans. (C)  | 8. Ans. (D)  | 9. Ans. (C)  | 10. Ans. (B) |
| 11. Ans. (B) | 12. Ans. (C) | 13. Ans. (C) | 14. Ans. (A) | 15. Ans. (A) |
| 16. Ans. (D) | 17. Ans. (D) | 18. Ans. (D) | 19. Ans. (B) | 20. Ans. (B) |
| 21. Ans. (D) | 22. Ans. (B) | 23. Ans. (A) | 24. Ans. (A) | 25. Ans. (C) |
| 26. Ans. (A) | 27. Ans. (D) | 28. Ans. (B) | 29. Ans. (B) | 30. Ans. (C) |
| 31. Ans. (C) | 32. Ans. (C) | 33. Ans. (D) | 34. Ans. (C) | 35. Ans. (A) |
| 36. Ans. (D) | 37. Ans. (B) | 38. Ans. (C) | 39. Ans. (A) | 40. Ans. (A) |
| 41. Ans. (B) | 42. Ans. (B) |              |              |              |

**EXERCISE # O-II**

- |   |                |                  |                |                |
|---|----------------|------------------|----------------|----------------|
| 1. Ans.(A,B,C,D)  | 2. Ans.(A,B,D) | 3. Ans.(A,B,C)   | 4. Ans.(A,B,D) | 5. Ans.(A,B,D) |
| 6. Ans.(A,B,C)  | 7. Ans.(B,C)   | 8. Ans.(A,B,C,D) | 9. Ans.(A,B,C) | 10. Ans.(B,D)  |
| 11. Ans. (D)  | 12. Ans.(A)    | 13. Ans.(D)      | 14. Ans.(B)    | 15. Ans.(C)    |
| 16. Ans.(A) → P, Q, S ; (B) → S ; (C) → R, S ; (D) → Q,R, S |                |                  |                |                |
| 17. Ans.(A) → R ; (B) → P ; (C) → S ; (D) → Q               |                |                  |                |                |

**EXERCISE # S-I****Assertion Reason**

- |             |             |             |             |             |
|-------------|-------------|-------------|-------------|-------------|
| 1. Ans. (A) | 2. Ans. (A) | 3. Ans. (A) | 4. Ans. (A) | 5. Ans. (D) |
| 6. Ans. (B) | 7. Ans. (C) | 8. Ans. (A) | 9. Ans. (C) |             |

**Match the Column**

10. Ans. (A) → S ; (B) → Q ; (C) → P ; (D) → R
11. Ans. (A) → Q, S ; (B) → Q, R, S ; (C) → P, R, T, U (D) → P, S, T, U
12. Ans. (A) → P, Q, R ; (B) → P ; (C) → P, S ; (D) → P, Q, R
13. Ans. (A) → Q, R (B) → P, (C) → S ; (D) → T
14. Ans. (A) → P, Q, R ; (B) → S ; (C) → R ; (D) → P, Q, S
15. Ans. (A) → S-W (B) → P-Y, R-X (C) → Q-Z

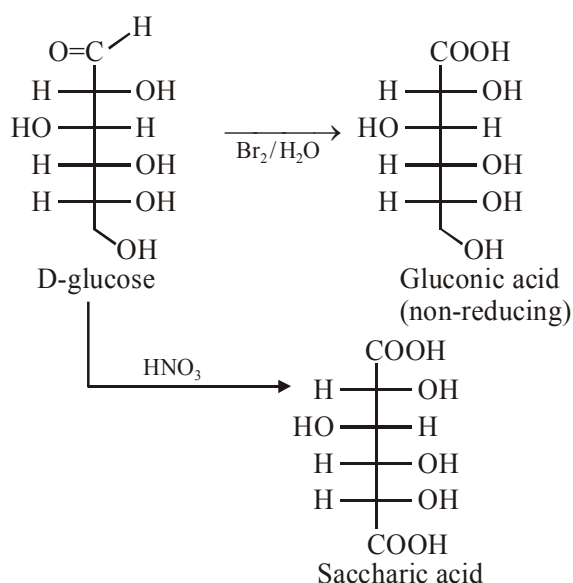
**Subjective Type :**

16. Ans. (3.25)

## EXERCISE # J-MAIN

- |              |              |              |              |              |
|--------------|--------------|--------------|--------------|--------------|
| 1. Ans. (2)  | 2. Ans. (2)  | 3. Ans. (4)  | 4. Ans. (3)  | 5. Ans. (3)  |
| 6. Ans. (3)  | 7. Ans. (3)  | 8. Ans. (4)  | 9. Ans. (1)  | 10. Ans. (1) |
| 11. Ans. (1) | 12. Ans. (1) | 13. Ans. (4) | 14. Ans. (2) | 15. Ans. (1) |
| 16. Ans. (4) | 17. Ans. (1) | 18. Ans. (4) | 19. Ans. (2) | 20. Ans. (4) |
| 21. Ans. (4) | 22. Ans.(2)  | 23. Ans.(3)  | 24. Ans. (1) | 25. Ans. (3) |
| 26. Ans. (2) | 27. Ans.(1)  | 28. Ans.(4)  | 29. Ans.(2)  | 30. Ans.(4)  |
| 31. Ans. (2) | 32. Ans. (2) | 33. Ans. (1) | 34. Ans.(1)  | 35. Ans. (1) |
| 36. Ans. (1) | 37. Ans. (1) | 38. Ans. (2) | 39. Ans. (4) | 40. Ans. (3) |

Sol.



42. Ans. (1)

Sol. (i) Riboflavin  $\longrightarrow$  (c) Cheilosis(ii) Thiamine  $\longrightarrow$  (a) Beriberi(iii) Pyridoxin  $\longrightarrow$  (d) Convulsions(iv) Ascorbic acid  $\longrightarrow$  (b) Scurvy

43. Ans. (3)

Sol. Two monomers in maltose are  $\alpha$ -D-glucose &  $\alpha$ -D-glucose.

44. Ans. (4)

Sol. Alanine does not show Biuret test because Biuret test is used for deduction of peptide linkage &amp; alanine is amino acid.

Albumine is protein so have paptide linkage so it gives positive Biuret test.

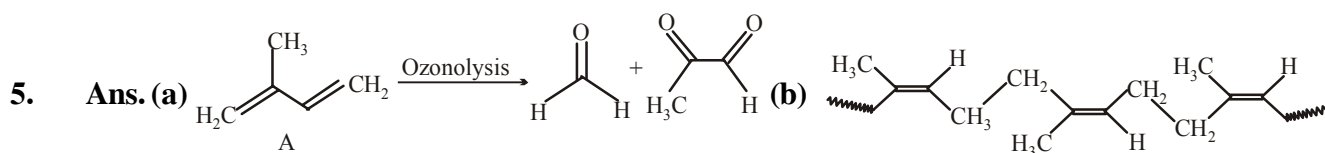
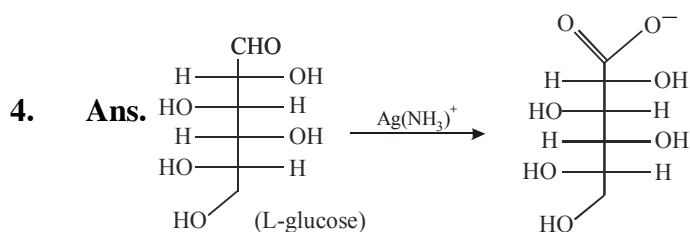
Positive Barfoed test is shown by monosaccharide but not disaccharide. Positive Molisch's test is shown by glucose.

## EXERCISE # J-ADVANCED\_(OBJECTIVE)

1. Ans.(D)      2. Ans.(A) → P, S ; (B) → Q, R ; (C) → P, R ; (D) → S  
 3. Ans.(A) → P, S ; (B) → Q ; (C) → Q, R, S ; (D) → Q, R      4. Ans.(A)  
 5. Ans.(A) → R, S ; (B) → P, Q ; (C) → P, Q, R ; (D) → P, S      6. Ans.(B,C)  
 7. Ans.(D)      8. Ans.(B)      9. Ans.(B)      10. Ans.(C)      11. Ans.(A,B,C,D)  
 12. Ans.(A)      13. Ans.(B,C)      14. Ans.(A)      15. Ans.(B)      16. Ans.(D)  
 17. Ans.(B,C,D)      18. Ans.(B,D)

## EXERCISE # J-ADVANCED\_(SUBJECTIVE)

2. Ans. (i) Amine, carboxylic acid, Amide, Ester



6. Ans.(6)      7. Ans.(4)      8. Ans.(8)      9. Ans.(4)      10. Ans.(6)  
 11. Ans.(1)

## CHEMISTRY IN EVERYDAY LIFE

### PART A : ANALGESIC DRUGS

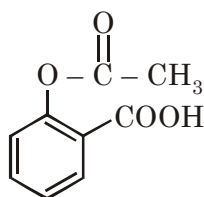
#### ANALGESIC DRUGS

(a) Non Narcotic Analgesic

(b) Narcotic Analgesic

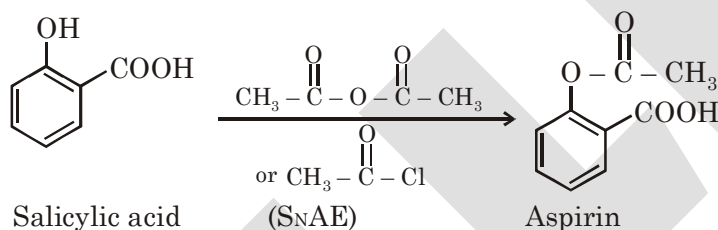
#### (a) NON NARCOTIC ANALGESIC

##### 1. ASPIRIN (IUPAC Name : 2-Ethanoyloxybenzoic acid)



**I. Medical use :** Analgesic (Non narcotic / Non addictive) & Antipyretic.

**II. Preparation :** Aspirin is prepared by acetylation of salicylic acid



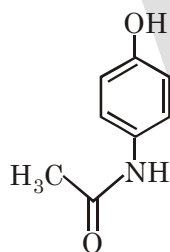
**III. Functional group :** Acid and ester

**IV. Test of Functional group :** All +ve tests for carboxylic acids

**V. Aromaticity :** Aromatic (Homocyclic)

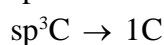
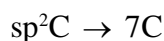
**VI. DOU :** 6

##### 2. PARACETAMOL (IUPAC Name : N-(4-Hydroxyphenyl)ethanamide)



**I. Medical use :** Analgesic (Non-narcotic / non-addictive) & Antipyretic.

**II. Hybridisation state :**



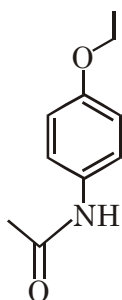
**III. Functional group :** Phenolic OH, secondary amide

**IV. Test of Functional group :** +ve test with neutral  $FeCl_3$

**V. Aromaticity :** Aromatic (Homocyclic)

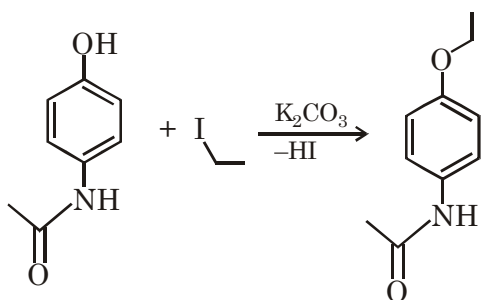
**VI. DOU :** 5

## 3. PHENACITIN (IUPAC Name : N-(4-Ethoxyphenyl)ethanamide)



I. **Medical use** : Analgesic (Non-narcotic / non-addictive) & Antipyretic.

II. **Preparation** :



Paracetamol

Phenacetin

III. **Hybridisation state**

$sp^2C \rightarrow 7C$

$sp^3C \rightarrow 3C$

IV. **Functional group / test** : Ether and  $2^\circ$  amide / -ve test with neutral  $FeCl_3$

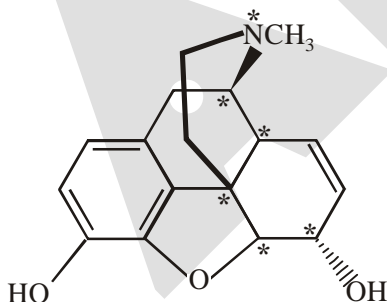
V. **Aromaticity** : Aromatic (Homocyclic)

VI. **DOU** : 5

**NOTE** : Quinine, Chloroquine, Paraquine and Primaquine are used as antimalaria.

## (b) NARCOTIC ANALGESIC

## 1. MORPHINE



I. **Medical use** : Morphine is used for relieve a post-operative pain, cardiac pan, child birth and pains of terminal cancer

II. **Number of chiral centre** : 6

III. **Number of chiral carbon** : 5

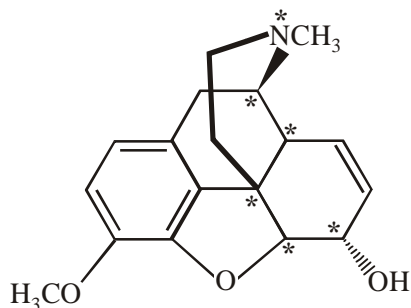
IV. **Functional group** : Morphin narcotics are also called opiates.

V. **Aromaticity** : Aromatic (Heterocyclic)

VI. **DOU** : 9

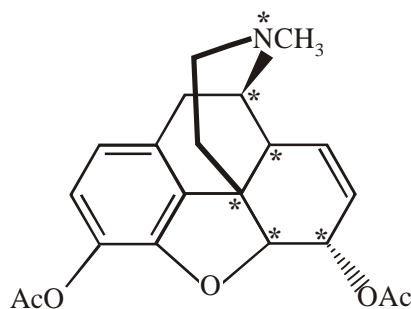


2. CODEINE



I. DOU : 9

3. HEROIN



I. DOU : 11

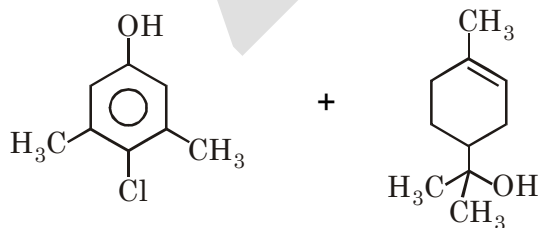
	Phenolic OH	Alcohol
Morphine	+	+
Codeine	-	+
Heroin	-	-

Acidic strength order : Morphine > Codeine > Heroin

**PART B : ANTISEPTIC, DISINFECTANTS & ANTI-FERTILITY DRUG**

1. ANTISEPTIC

I. Dettol (Chloroxylenol + Terpeneol)

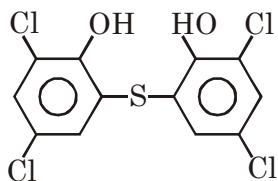


Chloroxylenol

Terpeneol

Medical use : Dettol, Soframicin are used as anticeptic

## II. Bithionol

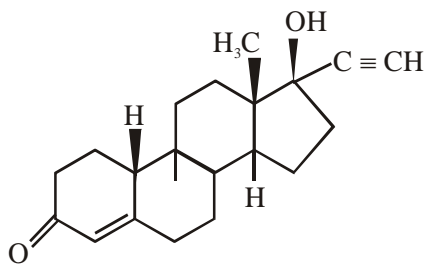


**Medical use :** Bithionol is added to soaps for antiseptic properties.

2. **NOTE :** 1% solution of phenol in disinfectant while 0.2% solution of phenol is antiseptic.

## 3. ANTI-FERTILITY DRUGS

### I



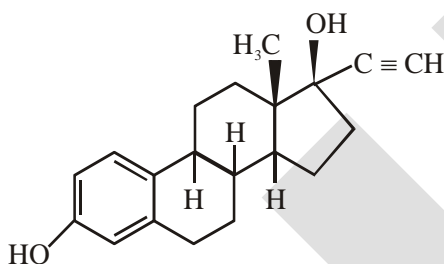
Norethindrone

**Medical Use :** It is present in birth control pills for family planning.

**Number of Chiral carbons :** 6

**Functional groups :** Ketone, Alcoholic-OH and terminal alkyne

### II



Ethynylestradiol (novestron)

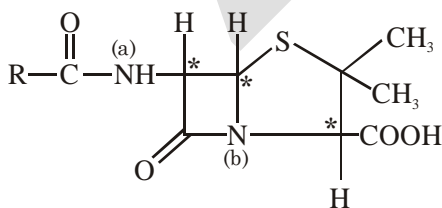
**Medical Use :** It is present in birth control pills for family planning.

**Number of Chiral carbons :** 5

**Functional groups :** Phenolic-OH, Alcoholic-OH and terminal alkyne

## PART C : ANTIBIOTICS

### 1. PENICILLIN



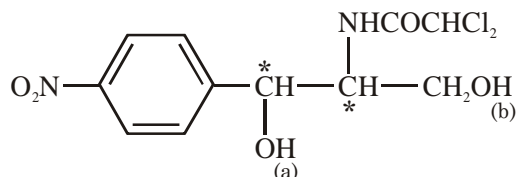
**I. Medical use :** Bactericidal Antibacterial (Killing effect on bacteria)

**NOTE :** Ampicillin and Amoxycillin are synthetic modifications of Penicilline

**II. Number of chiral carbon centre :** 3

**III. Functional group :**

(i) Carboxylic Acid (ii) 2° Amide (iii) 3° Amide (iv) Thioether

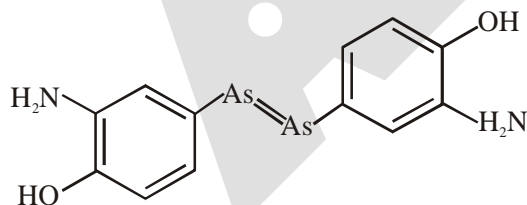
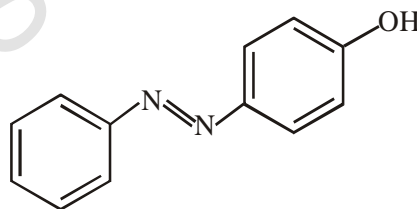
**IV. Aromaticity :** Non-aromatic (Heterocyclic)**V. DOU :** 5**VI. Basicity :**  $b > a$ **2. CHLORAMPHENICOL****I. Medical use :**

(i) Bacteriostatic antibiotic (Static / inhibitory effect on microbes)

(ii) Broad spectrum antibiotic (Covers wide range of diseases like typhoid, dysentery, acute fever, certain form of urinary infections, meningitis and pneumonia)

**II. Number of chiral carbon atoms :** 2**III. TSI :** 4 (OA)**IV. Functional group :**

(i) Alcohol (ii) Nitro (iii) 2° amide (iv) Chloro

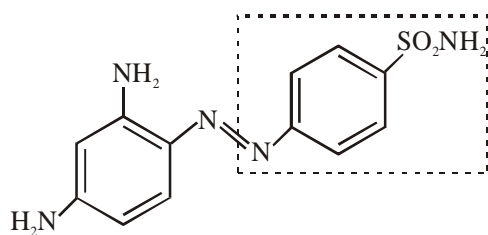
**V. Aromaticity :** Aromatic (Heterocyclic)**VI. DOU :** 6**VII. Acidic strength :**  $a > b$ **NOTE :** **DYSIDAZIRINE** antibiotic is toxic towards certain strains of cancer cells.**3. SALVARSAN****Structure similar to azodye****I. Medical use :**

(i) Effective for treatment against spirocheti (bacteria that causes syphilis)

(ii) Toxic to human beings

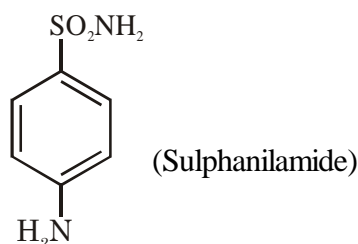
**II. Test of Functional group :** Phenolic OH (+ve test with neutral  $\text{FeCl}_3$ ), azodye test**III. Aromaticity :** Aromatic (Homocyclic)**IV. DOU :** 9

## 4. PRONTOSIL



## I. Medical use :

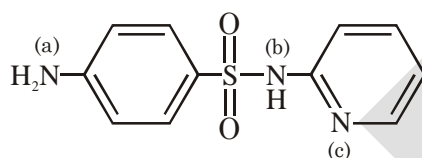
- (i) First effective antibacterial agent
- (ii) Converted to sulphanilamide in body which is the real active compound



## II. Aromaticity : Aromatic (Homocyclic)

## III. DOU : 11

## 5. SULPHAPYRIDINE



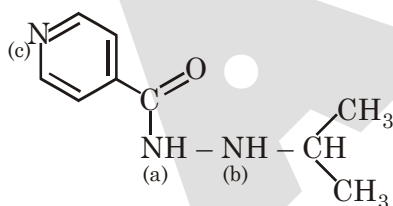
## I. Medical use : Sulphadrug

## II. Aromaticity : Aromatic (Heterocyclic)

## III. DOU : 10

IV. Most Basic site : N<sub>c</sub>**PART D : ANTIDEPRESSANT & TRANQUILIZERS**

## 1. IPRONIAZID



## I. Medical use :

- (i) Mood elevators (Antidepressant drugs)
- (ii) Catalyse the degradation of noradrenaline

## II. Number of chiral centre : 1

## III. Hybridisation state

$$sp^2C \rightarrow 6C$$

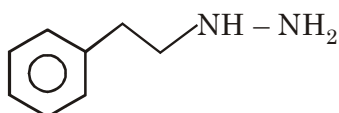
$$sp^3C \rightarrow 3C$$

## IV. Aromaticity : Aromatic (Heterocyclic)

## V. DOU : 5

VI. Basicity :  $b > c > a$

2. PHENELZINE (Nardil)



I. Medical use :

- (i) Mood elevators (Antidepressants)
- (ii) Catalyse the degradation of noradrenaline

II. Number of chiral centre : 1

III. Hybridisation state

$$sp^2C \rightarrow 6$$

$$sp^3C \rightarrow 2$$

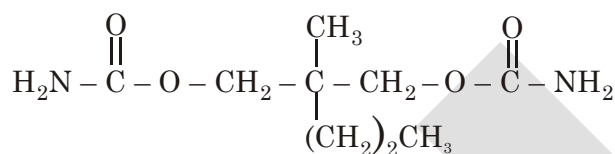
IV. Functional group : Amine

V. Test of Functional group : Diazotization ( $NH_2$ )

VI. Aromaticity : Aromatic (Homocyclic)

VII. DOU : 4

3. MEPROBAMATE



I. Medical use : Mild tranquilizer

II. Number of chiral centre : 0

III. Hybridisation state :

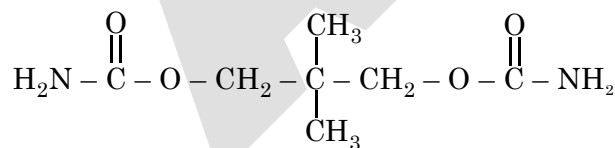
$$sp^2C \rightarrow 2$$

$$sp^3C \rightarrow 7$$

IV. Aromaticity : Non aromatic

V. DOU : 2

4. EQUANIL



I. Medical use : Controlling depression and hypertension

II. Number of chiral centre : 0

III. Hybridisation state :

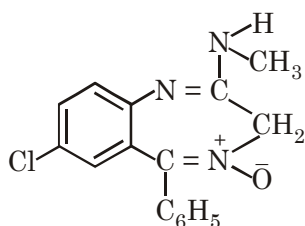
$$sp^2C \rightarrow 2$$

$$sp^3C \rightarrow 5$$

IV. Aromaticity : Non aromatic

V. DOU : 2

## 5. CHLORDIAZEPOXIDE



I. **Medical use** : Mild tranquilizer

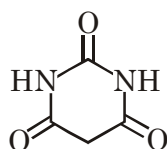
II. **Hybridisation state**



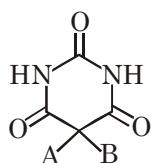
III. **Aromaticity** : Aromatic (Heterocyclic)

IV. **DOU** : 11

## 6. BARBITURIC ACID



## 7. BARBITURATES

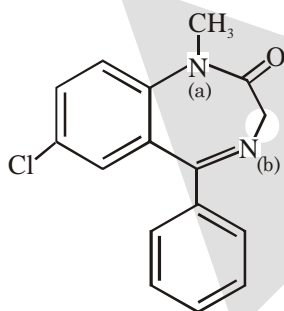


		A	B
1	Veronal	Ethyl	Ethyl
2	Luminal	Ethyl	Phenyl
3	Amytal	Ethyl	Isopentyl
4	Nembutal	Ethyl	Secondary active amyl
5	Seconal	Allyl	Secondary active amyl

They are derivatives of barbituric acid which are used as hypnotic (Sleep producing agents)

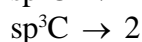
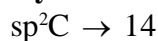
Tautomerism : Shows Tautomerism

## 8. VALIUM



I. **Medical use** : Tranquilizer

II. **Hybridisation state** :



III. **Test of Functional group** :

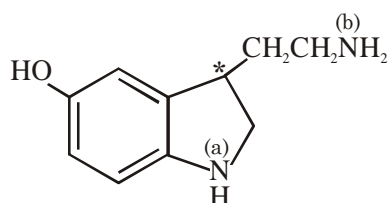
-ve test with  $AgNO_3$  (aq.)

IV. **Aromaticity** : Aromatic (Heterocyclic)

V. **DOU** : 11

VI. **Basicity** :  $b > a$

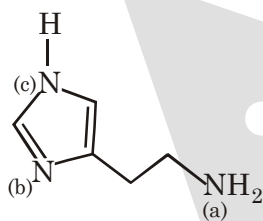
## 9. SEROTONIN



- I. **Medical use :** Tranquilizer
- II. **Number of chiral centre :** 1
- III. **TSI :** 2 (OA)
- IV. **Hybridisation state :**  
 $sp^2C \rightarrow 6$   
 $sp^3C \rightarrow 4$
- V. **Functional group :**  
 $1^\circ$  Amine  
 $2^\circ$  Amine  
 Phenolic OH
- VI. **Test of Functional group :**  
 +ve isocyanide test  
 +ve test with neutral  $FeCl_3$   
 Yellow dye with benzene diazonium chloride
- VII. **Aromaticity :** Aromatic (Heterocyclic)
- VIII. **DOU :** 5
- IX. **Basicity :**  $b > a$

**PART E : HISTAMINE, ANTI-HISTAMINE & ANTACIDS**

## (a) HISTAMINE

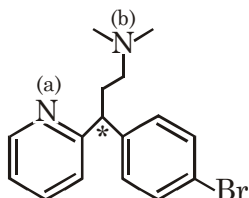


- I. **Medical use:**  
 (i) Stimulates secretion of pepsin and HCl in stomach  
 (ii) Contracts the muscles in bronchi and gut  
 (iii) Relaxes blood vessels (Vasodilator)  
 (iv) Nasal congestion and allergic reaction to pollen
- II. **Number of chiral centre :** 0
- III. **Hybridisation state:**  
 $sp^2C \rightarrow 3C$   
 $sp^3C \rightarrow 2C$

- IV. **Functional group** : Amine  
 V. **Test of Functional group** : Isocyanide test  
 VI. **Aromaticity** : Aromatic (Heterocyclic)  
 VII. **DOU** : 3  
 VIII. **Basicity**  $b > a > c$

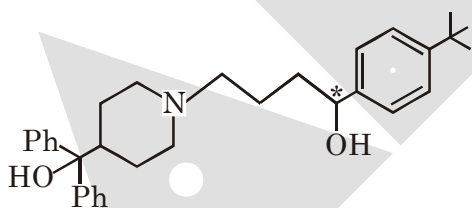
(b) **ANTI HISTAMINE**

1. **BROMPHENIRAMINE (Dimetapp, Dimetane)**



- I. **Medical use** : Antihistamine  
 II. **Number of chiral centre** : 1  
 III. **TSI** : 2 (OA)  
 IV. **Hybridisation state** :  
 $sp^2C \rightarrow 11C$   
 $sp^3C \rightarrow 5C$   
 V. **Functional group** :  $3^\circ$  amine, aryl bromide  
 VI. **Test of Functional group** :  $-ve$  test with  $AgNO_3$  (aq.)  
 VII. **Aromaticity** : Aromatic (Heterocyclic)  
 VIII. **DOU** : 8  
 IX. **Basicity** :  $N_b > N_a$

2. **TERFENADINE (Seldane)**

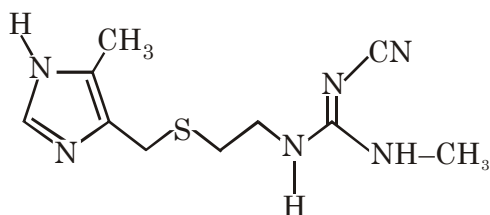


- I. **Medical use** : Antihistamine  
 II. **Number of chiral centre** : 1  
 III. **TSI** : 2  
 IV. **Hybridisation state** :  
 $sp^2C \rightarrow 18$   
 $sp^3C \rightarrow 14$   
 V. **Functional group** :  $3^\circ$  amine, alcohol  
 VI. **Test of Functional group** :  
 (i) Positive test of alcoholic OH (Including Lucas test)  
 VII. **Aromaticity** : Aromatic (Heterocyclic)  
 VIII. **DOU** : 13



## (c) ANTACIDS

## 1. CIMETIDINE (Tegamet)

**I. Medical use :**

(i) Antacid (against acidity)

**II. Number of chiral centre : 0****III. TSI : 2 (GI)****IV. Hybridisation state :**

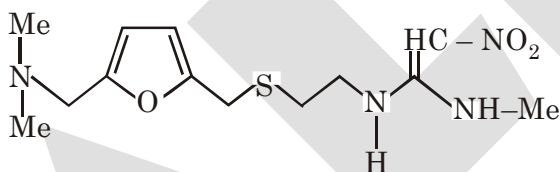
$sp^2C \rightarrow 1C$

$sp^2C \rightarrow 4C$

$sp^3C \rightarrow 5C$

**V. Functional group : Thioether, Cyanide etc.****VI. Aromaticity : Aromatic (Heterocyclic)****VII. DOU : 6**

## 2. RANITIDINE (Zantac)

**I. Medical use : Antacid****II. Number of chiral centre : 0****III. TSI : 2 (GI)****IV. Hybridisation state :**

$sp^2C \rightarrow 6C$

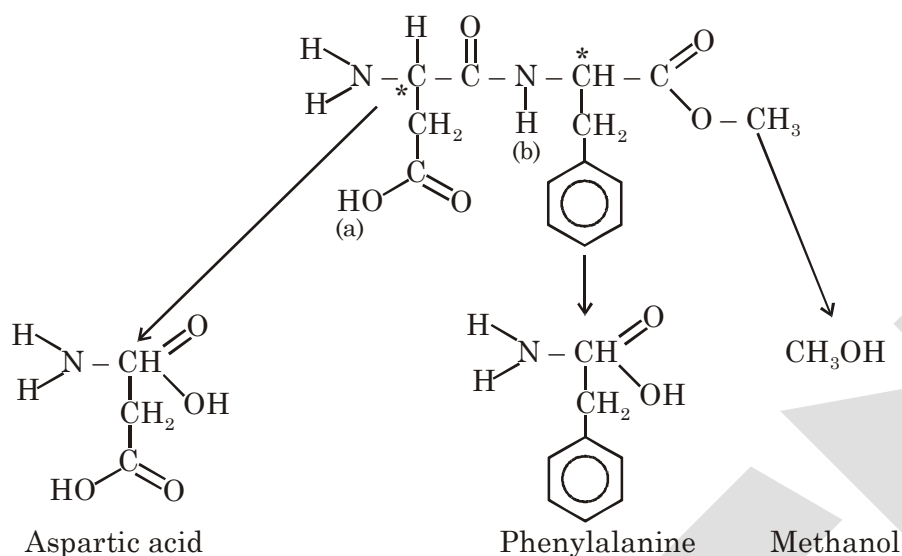
$sp^3C \rightarrow 7C$

**V. Functional group : Amines, Thiol, nitro etc.****VI. DOU : 5****VII. Aromaticity : Aromatic (Heterocyclic)**

**NOTE :**  $Al(OH)_3$ ,  $Mg(OH)_2$  are also used as antacids

## PART F : ARTIFICIAL SWEETNERS

### 1. ASPARTAME



#### I. Use :

- (i) Used as an artificial sweetener (100 times sweeter than cane sugar)
- (ii) Methyl ester of dipeptide formed from aspartic acid and phenylalanine
- (iii) Use of aspartame is limited to cold food and soft drinks because it is unstable at cooking temperature

#### II. Number of chiral centre: 2

#### III. TSI : 4

#### IV. Hybridisation state :

$$sp^2C \rightarrow 9$$

$$sp^3C \rightarrow 5$$

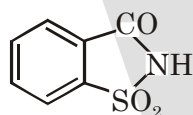
#### V. Functional group : Acid, Ester, Amide

#### VI. Aromaticity : Aromatic (Homocyclic)

#### VII. DOU : 7

#### VIII. Acidic strength : a > b

### 2. SACCHARIN (Ortho-sulphobenzimide)



#### I. Use :

- (i) Used as an artificial sweetener (550 times sweeter than cane sugar)
- (ii) Excreted from the body in urine unchanged.

#### II. Number of chiral centre : 0

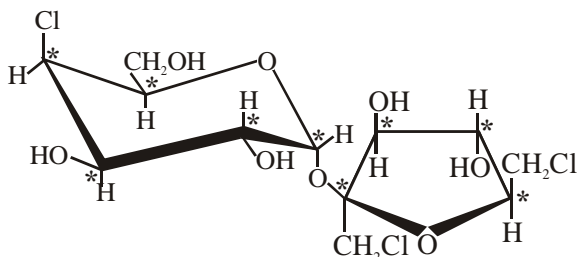
#### III. Hybridisation state :

$$sp^2C \rightarrow 7$$

#### IV. Aromaticity : Aromatic (Heterocyclic)

#### V. DOU : 8

3. SUCRALOSE



I. Use :

- (i) Used as an artificial sweetener (600 times sweeter than cane sugar)
- (ii) Appearance and taste like sugar
- (iii) Stable at cooking temperature
- (iv) Does not provide calories
- (v) Trichloro derivative of sucrose

II. Number of chiral centre : 9

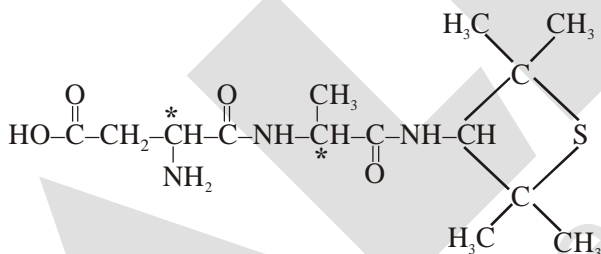
III. Functional group : Alcohol, ether, alkyl halide

IV. Aromaticity : Non aromatic (Heterocyclic)

V. DOU : 2

VI. Hybridisation :  $sp^3C \rightarrow 12C$

4. ALITAME



I. Use :

- (i) High potency sweetener (2000 times sweeter than cane sugar)
- (ii) Although it is more stable than aspartame, the control of sweetness of food is difficult while using it.

II. Number of chiral centre : 2

III. Hybridisation state :

$sp^2C \rightarrow 3$

$sp^3C \rightarrow 11$

IV. Functional group : Acid, amide, amine

V. Aromaticity : Non-aromatic (Heterocyclic)

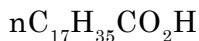
VI. DOU : 4

## PART G : SOAP, DETERGENT & PRESERVATIVES

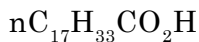
### (a) SOAPS

Sodium salt of

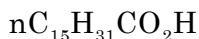
#### 1. Stearic acid



#### 2. Oleic acid

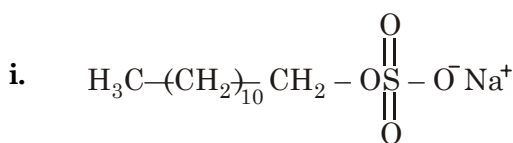


#### 3. Palmitic acid

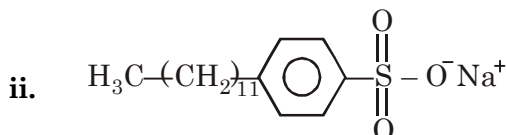


### (b) SYNTHETIC DETERGENTS

#### 1. Anionic

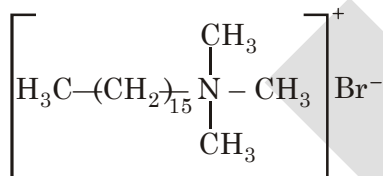


Sodium laurylsulphate



Sodium dodecylbenzenesulphonate

#### 2. Cationic



Cetyltrimethylammonium bromide

#### i Non ionic

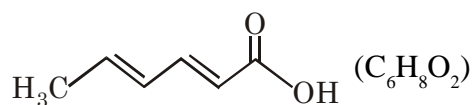


(non-ionic detergent), it is dishwashing detergent

**Note :** Synthetic detergents are better than soaps because synthesis detergents gives foam in both soft and hard water while soap do not give foam in hard water.

### (c) FOOD PRESERVATIVES

#### 1. SORBIC ACID



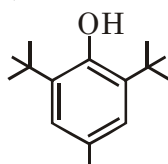
#### I. Use :

Salts of sorbic acid and propanoic acid are used as food preservatives (prevent microbial growth on food)

- II. Number of chiral centre : 0  
 III. TSI : 4 (GI)  
 IV. Hybridisation state :  
 $sp^2C \rightarrow 5$   
 $sp^3C \rightarrow 1$   
 V. Functional group : Carboxylic acid  
 VI. Aromaticity : Non-aromatic  
 VII. DOU : 3

2. Butylatedhydroxytoluene (BHT)

(IUPAC Name : 2,6-Bis(1,1-dimethylethyl)-4-methylphenol)



I. Use :

- (i) Used as antioxidants (Help in food preservation by retarding the action of oxygen on food)  
 (ii) Sometimes citric acid added along BHT to produce more effect

II. Number of chiral centre : 0

III. Hybridisation state :

- $sp^2C \rightarrow 6$   
 $sp^3C \rightarrow 9$

IV. Functional group : Phenolic OH (SIR)

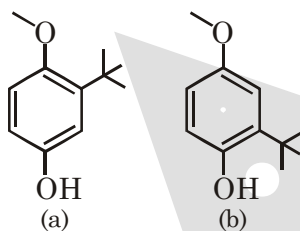
V. Aromaticity : Aromatic (Homocyclic)

VI. DOU : 4

3. Butylated hydroxy anisole (BHA)

(IUPAC Name : (a) 3-(1,1-Dimethylethyl)-4-methoxyphenol

(b) 2-(1,1-Dimethylethyl)-4-methoxyphenol)



I. Use :

- (i) Used as antioxidants (Help in food preservation by retarding the action of oxygen on food)  
 (ii) Sometimes citric acid added along BHA to produce more effect

II. Number of chiral centre : 0

III. Hybridisation state :

- $sp^2C \rightarrow 6$   
 $sp^3C \rightarrow 5$

IV. Functional group : Phenolic OH, ether

V. Aromaticity : Aromatic (Homocyclic)

VI. DOU : 4

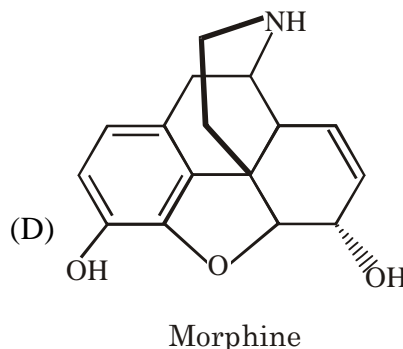
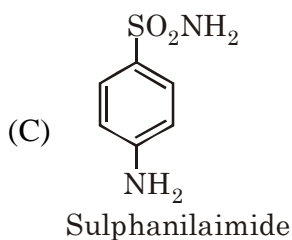
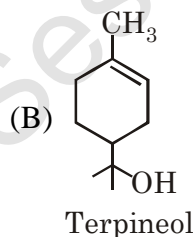
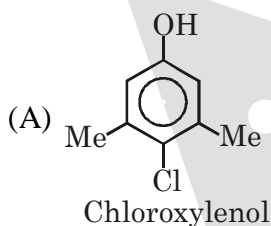
## EXERCISE # O-1

- An antipyretic is –  
(A) Seldane (B) Paracetamol (C) Luminal (D) Aspartame
- Medicine which is an antibiotic is –  
(A) Ampicillin (B) Aspirin (C) Dimetapp (D) None of these
- Paracetamol is –  
(A) Both antipyretic and analgesic (B) Analgesic  
(C) Antipyretic (D) Antimalarial
- Sulpha drugs are derivatives of –  
(A) Benzene sulphonamic acid (B) Sulphanillic acid  
(C) Sulphanilamide (D) p - aminobenzoic acid
- Aspirin is called –  
(A) Pyretic (B) Antiseptic (C) Antibiotic (D) Antipyretic
- Which of the following is an antidiabetic drug –  
(A) Insulin (B) Penicillin (C) Sucralose (D) Aspirin
- 2-Acetoxybenzoic acid is called –  
(A) Antiseptic (B) Aspirin (C) Antibiotic (D) Mordant dye
- Arsenic drugs are mainly used in the treatment of–  
(A) Jaundice (B) Typhoid (C) Syphilis (D) Cholera
- Aspirin is an acetylation product of –  
(A) p-dihydroxybenzene (B) o-hydroxybenzoic acid  
(C) o-dihydroxy benzene (D) m-hydroxybenzoic acid
- Chloramphenicol is an –  
(A) Analgesic (B) Anaesthetic (C) Antibiotic (D) Antiseptic
- Substances which bring body temperature down are known as –  
(A) Antipyretics (B) Analgin (C) Antibiotics (D) Hypnotics
- The drug given during hypertension is –  
(A) Salvarsan (B) Chloroxylenol (C) Equanil (D) Aspirin
- Which of the following is known as narrow spectrum antibiotic –  
(A) Ofloxacin (B) Ampicillin (C) Chloramphenicol (D) Penicillin
- Phenol is used as –  
(A) An antiseptic (B) A disinfectant (C) Both (A) and (B) (D) None of these
- Mixture of chloroxylenol and terpineol acts as  
(A) antiseptic (B) antipyretic (C) antibiotic (D) analgesic
- Bithional is generally added to the soaps as an additive to function as a/an  
(A) buffering agent (B) antiseptic (C) softener (D) dryer.
- Artificial sweetner which is stable under only cold conditions is  
(A) saccharine (B) sucralose (C) aspartame (D) alitame.
- Antiseptics and disinfectants either kill or prevent growth of microorganisms. Identify which of the following statements is not true.  
(A) Dilute solution of boric acid is strong antiseptic.  
(B) Disinfectants harm the living tissues.  
(C) A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant.  
(D) Chlorine and iodine are used as strong disinfectants.
- Dettol is the mixture of  
(A) chloroxylenol and bithional (B) chloroxylenol and terpineol  
(C) phenol and iodine (D) terpineol and bithional

20. Chloramphenicol is an  
(A) antifertility drug (B) antihistamine  
(C) antiseptic and disinfectant (D) antibiotic-broad spectrum
21. Which of the following forms cationic micelles above certain concentration?  
(A) Sodium dodecyl sulphate (B) Sodium acetate  
(C) Urea (D) Cetyltrimethylammonium bromide.
22. Aspirin is an acetylation product of  
(A) m-Hydroxybenzoic acid (B) o-Dihydroxybenzene  
(C) o-Hydroxybenzoic acid (D) p-Dihydroxybenzene
23. Which of the following can possibly be used as analgesic without causing addiction and mood modification?  
(A) Codeine (B) Heroin  
(C) Morphine (D) N-Acetyl-para-aminophenol.
24. Diazo coupling is useful to prepare some  
(A) pesticides (B) dyes (C) proteins (D) vitamins.
25. Which one of the following statements is not true?  
(A) Penicillin is a natural antibiotic  
(B) Aspirin is both analgesic and antipyretic  
(C) Sulphadiazine is a synthetic antibacterial drug  
(D) Some disinfectants can be used as antiseptics.
26. Which of the following is a correct match?  
(A) Anionic detergent : Glyceryl ester of stearic acid  
(B) Fat : Sodium stearate  
(C) Soap : Sodium salt of oleic acid  
(D) Soap : Sodium Lauryl Sulphate
27. Which of the following compounds is not a food preservative?  
(A) Table salt (B) Sugar (C) Vegetable oil (D) Sodium oleate
28. What is the normal range of molecular masses of drugs?  
(A) (~0–100) u (B) (~100–500) u (C) (~500–1000) u (D) > 1000 u
29. Which of the following is not used as an anti-oxidant?  
(A) Butylated Hydroxy Toluene (BHT)  
(B) Sulphur Dioxide  
(C) Sulphite  
(D) Sodium Palmate
30. Abrasive is a :  
(A) Scouring agent (B) Drug to reduce fever  
(C) Drug to kill bacteria (D) Gum

## EXERCISE # O-2

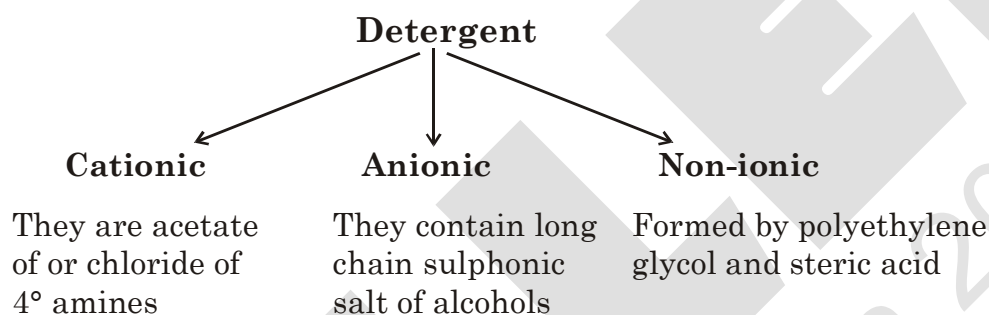
- Which of the following are used as analgesics?  
(A) Aspirin (B) Heroin (C) Promethazine (D) Serotonin
- Select the correct statements :  
(A) Drugs are chemicals of low molecular mass.  
(B) Drugs produce biological response.  
(C) Drugs which are used in diagnosis, prevention and treatment of diseases are called medicines.  
(D) Chemotherapy is the use of chemical for therapeutic effect.
- Which of the following pairs are bacteriostatic antibiotics?  
(A) Penicillin, tetracycline (B) Erythromycin chloramphenicol  
(C) Ofloxacin, aminoglycosides (D) Tetracycline, chloramphenicol
- Which of the following can be used as artificial sweeteners?  
(A) Aspartame (B) Alitame (C) Sucralose (D) Saccharin
- Which of the following is known as broad spectrum antibiotic –  
(A) Streptomycin (B) Ampicillin (C) Chloramphenicol (D) Penicillin
- Medicine which is an antibiotic is –  
(A) Ampicillin (B) Ofloxacin (C) Aminoglycoside (D) Penicillin
- Bactericidal antibiotics are -  
(A) Penicilline (B) Ofloxacin (C) Aminoglycosides (D) Only (B) and (C)
- Bacteristatic antibiotics are -  
(A) Chloramphenicol (B) Tetracydine (C) Penicillin (D) Erythromycin
- Which one drugs have one or more then one chiral atom -  
(A) Penicillin (B) Chloramphenicol (C) Terpeneol (D) Phenelzine (Nardil)
- How many drugs have even number of degree of unsaturation -



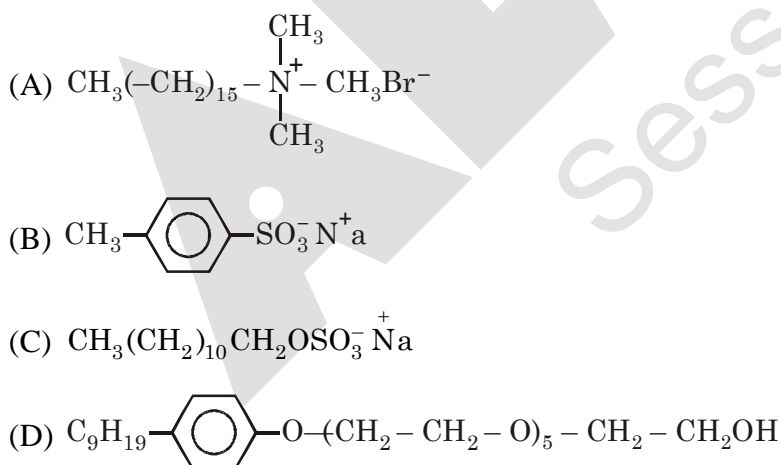


11. Which pair is combination of non narcotic and narcotic drug?  
 (A) Paracetamol, Aspirin (B) Paracetamol, Herion  
 (C) Aspirin, Morphine (D) Morphine, Codeine
12. Which one is/are used as food preservative?  
 (A) Sodium benzoate (B) Vegetable oil (C) Sorbic acid (D) Propanoic acid
13. Choose the incorrect statement?  
 (A) Saccharin is 650 times sweeter than cane sugar.  
 (B) Alitame is 2000 times sweeter than cane sugar  
 (C) Sucralose is 160 times sweeter than cane sugar.  
 (D) Aspartame is 550 times sweeter than cane sugar.
14. Antiseptic chloroxylenol is :  
 (A) 4-chloro-3,5-dimethyl phenol (B) 3-chloro-4, 5-dimethyl phenol  
 (C) 4-chloro-2, 5-dimethyl phenol (D) 5-chloro-3,4-dimethyl phenol

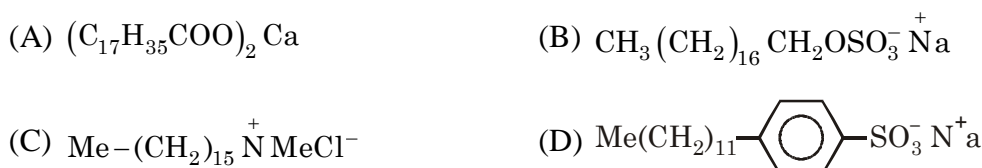
Paragraph for Question No. 15 to 17



15. Used in liquid dishwashing detergent?



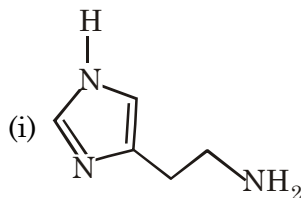
16. Which is not used in synthetic detergent?



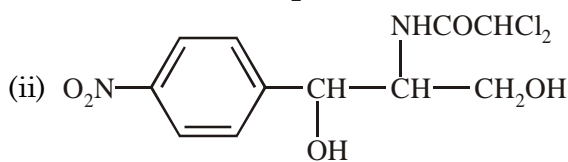
17. Which of the following is non-ionic detergent?

- (A)  $\text{Me}(\text{CH}_2)_{16}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_3 - \text{CH}_2\text{CH}_2\text{OH}$       (B)  $\text{Me}(\text{CH}_2)_{16}\text{CH}_2\text{SO}_3\text{Na}$   
 (C)  $\text{Me}(\text{CH}_2)_{15} - \text{NMe}_3\text{Br}$       (D)  $\text{Me}(\text{CH}_2)_{11} - \text{C}_6\text{H}_4 - \text{SO}_3\text{Na}$

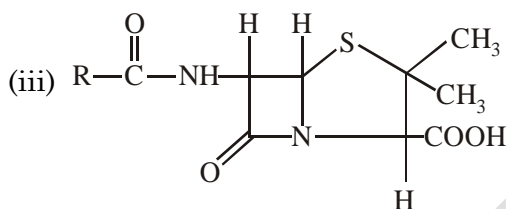
18. How many organic compound(s) is/are correctly matched with number of chiral carbon(s) present in its structure :



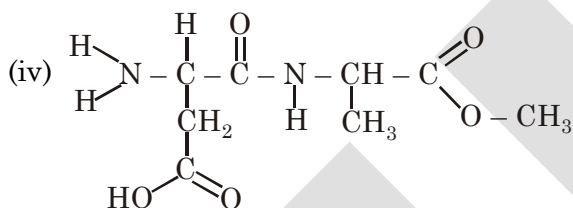
Histamine = 0



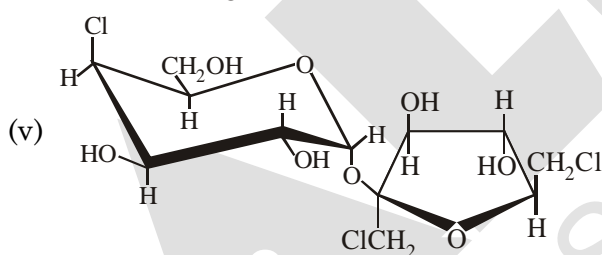
Chloramphenicol = 2



Penicillin = 3



Aspartame = 4



Sucralose = 9

Matrix match :

19. Column-I

- (A) Aspirin  
 (B) Paracetamol  
 (C) Soframycin  
 (D) Penicillin

Column-II

- (P) Antiseptic and Disinfectant  
 (Q) Analgesic  
 (R) Antibiotic  
 (S) Antipyretic

20. Match list-I and list-II and select the correct answer using the codes given below the list?

Column-I

- (A) Penicillin  
 (B) Chloramphenicol  
 (C) 0.2 % solution of phenol  
 (D) 1 % solution of phenol

Column-II

- (P) Antiseptic  
 (Q) Antibiotic  
 (R) Bacteriocidal  
 (S) Disinfectant

EXERCISE # JEE MAIN'S & ADVANCE

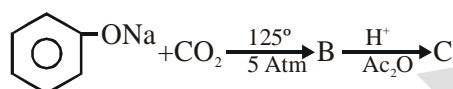
1. Which one of the following types of drugs reduces fever- [AIEEE-2005]

- (1) Tranquilizer (2) Antibiotic (3) Antipyretic (4) Analgesic

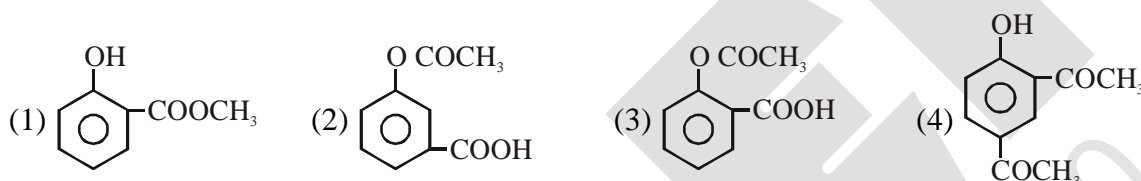
2. Aspirin is known as :- [AIEEE-2012]

- (1) Methyl salicylic acid (2) Acetyl salicylic acid  
(3) Phenyl salicylate (4) Acetyl salicylate

3. Sodium phenoxide when heated with CO<sub>2</sub> under pressure at 125°C yields a product which on acetylation produces C. [J-Main- 2014]



The major product C would be :



4. Which of the following compounds is not an antacid? [J-Main- 2015]

- (1) Phenelzine (2) Ranitidine  
(3) Aluminium hydroxide (4) Cimetidine

5.  is used as : [J-Main-2015]

- (1) Insecticide (2) Antacid (3) Antihistamine (4) Analgesic

6. Which of the following is an anionic detergent ? [J-Main-2016]

- (1) Glyceryl oleate  
(2) Sodium stearate  
(3) Sodium lauryl sulphate  
(4) Cetyltrimethyl ammonium bromide

7. The artificial sweetener that has the highest sweetness value in comparison to cane sugar is:

- (1) Saccharin (2) Alitame [J-Main-2016]  
(3) Aspartane (4) Sucralose

8. The correct match between Item(I) and Item(II) is : [JEE-MAIN-(Jan)-2019]

Item-I

Item-II

- (A) Norethindrone (P) Anti-biotic  
(B) Ofloxacin (Q) Anti-fertility  
(C) Equanil (R) Hypertension  
(S) Analgesics

- (1) A-R, B-P, C-S (2) A-Q, B-P, C-R (3) A-R, B-P, C-R (4) A-Q, B-R, C-S

9. The correct match between Item -I and Item-II is :

[JEE-MAIN-(Jan)-2019]

Item – I (drug)		Item – II (test)	
(A)	Chloroxylenol	(P)	Carbylamine Test
(B)	Norethindrone	(Q)	Sodium Hydrogen carbonate Test
(C)	Sulphapyridine	(R)	Ferric chloride test
(D)	Penicillin	(S)	Bayer's test

(1) A→Q ; B→P ; C→S ; D→R

(2) A→R ; B→P ; C→S ; D→Q

(3) A→R ; B→S ; C→P ; D→Q

(4) A→Q ; B→S ; C→P ; D→R

10. Noradrenaline is a/an

[JEE-MAIN-(April)-2019]

(1) Neurotransmitter

(2) Antidepressant

(3) Antihistamine

(4) Antacid

11. The number of  $sp^2$  hybridised carbons present in "Aspartame" is \_\_\_\_\_. [JEE-MAIN-(Jan)-2020]

12. The number of chiral carbons in chloramphenicol is \_\_\_\_\_. [JEE-MAIN-(Jan)-2020]

13. The number of chiral centres in penicillin is \_\_\_\_\_. [JEE-MAIN-(Jan)-2020]

14. The mass percentage of nitrogen in histamine is \_\_\_\_\_. [JEE-MAIN-(Jan)-2020]

ANSWER KEY

EXERCISE # O-1

- |             |             |             |             |
|-------------|-------------|-------------|-------------|
| 1. Ans. B   | 2. Ans. A   | 3. Ans. A   | 4. Ans. C   |
| 5. Ans. D   | 6. Ans. A   | 7. Ans. B   | 8. Ans. C   |
| 9. Ans. B   | 10. Ans. C  | 11. Ans. A  | 12. Ans. C  |
| 13. Ans. D  | 14. Ans. C  | 15. Ans. A  | 16. Ans. B  |
| 17. Ans. C  | 18. Ans. A  | 19. Ans. B  | 20. Ans. D  |
| 21. Ans. B  | 22. Ans. C  | 23. Ans. D  | 24. Ans. B  |
| 25. Ans. A  | 26. Ans.(C) | 27. Ans.(D) | 28. Ans.(B) |
| 29. Ans.(D) | 30. Ans.(A) |             |             |

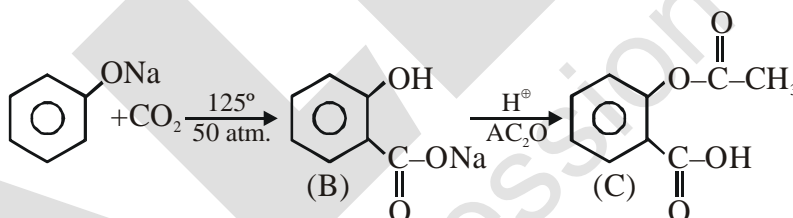
EXERCISE # O-2

- |                                   |                  |                                |                   |
|-----------------------------------|------------------|--------------------------------|-------------------|
| 1. Ans. (A,B)                     | 2. Ans.(A,B,C,D) | 3. Ans. (B,D)                  | 4. Ans.(A,B,C,D)  |
| 5. Ans.(B,C)                      | 6. Ans.(A,B,C,D) | 7. Ans.(A,B,C)                 | 8. Ans.(A,B,D)    |
| 9. Ans. (A,B)                     | 10. Ans.(A,B,C)  | 11. Ans.(B,C)                  | 12. Ans.(A,B,C,D) |
| 13. Ans.(A,C,D)                   | 14. Ans.(A)      | 15. Ans. (D)                   | 16. Ans.(A)       |
| 17. Ans.(A)                       | 18. Ans. (4)     | 19. Ans. A→Q ; B→S ; C→P ; D→R |                   |
| 20. Ans. (A) A→Q,R; B→Q; C→P; D→S |                  |                                |                   |

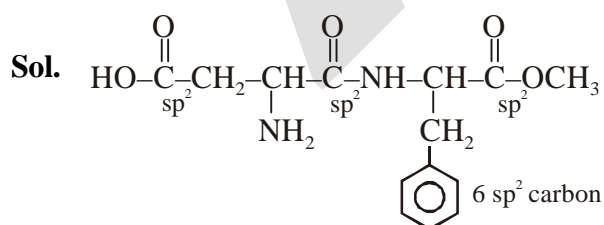
EXERCISE # JEE MAIN'S & ADVANCE

- |             |            |
|-------------|------------|
| 1. Ans.(3)  | 2. Ans.(2) |
| 3. Ans. (3) |            |

Sol. First step is carboxylation (Kolbe schmidt reaction) & second step is acetylation of sodium salt of aspirin (B).

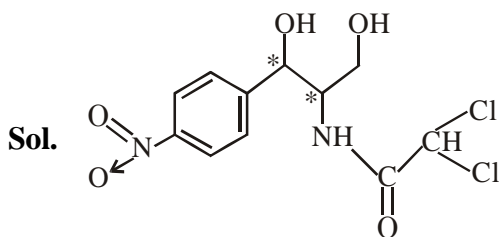


- |                 |             |              |             |
|-----------------|-------------|--------------|-------------|
| 4. Ans. (1)     | 5. Ans. (4) | 6. Ans. (3)  | 7. Ans. (2) |
| 8. Ans. (2)     | 9. Ans. (3) | 10. Ans. (1) |             |
| 11. Ans. (9.00) |             |              |             |



no. of sp<sup>2</sup>-carbon → 9

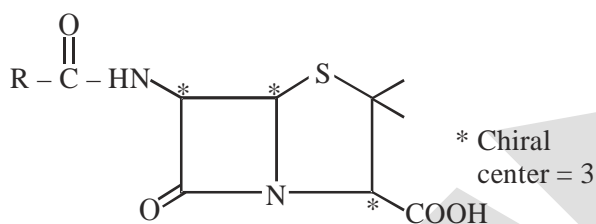
12. Ans. (2.00)



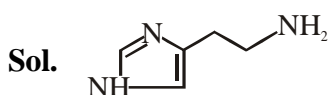
Chloramphenicol

13. Ans.(3.00)

Sol. The structure of penicillin is



14. Ans.(37.80 to 38.20)

M.F. of Histamine is  $C_5H_9N_3$ 

Molecular mass of Histamine is 111

$$\text{Now, mass \% of nitrogen} = \left( \frac{42}{111} \right) \times 100 = 37.84\%$$