CHEMISTRY - I
(DSCHE11)
(BSC)

ACHARYA NAGARJUNA UNIVERSITY

CENTRE FOR DISTANCE EDUCATION

NAGARJUNA NAGAR,

GUNTUR

ANDHRA PRADESH

UNIT – I

Lesson – 1

P- Block Elements

Group - 13 : Synthesis and Structure of diborane and higher boranes (B_4H_{10} and B_5H_9) and boron - nitrogen compounds ($B_3N_3H_6$ and BN)

1.1.1 Synthesis and Structure of diborane and higher boranes(B_4H_{10} and B_5H_9):

The volatile compounds formed by the combination of boron with hydrogen are called boron hydrides. By analogy with the alkanes, boron hydrides are known as boranes. There are eight boranes which are well characterised. They fall into two series having general formula B_nH_{n+4} (Boranes) and a less stable B_nH_{n+6} (hydroboranes).

B_2H_6 - Diborane

B_4H_{10} - Tetraborane

B_6H_{10} - Hexaborane

B_9H_{15} - Enneaborane

B_5H_9 - Stable penta borane

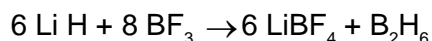B_5H_{11} - Unstable Pentaborane

$B_{10}H_{14}$ - Decaborane

$B_{10}H_{16}$ - Decaborane

1.1.2 Preparation of Diborane, B_2H_6 :

Boranes have great affinity for water and oxygen and hence they do not occur in nature -

1. Diborane can be obtained by the reaction of lithium hydride with boron trifluoride.

$$6 \, Li \, H + 8 \, BF_3 \rightarrow 6 \, LiBF_4 + B_2H_6$$

2. Diborane can also be prepared by the reaction of lithium aluminium hydride with boron trichloride

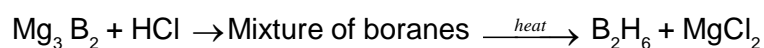$$4 \, B \, Cl_3 + 3 \, Li \, Al \, H_4 \rightarrow 2 \, B_2H_6 + 3 \, Al \, Cl_3 + 3 \, Li \, Cl$$
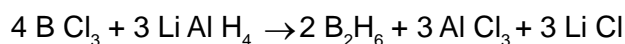
3. Diborance may also be prepared by passing silent electric discharge through a mixture of hydrogen and boron trichloride at a low pressure.

$$6 H_2 + 2 B Cl_3 \rightarrow B_2H_6 + HCl$$
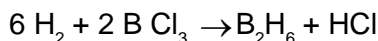
4. Diborane can also be prepared by the action of dilute sulphuric acid on sodium borohydride.

$$3 Na BH_4 + H_2 SO_4 \rightarrow Na_2 SO_4 + 2H_2 + B_2 H_6$$
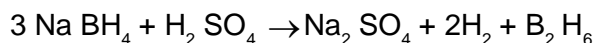
5. Diborane can also be prepared by heating the mixture of boranes formed by heating magnesium boride with HCl or $H_3 PO_4$.

$$Mg_3 B_2 + HCl \rightarrow \text{Mixture of boranes} \xrightarrow{heat} B_2H_6 + MgCl_2$$

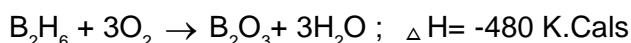$$Mg_3 B_2 + H3 PO_4 \rightarrow \text{Mixture of boranes} \xrightarrow{heat} B_2H_6 + Mg_3 (PO_4)_2$$
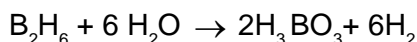
Properties of diborane :

1. Diborane is a gas and is stable only at low temperatures. When heated at temperatures between 100 and 250°C it changes into a number of other boranes.
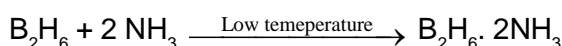
$$B_2H_6 \xrightarrow{heat} \text{Other boranes}$$
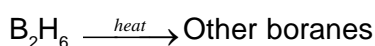
2. On Combustion of diborane and other boranes a large amount of heat is released.

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O ; \quad \triangle H = -480 \text{ K.Cals}$$

3. It undergoes hydrolysis to give boric acid.

$$B_2H_6 + 6 H_2O \rightarrow 2H_3 BO_3 + 6H_2$$

4. Diborane reacts with ammonia and gives the product depending upon the experimental conditions.

$$B_2H_6 + 2 NH_3 \xrightarrow{\text{Low temeperature}} B_2H_6 . 2NH_3$$

Diammoniate of diborane

$$3B_2H_6 + 6 NH_3 \xrightarrow{\text{High temeperature}} 2B_3N_3H_6 + 12H_2$$
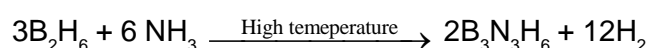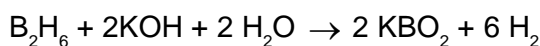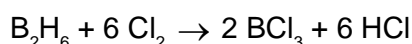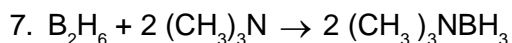
Borazole or Borazine or Inorganic Benzene

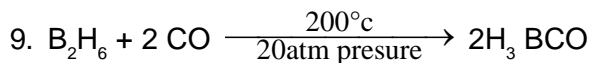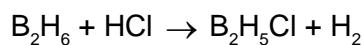5. Diborane dissolves in strong alkali solutions giving borates along with the evolution of hydrogen.

$$B_2H_6 + 2KOH + 2 H_2O \rightarrow 2 KBO_2 + 6 H_2$$

6. Diborane, when treated with chlorine at 25°c it gives boron trichloride.

$$B_2H_6 + 6 Cl_2 \rightarrow 2 BCl_3 + 6 HCl$$

7. $B_2H_6 + 2 (CH_3)_3N \rightarrow 2 (CH_3)_3NBH_3$

8. Diborane, reacts with hydrogen chloride and form chlorodiborane.

$$B_2H_6 + HCl \rightarrow B_2H_5Cl + H_2$$

9. $B_2H_6 + 2 CO \xrightarrow[\text{20atm presure}]{200°c} 2H_3 BCO$

Boron Carbonyl

Structure of Diborane :

The structure of boranes are of great interest. They do not possess enough valency electrons to form the required number of covalent bonds and hence they are called electron deficient compounds.

In diborane, there are twelve valency electrons, three from each boron atom and six from the hydrogen atoms. Thus each boron in diborane molecule can link to itself three hydrogen atoms, there are no electrons left to form a bond between the two boron atoms, as shown below.
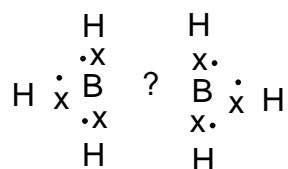
Form electron diffraction and infrared spectroscopic experiments the structure of diborane is a shown below -
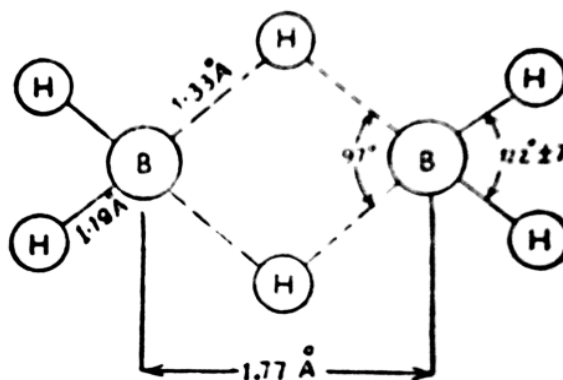

Fig 1.1 Structure of diborane molecule

The four terminal hydrogen atoms, two on the left and two on the right are different from the other two hydrogen atoms called as bridging atoms. The four terminal hydrogen atoms and the two boron atoms lie in the same plane while the two bridging hydrogen atoms lie one above and one below in a plane perpendicular to this plane.

The above given bridge structure is supported by the following facts -

1. Diborane can not be methylated beyond $Me_4B_2H_2$. Thus the bridge hydrogen atoms can not be methylated.

2. The terminal B - H distances are the same as the bond lengths measured in non electrons deficient compounds. These can be considered to be normal covalent bonds, with two electrons shared between two bonds. Hence, these bonds are known as two - centre two electron bonds (2c- 2e).

Nature of bonds in hydrogen bridges :

The electron deficiency must be associated with the bridge groups.

The B – H– B bond is a three centre electron pair bond i.e, one electron pair binds three atoms (B,H and B). These are called abnormal bonds as the two bridges involve only one electron from each boron atom and one electron from each hydrogen atom. There are two such three - centre electron pair bonds in diborane molecule.

The complete structure of diborane can be explained on the basis of molecular orbital theory.

Fig 1.2 Orbital picture of a three - centre electron pair bond

According to the molecular orbital theory the boron atoms undergoes SP3 hybridisation. Out of the four SP^3 hydrid orbitals three contain one electron each while the fourth SP^3 hydrid orbital is empty. Two of the SP^3 hybrid orbitals of each boron atom overlap with 1S orbitals of the two terminal hydrogen atoms forming the two normal B –H sigma (σ) bonds. One of the remaining SP^3 hybrid orbital (filled) of one of the boron atoms, the 1S orbital of the bridge hydrogen atom and one of the SP^3 hybrid orbital (empty) of the other boron atom overlap to form a delocalised orbital covering the three nuclei. Thus a pair of electrons (One electron from boron and the other from hydrogen atom) acts as a bond between the three atoms (B ; H ; B) and such a bond is known as three - centre two electron bonds (3C- 2C bonds). Due to repulsion between the two hydrogen nuclei, the delocalised orbitals of bridges are bent away from each other in the middle thus giving the shape of banana and thus the three - centre two electron bonds are also known as tau bonds or banana bonds.
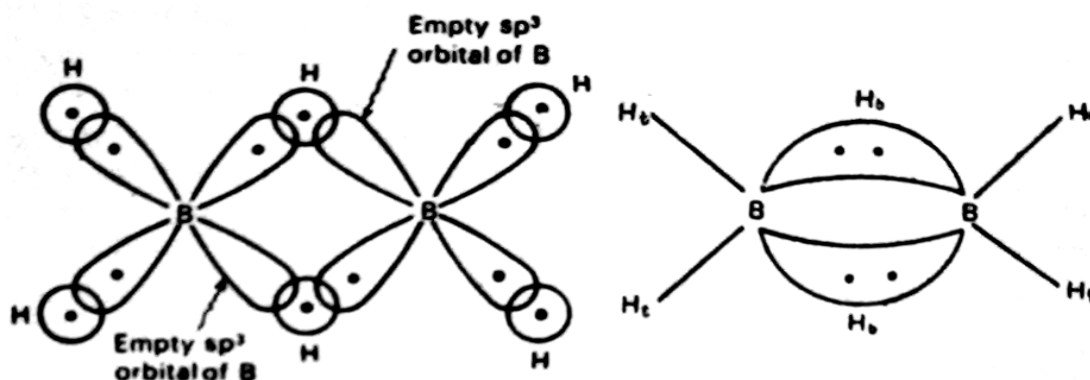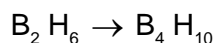
Fig 1.3 Structure of diborane showing two three - centre bonds.

1.1.3 Synthesis and structure of Higher boranes :
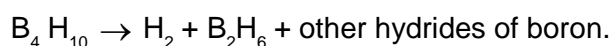
Tetra borane, $B_4 H_{10}$:

I Method : It can be prepared by heating diborane in a sealed tube at 80 - 90°c and 200 atmospheres.

$$B_2 H_6 \rightarrow B_4 H_{10}$$

II Method : Tetra borane is prepared by the action of dilute hydrochloric acid on magnesium boride. The gaseous product obtained is a mixture of a number of hydrides of boron which is then condensed by cooling in liquid air. Tetraborane can be obtained from the condensed product by fractional distillation.

Properties of tetraborane :

Tetraborane is highly unstable and decomposes at ordinary temperatures to give hydrogen and lower hydrides.

$$B_4 H_{10} \rightarrow H_2 + B_2 H_6 + \text{other hydrides of boron.}$$

It undergoes hydrolysis very slowly giving boric acid along with the evolution of hydrogen.

$$B_4 H_{10} + 12 H_2O \rightarrow 4H_3 BO_3 + 11H_2$$
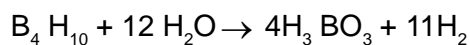
Structure of tetraborane :

Tetraborane has almost a planar structure. In tetraborane, there are four three - centre B----H---B bonds and one B – B bond. Each of the four boron and the four H μ contribute one electron to the B----H---B bonds. The two joint BHt groups each have one remaining electron and an orbital which interact to give a two centre B – B bond.
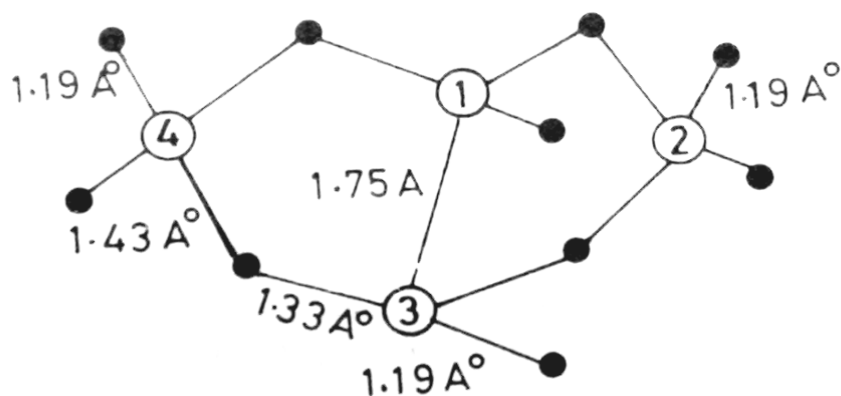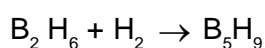
Fig 1.4

Pentaborane (9), B_5H_9 :

It is prepared by heating diborane in a sealed tube at 200 - 250°c.

$$B_2H_6 + H_2 \rightarrow B_5H_9$$

Structure :

Here, the boron atoms form a square based pyramid with four three centre B ----- H -----B bonds and multi centre bonds from the apical boron atom to the four boron atoms in the square. The B – B distance in the square base has 1.78A°length.
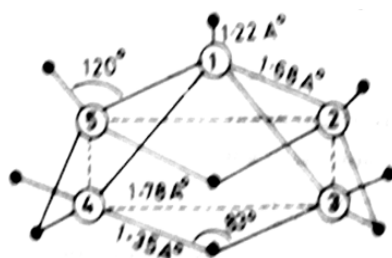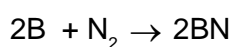

Fig 1.5

The pyramidal apex B is 1.68A° away from the basal boron atoms. The B–H_t distance is 1.22A° and B-H μ distance is 1.35A°. The BH_tB angle is 120° and BH μ B angle is of 83°

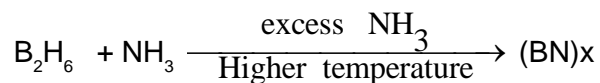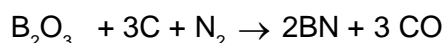# Boron - nitrogen compounds :

1.1.4 Boron nitride , BN :

1. Boron nitride is prepared directly by burning boron in nitrogen.

$$2B + N_2 \rightarrow 2BN$$

2. It can also be prepared by heating diborane with excess of ammonia at high temperature.

$$B_2H_6 + NH_3 \xrightarrow[\text{Higher temperature}]{\text{excess } NH_3} (BN)x$$

3. It can also be prepared by heating boric oxide and carbon in presence of N_2 at 1300 - 1500°c.

$$B_2O_3 + 3C + N_2 \rightarrow 2BN + 3\ CO$$

4. It is obtained by heating anhydrous borax and dry ammonium chloride together.

$$Na_2B_4O_7 + 2NH_4Cl \rightarrow 2BN + 2\ NaCl + B_2O_3 + 4\ H_2O$$

5. It can be prepared by heating boron halide with ammonia.

$$BCl_3 + NH_3 \rightarrow BN + 3\ HCl$$
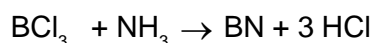
Properties :

It is a white powder, insoluble in water but reacts with steam evolving ammonia.

$$BN + 3\ H_2O \rightarrow B_2O_3 + 2\ NH_3$$
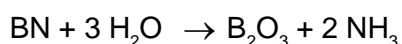
It is easily oxidised in air at 800° to 900°c after two hours to form B_2O_3.

Structure :

Boron nitride has a structure similar to graphite. The hexagons forming the layers are composed of alternate boron and nitrogen atoms.

A boron atom bonded together with nitrogen atom has 8 valency electrons, 3 from boron and 5 from nitrogen. The same number of electrons are present between two adjuscent carbon atoms in graphite.

Fig 1.6 Similarity in the structure of boron nitride and graphite

The inter atomic distances in the layers are 1.45A° and the distance between the two adjuscent layers is 3.33 A°. However boron nitride structure differ from that of graphite in the case the atoms in successive layers in boron nitride are eclipsed unlike in that of graphite where they are staggered.

1.1.5 Borazole or borazine or Inorganic benzene :

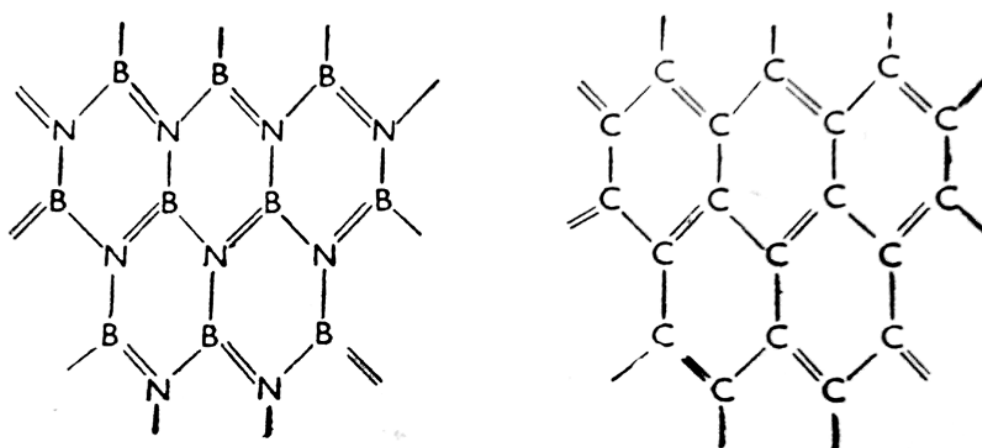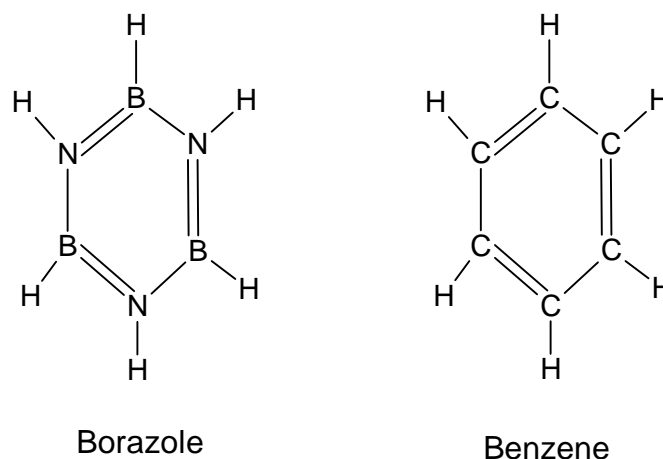Borazole   Benzene

Fig 1.7 Similarity in the structure of borazole and benzene

Borazole can be prepared by heating diborane with ammonia in 1: 2 ratio at a very high temperature.

$$2B_2H_6 + 6NH_3 \xrightarrow[\text{Very higher temperature}]{1:2 \text{ mixture}} 2B_3N_3H_6 + 9H_2$$
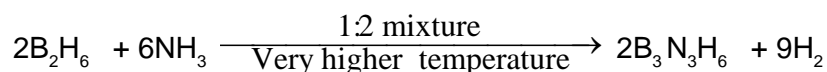
It can also be prepared by the reaction of sodium tetrahydrato borate with ammonium and heating the compound obtained chloride.

$$Na\,BH_4 + NH_4\,Cl \rightarrow H_3NBH_3 + H_2 + NaCl$$
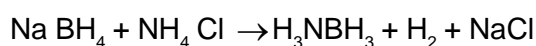
It can also be prepared by treating $NaBH_4$ with NH_4Cl.

Borazole can be prepared by heating BCl3 with ammonium chloride in presence of chlorobenzene solvent at 150° and reducing the product tri chloro borazine obtained.

$$2\,BCl_3 + 3NH_4\,Cl \xrightarrow{150°} B_3N_3\,Cl_3\,H_3$$

$$B_3N_3\,Cl_3\,H_3 \xrightarrow{\text{reduction}} B_3\,N_3\,H_6 + 3\,HCl$$
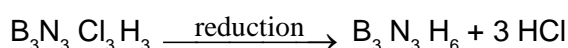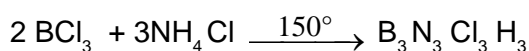
Properties :

It is a colourless liquid.

It resembles benzene in some of its physical properties and structure.

On account of the polarity of N$\rightarrow$ B bond (C = C bonds in benzene are non polar) it is more reactive than benzene. Thus it adds three molecules of HCl, CH_3OH, H_2O or CH_3I, the more negative group adds to boron atoms.

$$B_3N_3H_6 + 3\ HCl \rightarrow B_3N_3H_6.\ 3\ HCl$$

It undergoes hydrolysis to give boric acid and ammonia. Benzene does not undergo hydrolysis.

$$B_3N_3H_6 + 3\ H_2O \rightarrow H_3BO_3 + 2NH_3 + 3\ H_2$$

Structure of borazole :

Borazole is commonly known as inorganic benzene because of its analogous behaviour to benzene with respect to the isoelectronic structures. It is a planar molecule in which boron and nitrogen atoms are SP2 hybridized. In benzene there is pi (π) bond present but in borazole there the double bond arises by the overl apping of empty P - orbitals of boron with filled P - orbita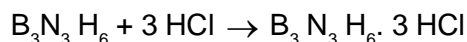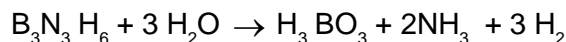ls of nitrogen. Thus the six electrons in the Pi (π) orbitals of borazole are derived from the three nitrogen atoms only.

1.1.6 Model Questions :

1) What are electron deficient molecules ? Discuss the preparation, properties and structure of diborane.

2) What is electron deficient bond? Explain the bonding and structure taking one example of electron deficient molecule.

3) How is diborane prepared ? Discuss its structure.

4) Write an explanatory note on a three centered bonds.

5) What are electron deficient compounds ? Discuss the electron deficiency in boranes.

6) Describe the preparation and structure of higher boranes i.e. B_4H_{10} and B_5H_9.

7) What is meant by three - centre electron pair bond ? Discuss in detail the nature of bonds in hydrogen bridges.

8) Discuss the structure of boron nitride. Give its hydrolysis reaction.

9) Give the preparation ; Properties and structure of borazole.

10) How is boron nitride prepared ? Give its structure.

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UNIT – I

Lesson – 2

P - Block Elements

Group - 14 : Preparation and applications of Silanes ; Silicones and graphitic compounds.

1.2.1 Preparation and applications of Silanes:

All the elements of group 14 forms covalent hydrides of the type MH_4. The number of hydrides formed and the ease with which they form decreases from carbon to lead.

Carbon forms a large number of hydrides i.e. alkanes, alkenes, alkynes and aromatic hydrocarbons. silicon forms a limited number of volalile hydrides, called silanes having the general formula $Si_n H_{2n+2}$. where 'n' stands for number of silicon atoms. These silanes are similar to hydrocarbons i.e alkanes but they are less stable. The individual members are known as silane, SiH_4, disilane $Si_2 H_6$ and trisilane, $Si_3 H_8$ etc. Germanium forms hydrides known as germanes. Eg. : GeH_4 (Monogermane), Digermane, Ge_2H_6 and Trigermane, Ge_3H_8 etc.

Tin forms only two hydrides namely stannane ; $Sn H_4$ and distannane, $Sn_2 H_6$.

Lead forms only one hydride known as Plumbane, PbH_4.

Preparation of Silanes:

Silicon with hydrogen are called silanes.

1. The monosilane, SiH_4 and disilane, $Si_2 H_6$ are colourless gases while trisilane, Si_3H_8 is liquid.

   A mixture of silanes is obtained by the action of acids HCl or $H_3 Po_4$ on silicides.

   $$Mg_2 \, Si + 4 \, HCl \rightarrow 2 \, MgCl_2 + Si \, H_4$$
   $$\text{Magnesium silicide}$$
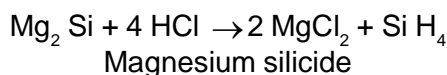
   The monosilane can be separated by fractionating in vacuum.

2. Pure monosilane can be prepared by the reaction of silicon tetra chloride with lithium aluminium hydride in ether.

   $$Si \, Cl_4 + Li \, Al \, H_4 \rightarrow SiH_4 + Li \, Cl + Al \, Cl_3$$
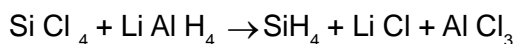
Properties :

The Silanes are much reactive than the alkanes.

Since the thermal stability of hydrides decreases from carbon to lead in the group, their ability to act as reducing agent increases. Thus, Silanes are strong reducing agents and are readily hydrolysed by alkaline Solution to liberate hydrogen.

$$Si\ H_4 + 2NaOH + H_2O \rightarrow Na_2\ SiO_3 + 4\ H_2$$

$$Si_2\ H_6 + 4KOH + 2H_2O \rightarrow 2K_2\ SiO_3 + 7\ H_2$$
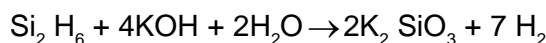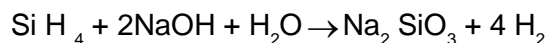
Among the hydrides of the group, silanes are least stable to hydrolysis, and hence silanes are hydrolysed even by neutral water.

$$Si\ H_4 + 3H_2O \rightarrow H_2\ SiO_3 + 4\ H_2$$

Monosilane is unstable, decomposing spontaneously on coming into contact with air.

$$Si\ H_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$$

Applications :

Compounds with Si – H bonds undergo a hydrosilation reaction with alkenes, in the presence of platinum catalyst and the products may be used to make silicones.

$$RCH = CH_2 + Si\ HCl_3 \rightarrow R.CH_2.CH_2\ SiCl_3$$
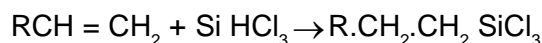
1.2.2 Silicones - Preparation - a) direct silicon process b) use of Grignard reagent c) aromatic sililation, classification - straight chain, Cyclic and cross - linked. Types - Oils, grease, resins and rubbers-uses.
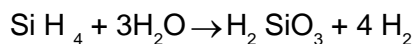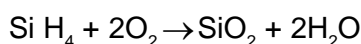
Organo silicon polymers containing Si-O-Si linkage are called silicones. They may be linear, cyclic or cross- linked polymers.

preparation of silicones :

These are prepared from alkyl or aryl chlorosilanes which in turn can be obtained by the following methods.

a) Direct silicon process :

Chlorinated hydro carbons react with silicon in the presence of metal catalyst like copper at 300°c.

$$Si + 2CH_3\ Cl \xrightarrow[300°c]{cu} (CH_3)_2\ Si\ Cl_2\ .$$
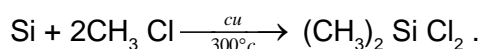
b) use of Grignard reagent :

Alkyl chlorosilanes are prepared by the reaction of Grignard reagent with Si Cl_4.

$$Si\ Cl_4 + CH_3\ MgCl \rightarrow CH_3\ SiCl_3 + MgCl_2.$$

$$CH_3\ Si\ Cl_3 + CH_3\ MgCl \rightarrow (CH_3)_2\ SiCl_2 + MgCl_2.$$

$$(CH_3)_2\ Si\ Cl_2 + CH_3\ MgCl \rightarrow (CH_3)_3\ SiCl + MgCl_2$$
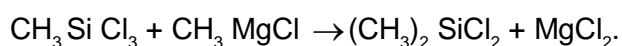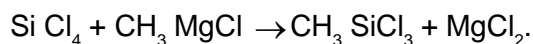
c) Aromatic sililation :

Aryl chlorosilanes are prepared by the reaction of benzene and other aromatic hydrocarbons with compounds containing Si - H bonds at 250 -300°c.

$$C_6 H_6 + H Si Cl_3 \rightarrow C_6 H_5 Si Cl_3 + H_2.$$
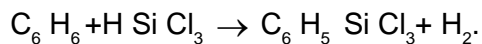
Classification of Silicones :-

Silicones are classified into straight chain, cyclic and cross linked silicones .

Straight chain silicones :

Hydrolysis of dialkyl - dichlorosilanes is as follows :
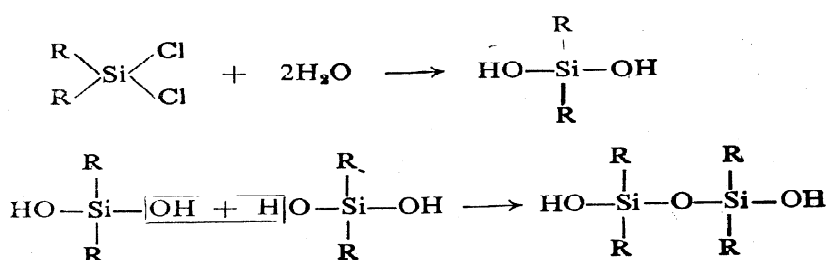
An active OH group is left at each end of the chain and hence polymerisation reaction continues and increases the length of the chain as shown below
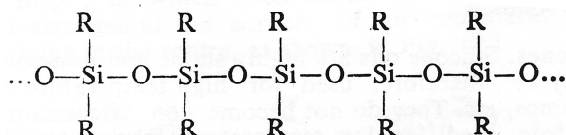
Cyclic Silicones :

Cyclic Silicones are formed when water molecule is eliminated from the terminal - OH groups of the straight chain silicones.
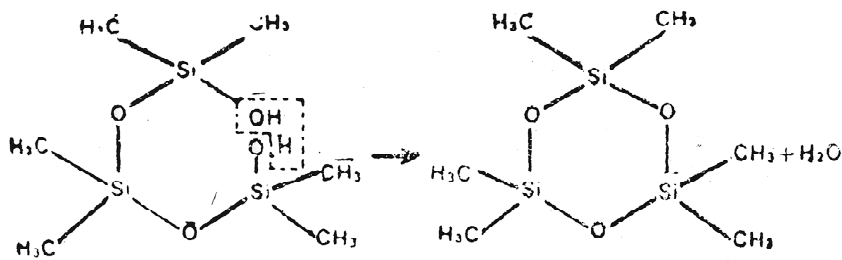
Fig 2.1

Cross linked silicones :-

complex cross - linked silicones are obtained by the hydrolysis of mono alkyl trichlorosilane, $RSi\,Cl_3$
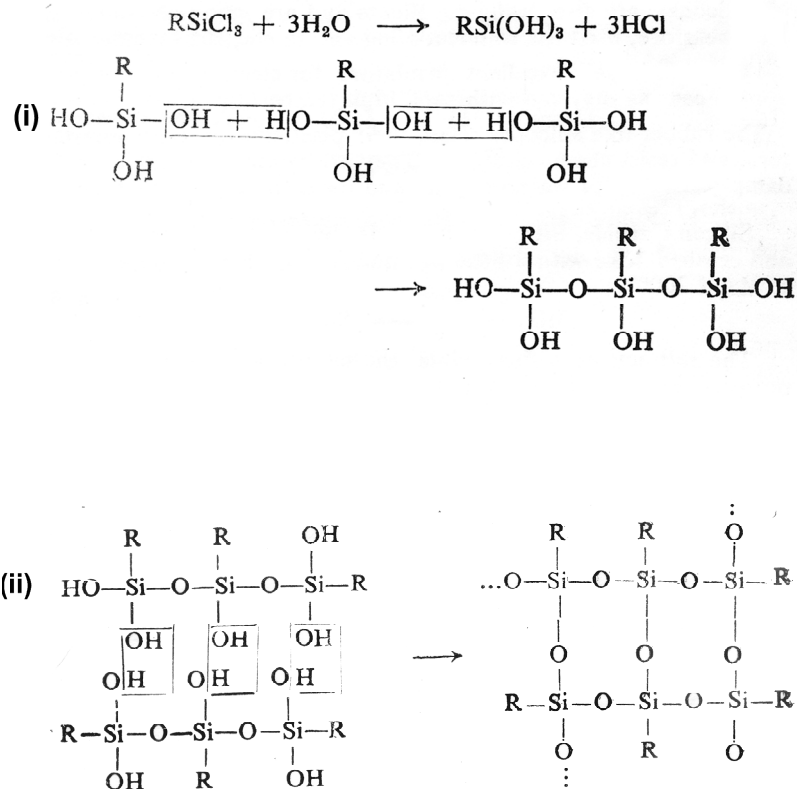
Fig 2.2

The sturcture can be extended to any length in two dimensional manner.

Types :-

Silicone Oils :-

Straight chain polymers of 20 to 500 silicone units are used as silicon fluids. silicone Oils are highly stable and non volatile even on heating . They have very less temperature coefficient of Viscosity when compared to the hydrocarbon Oils and are therefore used as hydraulic fluids and lubricants. Silicone oils are also used in water proofing textiles and as mould releasing agents and silicone rubber.

Silicone rubbers are made of long straight chain polymers, 6000-7000 silicone units long, with occasional cross - links. They are also known as silicon elastomers. Silicon rubbers retain their elasticity over a wide range of temperature and hence they are good electrical insulators. Silicon rubbers are resistant to chemical solvents.

Silicone greases :-

Silicone greases are made from mixture of silicone fluids and filters such as silica, lithium soap and carbon black. Silicone greases made from phenyl oil and lithium soap are used for ball bearings operating at high speeds and high temperatures.

Silicone resins :

Silicone resins are rigid polymers and are highly cross linked. They are used as electrical insulators. They are also used as non - stick coatings for pans and are used in points and varnish and as water repellents for treating masonry.

1.2.3 Prepartion and Applications of graphitic compounds :

The structure of graphite consists of flat two - dimensional sheets of carbon atoms. In graphite, Only three of the valency electrons of each carbon atom form sigma bonds (σ bonds) using SP_2 hybrid orbitals. The fourth electron forms a π bond. These π electrons are delocalised over the whole sheet i.e the π electrons are shared by the entire layer of carbon atoms. Since the π electrons are mobile, graphite conducts electricity. These electrons can react with other elements without breaking either the ring or the layers. During these reactions, the reacting atoms, molecules or ions enter in between the layers and causes an increase in distance between the layers. Some of these compounds have a higher electrical conductivity than graphite whilst the others are non conducting.

When graphite is heated to about 300°c with the vapours of the I group metals like potassium, Rubidium and cesium, graphite absorbs the metal forming a bronze coloured compound, C_8 M.

$$8C + M \rightarrow C_8M$$
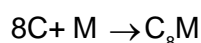
The halogens i.e chlorine and bromine, halides, like $FeCl_3$, sulphides like $Fe\,S_2$ and oxides like MoO_3 and ammonia may penetrate the graphite structure like potassium.

For example, ferric chloride, $FeCl_3$ reacts with graphite at 200 - 300°c to from a compound of the formula, $C_3 FeCl_3$. The presence of the above two types of atoms increases the conductivity of graphite.

Alkali and alkaline earth metals in liquid ammonia are found to penetrate the graphite structure.

Ex : $C_{12} K (NH_3)_2$ and $C_{12} Ca (NH_3)_2$

On heating graphite in fluorine at 450°c in the absence of HF, graphite fluoride is formed.

At room temperature or below 100°c, CF_4 a solid fluoride is formed. Graphitic acid or graphitic oxide, which is also a non conducting compound is formed, when graphite is oxidised with strong reducing agents like concentrated nitric acid, perchloric acid or potassium permanganate. Graphitic acid or graphitic oxide is an unstable, pale lemon coloured and non - stoichiometric compound. It decomposes slowly at 70°C and catches fire at 200°c giving H_2O, Co, CO_2 and C.

Oxidation of graphite in the presence of strong acids like H_2SO_4, HNO_3 and $HClO_4$ forms the graphitic salts. In presence of H_2SO_4, the graphite under goes oxidation to form the sulphate, $C_{24}HSO_4 . 2H_2SO_4$. The graphite salts are stable in the presence of concentrated acids but are decomposed by water to graphite which retains some oxygen.

1.2.4 Model Questions :

1) What are silanes ? How are they prepared ? Give their important applications.

2) What are silicones? How are they classified ? Give one method of preparation for each type.

3) What are silicones ? Mention their important applications.

4) Write notes on graphitic compounds.

5) What are silicones ? Discuss their important properties and uses.

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Tenali, Guntur- (Dt)

UNIT – I

Lesson – 3

P- Block Elements

Group -15: Preparation and reactions of Hydrazine, Hydroxylamine and Phosphazenes.

1.3.1:

All the elements of group 15 form volatile gaseous hydrides of the type MH_3, Ammonia (NH_3), Phosphine (PH_3), Arsine (AsH_3), Sliibine (SbH_3) and Bismuthine (BiH_3).

In addition to ammonia, nitrogen also forms two other hydrides namely hydrazine and hydroxylamine.

Preparation and reactions of hydrazine or Diamide, $H_2N. NH_2$ or N_2H_4 :

Hydrazine is prepared in the laboratory as well as on industrial scale by Rashing method i.e by boiling aqueous ammonia solution with an alkaline solution of sodium hypochlorite in the presence of a small amount of gelatin or glue.

$$NH_3 + NaOCl \rightarrow NaOH + NH_2Cl$$

$$NH_3 + NaOH + NH_2Cl \rightarrow N_2H_4 + NaCl + H_2O$$
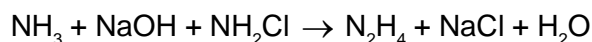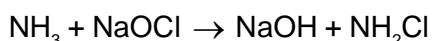
The hydrazine so produced may react with chloramine to give nitrogen thus decreasing the yield of hydrazine. Hydrazine from the solution is precipitated as sparingly soluble hydrazine sulphate by reaction with sulphuric acid.

$$N_2H_4 + H_2SO_4 \rightarrow H_2N . NH_3. HSO_4 \text{ or } N_2H_4. H_2SO_4$$
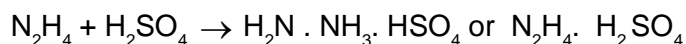
Hydrazine sulphate

An hydrous hydrazine can be prepared by treating hydrazine sulphate with liquid ammonia when ammonium sulphate is precipitated quantitatively.

On reduction of the product obtained by the reaction of potassium sulphite and nitric oxide with sodium amalgam and water, gives hydrazine.

$$NH_2 \cdot \overset{+}{NH_3} \cdot HS\overset{-}{O_4} + 2NH_3 \rightarrow N_2H_4 + (NH_4)_2SO_4 \downarrow$$
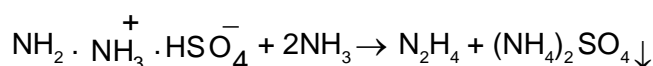
Properties :

1. An hydrous hydrazine is a colourless fuming liquid soluble in H_2O in all proportions. It is also soluble in alcohol. It is hygroscopic.

2. On heating hydrazine decomposes to ammonia and nitrogen.

$$3N_2H_4 \rightarrow N_2 + 4 NH_3$$

3. Hydrazine may be regarded as derived from ammonia by the replacement of one hydrogen atom by - NH_2 group.

   It behaves as a weak diacid base. Thus hydrazine forms two series of hydrazinium salts. Thus with hydrochloric acid, it forms hydrazine monochloride H_2N - NH_3Cl and hydrazine dichloride, $Cl\,NH_3. NH_3Cl$.

4. **Oxidation :**

   a) It burns in air with a considerable evolution of heat.

   $$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \; ; \; \Delta H = - 148.6 \; K.Cal$$

   Hence its alkylated derivatives are used as potential rocket fuels.
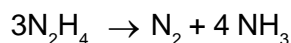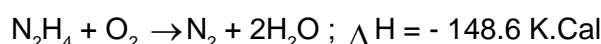
   b) Ozone and hydrogen peroxide react with hydrazine and oxidises it to hydrazoic acid, N_3H.

   $$3N_2H_4 + 5O_3 \rightarrow 2N_3H + 5H_2O + 5O_2$$

   $$3N_2H_4 + 5H_2O_2 \rightarrow 2N_3H + 10H_2O$$
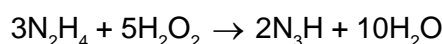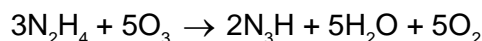
5. It reacts with nitrous acid and gives hydrazoic acid.

   $$N_2H_4 + H\,NO_2 \rightarrow 2H_2O + N_3H$$
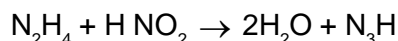
7. It reacts with sodium in an inert atmosphere giving sodium hydrazide.

   $$2NH_2 . NH_2 + 2Na \rightarrow 2NH_2. NHNa + H_2$$
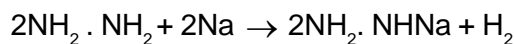
8. Hydrazine and its salts are powerful reducing agents since they can be readily oxidised to nitrogen. Thus -

   a. It reduces salts of platinum, gold and silver to the metallic state.

   $$Pt\,Cl_4 + N_2H_4 \rightarrow Pt + N_2 + 4HCl$$

   $$4Au\,Cl_3 + 3N_2H_4 \rightarrow 4Au + 3N_2 + 12HCl$$

   $$4AgNO_3 + N_2H_4 \rightarrow 4Ag + N_2 + 4HNO_3$$
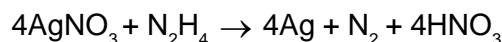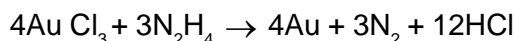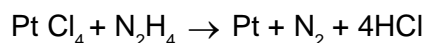
   b. It reduces Fehling solution to red cuprous oxide and iodates to iodides.

   $$4Cu^{2+} + H_2N. NH_2 \rightarrow 4Cu^+ + 4H^+ + N_2$$

   $$2\,IO^-_3 + 3H_2N. NH_2 \rightarrow 2\,I^- + 6H_2O + 3\,N_2$$
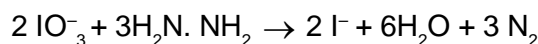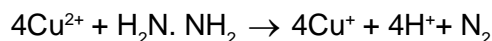
   c. It reduces acidified potassium permanganate solution to colourless manganese salt.

   $$4\,KMnO_4 + 6\,H_2SO_4 + 5\,NH_2. NH_2 \rightarrow 2\,K_2SO_4 + 4\,MnSO_4 + 16\,H_2O + 5\,N_2$$
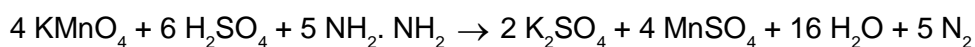
d. It reacts violently with halogens and reduces them to the corresponding halogen acids.

$$H_2N. NH_2 + 2 Cl_2 \rightarrow N_2 + 4 HCl$$
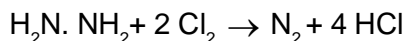
Uses :

1. Hydrazine is used as a reducing agent.

2. Used as a rocket fuel.

3. Used as a reagent in organic chemistry.

Structure :
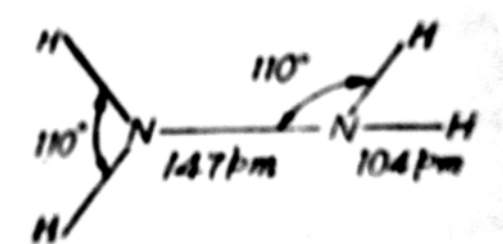
Fig 3.1 Structure of Hydrazine

1.3.2 Preparation and reactions of Hydroxylamine ; NH_2OH:

It is prepared by the reduction of nitrites with sulphur dioxide. A Concentrated solution of sodium nitrite is mixed with a solution of sodium carbonate and sulphur dioxide till the solution becomes just acidic.

$$Na_2CO_3 + SO_2 + H_2O \rightarrow NaHSO_3 + NaHCO_3$$

$$NaNO_2 + 3NaHSO_3 \rightarrow HON (SO_3 Na)_2 + Na_2SO_3 + H_2O$$
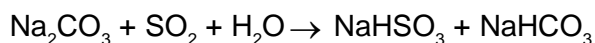
Hydroxylamine sodium sulphonate

Hydroxylamine sodium sulphonate is then hydrolysed with dilute sulphuric acid to form hydroxylammonium bisulphate which is decomposed by baryta water $(Ba(OH)_2)$ to form free hydroxylamine.

$$HON (SO_3Na)_2 + 2H_2O \rightarrow H_3N(OH). HSO_4 + Na_2SO_4$$

$$H_3N (OH) HSO_4 + Ba(OH)_2 \rightarrow H_2NOH + BaSO_4 + 2H_2O$$
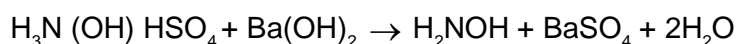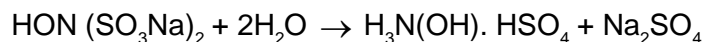
It can be prepared by the electrolytic reduction of nitric acid in 50% H_2SO_4 using amalgamated lead cathode.

$$HO : NO_2 + 6H^+ + 6e^- \rightarrow HO. NH_2 + 2H_2O$$
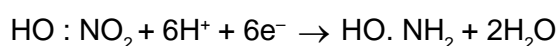
Properties :

1. It is a colourless, poisonous solid.

2. It is soluble in water, alcohol and ether.

   Due to hydrolysis, its aqueous solution is alkaline in nature.

   $$NH_2OH + H_2O \rightleftharpoons {}^+NH_3OH. OH \rightleftharpoons {}^+NH_3OH + OH^-$$
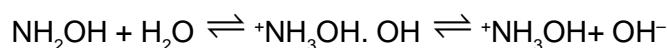
3. It is an unstable mono acid i.e base. It decomposes (auto - oxidation) Violently even at 20°c into ammonia, nitrogen and water.

   $$3NH_2OH \rightarrow NH_3 + N_2 + 3H_2O$$

4. It explodes with halogens and reduces them to the corresponding hydracids.

   $$2NH_2OH + 2\ Cl_2 \rightarrow N_2O + H_2O + 4\ HCl$$
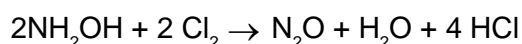
5. In alkaline medium it is a powerful reducing agent and reduces

   $$2NH_2OH + 4\ OH^- \rightleftharpoons N_2O + 5H_2O + 4\ e^-$$
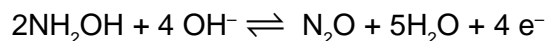
   It reduce Fehlings solutions to Cu (1) oxide, ammoniacal silver nitrate to silver, mercuric chloride to mercurous chloride and mercury.

   $$4\ Cu^{2+} + 2NH_2OH + 8OH^- \rightarrow 2\ Cu_2O + N_2O + 7H_2O$$
   $$\text{Red}$$

   $$4\ Ag^+ + 2NH_2OH + 4OH^- \rightarrow 4Ag + N_2O + 5H_2O$$
   $$\text{Silver mirror}$$

   $$4\ Hg\ Cl_2 + 2NH_2OH + 4OH^- \rightarrow 2\ Hg_2\ Cl_2 + N_2O + 5H_2O + 4\ Cl^-$$

   $$2\ Hg_2\ Cl_2 + 2NH_2OH + 4OH^- \rightarrow 4\ Hg + N_2O + 5H_2O + 4\ Cl^-$$
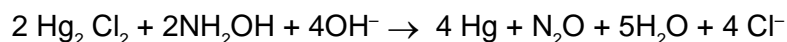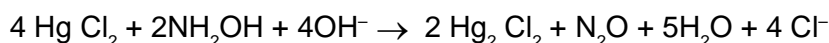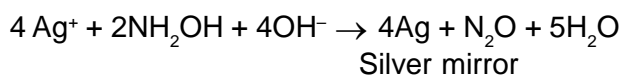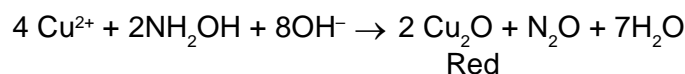
6. Aqueous solution of hydroxylamine is an oxidising agent.

   $$NH_2OH + H_2O + 2\ e^- \rightleftharpoons NH_3 + 2OH^-$$
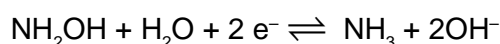
   It oxidizes Ferrous salts to ferric salts.

   $$2\ Fe(OH)_2 + NH_2OH + H_2O \rightarrow 2Fe\ (OH)_3 + NH_3$$
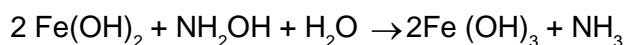
   Sodium arsenite to sodium arsenate.

   $$Na_3\ AsO_3 + NH_2OH \rightarrow Na_3\ AsO_4 + NH_3$$
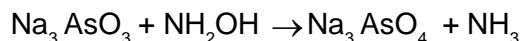
7. Hydroxylamine reacts with aldehydes and ketones to form the corresponding oximes.

   $$(CH_3)_2\ C=O + H_2NOH \rightarrow (CH_3)_2\ C= NOH + H_2O$$
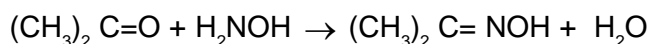
   Acetone   Acetoxime

Structure :

Uses :

1. Used as analytical reagent in the identification of carbonyl compounds.

2. Used for the preparation of crystalline derivatives of aldehydes and ketones called oximes. For example, dimethyl glyoxime used in the estimation of metal ions.

3. Used for the preparation of caprolactam, a raw material for nylon - 6.

1.3.3 Phosphazenes :

Nitrogen and phosphorus undergo catenation (or self linkage) to a little extent only. The maximum chain length for nitrogen is three in the azide N_3^- ion and two for phosphorus in compounds like P_2H_4. A few ring compounds exist where four, five or six phosphorus atoms are joined together.

Nitrogen and phosphorus may bond together to form a large number of compounds known as phosphozenes. These are formally unsaturated in nature and contain nitrogen atom in (+III) oxidation state and phosphorus atom in (+V) oxidation state.

Monophosphazines can be prepared by the reaction of an azide with PCl_3 ; $P(C_6H_5)_3$ or POR_3.

$$PCl_3 + C_6H_5N_3 \rightarrow Cl_3P = NC_6H_5 + N_2$$

$$P(C_6H_5)_3 + C_6H_5N_3 \rightarrow (C_6H_5)_3P = NC_6H_5 + N_2$$
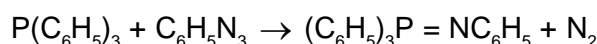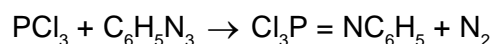
Diphosphazenes can be prepared by the reaction of PCl_5 with NH_4Cl

$$3PCl_5 + 2NH_4Cl \rightarrow [Cl_3P = N\text{-}P\,Cl_2 = N \text{-} P\,Cl_3]^+Cl^- + 8\,HCl$$

Nitrogen and phosphorus catenate together to form a series of polymers namely ring compounds (Cyclophosphazenes) and chain compounds (Polyphosphazenes)

$$nPCl_5 + nNH_4Cl \xrightarrow{\;120\text{-}150^0C\;} (nPCl_2)_n + Cl_4P\,(NP\,Cl_2)_n \,.\, NP\,Cl_3 + 4nHCl$$

                       Cyclophosphazenes   Polyphosphazenes
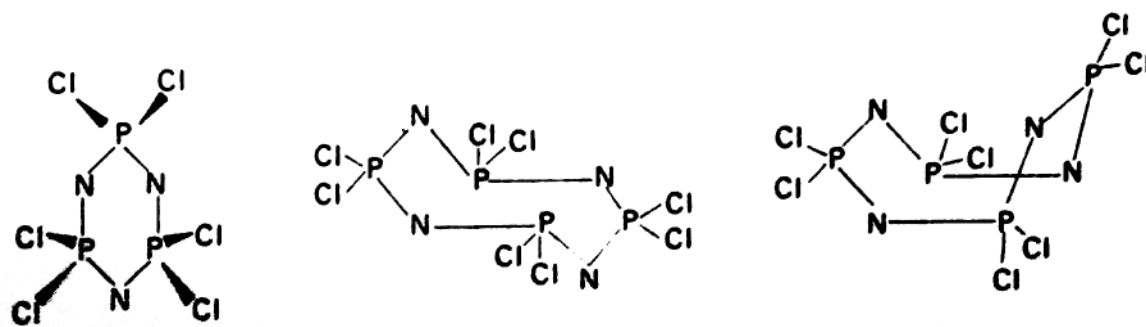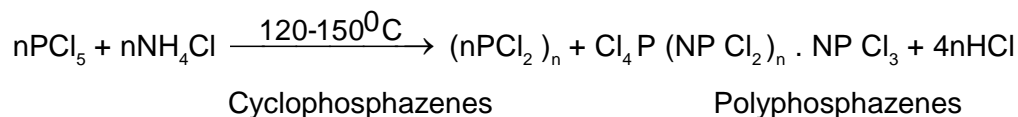
Fig 3.2 Some Cyclophosphazene compounds

A large number of chain compound which are originally called phosphonitro halides are known. But now they were named systematically as poly (chlorophosphazenes).

Phosphonitrilic chlorides can also be prepared by heating $(P_3N_5)_n$ in chlorine at 700°c.

$(P_3N_5)N + nCl_2 \rightarrow (PNCl_2)n$ + other products

Triphosphonitrilic chloride may also be prepared by the reaction of S_4N_4 with $SOCl_2$ in PCl_3

$3S_4N_4 + 6 SOCl_2 + 12 PCl_3 \rightarrow 4(PNCl_2)_3 + 18S + 3 O_2 + 12Cl_2$
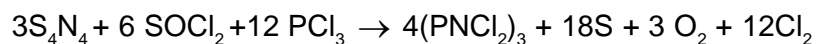
Properties :

1. On heating to about 300°c all the phosphonitrilic chlorides are converted to an elastic product having rubber like properties. Such elastic product is made up of long spiral (Zig - Zig) chains.

   The chlorine atoms are very reactive and most of the reactions of trimer and tetramer involve the partial or complete removal of the chlorine by other groups. The reactions involve replacement of cl by groups such as alkyl aryl, OH , OR, NCS etc.

Hydrolysis :

On hydrolysis some or all the chlorine atoms can be replaced by hydroxyl groups.
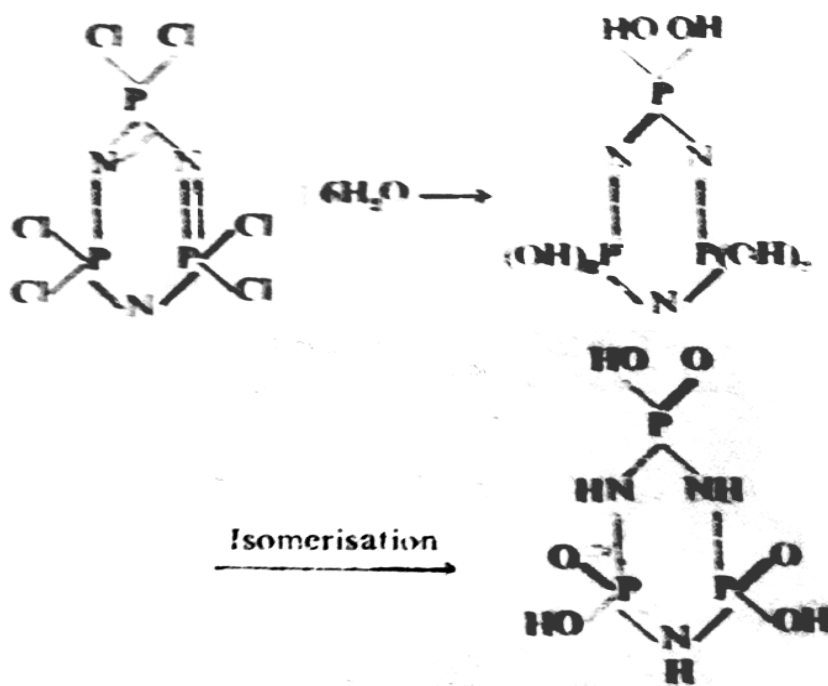
Fig 3.3

The trimer is very slowly attacked by water due to the fact that it is not wetted by water.

The tetramer is rapidly hydrolysed by boiling water.
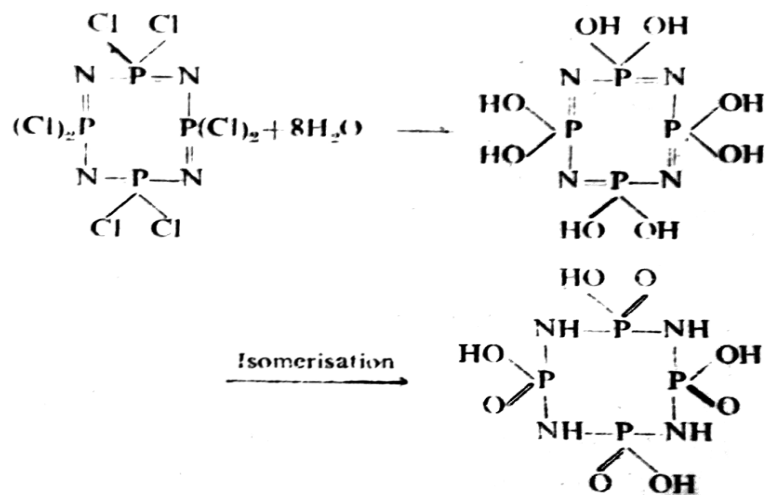
Fig 3.4

Reaction with ammonia :

When treated with liquid ammonia, all or some of the chlorine atoms of the trimer and tetramer are replaced by the amino group. For example, in case of trimer the fully aminated product, loses three molecules of ammonia to form phospham which on further heating loses ammonia and form phosphorus nitride.
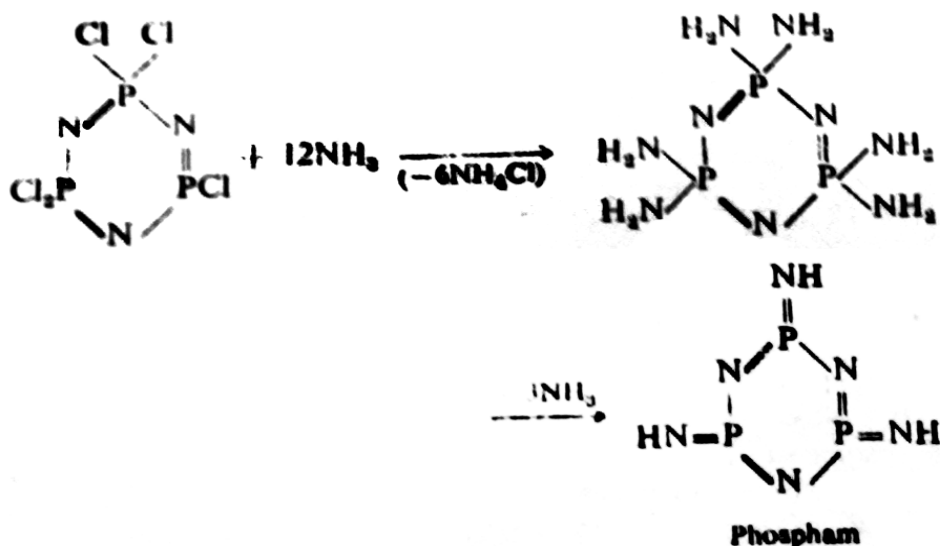
Fig 3.5

Reaction with alcohols and alkoxides :

On reaction with alcohols and alkoxides, the chlorine atoms may be replaced by alkoxy groups.
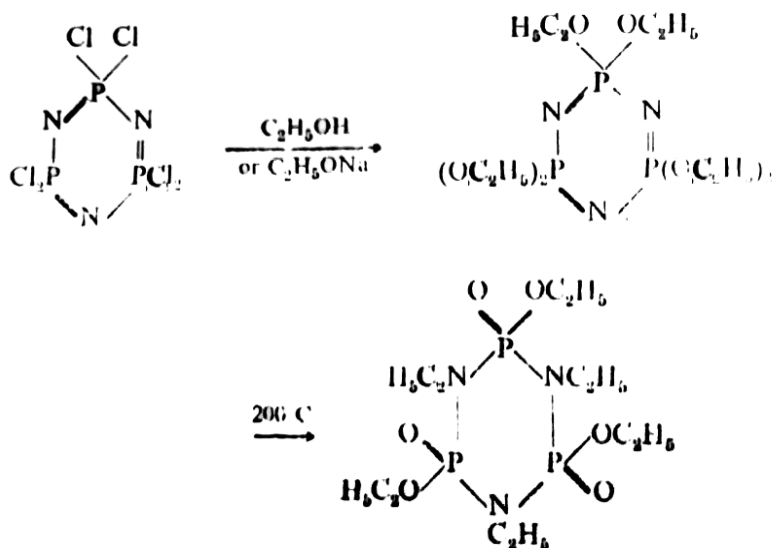
Fig 3.6

Reaction with potassium thiocyanate :

$(PNCl_2)_3$ react with potassium thiocyanate in acetone to form $[PN(CNS)_2]_3$.

$$(PNCl_2)_3 + 6\ KCNS \rightarrow [PN(CNS)_2]_3 + 6\ KCl$$
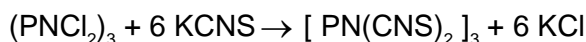
Reaction with phenyl magnesium bromide :

     a. Phosphonitrilic chlorides react with phenyl magnesium bromide at about 115°c to form partially or completely phenylated product.

     b. Partially or completely phenylated product may also be formed by reaction with benzene in the presence of catalyst $AlCl_3$.

$$(PNCl_2)_3 + 6\ C_6H_6 \xrightarrow{\quad AlCl_3 \quad} [(PN(C_6H_5)_2]_3 + 6\ HCl$$
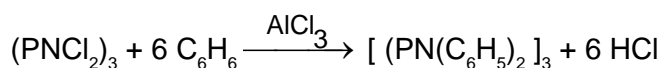
Basic Properties :

The lone pairs of electrons on the nitrogen atoms of phosphonitrilic derivatives are potential sites for attack by Lewis acids. Although the basic properties of the halides are very weak, the trimeric chloride forms adducts with $HClO_4$.

$$(PNCl_2)_3 + HClO_4 \rightarrow (PN(Cl_2)_3 + HClO_4$$
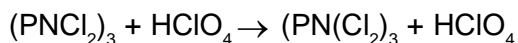
Structure of phosphonitrilic chlorides :

X - ray examination shows that the trimer and tetramer have cyclic structures. The P-N bond distance 1.59°A is shorter than the usual single P–N bond distance i.e 1.77°A. The bonding in trimeric phosphonitrilic chloride is interesting. The four electrons of the individual nitrogen atoms occupy SP^3 hybrid orbitals, two in two P-N bonds and two in a lone pair. The fifth electron in Pz orbital is available for π bond formation. The four electrons around every phosphorus atom are distributed in a tetrahedral way leaving the fifth electron in d - orbital for π bonding. The Pz orbital of nitrogen overlap with d electron of phosphorus to form $P\pi$ - $d\pi$ bond between phosphorus and nitrogen. The π bonding in these compounds are different from those in benzonoid structures where $P\pi$ - $P\pi$ bonding occurs. The trimer is square planar where as the tetramer is also cyclic but the ring is puckered.
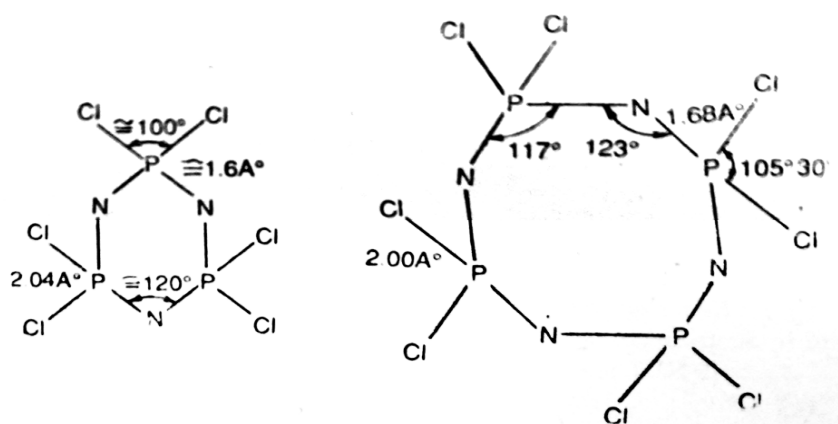
Fig 3.7

1.3.5 Model Questions :

1) How is hydrazine prepared ? Give its properties and structure.

2) Give the preparation , properties and uses of hydroxylamine.

3) Give equations to show that hydroxylamine and hydrazine behave as oxidising and reducing agents.

4) What are phosphazenes ? How are they prepared ?

5) Discuss the bonding and structure in phosphonitrilic chloride.

6) Discuss the preparation and properties of phosphazenes.

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UNIT – I

Lesson – 4

P- Block Elements

Group -16: Classification of oxides based on (i) Chemical behaviour and (ii) oxygen content :

1.4.1:

Binary compounds of oxygen with other elements are called oxides. They are classified into two types namely (1) classification based on chemical behaviour and (2) classification on the basis of oxygen content.

1.4.2 Classification based on chemical behaviour :

These oxides contain bond only between element and oxygen atom.

(a) Acidic oxides (Acid anhydrides) :

These oxides are formed by non - metals

Eg : CO_2 ; NO_2 etc and metals of high oxidation state, CrO_3, V_2O_5 etc.

These oxides dissolve in water forming acids. Hence they are called acid anhydrides.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

They react with alkalies to form salt and water.

$$Si\,O_2 + 2\,NaOH \rightarrow Na_2\,Si\,O_3 + H_2O$$
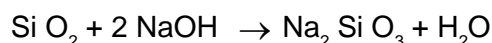
Their aqueous solutions turn blue litmus red.

Some of the acidic oxides give a mixture of two acids when dissolved in water and such oxides are known as mixed anhydrides.

$$2NO_2 + H_2O \rightarrow \underset{\text{Nitrous Acid}}{HNO_2} + \underset{\text{Nitric acid}}{HNO_3}$$

(b) Basic oxides :

Metals form basic oxides and they give alkalies or bases on reaction with water.

Eg : Na_2O , CaO etc.

$$Na_2O + H_2O \rightarrow 2NaOH$$

Their aqueous solutions turn red litmus blue.

They react with acids to form salt and water.

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$
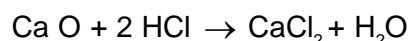
(c) Amphoteric oxides :

These oxides behave as acid as well as base depending on the conditions.

Eg : Al_2O_3 ; ZnO, SnO and SnO_2

Metalloids generally form amphoteric oxides. ZnO behaves as acidic oxide When treated with NaOH and as basic oxide when treated with HCl.

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$$

Sodium Zincate

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2$$
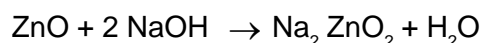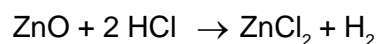
(d) Neutral oxides :

Neutral oxides give neither acid nor base with water

Eg : NO, CO, H_2O, N_2O

These oxides are neutral towards litmus.

They do not form salts when treated with acids or bases.

1.4.3 Classification of oxides basing on oxygen content :

(a) Normal oxides :

These oxides contain just as much oxygen as permitted by the normal valency of the metal or non - metal or hydrogen.

They contain only M – O bonds.

Eg : H_2O, MgO, Al_2O_3 etc.

(b) Mixed oxides :

These are made up of two simple oxides. These oxides on reaction with acids give two compounds corresponding to the constituents.

Eg : Pb_3O_4 ($2PbO + PbO_2$)

Fe_3O_4 ($FeO + Fe_2O_3$)

Mn_3O_4 ($MnO + Mn_2O_3$)

$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O$

(c) Sub oxides :

These oxides contain less oxygen than allowed from the normal valency of its metal or non-metal.

Eg : N_2O ; C_3O_2 (Carbon suboxide)

(d) Polyoxides :

These oxides contain more oxygen than permitted by normal oxidation number of the metal. They contain both M-O as well as O – O bonds and are further calssified into peroxides, super oxides and dioxides.

(i). Peroxides : Peroxides contain O_2^{2-} ions and are called as derivatives of hydrogen peroxide and produce H_2O_2 on reaction with dilute acids.

Eg : Na_2O_2 ; $Ba\ O_2$ etc.

$$Ba\ O_2 + H_2\ SO_4 \rightarrow Ba\ SO_4 + H_2\ O_2$$
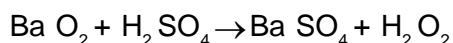
(ii) Super oxides : These oxides contain O_2^- ions and react with H_2O to give H_2O_2 and O_2

Eg : $2KO_2$; RbO_2 ; CsO_2 etc.

$$2KO_2 + 2H_2\ O \rightarrow 2\ KOH + H_2\ O_2 + O_2$$
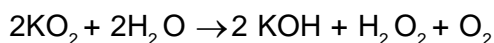
(ii) Dioxides : These oxides do not give H_2O_2 with dilute acids but liberate oxygen on treatment with concentrated nitric acid.

Eg : MnO_2 ; PbO_2 etc.

$$2MnO_2 + 2H_2\ SO_4 \rightarrow 2MnSO_4 + 2H_2\ O + O_2$$
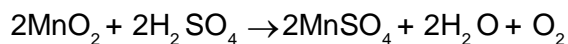
1.4.4   Model Questions :

1)   How do you classify the oxides basing on their chemical behaviour ? Give examples

2)   Explain the nature and properties of the following oxides - ZnO, Pb_3O_4, SO_3, MgO.

3)   How do you calssify the oxides basing on their oxygen contents. Give examples.

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UNIT – I

Lesson – 5

P- Block Elements

Group -17: Interhalogen compounds and pseudohalogens

1.5.1   Inter halogen compounds :

1.4.v) Interhalogens - classification, general preparation, structures of AB, AB_3, AB_5, AB_7 type and reactivity.

The difference in electronegativity value of halogens gives rise to formation of compounds among themselves and the compounds so formed are known as interhalogen compounds. In naming the compounds the less electronegative halogen is mentioned first.

Classification of interhalogens :

Depending upon their molecular formula they are classified into four types namely AB, AB_3, AB_5 and AB_7. Fluorine never become the central atom in these compounds because it never exhibits a positive oxidation state and cannot show co-ordination number more than 4.

Table 4.2 : Interhalogen compounds and their physical state at 25°c

AB	AB_3	AB_5	AB_7
Cl F (g)	Cl F_3 (g)	Cl F_5 (g)	
Br F (g)	Br F_3(L)	Br F_5(L)	
Br Cl (g)	IF_3 (s) (unstable)	IF_5 (L)	IF_7 (g)
ICl (s)			
IBr (s)			
IF (unstable)			

Table 5.1

General preparation :-

Inter halogen compounds are perpared by the direct combination of two halogens or by heating lower interhalogen compound with halogen. The product fomed depends on the conditions of the method.

$Cl_2 + F_2 \xrightarrow{200°c} 2Cl\ F$

(equal volumes)

$Cl_2 + 3F_2 \rightarrow 2Cl\ F_3$

(excess)

$I_2 + Cl_2 \xrightarrow{300°c} 2\ I\ Cl$

$Br_2 + 3F_2 \rightarrow 2Br\ F_3$

$F_2 + Cl\ F \rightarrow Cl\ F_3$

$Cl_2 + I\ Cl \rightarrow I\ Cl_3$

$Br_2 + 5F_2 \rightarrow 2Br\ F_5$

(excess)

$F_2 + Br\ F_3 \rightarrow Br\ F_5$

$I_2 + 5F_2 \rightarrow 2I\ F_5$

$I_2 + IF_3 \rightarrow I\ F_5$

$IF_5 + F_2 \rightarrow I\ F_7$
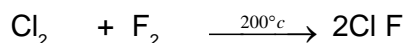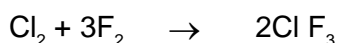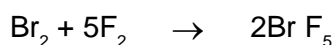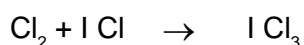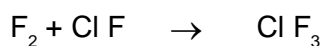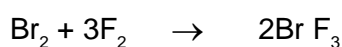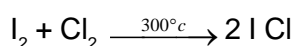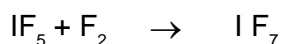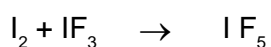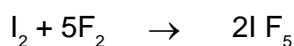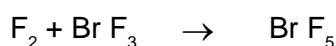
Reactivity :-

i) Interhalogen compounds are volatile in nature. They are covalent liquids or gases.

ii) The m.pts and b.pts of the interhalogen compounds increase with increase in electronegativity difference

iii) Halogen molecules are non-polar but interhalogen compounds are polar and the polarity increases with increase in electronegativity difference.

iv) Some of these compounds ionize in the liquid state and are electrical conductors in molten state.

$2\ I\ Cl \rightleftharpoons I^+ + I\ Cl_2^-$

$2Br\ F_3 \rightleftharpoons Br\ F_2^+ + Br\ F_4^-$

$2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$
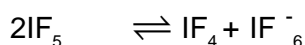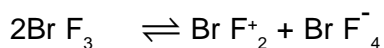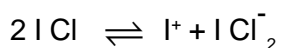
v) Their chemical properties are similar to those of halogens. Interhalogen compounds are more reactive than halogens (except F_2). The more reactivity is due to weak nature of A -B bond than the corresponding B - B bond in halogens. The more polar is the bond in the interhalogen compound, greater is its thermal stability and it decreases in the following order.

IF > BrF > Cl F > I Cl > I Br > BrCl > Br F_3 > Cl F_3 > I Cl_3 .
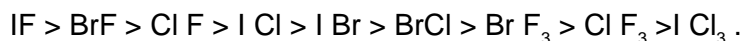
vi) These compounds are hydrolysed to form halide and oxyhalide ions.

I Cl + H_2O $\rightarrow$ H^+ + Cl^- + HOI

Br F_5 + 3H_2O $\rightarrow$ 5H^+ + 5F^- + H Br O_3
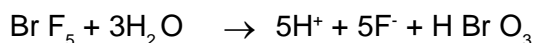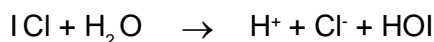
vii) Halogen fluorides act as fluorinating agents eg : Cl F_3 ;Br F_5 ; IF_5 etc

viii) AB type compounds, often add to the ethylenic bond

$$\begin{array}{ccc} CH_2 & & CH_2I \\ \| & + I\,Cl \rightarrow & | \\ CH_2 & & CH_2Cl \end{array}$$
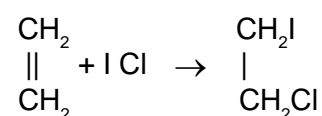
Structure of interhalogen compounds :-

Structure of AB type

The interhalogen compounds are generally covlent and the larger halogen atom forms the central atom. eg : IF ; I Cl ; I Br etc.

Electron structure of iodine atom   5s   5p   5d

in ground state

Iodine, the central atom with its one unpaired electron forms a covalent bond with the second halogen atom (F, Cl or Br) and the molecule is linear in shape.

structure of AB_3 type :

Cl F_3 molecule :

Electronic structure of chlorine atom   3s   3p   3d

in ground state :

In excited state :

Cl F_3 molecule :

Sp3 d hybridisation

Fig 5.1

Chlorine atom undergoes $Sp^3 d$ hybridisation and the three unpaired electrons of chlorine atom form covalent bonds with the three fluorine atoms. $Cl F_3$ assumes trigonal.
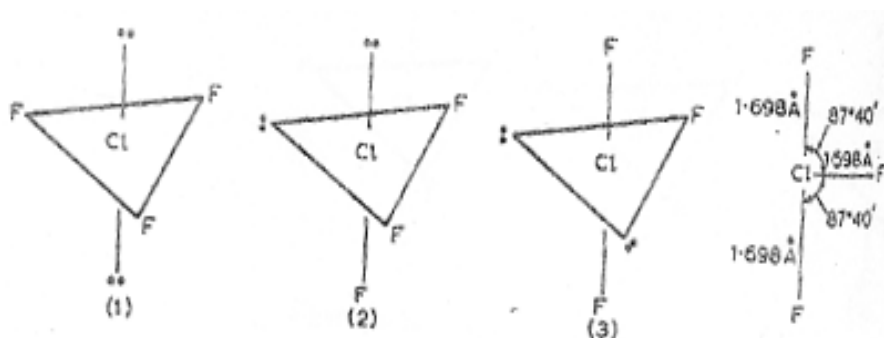
Fig 5.2 possible structure of Cl F$_3$ molecule

$Cl F_3$ is planar and T- shaped with bond angle 90°. The lone pairs of electrons distort the angle slightly to 87.5°. The structures of $Br F_3$ and $I F_3$ are also T- shaped.

But X ray analysis of $I Cl_3$ has established that the molecule is dimeric in crystalline and is a planar molecule.
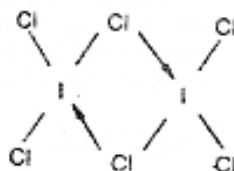
Fig 5.3 structure of I$_2$ Cl$_6$ molecule

Structure of AB$_5$ type :-

eg : IF$_5$

In these compounds the central atom undergoes $Sp^3 d^2$ hybridisation and gets octahedral structure with one position occupied by lone pair of electrons.

Electronic structure of iodine atom   5s   5p   5d

In ground state -

In excited state -

IF_5 molecule -

$Sp^3 d^2$ hybridisation

The five unpaired electrons of the central atom, iodine are shared with the unpaired electrons of the fluorine atoms. Due to the presence of lone pair the octahedral structure is slightly distorted.
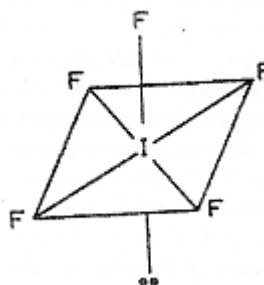
Fig 5.4 structure of I F$_5$ molecule

Structure of AB$_7$ type :

eg : IF$_7$.

In IF$_7$ molecule , iodine undergoes $Sp^3 d^3$ hybridisation and assumes pentagonal bipyramidal structure. The seven unpaired electrons of iodine atom are shared with the unpaired electrons of the fluorine atoms

Electronic structure of iodine atom   5s   5p   5d

In ground state -

In excited state -

IF_7 molecule -

$Sp^3 d^3$ hybridisation

and form covalent bonds. The five fluorine atoms and iodine atom are in one plane while the other two fluorine atoms are situated one above and one below the plane. This structure has been Confirmed by infrared spectral studies.
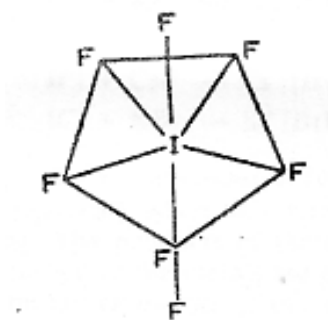
Fig 5.5 Structure of IF_7 molecule.

1.5.2 Basic Iodine - Basic nature and evidence of +1 and +3 iodine :

The metallic nature or basic properties increases on descending the group i.e. from fluorine to iodine. As the electronegativity and ionization energy values are decreasing from F to I, the basic character increases on descending the group. F_2 ; being the most electronegative element has no basic character. It has no tendency to form positive ions. Iodine being the least electronegative or most electropositive or metallic, exhibit maximum basic nature. The properties of iodine indicates that it is capable of forming positive ions. iodine exist as unipositive ion (I^+) ans tripositive ion (I^{3+}) evidences in favour of these ions are available.

Evidences for unipositive ion, I^+ :-

i)I Cl in molten state conducts electricity. on electrolysis, iodine is liberated at the cathode.

$$2\, I\, Cl \rightleftharpoons I^+ + I\, Cl_2^-$$

$$2I^+ + 2e^- \rightarrow I_2 \text{ (at cathode)}$$

$$2I\,Cl^-_2 \rightarrow I_2 + 2Cl_2 + 2e^- \text{ (at anode)}$$
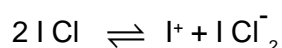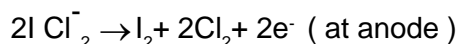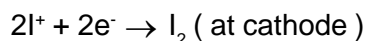
ii) Electrolysis of ICN in pyridine liberates iodine at cathode.

$$I\,CN \rightleftharpoons I^+ + CN^-$$
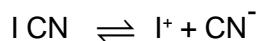
iii) when iodine dissolved in an inert solvent is passed through a cationic ion exchange resin, some iodine is retained on the resin, shows the formation of cationic iodine

$$H^+Resin + I_2 \rightarrow I^+ Resin + HI$$
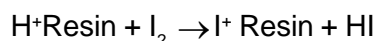
iv) Many compounds have been known containing I^+ ion stabilised by coordination.

eg :- [I (Pyridine) NO^-_3]

[I (pyridine)$_2$ NO^-_3]$^+$; [I (pyridine) acetate$^-$]etc

Electrolysis of these complexes liberate iodine at cathode.

v) When I Cl is added to oleum, a blue colour is observed due to the presence of unipositive ion, I^+.

i) I Cl_3 in molten state conducts electricity liberating iodine and chlorine at the electrodes.

$$2I\,Cl_3 \rightleftharpoons I\,Cl^+_2 + I\,Cl^-_4$$

ii) Many compounds containing I^{3+} ion have been obtained

a) Iodine acetate

when saturated solution of the compound in acetic acid is electrolysed using silver electrodes, one equivalent of Ag I is formed for every three Faradays of electrolysis which is in good agreement with Faraday's calculations.

$$I (CH3\,COO)_3 \rightleftharpoons I^{3+} + 3CH_3\,COO^-$$

$$I^{3+} + Ag + 3e^- \rightarrow Ag\,I$$
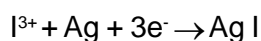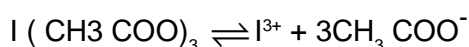
Iodine phosphate

I PO_4 containing tripositive ion, I^{3+} is formed when iodine is oxidised with concentrated nitric acid in the presence of acetic anhydride and phosphoric acid.

Iodine perchlorate

I Cl O_4 is prepared by passing ozone into a solution of iodine dissolved in anhydrous perchloric acid.

$$I_2 + O_3 + 6HCl\ O_4 \rightarrow 2\ I\ (Cl\ O_4)_3 + 3H_2O$$
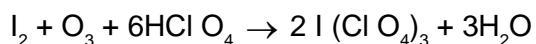
Now, It has been established that in addition to I^+ and I^{3+} other cationic species such as I^+_2, I^+_4, I^+_3, and I^+_5, can exist in solvents with low nucleophilic properties.

1.5.3 Polyhalides - Definition and structure of $[I\ Cl_2]^-, [I\ Cl_4]^-, I^-_3$:

Halogen or interhalogen molecules when associate with halide ions form univalent ions called polyhalide ions. The compounds of these polyhalide ions are called polyhalides.

eg : when iodine is dissolved in aqueous solution of potassium iodide, potassium triiodide, KI_3 is formed.

$$K\ I + I_2 \rightarrow KI_3$$
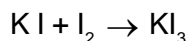
Classification of polyhalides :-

Polyhalides are classified into three types, depending upon the type of polyhalide ion present.

Type I : Compounds containing polyhalide ion of the type $(X_n)^{-1}$ ions

eg: RbI_3 , $KI_3 .2H_2O$, CsI_3 etc.

Type II : Compounds containing $(XX^I_n)^{-1}$ ions

eg: ICl^-_2 , IBr_2^- : ICl^-_4 , $Br\ F^-_4$ etc.

Type III : Compounds containing $(XX^I X^{II}_n)^{-1}$ ions

eg : Cs $FIBr_3$; Rb FI Cl_3

In addition to the abouve polyhalides,containing polyhalide anions, there are also compounds containing polyhalide cations.

eg: Br F_2^{+1} ; ICl_2^{+1} etc

unusual dissaciation of certain interhalogen compounds result in the formation of polyhalide cations.

ICl_3 $\rightleftharpoons$ I $Cl^+_2 + Cl^-$

$2IF_5$ $\rightleftharpoons$ $IF^+_4 + IF^-_6$
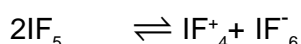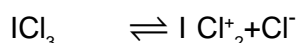
Structure of polyhalides :

Polyhalides containing three halogens are linear in shape.

Structure of ICl_2^-

Electronic structure of iodine atom   5s   5p   5d

in ground state :   ↑↓   ↑↓ ↑↓ ↑   ☐ ☐ ☐ ☐ ☐

Iodine in ICl_2^- ↑↓   ↑↓ ↑↓ ↑↓   ↑↓ ☐ ☐ ☐

Sp3 d hybridisation

In ICl_2^- ion, iodine atom undergoes Sp3 d hybridisation and assumed trigonal bipyramidal shape with
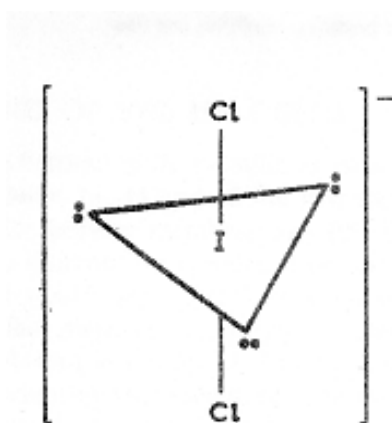
Fig 5.6 Structure of ICl_2^- ion

lone pairs in three positions. The two chlorine atoms form one covalent bond and one coordinate bond (Cl^-) with iodine atom and in a straight line. Thus the ion is linear.

Structure of ICl_4^- ion :-

In ICl_4^-

In ICl_4^- ion, the central iodine atom is surrounded by four chlorine atoms occupy the corners of a square.

Elecronic structre of iodine atom   5s   5p   5d

in ground state

in excited state

iodine in ICl_4^- ion

sp^3d^2 hybridisation

Iodine undergoes sp^3d^2 hybridisation and the lone pairs are directed towards the apices of a octahedron resulting in a square planar structure. Three chlorine atoms form covalent bonds with iodine atom while the chloride ion forms a coordinate bond.
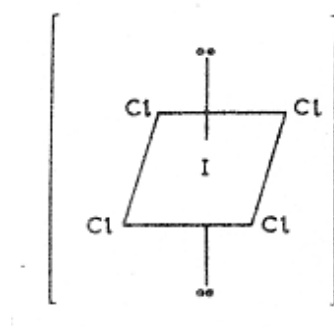
Fig 5.7 Structure of Icl⁻₄ ion

structure of I_3^- ;-

I-I-I bond angle in I⁻₃ ion is not equal to 180° and the two I-I bond lengths are unequal.
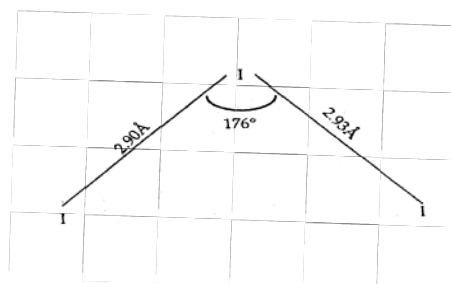
Fig 5.8 Structure of I_3^- ion

1.5.4 Pseudohalogens :

The term pseudohalogen was first suggested by Birckenbach and kellerman. pseudohalides or psendohalide ions are the uni - negative groups which show certain characteristics of halide ions. Psendohalogens are the covalent dimers of the pseudohalide ions. Psendohalogen is a molecule consisting of more than two electronegative atoms which in its free state resembles halogens in their chemical reactivity.

Psendohalide ions and Psendohalogens

Pseudohalide ions	Formulae	Pseudohalogens	Formulae
(i) Cyanide	CN^-	Cyanogen	$(CN)_2$
(ii) Cyanate	OCN^-		
(iii) Thiocyanate	SCN^-	Thiocyanogen	$(SCN)_2$
(iv) Selenocyanate	$SeCN^-$	Selenocyanogen	$(SeCN)_2$
(v) Azide	N_3^-		
(vi) Azidothiocarbonate	$SCSN_3^-$	Azidocarbondisulphide	$(SCSN_3)_2$
(vii) Isocyanate	ONC^-		

Pseudohalide ions form salts resembling the halide salts. Pseudohalogens include cyanogen $(CN)_2$, Oxycyanogen $(OCN)_2$, Sulphocyanogen $(SCN)_2$, Selenocyanogen $(SeCN)_2$ and azido carbon disulphide $(SCSN_3)_2$.

Characteristic reactions of Pseudohalogens and Pseudohalides :

1. Pseudohalogens are volatile like the halogens.

2. Like the halide ions, Pseudohalide ions react with hydrogen to form hydroacids which however are very weak than the halogen acids.

Pseudohalide or Halide in – N_3^- C^-N C^-l

Hydroacid   – HN_3 HCN   HCl

Pka Value   –   4.4   8.9   -7.4

3. Pseudohalogens like halogens, add at ethylenic double bond linkages.

$$H_2C = CH_2 + (SCN)_2 \rightarrow$$

$$\begin{array}{ccc} H_2C & \text{———} & CH_2 \\ | & & | \\ SCN & & SCN \end{array}$$
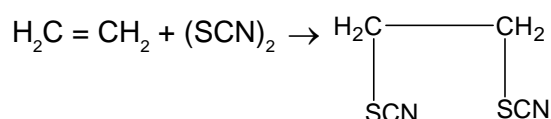
4. Lead (1), Silver (1) and mercury (1) salts, [Eg AgCN, Pb (CNS)2, Hg (CNS) are insoluble like that of halide (eg; AgCl, $PbCl_2$, HgCl)].

5. Pseudohalides form complexes similar to the halide complexes.

   eg : [Co $(SCN)_4]^{2-}$ and [$Hg(CN)_4]^{2-}$. The corresponding halide complexes are $[COCl_4]^{2-}$ and $[Hg\ I_4]^{2-}$.

6. Pseudohalogens and halogens form covalent compounds of similar composition and properties. eg : ICN, Si $(NCS)_4$; CO $(N_3)_2$. The corresponding covalent halides are ICl, $SiCl_4$ and $COCl_2$.

7. Pseudohalogens like the halogens react with alkalies.

$$(SCN)_2 + 2\ KOH \rightarrow KSCN + KOSCN + H_2O$$

$$Cl_2 + 2\ KOH \rightarrow KCl + KClO + H_2O$$

$$3(SCN)_2 + 6\ KOH \rightarrow 5\ KSCN + K(SCN)O_3 + 3H_2O$$

$$3Cl_2 + 6\ KOH \rightarrow 5\ KCl + KClO_3 + 3H_2O$$
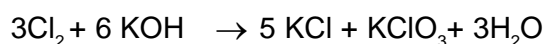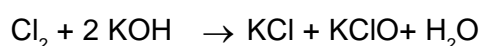
8. Certain lead (IV) compounds decompose on heating to give lead (II) salt and the free pseudohalogen.

$$Pb(SCN)_4 \rightarrow Pb(SCN)_2 + (SCN)_2$$

$$Pb(SeCN)_4 \rightarrow Pb(SeCN)_2 + (SeCN)_2$$
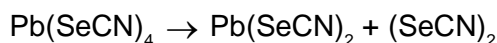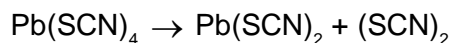
The above given recaction is similar to the decomposition of lead(IV) halides.

$$PbCl_4 \rightarrow PbCl_4 + Cl_2$$

9. A Pseudohalide ion is oxidised by suitable oxidising agent to the parent psendohalogen.

$$2Fe^{3+} + 2\ SCN^- \rightarrow 2Fe^{2+} + (SCN)_2$$

$$Pb(SeCN)_4 \rightarrow Pb(SeCN)_2 + (SeCN)_2$$
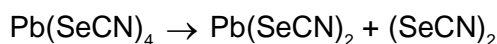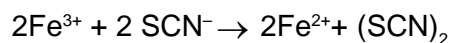
Similar reaction of halide ion is

$$2Fe^{3+} + 2Cl^- \rightarrow 2Fe^{2+} + Cl_2$$
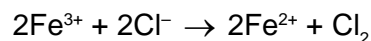
Cyanogen $(CN)_2$

The most important pseudohalogen is cyanogen.

It is prepared by heating silver cyanide alone or a mixture of mercuric cyanide and mercuric chloride.

$$2AgCN \rightarrow 2Ag + (CN)_2$$

$$Hg\ (CN)_2 + HgCl_2 \rightarrow Hg_2\ Cl_2 + (CN)_2$$
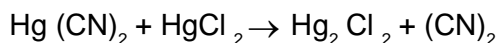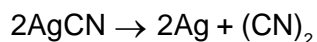
It is a colourless, poisonous gas soluble in water.

On heating it polymerises to give insoluble paracyanogen $(CN)_x$.

Except in the formation of covalent cyanides of the non metals, cyanogen resembles halogens in general chemical properties.

Thiocyanogen $(SCN)_2$:

1. It can be prepared by the action of bromine on silver sulphocyanide suspended in ether.

$$2\,AgSCN + Br_2 \rightarrow 2\,AgBr + (SCN)_2$$
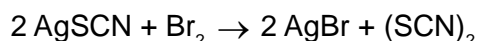
2. It can also be prepared by the electrolysis of alcoholic potassium thiocyanate.

$$2\,KSCN \rightarrow (SCN)_2 + 2K$$
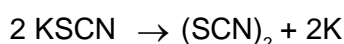
1. It is an yellow solid. It oxidises iodides to iodine and H_2S to sulphur.

$$(SCN)_2 + 2KI \rightarrow 2\,KSCN + I_2$$

$$(SCN)_2 + H_2S \rightarrow 2H^+ + S + 2(SCN)^-$$
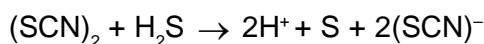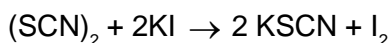
2. It undergoes hydrolysis to give thiocyanic acid and hydroxythiocyanic acid.

$$(SCN)_2 + H_2O \rightarrow HSCN + HOSCN$$
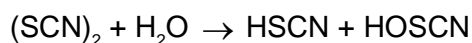
Selenocyanogen $(SeCN)_2$:

1. It can be prepared by heating the corresponding lead (IV) salt.

$$Pb(SeCN)_4 \rightarrow Pb(SeCN)_2 + (SeCN)_2$$
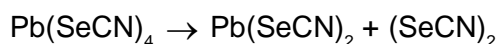
2. It can also be prepared by the action of iodine on silver selino cyanate.

$$2\,AgSe\,CN + Br_2 \rightarrow 2\,AgBr + (Se\,CN)_2$$
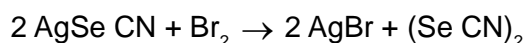
It is an yellow crystalline substance which turns red on standing.

It is quite stable when dry but reacts with water to form H_2SeO_3.

$$2(SeCN)_2 + 3H_2O \rightarrow H_2SeO_3 + 3HSeCN + HCN$$
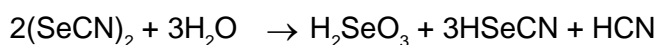
Pseudohalogen - halogen compounds :

Pseudohalogen - halogen compounds like CNCl and CNBr can be prepared by the action of chlorine and bromine on HCN.

$$Cl_2 + 2HCN \rightarrow 3CNCl + H_2$$

$$Cl_2 + 2HCN \rightarrow 3CNBr + H_2$$
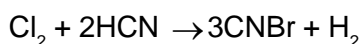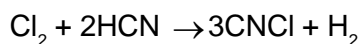
1.5.5 Model Questions :

1) What are interhalogen compounds ? How are they classified ? Give examples.

2) Discuss the structure of ClF_3 and IF_7 molecules.

3) Draw the shapes of the following molecules and ions. IF_5, ICl_4^- and I_3^-. Iodine is almost insoluble in water but it dissolves readily in aqueous solution of KI. Give reasons.

4) Discuss the structure of interhalogen compounds formed by iodine and fluorine atoms.

5) What are polyhalides ? Discuss the structure of ICl_2^- ion.

6) Discuss the structure of BrF_3 and IF_5.

7) Give an account of pseudohalogens.

8) What are Pseudohalogens and Pseudohalogens ? Name the important pseudohalogens and pseudohalides.

9) Describe briefly the preparation and properties of some typical pseudohalogens.

10) What are pseudohalogens ? Why are they so called? Describe the important characteristics of pseudohalogens.

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UNIT – I

Lesson – 6

ORGANOMETALLIC CHEMISTRY

1.6.1 Definition and nomenclature of organometallic compounds :

Organometallic compounds are those in which a metal atom is bonded directly to a carbon atom of a hydrocarbon radical or molecule. The organometallic compound should involve at least one close M- C inter action. Organic groups can be bound through carbon to virtually all the elements in the periodic table, excluding the inert gases.

$$—\overset{|}{\underset{|}{C}}—Metal \quad \textbf{or} \quad —\overset{|}{\underset{|}{C}}—M$$
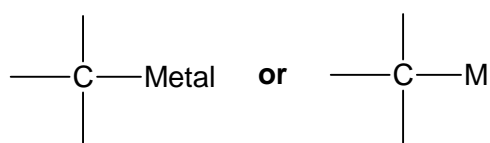
Where M = Mg ; Zn ; Li ; Pb ; Na etc.

The compounds like acetates and alkoxides do not come under this category because, in these compounds metal is not directly attached to carbon.

$$H_3C—\overset{\overset{\textstyle O}{\|}}{C}—ONa \qquad H_5C_2 — ONa$$
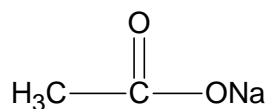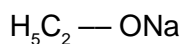
Sodium acetate   **Sodium ethoxide**

Compounds like carbides, cyanides and carbonyls although contain metal - carbon bonds are not considered as organometallic compounds, because metal is not attached to carbon of alkyl group, in these compounds. Similary, trimethyl orthoborate, B(OCH3)3 is not an organometallic compound while CH_3–B $(OCH_3)_2$ is an organometallic compound due to the attachment of boron to carbon of alkyl group.

Eg :

H$_3$C — Mg — I   H$_3$C — Zn — CH$_3$
Methyl magnessium iodide   Dimethyl zinc
(Alkyl magnesium halide)   (Dialkyl zinc)

$$C_2H_5$$
$$|$$
$$H_5C_2 \!\!-\!\!-\!\! Pb \!\!-\!\!-\!\! C_2H_5$$
$$|$$
$$C_2H_5$$
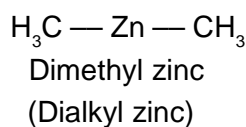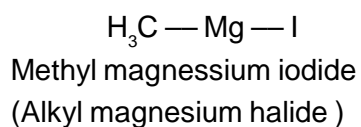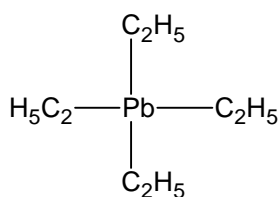
Tetra ethyl lead

(Tetra - alkyl lead)

Organometallic compounds are grouped into two classes namely " Simple " and " mixed".

Simple organo metallic compounds have only alkyl groups or hydrogen atoms attached to the metal and are represented as RnM ; $(CH_3)_2$ ZN ; $(C_2H_5)_4$ Pb ; $(CH_3)_3$ SnH etc. These simple organometallic compounds are either symmetrical, eg : $(C_2H_5)_2$Hg or unsymmetrical, eg: $C_2H_5.Hg.C_4H_9$. Mixed organometallic compounds contain both alkyl (R) and other (x) groups attached to the metal and are represented by Rn Mxn.

Eg : CH_3 Mg Br ; $(C_4H_9)_2$ $SnCl_2$ etc.

1.6.2 Types of metal - carbon bonds :

The organometallic compounds are of three types depending upon the nature of the metal carbon bond which in turn depends upon the nature of the metal.

(i) Ionic organo metallic compounds :

The organo metallic compounds of highly electropositive metals are ionic in nature and the hydrocarbon residue being negatively charged exists as a carbanion and is attracted to the metal by electrostatic forces. Examples are organometallic compounds represented by the alkali (except lithium) and alkaline earth metals i.e Ca, Sr and Ba. These compounds are colourless, salt like solids, unstable in air and are readily hydrolysed in water to liberate hydrocarbon with the formation of hydroxide. Compounds containing stable anions are highly reactive and the metal derivatives are more stable and less reactive.

Ex : Cyclopentadienyl sodium.

(ii) σ bonded covalent organometallic compounds :

Most of the organometallic compounds of non transition elements are covalent compounds with M- C σ - bonds. These compounds are formed by non transition elements other than alkali and alkaline earth metals. The bonding consist of localised carbon - metal σ - bonding formed by sharing of an electron pair.

Ex :
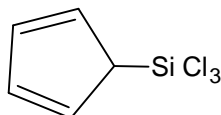
σ - bonded structure of trichloro cyclopenta dienyl silicon

The strength of the M - C bond depends on the nature of the R group and also on the nature of other ligands present on M.

The polarity of the bond depends not only on the difference in electronegativity between M and C, but also on the metal orbitals that are available, the polarisability of the electron cloud.

(iii) π bonded organometallic compounds :

This type of organometallic compounds are formed by transition metals.

Ex : Ferrocene or bi (Cyclo - pentadienyl) iron ; $(C_5H_5)_2$ Fe has a ' Sand wich' structure in which the iron atom lies between two planar $C_5 H_5$ rings. There is overlap of electrons of the cyclo pentadienyl rings with vacant d - orbitals of the metal and hence the bonding is called π bonding.

(iv) Bridge bonded organometallic compounds :

The organometallic compounds having bridging alkyl groups comes under this category.

Ex : Dimeric dialkyl aluminium, $Al_2 R_6$ and the polymeric diethyl magnesium $(MgEt_2)_n$;
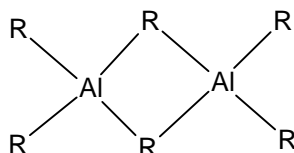
Fig 6.1

The bonding can be explained on the basis of molecular orbital theory in which M – C–M bond is formed by using SP^3 hybrid orbitals of carbon atom and of orbitals of each one of the M atoms.

1.6.3 Preparation of organometallic compounds of Lithium and Magnesium :

1. By the interaction of alkyl halides with metals.

Methyl iodide on reaction with lithium in ether gives methyl lithium.

$$2 CH_3 I + 2 Li \xrightarrow[ether]{-10^0 c} 2 CH_3 Li + Li I$$
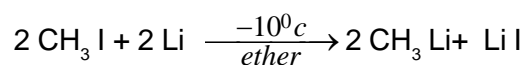
Ethyl iodide on reaction wiht magnesium in dry ether gives ethyl magnesium iodide.

$$C_2H_5 I + Mg \xrightarrow{dry\ ether} C_2H_5 Mg I$$
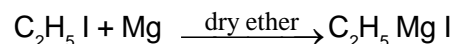
2. By metal halogen exhange :

The lithium aryls are best prepared by metal halogen exchange.

$$C_6H_5 Br + C_4H_9 Li \rightarrow C_6H_5 Li + C_4H_9 Br$$
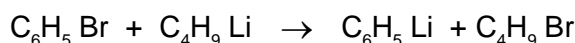
Phenyl bromide n- butyl lithium   phenyl lithium

$$CH_2 = CH Br + C_3H_7 Li \rightarrow CH_2 = CH Li + C_3H_7 Br$$
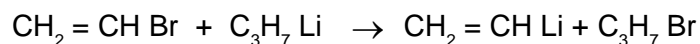
Vinyl bromide   Vinyl lithium

3. Metalation by Phynyl lithium :

The method is suitable for the preparation of lithium derivatives of comparatively acidic hydrocarbons. The metal displaces hydrogen to form a bond with carbon.

Phenyl lithium
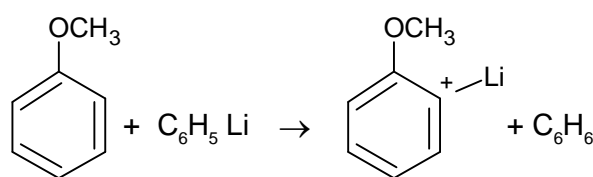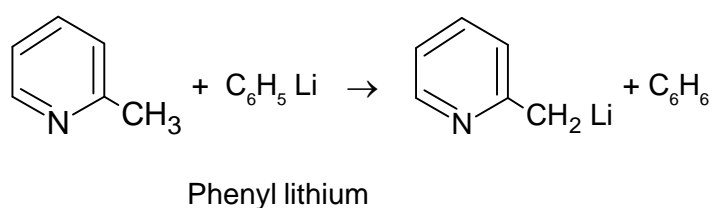
Fig 6.2

From Organo mercury compounds :

Organolithium compounds can also be prepared by treating the lithium metal with an organo mercury compound.

$$R_2Hg + 2 Li \rightarrow 2R Li + Hg$$
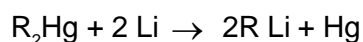
Preparation of alkyl magnesium halides (Grignard reagents) :

Grignard reagents are magnesium organometallic compounds and their general formula is RMg x. Grignard reagents are prepared by the action of alkyl halides on magnesium in dry ether.

$$RX + Mg \xrightarrow{\text{dry ether}} RMg X$$

$$Ar X + Mg \xrightarrow{\text{dry ether}} Ar Mg X$$

$$CH_3 Cl + Mg \xrightarrow{\text{ether}} CH_3 Mg Cl$$

$$C_2H_5 Br + Mg \xrightarrow{\text{ether}} C_6H_5 Mg Br$$
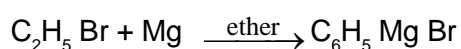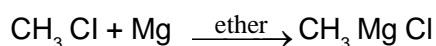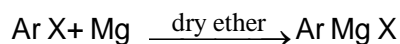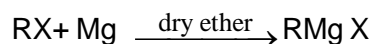
Grignard reagents, have a wide range of application in the synthesis of alcohols, aldehydes, ketones, carboxylic acids, esters and amides. Grignard reagent is the most versatile reagent for construction of the C – C bonds by carbanion mechanisms.

1.6.3 Preparation of ethyl magnesium iodide; C_2H_5MgI - Experimental details :

The opparatus consists of a round bottomed flask fitted with a water condenser carrying a calcium chloride tube at the top. Dry and pure magnesium wire suspended in dry and pure ether are placed in the flask. A required amount of ethyl iodide dissolved in ether is added slowly through the condenser by removing the $CaCl_2$ tube for a moment. To start the reaction the mixture is warmed for some time and then cooled. When the whole of the magnesium is dissolved a clear solution of Grignard reagent is formed. Grignard reagent in solid state can be prepared by evaporating tha above ethereal solution in an inert atmosphere.
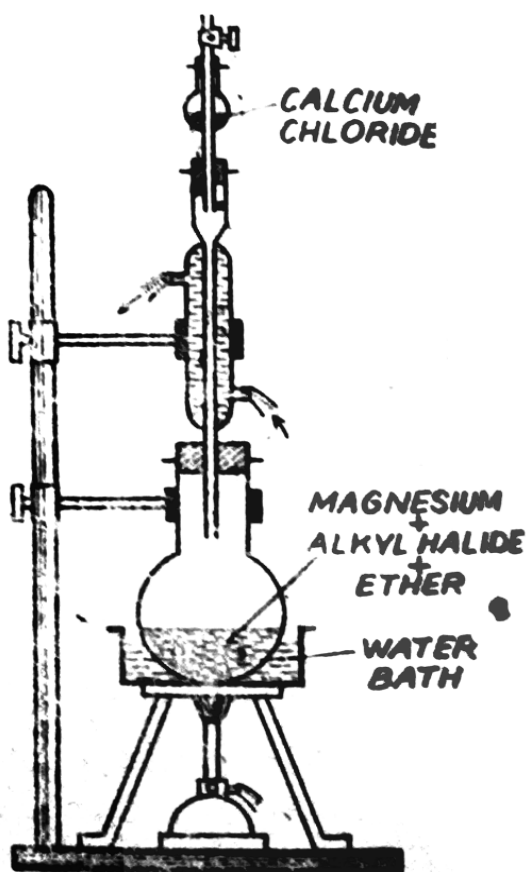
Fig 6.3

Precautions :

All the reagents and apparatus used must be completely dry. Because the presence of moisture will form a film of magnesium oxide on the surface of magnesium and thus prevents the reaction.

Alkyl halide is dried over anhydrous $CaCl_2$ and then distilled over phosphorus pentoxide.

Ether is washed with water to remove any alchohol and then dried over anhydrous $CaCl_2$ and finally distilled over P_2O_5 to remove final traces of alcohol and water.

Magnesium wire is rubbed with sand paper and then treated with dilute acid to remove the magnesium oxide film. It is then washed with sodium dried ether to remove grease and dried in an air oven at 110°c. Since diethyl ether catches fire there should be no naked flame in the surrounding places.

$$C_2H_5 I + Mg \xrightarrow{\text{dry ether}} C_2H_5 Mg I$$
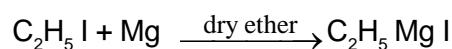
1.6.5 Synthetic uses of organometallic compounds :

Except with few differences, organolithium compounds give most of the reactions of Grignard reagents or organo magnesium compounds.

1. Preparation of Hydrocarbons :

Like Grignard reagents, organolithium compounds react with compounds containing active hydrogen to form the corresponding hydrocarbon. The reactions of Grignard reagents were given in the brackets.

$$R Li + H_2O \rightarrow R - H + Li OH$$

$$R Li + R^l OH \rightarrow R - H + Li OR^l$$

$$R Li + CH_3 Br \rightarrow R - CH_3 + Li Br$$

$$(CH_3 Mg I + C_2H_5 OH \rightarrow CH_4 + Mg I OC_2H_5)$$
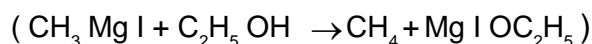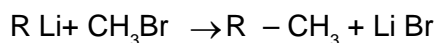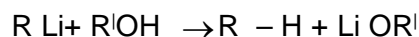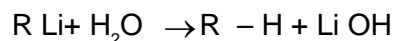
2. Primary, secondary and tertiary alcohols can be prepared by the action of organolithium compounds on formaldehyde, acetaldehyde and acetone respectively.

Formation of primary alcohol :

Primary alcohol

$$
\left[\; H-\overset{\overset{\displaystyle O}{\|}}{C}-H \; + \; CH_3Mg\,I \; \longrightarrow \; H-\overset{\overset{\displaystyle OMg\,I}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-H \; \xrightarrow{H_2O} \; H-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-H \; \right]
$$

<div align="center">ethyl alcohol</div>
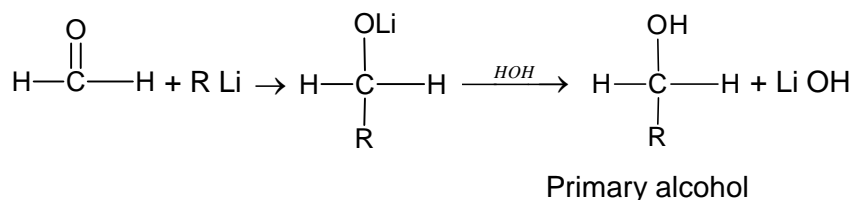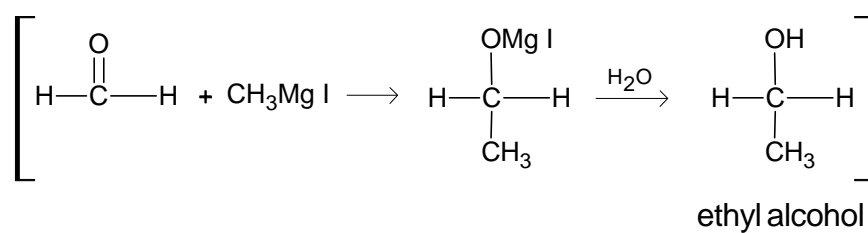
Formation of Second alcohol :

$$
CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \; + \; R\,Li \; \longrightarrow \; CH_3-\overset{\overset{\displaystyle OLi}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-H \; \xrightarrow{H_2O} \; CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-H
$$

<div align="center">Secondary alcohol</div>

$$
\left[\; CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \; + \; CH_3Mg\,I \; \longrightarrow CH_3-\overset{\overset{\displaystyle OMg\,I}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-H \; \xrightarrow{H_2O} \; CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-H \; \right]
$$

<div align="center">Iso - Propanol</div>
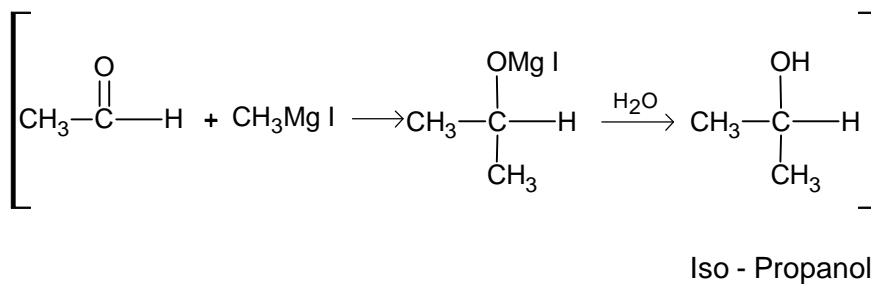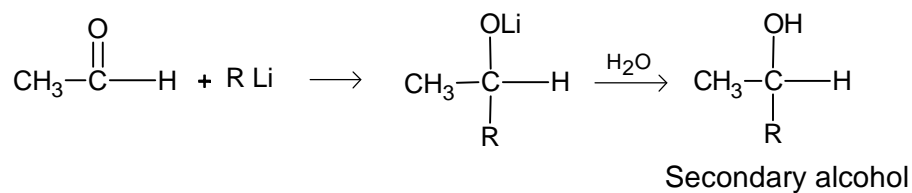
Formation of tertiary alcohol :

$$
CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-R^{|} \; + \; R\,Li \; \longrightarrow \; CH_3-\overset{\overset{\displaystyle OLi}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-R^{|} \; \xrightarrow{H_2O} \; CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-R^{|}
$$

<div align="center">Tertiary alcohol</div>

$$
\left[\; CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-R^{|} \; + \; CH_3Mg\,I \; \longrightarrow CH_3-\overset{\overset{\displaystyle OMg\,I}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-R^{|} \; \xrightarrow{H_2O} \; CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-R^{|} \; \right]
$$
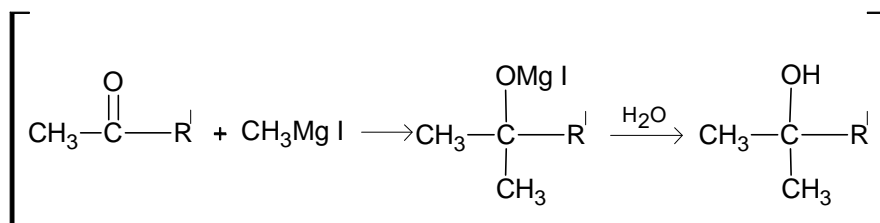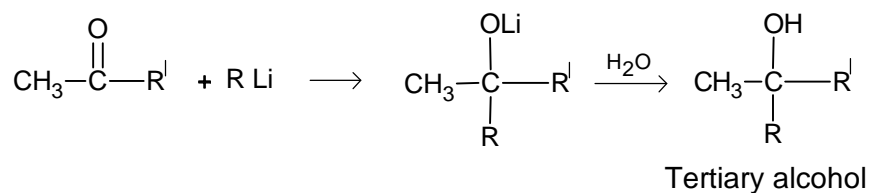
3. Formation of ethers :

Higher ethers are prepared by the action of organolithium compounds on a monochloroether.

$$R \, OCH_2 \, Cl + R^I \, Li \longrightarrow R \, OCH_2R^I + Li \, Cl$$
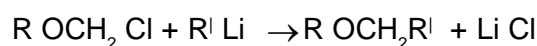
4. Formation of aldehydes :

Organolithium compounds react with hydrogen cyanide to form aldehydes.

$$HC{\equiv}N \; + R \, Li \longrightarrow \underset{R}{CH{=}N.\,Li} \; \xrightarrow[- \, Li \, OH]{H_2O} \; RCH{=}NH \xrightarrow{H_2O} RCHO + NH_3$$

$$\left[HC{\equiv}N \xrightarrow{CH_3 \, Mg \, I} \underset{CH_3}{HC{=}N \, Mg \, I} \xrightarrow{H_2O} \underset{CH_3}{HC{=}O} \right]$$
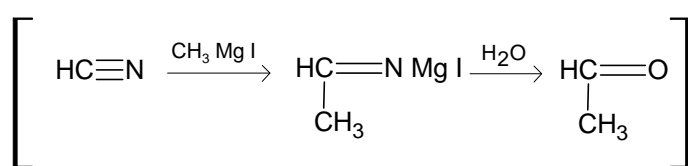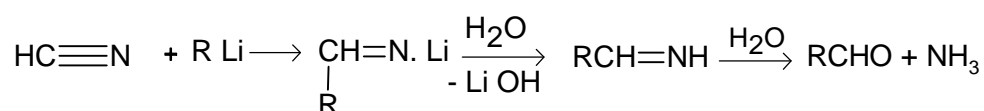
Acetaldehyde

5. Formation of ketones :

Organolithium compounds react with alkyl cyanide to form ketones.

$$H_3C{-}C{\equiv}N \; + R \, Li \longrightarrow \underset{R}{H_3C{-}C{=}N.\,Li} \; \xrightarrow[- \, Li \, OH]{H_2O} \; \underset{R}{CH_3.C{=}NH} \xrightarrow{H_2O} \underset{R}{CH_3.C{=}O} + NH_3$$

$$\left[CH_3.C{\equiv}N \xrightarrow{CH_3 \, Mg \, I} \underset{CH_3}{CH_3.C{=}N \, Mg \, I} \xrightarrow{H_2O} \underset{CH_3}{CH_3.C{=}O} \right]$$
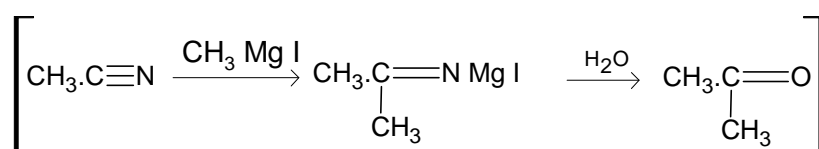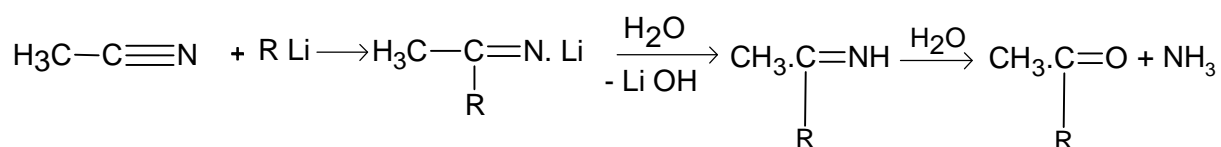
Acetone

6. Formation of alkyl cyanides :

Organolithium compounds react with Cyanogen chloride to form alkyl cyanide.

$$R \, Li \; + Cl \, CN \longrightarrow R \, CN + Li \, Cl$$

7. Formation of amines :

Organolithium compounds react with Chloramine to form amines .

$$R \, Li \; + Cl \, NH_2 \longrightarrow R \, NH_2 + Li \, Cl$$
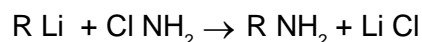
8. Formation of alkyl iodides :

Organolithium compounds react with iodine gives alkyl iodides.

$$R\,Li + I_2 \rightarrow R\,I + Li\,I$$
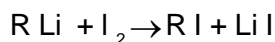
9. Formation of Thio alcoholos :

By the action of Organolithium compounds on sulphur and hydrolysing the product gives thioalcohols.

$$R\,Li + S \rightarrow R\,S\,Li \xrightarrow{H_2O} RSH + LiOH$$
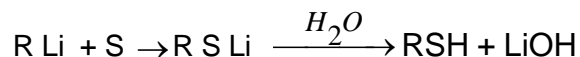
b) Differences from Grignard reagents :

As organolithium compounds are more reactive than Grignard reagents, they undergo some additional reactions. They also differ in some of the Grignard reagent reactions.

1. Formation of Ketones :

Organolithium compounds on reaction with carbon dioxide gives ketones. Grignard reagents react with CO_2 to give carboxylic acids.

Ketone

Acetic acid
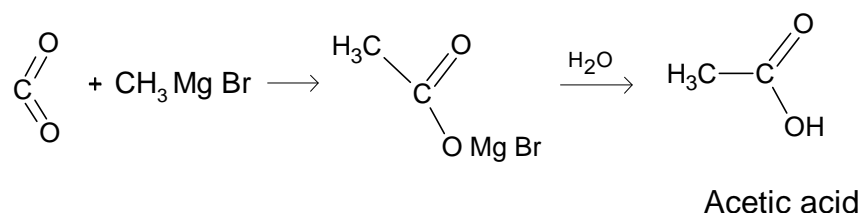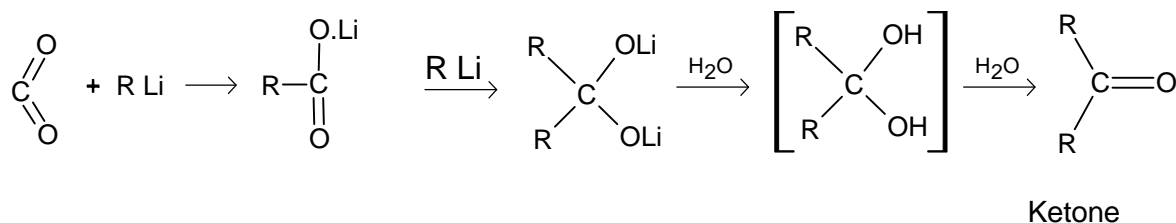
2. Addition on olefinic double bonds :

At high pressure, organolithium compounds add on ethylenic double bonds. No such reaction is given by Grignard reagents.

$$C_4H_9\,Li + CH_2 = CH_2 \rightarrow C_4H_9. CH_2 - CH_2Li \xrightarrow{CH_2=CH_2} C_4H_9\,(CH_2)_4\,Li \xrightarrow{CH_2=CH_2}$$
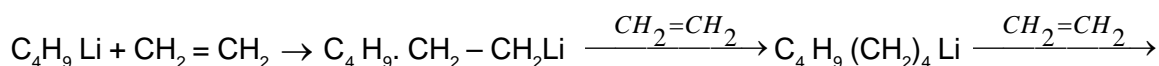
1.6.6 Organoaluminium compounds :

On commercial scale, organo aluminium compounds are prepared by heating aluminium powder, hydrogen and an alkene.

$$3(CH_3)_2 \, C = CH_2 + Al + \frac{3}{2} \, H_2 \rightarrow \left[\begin{array}{c} H_3C \\ \\ H_3C \end{array} \!\!\! CH.CH_2 \!\!-\!\! \right]_3 \!\!\!\!-\!\! Al$$
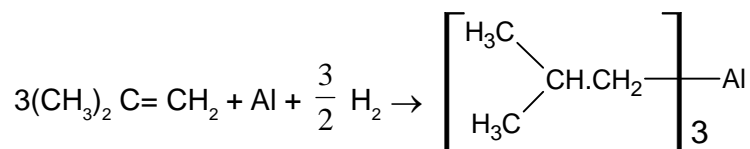
Isobutene   Tri- isobutyl aluminium

Mono, di and trialkyl aluminium compounds are prepared by treating aluminium chloride with Grignard reagent.

$$CH_3 \, Mg \, Cl + Al \, Cl_3 \; \rightarrow CH_3 \, AlCl_2 + Mg \, Cl_2$$

$$2CH_3 \, Mg \, Cl + Al \, Cl_3 \; \rightarrow (CH_3)_2 \, AlCl + 2Mg \, Cl_2$$

$$3CH_3 \, Mg \, Cl + Al \, Cl_3 \; \rightarrow (CH_3)_3 \, Al + 3Mg \, Cl_2$$
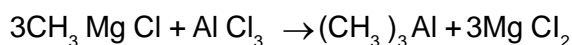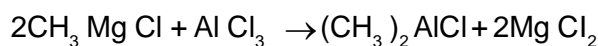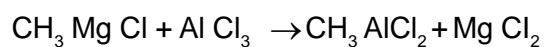
Since aluminium atom in trialkyl aluminium has formerly six electrons in its valency shell, such organometallic compounds have only partly covalent carbon metal bonds.

$$\begin{array}{c} CH_3 \\ \cdot\cdot \\ Al \\ CH_3 \qquad CH_3 \end{array}$$
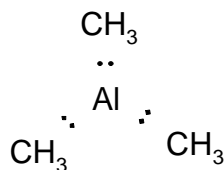
Trimethyl aluminium

Some organometallic compounds of this type have a tendency to exist as dimers.
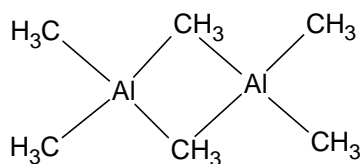
Trimethyl aluminium
(dimer)

$$H_3C, \quad Cl \quad CH_3$$
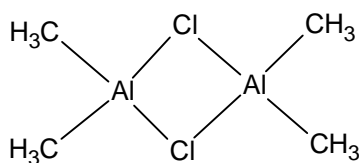
Dimethyl aluminium Chloride
(dimer)

The dimers are examples of electrons deficient compounds. The dimers dissociate to a small extent in solution but to a greater extent in the gaseous phase.

Trialkyls aluminium decompose reversibly on heating to form alkenes.

$$\left[(CH_3)_3 \, C \!\!-\!\! \right]_3 \!\! Al \quad \xrightarrow{150^0C} \quad \left[(CH_3)_3 \, C \!\!-\!\! \right]_2 \!\! Al \, H + (CH_3)_2 \, C = CH_2$$

di- ter - butyl
aluminium
hydride

Isobutene
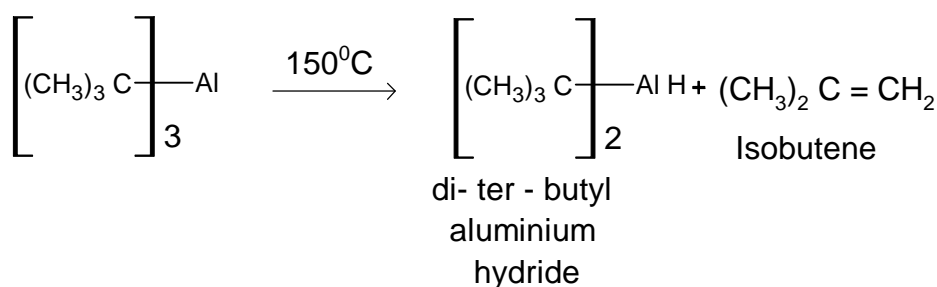
Di- isobutyl aluminium hydride acts as a reducing agent for functional groups i.e. aldehydes, ketones, esters to alcohols or aldehydes and cyanides to aldehydes or amines.

The trialkyl aluminium is used as a catalyst (Ziegler/ Natta type catalysts) for the low temperature polymerisation of alkenes.

Some alkyl aluminiums are used as jet fuel igniters and to help in preventing flame out of jet engines.

1.6.7 Other uses of Organometallic compounds :

1. Tetra ethyl lead is added in small proportion to petrol as an antiknocking agent. The Petrol after adding tetraethyl lead in known as leaded petrol or ethyl petrol.

2. Many organometallic compounds are used as catalysts in polymerisation reactions.

3. Butyl sodium is used for the conversion of butadiene to buna rubber.

4. Trialkyl aluminium is used for the low temperature polymerisation of alkenes.

5. Mercurials find an important place in medicine. Several organometallic compounds are medicinally important.

   Eg : Mercurochrome (antiseptic); Salvarsan and neosalvarsan are used in the treatment of syphilis etc.

Mercurochrome and merthiolate are very useful for open wounds.

Mercuryhydrin and chlormosadran are used in diuretics, in the treatment of edema etc.

Trialkyl germanium compounds destroy certain kinds of bacteria.

1.6.8 Model Questions :

1) What are organometallic compounds ? How is organometallic compound of magnesium prepared?

2) Explain the nature of metal - carbon bond in organometallic compounds.

3) Give any three synthetic applications of organolithium compounds.

4) What are Grignard reagents ? How are they prepared ? Give any two synthetic applications of Grignard reagents.

5) Out line the synthesis of ethyl magnesium bromide with experimental details and give the synthesis of a ter - alcohol from it.

6) Give a method of preparation of organo lithium compound. Give any two synthetic application of organo - lithium compounds.

7) What are organo metallic compounds ? Describe the preparation and uses of alkyl lithium.

8) How are Grignard reagents prepared ? Explain the synthetic uses of Grignard reagents.

9) Describe the general methods to prepare organomagnesium compounds. What are their synthetic uses?

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UNIT- II

Lesson -1

STRUCTURAL THEORY IN ORGANIC CHEMISTRY

2.1.0 Types of bond fission and organic reagents (Electrophilic, Nucleophilic, and free radical reagents including neutral molecules like H_2O, NH_3 & $AlCl_3$).

Bond Polarization : Factors influencing the Polarization of covalent bonds, electro negativity - inductive effect. Application of inductive effect

(a) Basicity of amines

(b) Acidity of carboxylic acides

(c) Stability of carbonium ions.

Resonance or Mesomeric effect, application to

(a) acidity of phenol, and

(b) acidity of carboxylic acids.

Hyper conjugation and its application to stability of carbonium ions, Free radicals and alkenes, carbanions, carbenes and nitrenes.

Types of Organic reactions : Addition - electrophilic, nucleophilic and free radical. Substitution - electrophilic, nucleophilic and free radical. Elimination - Examples (with mechanisms).

2.1.1 BOND FISSION (OR) BOND CLEAVAGE.

There are two types of Bond cleavage depending on the relative electronegativities of the concernd atoms. They are

1) Homolytic bond cleavage

2) Heterolytic bond cleavage

Homolytic bond cleavage :

In homolytic bond cleavage each of the departing atom or group retains one electron from the shared pair forming free radicals.

Homolytic fission takes place when the two bonded atoms have similar electronegativity values.
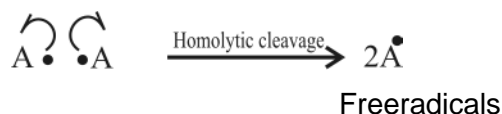
Freeradicals

A freeradical is defined as an atom or a group of atoms containing single electron.

Heat or U.V. light (h ν) is used to produce free radicals. Halogens with low bond dissociation energy easily produce free radicals.

Mechanism :

Reactions in which free radicals are produced as intermediate proceed through radical mechanism .It takes places in three steps.

i) **Initiation :** In initiation free radicals are produced
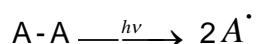
$$A\text{-}A \xrightarrow{\;hv\;} 2\overset{\bullet}{A}$$

ii) **propagation** : In propagation chain reaction takes place.

$$B\text{-}C + \overset{\bullet}{A} \rightarrow A\text{-}B + \overset{\bullet}{C}$$

$$\overset{\bullet}{C} + A\text{-}A \rightarrow A\text{-}C + \overset{\bullet}{A}$$
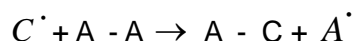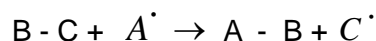
iii) Termination : In termination no free radicals are produced.

$$\overset{\bullet}{C} + \overset{\bullet}{C} \rightarrow C\text{-}C$$
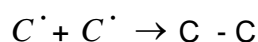
Heterolytic bond eleavage :

In heterolytic bond cleavage, both the bonded electrons are retained by one of the departing atom or group forming ions.

Heterolytic bond cleavage takes place when the two bonded atoms have different electronegativities.

$$C \overset{\curvearrowright}{\textbf{:}} A \longrightarrow \overset{+}{C} + \bar{A}$$

Carboniumion

$$\overset{\curvearrowleft}{C} \textbf{:} A \longrightarrow \bar{C} + \overset{+}{A}$$
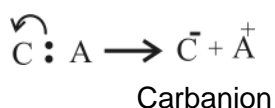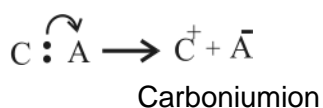
Carbanion

Carbon atom with positive charge is called Carbonium ion. Carbon atom with negative charge is called Carbanion. In carbonium ion the carbon atom has only three pairs of electrons. In carbanion the carbon atom has four pairs of electrons.

Mechanism :

Reactions in which ions are produced as intermediate proceed through ionic mechanism.

According to the principle of electrostatistics like charges repel and unlike charges attract.
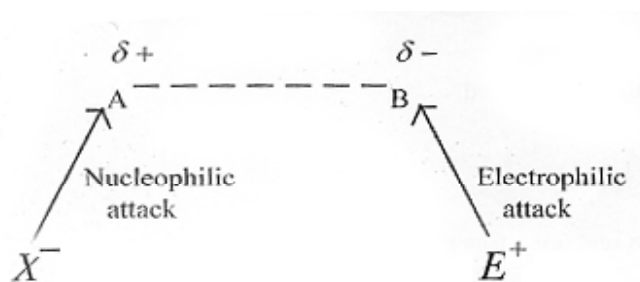
Radical and Ionic reactions

Radical reactions (Homolytic fission)	Ionic reactions (Heterolytic fission)
1.They Involve free radicals	1. They involve ions.
2.Heat or U.V. light initiates the reaction.	2. Acid or Base initiates the reaction.
3.They take place in non- polar medium	3. They take place in polar medium
4.They are auto catalytic	4. They follow kinetics.
5. They oppose Markownikov's rule	5. They follow Markownikov's rule
6. They violate orientation rules	6. They follow orientation rules.

2.1.2 ORGANIC REAGENTS

Organic reagents are classified as

1. Electrophiles
2. Nucleophiles.

Electrophiles :

Electrophiles are electron liking reagents (phile = like). They have an electron defficient atom or centre. They may be positively charged or neutral.

Ex: Positively charged electrophiles

H^+ , H_3O^+ , R_3C^+ , NO_2^+ .

Neutral eletrophiles

BF_3 , $AlCl_3$, $ZnCl_2$, $FeCl_3$.
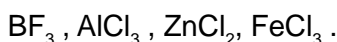
Electrophiles accept electrons . $\therefore$ They are lewis acids.

Nucleophiles:

Nucleophiles are nucleous liking reagents.   They have an electron rich atom or centre. They may be negatively charged or neutral.

Ex: Negatively charged Nucleophiles - $\overline{OH}$, $\overline{X}$, R_3C^-, CN^- .

Neutral Nucleophiles- $H_2\ddot{O}$, $\ddot{N}H_3$, $R—\ddot{N}H_2$, $R—\ddot{O}H$, $\ddot{N}H_3$, R- Mgx .

Nucleophiles donate electrons. $\therefore$ They are lewis bases.

The reactions involving the attack of electrophiles are called Electrophilic reactions and those involving the attack of nucleophiles are called nucleophilic reactions.

Nucleophiles	Electrophiles
1. Electron rich	1. Electron defficient
2. Provide electron pair .	2. Accept electron pair
3. Lewis bases	3. Lewis acids .
4. Attack positive ions	4. Attack negative ions .
5. They are Anions or Contain unshared pair of electrons.	5. They are Cations or Contain an empty orbital to accept electronpair.

2.1.3. Factors influencing polarity of Covalent bond :

A Covalent bond is formed between two atoms by mutual sharing of electron pair . The polarity of a covalent bond depends on the electronegativities of the atoms participating in the bond formation.

The magnitude of polarity of the bond depends upon the difference in electronegativities of the atoms concernd. The greater the difference in electronegativities, the greater the polarity.

The covalent bond is two types depending on the electronegativities of the bonded atoms.

1. Non polar covalent bond

2. Polar covalent bond.

Non-Polar Covalent bond :

Non- Polar covalent bond is formed between two atoms of same or almost equal electronegativity values.

Ex: H - H   Cl - Cl

non - polar covalent bonds .
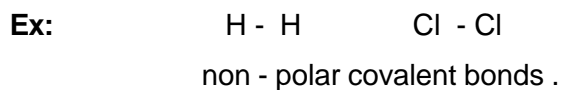
Polar Covalent bond :

Polar covalent bond is formed between two atoms of different electronegativity values.

$$\overset{\delta +}{H} - \overset{\delta -}{Cl} \qquad \overset{\delta +}{C} - \overset{\delta -}{Cl}$$

Ex:

Polar Covalent bonds
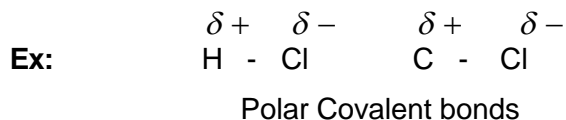
The atom having high electronegativity gets partial negative charge and the other atom gets partial positive charge .

In single bonds partial charges are formed on atoms due to polarity . But in double and triple bonds complete charges are formed on atoms due to shifting of electrons.

$$> C = O \longrightarrow > \overset{+}{C} - \bar{O}$$

$$- C \equiv N \longrightarrow - \overset{+}{C} = \bar{N}$$
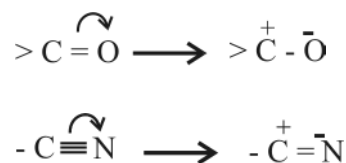
These electronic displacements are two types .

1. Permanent electronic displacements

2. Temporary electronic displacements.

Permanent electronic diplacements:

These are permanently operating in the molecule known as polarisation effects.

Ex: Inductive effect

Mesomeric effect

Temporary electronic displacements :

These are brought in to play by the attacking reagent and disappears as soon as the attacking reagent is removed known as polarisability effects.

Ex.   Electromeric effect.

2.1.4. INDUCTIVE EFFECT : (Transmission effect)

Inductive effect is defined as permanent effect in which displacement of electrons of a σ covalent bond takes place towards more electronegative atom or group .

Ex: 1. Chlorobutane

$$C H_3 - C H_2 \longrightarrow C H_2 \ggg CH_2 \ggg Cl$$
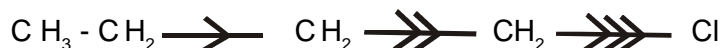
Explanation :

Electronegativity of Carbon = 2.5

Electronegativity of Chlorine = 3.0

$\therefore$ Electrons are displaced towards chlorine . Thereby C_1 Carbon becomes electronically deffificient. It attracts electrons from C_2 Carbon . Now C_2 Carbon becomes electronically deffificient and soon. Thus the polarity of one bond is transmitted to neighbouring bonds.

There are two types of inductive effects .
1. Positive inductive effect (+ I effect)
2. Negative inductive effect (- I effect)

+ I Effect : Inductive effect caused by electron releasing group is called + I effect.

Ex: All Alkyl Radicals (R-), - H

- I Effect : Inductive effect Caused by electron withdrawing group is called - I effect.

Ex: - X, - OH, - NO_2

Characters :

1. Electrons of σ covalent bond participate in this effect.

2. It is a permanent effect .

3. it dies away quickly . So , it can be neglected beyond third carbon.

4. It effects physical properties of the molecule.

Applications :

1. Basicity of Amines : (R-NH$_2$).

   Basic nature of Amines is due to the presence of lonepair of electrons on Nitrogen atom which accept proton.

$$R \longrightarrow \overset{\cdot\cdot}{N}H_2$$
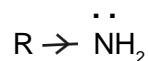
+ I effect : Alkyl group (R-) is an electron releasing group.

   Due to positive Inductive effect of the alkyl group the nitrogen atom becomes more rich in electrons . So , Amines are more basic than Ammonia .

   $RNH_2 > NH_3$
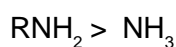
   According to + I effect the relative basic Character of Amines must be T > S > P . But practically it is Secondary > Primary > Tertiary

   $R_2NH > R NH_2 > R_3N$

   This anamalous behavior is due to Steric effect

2. Acidity of Carboxylic acids:

   Acidic nature is due to the tendency to lose proton. So ,the strength of an acid depends on the ease with which it gives proton .

   $RCOOH \rightleftharpoons RCOO^- + H^+$
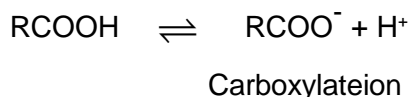
             Carboxylateion

   Electron releasing group decreases the stability of carboxylateion due to + I effect. So Acidic nature decreases .

$$R \longrightarrow C \overset{O}{\underset{O}{\big<}} -$$

   Ex : $HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH$
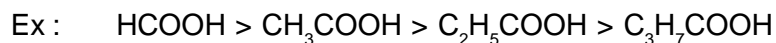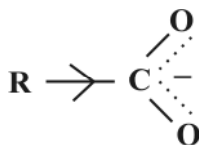
   Here Alkyl groups are electron releasing groups they decrease acidic streanth due to + I effect.

- I effect : Electron with drawing group increases the stability of carboxylate ion due to - I effect

∴ Acidic strength increases.

Ex : a) Cl CH$_2$ COOH > CH$_3$COOH
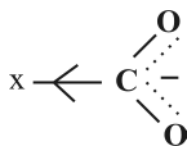
Here chlorine is Electron with drawing group. It increases acidic strength due to -I effect.
∴ Chloro acetic acid is more acidic than acetic acid.

b) di- and tri- choloro acetic acids are still more stronger acids due to cumulative -Ieffect.

Cl ← C COOH > Cl ← CH COOH > Cl ← CH$_2$ COOH > CH$_3$ COOH .
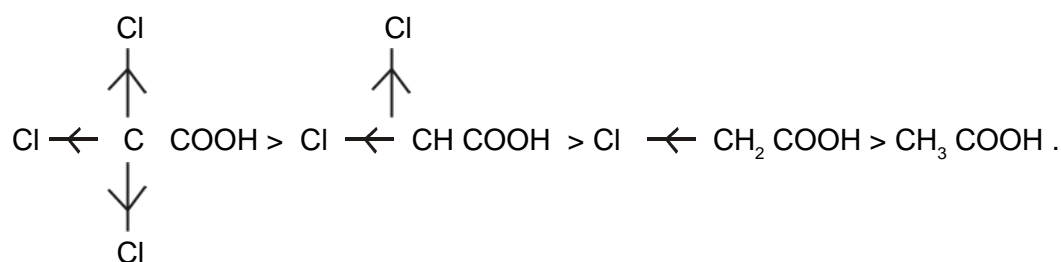
trichloroacetic acid is as strong as Hydrochloric acid .

c) Inductive effect dies away quickly ,

Ex : α - > β - > γ - n Chloro Butyric acids .

The strength of the acid is proportionately decreased as position of the halogen atom is away from the -COOH Group.

3. Stability of Carbonium ions ;

Due to + I effect , alkyl group releases electrons to the posistively charged carbonium ion and reduces charge. The carbonium ion is stabilised by dispersal of charge. Thus a tertiary car-bonium ion with three alkyl groups is more stable than secondary Carbonium ion with two alkyl groups which is more stable than primary Carboniumion with one alkyl group.

R   H   H   H

R $\rightarrow$ C$^+$ > R $\rightarrow$ C$^+$ > R $\rightarrow$ C$^+$ >   H - C$^+$

R   R   H   H
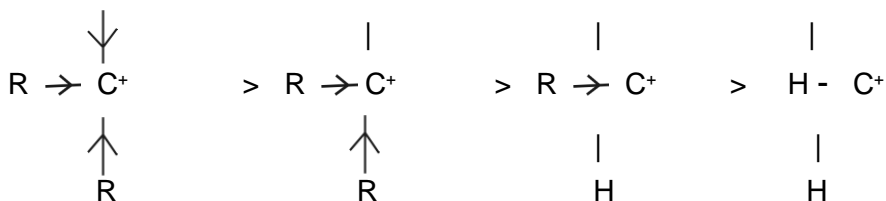
T- Carboniumion   S - Carboniumion.   P - Carboniumion Methyl cation

2.1.5 .RESONANCE OR MESOMERIC EFFECT :

Mesomenic effect is defined as a pemanent effect in which transfer of π electrons or lone pair of electrons takes place through multiple bonds. This effect is as long as conjugation exists. It is also called Conjugative or Resonance effect.

Alternative arrangement of double bonds in a molcule is called conjugation.

Ex :   Crotonaldehyde

CH_3 - CH = CH - CH = O $\rightarrow$ CH_3 - $\overset{+}{CH}$ - CH = CH - $\overset{-}{O}$
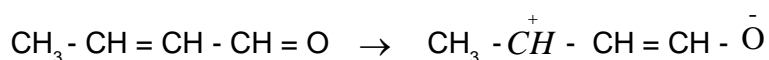
There are two types of Mesomeric effects

1) Positive mesomeric effect (+M effect)

2) Negative mesomeric effeect (-M effect)

+Meffect : Mesomeric effect caused by electron releasing groups is called +M effect.

Ex : - $\ddot{\underset{..}{X}}$: - $\ddot{O}$H - $\ddot{N}H_2$ are electron releasing groups in mesomeric effect.

-M effect : Mesomeric efect caused by electron withdrawing groups is called - M effect.

Ex : -NO_2, -CN, >CO are electron with drawing groups.

Explanation : The mesomeric effect takes place in conjugated system through π - orbitals. Conisder a carbonyl group which is the resonance hybrid of the two forms I and II

> C = O   > $\overset{+}{C}$ — $\overset{-}{O}$ > C $\overline{\underline{\,\,\,}}$ O

I   II   Resonance hybrid
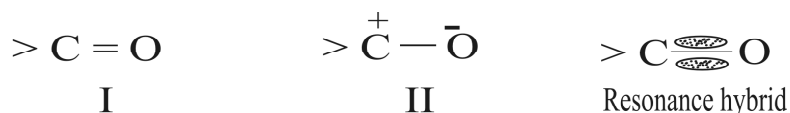
Now if carbonyl group is conjugated with C = C, then tranfer of π - electrons takes place.

$$CH_3 - CH = CH - CH = O \leftrightarrow CH_3 - CH = CH - \overset{+}{C}H - \overset{-}{O}$$

$$\updownarrow$$

$$CH_3 - \overset{+}{C}H - CH = CH - \overset{-}{O}$$
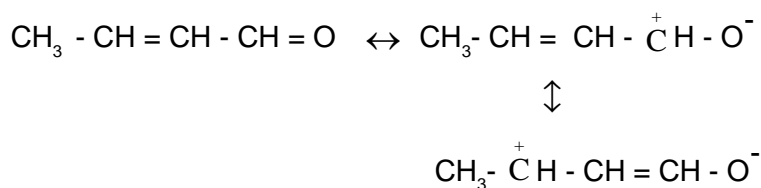
Characters :

1. It is a permanent effect

2. π - electrons or lone pair of electrons participate in this effect

3. It is from one end to other end of the molecule as long as conjugation exists.

4. It effects Physical properties of molecules.

Applications :

1) Acidity of Phenol :

Acidic nature is due to the tendency to lose proton.
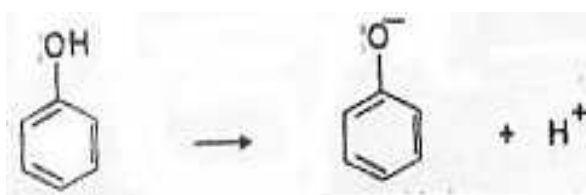
Phenoxide ion

Phenol is acidic because Phenoxide ion is stabilised by resonance due to +M effect.
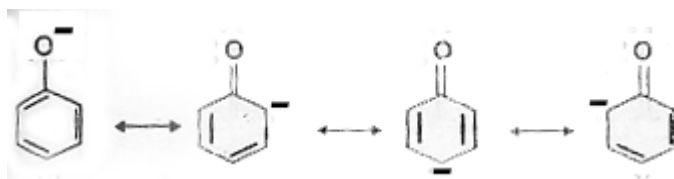
As this resonance stabilisation is not possible in alkoxide ion (RO^-), Alcohols are neutral.

Acidity of Carboxylic acids :

The strength of an acid depends on the ease with which it gives proton.

$$RCOOH \rightleftharpoons RCOO^- + H^+$$
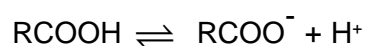
Carboxylic acids are acidic because the carboxylate ion is stabilised by resonance due to +M effect

$$
\begin{array}{ccc}
\overset{\textstyle O}{\overset{\|}{R-C-O^-}} & \longleftrightarrow & \overset{\textstyle O^-}{\overset{|}{R-C=O}}
\end{array}
$$
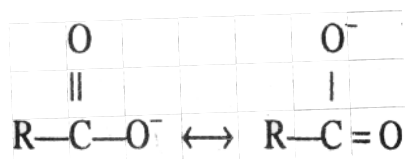
The resonating structures of carboxylate ion are equivalent where as the resonationg structures of phenoxide ion are not equivalent. Hence Carboxylic acids are stronger acids than phenol.

2.1.6 HYPER CONJUGATION : (No- bond resonance)

Hyper conjugation is a kind of resonance which involves hydrogen atoms alpha (α -) to the unsaturated or elctronically defficient atom. it is also knwn as conjugation

Ex:
$$
\overset{\textstyle H}{\overset{|}{\underset{\underset{\textstyle H}{|}}{H-C-CH=CH_2}}} \rightarrow \overset{H^+}{\overset{\textstyle H}{\overset{|}{\underset{\underset{\textstyle H}{|}}{H-C=CH-\bar{C}H_2}}}} \longleftrightarrow \overset{\textstyle H}{\overset{|}{\underset{\underset{\textstyle H}{|}}{H^+C=CH-\bar{C}H_2}}}
$$

Propene $\updownarrow$

$$
\overset{\textstyle H}{\overset{|}{H-C=CH-\bar{C}H_2}}
$$
$$
H^+
$$
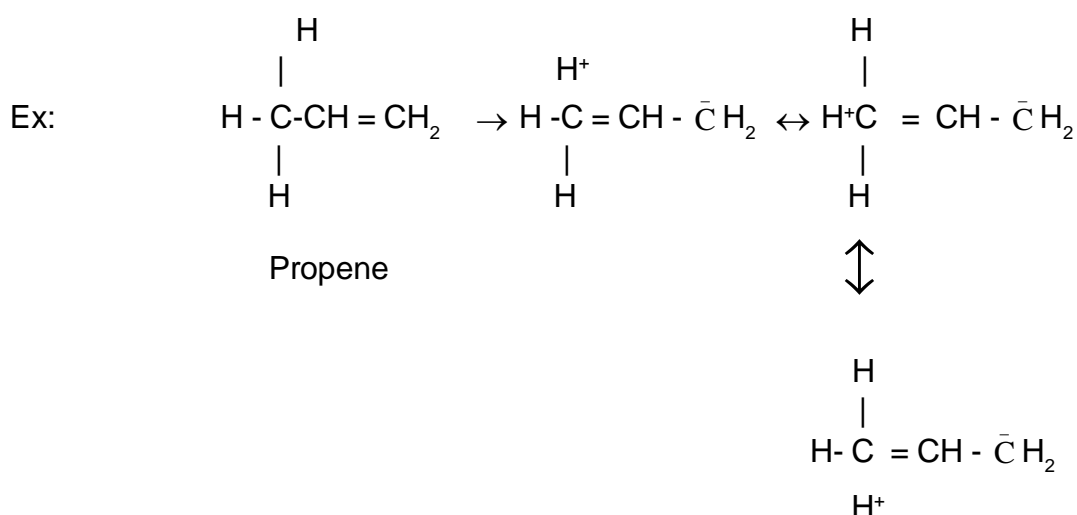
In these resonance structures there is no bond between the α - carbon and one of the hydrogen atoms. Hence Hyper conjugation is also Known as no- bond resonance.

Applications :

1) Stablilty of carboniumions :

A Carboniumion is a cation in which positive charge is carried by a carbon atom with only 6 electrons in its valency shell.

The more the number of Hyperconjugative structures, the higher is its stability.

The t- Carbonium ion has a maximum number of Hyperconjugative structures compared to that of secondary or primary. Hence Tertiaty Carbonium ion has more stability than secondary carbonium ion which in turn has more stability than Primary Carbonium ion.

$$
\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3-C+}} \leftrightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{\overset{H^+}{}}{\overset{CH_2}{\|}}}{H_3C-C}} \leftrightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{\overset{H^+}{}}{CH_3}}{CH_2=C}} \leftrightarrow \underset{\underset{\underset{H^+}{}}{\overset{CH_2}{\|}}}{\overset{\overset{CH_3}{|}}{CH_3-C}} \leftrightarrow \text{Total 10 structures}
$$

Tertiary Carboniumion

$$
\underset{\underset{CH_3}{|}}{\overset{\overset{H^+}{}}{CH_3-\overset{+}{C}H}} \leftrightarrow \underset{\underset{CH_3}{|}}{CH_2=CH} \leftrightarrow \underset{\underset{\underset{H^+}{}}{\overset{CH_2}{\|}}}{CH_3-CH} \quad \text{Total 7 sturctures.}
$$

Secondary carboniumion

$$
\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{H-C}}-\overset{+}{C}H_2 \leftrightarrow \underset{\underset{H}{|}}{\overset{\overset{H^+}{}}{H-C}}=CH_2 \leftrightarrow \underset{\underset{H}{|}}{H^+C}=CH_2 \leftrightarrow \underset{\underset{H^+}{}}{\overset{\overset{H}{|}}{H-C}}=CH_2
$$
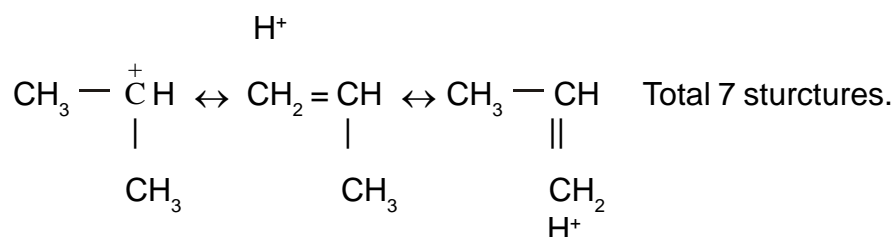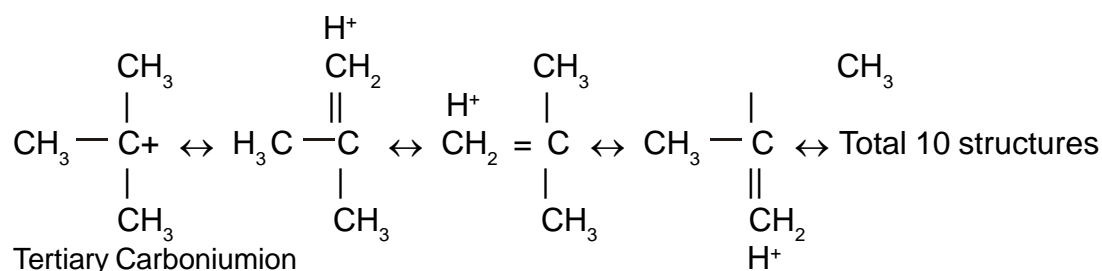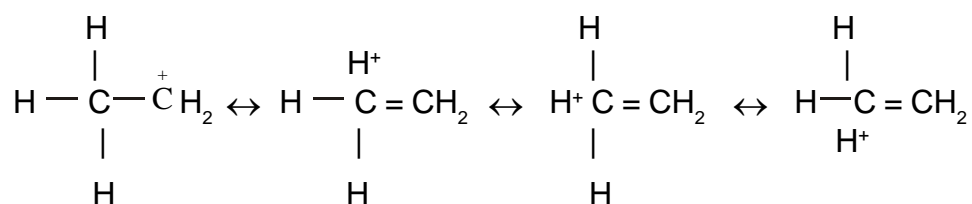
Primary carboniumion

Thus t- > s- > p- carboniumion

2) Stability of freeradicals :

Any species having an odd or unpaired electron is called a free radical.

The stability of free radicals is in the order tertiary > secondary > primary.

This has been explained on the basis of Hyper conjugation. The number of Hyperconjugative structures for tertiary radical is more than that of secondary or Primary radicals. Hence tertiary radicals are more stable than secondary radicals which in turn are more stable than primatry radicals.

$$CH_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{\overset{\bullet}{C}}}}} \leftrightarrow CH_3 - \overset{\displaystyle \overset{H^{\bullet}}{CH_2}}{\underset{\displaystyle CH_3}{\overset{||}{\underset{|}{C}}}} \leftrightarrow \overset{H^{\bullet}}{CH_2} = \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} \leftrightarrow CH_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle \underset{H^{\bullet}}{CH_2}}{\overset{|}{\underset{||}{C}}}} \leftrightarrow \text{Total 10 sturctures.}$$

Tertiary radical

$$CH_3 - \overset{\displaystyle H^{*}}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{\overset{\bullet}{C}H}}}} \leftrightarrow CH_2 = \overset{\displaystyle}{\underset{\displaystyle CH_3}{\overset{}{\underset{|}{CH}}}} \leftrightarrow CH_3 - \overset{\displaystyle}{\underset{\displaystyle \underset{H^{*}}{CH_2}}{\overset{}{\underset{||}{CH}}}} \leftrightarrow \text{Total 7 sturctures.}$$

Secondary radical

$$H - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \overset{\bullet}{C}H_2 \leftrightarrow H - \overset{\displaystyle \overset{H^{*}}{}}{\underset{\displaystyle H}{\overset{}{\underset{|}{C}}}} = CH_2 \leftrightarrow \overset{\bullet}{H} \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} = CH_2 \leftrightarrow H - \overset{\displaystyle H}{\underset{\displaystyle H^{*}}{\overset{|}{C}}} = CH_2 \quad \text{Total 4 sturctures.}$$

Primary radical
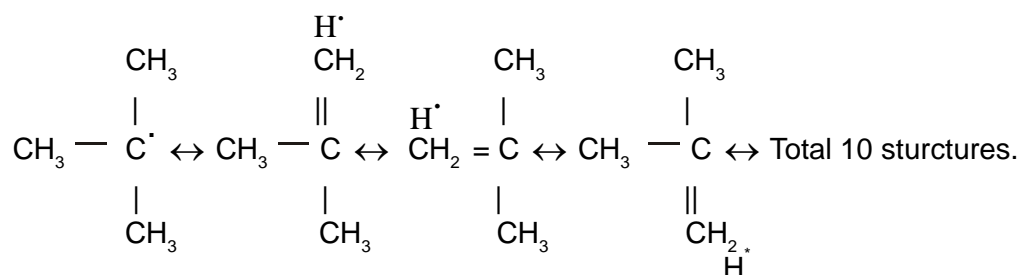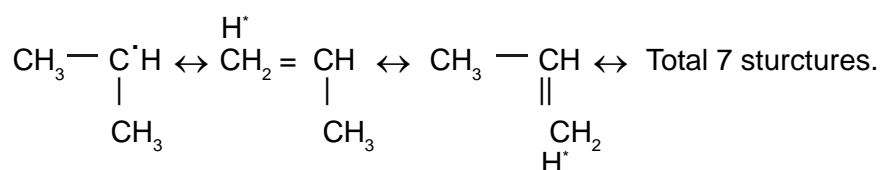
Thus Tertiary radical **>** Secondatry radical **>** Primary radical.

Stabililty of Alkenes :

    The unsaturated Hydrocarbons which contain carbon- carbon double bonds are called Alkenes.

    The greater the number of alkyl groups attached to the doubly bonded carbon atoms, greater is the stability of the alkene because they have greater number of Hyperconjugative structures. Ex :

$$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{C}} = \overset{\displaystyle CH_3}{\overset{|}{C}} - CH_3 \quad > \quad CH_3 - \overset{\displaystyle CH_3}{\overset{|}{C}} = CH - CH_3 \quad > \quad CH_3CH = CH\,CH_3 \quad >$$

2,3 -dimethylbutene -2   2- methylbutene -2   Butene -2

It has 12 α - H   It has 9 α -H   It has 6 α -H

$$CH_3 CH = CH_2 \qquad > \qquad CH_2 = CH_2$$
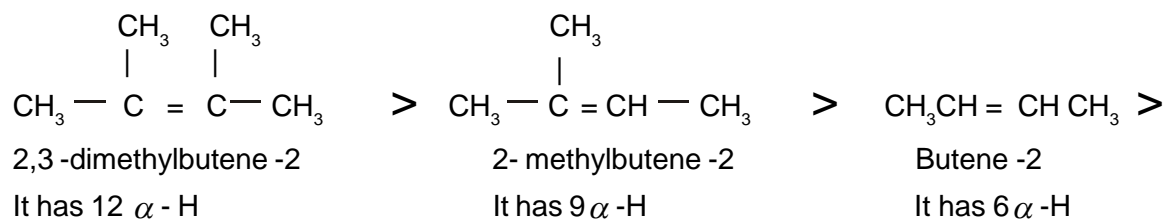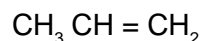
Propene   Ethylene
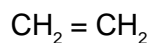
it has 3α -H   It has no α -H

The number of Hyper conjugative structures is equal to the number of α - hydrogens a molecule contains.

2.1.7. CARBANIONS :

An organic ion with unshared pair of electrons and a negative charge on the central carbon atom is called cabanion.

Ex :

$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}:^-$$
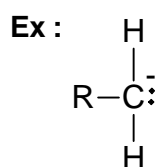
Formation :

i) From Alkynes :

Acetylene forms carbanion by the action of sodamide.

$$HC\equiv CH \xrightarrow{\overset{-}{N}H_2} HC\equiv \overset{-}{C} + NH_3$$
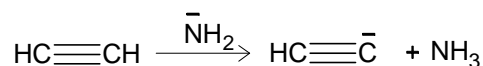
ii) From Nitriles :

Nitriles form carbanions by the action of a strong base.

$$CH_3CN \xrightarrow{\overset{-}{O}H} \overset{-}{C}H_2CN + H_2O$$
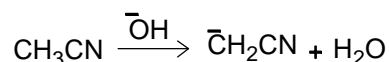
Stability :

a) Based on Inductive effect :

Alkyl groups decreases the stability of Carbanions due to +I effect.$> R_2C^-$

$$R - \overset{-}{C}H_2 \quad > \quad R_2\overset{-}{C}H \quad > \quad R_3C^-$$
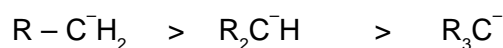
1° Carbanion 2°- carbanion3° - carbon

b) Base on Resonance :

As resonance increases stability of carbanion increases.

$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{C}H_2 \longleftrightarrow CH_3-\overset{\overset{\displaystyle \overset{-}{O}}{|}}{C}=CH_2$$

2.1.8 CARBENES:

Carbenes are defined as neutral organic species containing a divalent carbon atom having a sextet of electrons.

Ex : $:CH_2$ $:CCl_2$

       Methyl carbene   dichlorocarbene

Formation :

i) From diazomethane :

Diazomethane forms carbene by the action of U.V. light.

$$CH_2N_2 \xrightarrow{hv} :CH_2 + N_2$$
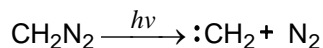
ii) From Chloroform :

Chloroform forms dichlorocarbene by the action of sodium ehtoxide.

$$CHCl_3 + C_2H_5ONa \longrightarrow :C_2H_5OH + NaCl$$

Stability :

These are highly reactive speciesl. Two types carbenes are known.

Singlet carbene :

In singlet carbene two unbonded electrons on the carbon atom are paired.

$$H-C:-H$$
Singlet methylene
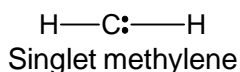
Triplet carbene :

In triplet carbene two unbonded electrons on the carbon atom are unpaired.

$$H—\overset{\bullet}{\underset{\bullet}{C}}—H$$

Triplet methylene
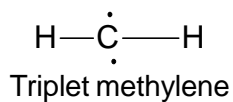
Triplet carbene is relatively more stable because it has lower energy.

2.1.9 NITRENES :

Nitrenes are defined as neutral organic species containing sextet of electrons around nitrogen atom. These are analogous to carbenes and are also known as azocarbenes.

Ex : $CH_3—N\colon$
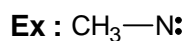
Formation :

i) From Azides :

Azides form nitrenes by photolysis or thermolysis.

$$RN_3 \xrightarrow{hv} R—\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}} + N_2$$
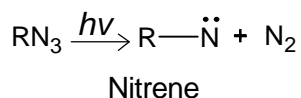
Nitrene

ii) From isocyanates :

Nitriles form carbanions by the action of a strong base.

$$R\text{-}NCO \xrightarrow{hv} R—\overset{\bullet\bullet}{\underset{\bullet\bullet}{N}} + CO$$
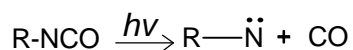
Stability :

These are highly reactive species. Two types of nitrenes are known

a) Singlet nitrene :

In singlet nitrene unbonded electrons on the nitrogen atom are paired

$$R—\ddot{\underset{..}{N}}$$

Singlet nitrene

b) Triplet nitrene :

In triplet nitrene two unbonded electrons on the nitrogen atom are unpaired.

$$R—\ddot{\underset{.}{N}}·$$
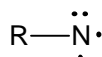
Triplet nitrene

Triplet nitrene is relatively more stable because it has lower energy. Aryl nitrenes are less reactive that Alkyl nitrenes.

TYPES OF ORGANIC REACTIONS :

2.1.10 Addition reaction :

The recation in which combination of two reacting molecules takes place forming a single product molecule is called addition reaction.

Ex : $CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$

      Ethylene   Ethane
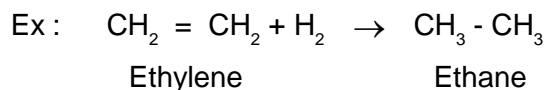
Depending on the nature of the attacking species addition reactions are three types.

1. Electrophilic addition reactions

2. Nucleophilic addition reactions

3. Free radical addition reactions.

Electrophilic addition reactions :

Addition reactions initiated by electrophiles are called electrophilic addition reactions.

a) Addition with non-polar molecules.

$$CH_2 \quad \delta+ \quad \delta-$$
$$|| + Br > Br \xrightarrow[\text{attack}]{\text{Electrophilic}} | \quad + \quad B\dot{r} \rightarrow |$$
$$CH_2 \qquad\qquad CH_2\,Br \qquad CH_2\,Br$$

CH₂ ... CH₂ Br ... CH₂ Br

Ethylene   Ethylenedibromide

Mechanism :

It was found that either impurites or surface of the vessel polarise bromine. So, a π - complex is formed due to the attraction between π bond of ethylene and polarised bromine.
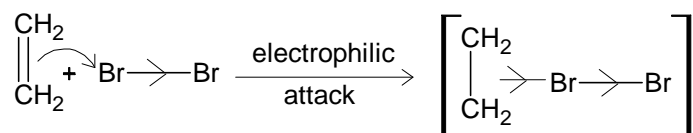
1st stage : In the first stage π - Complex decomposes forming carboniumion.
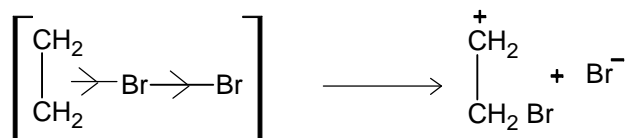
2nd stage : In the second stage nucleophile attacks the carboniumion.
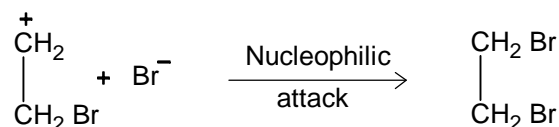
b) Addition with polar molecules.

CH₂ || + H⁺ ..... CH₃ | .... CH₃ | CHBr | CH₃

CH | CH₃ ..... CH | CH₃
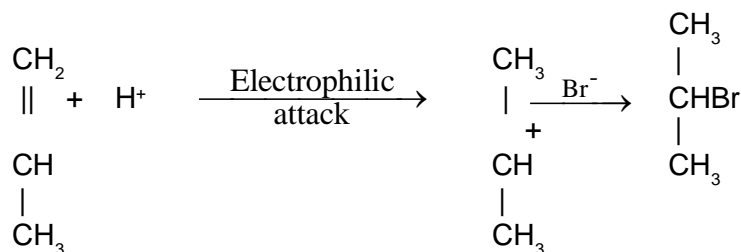
S-Carboniumion more stable   2- bromopropane

It is called Markownikov's addition. Here negative part of the reagent is added to the doubly bonded carbon atom containing minimum number of Hydrogen atoms.

Mechanism :

Addtion of HX to ethylene

$$HX \rightarrow H^+ + X^-$$
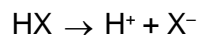
1st stage : In the first stage electrophile attacks forming carbonium ion.

$$
\begin{array}{c}
CH_2 \\
\| \\
CH_2
\end{array}
+ \ H^+ \quad \xrightarrow[\text{attack}]{\text{electrophilic}} \quad
\begin{array}{c}
\overset{+}{C}H_2 \\
| \\
CH_3
\end{array}
$$
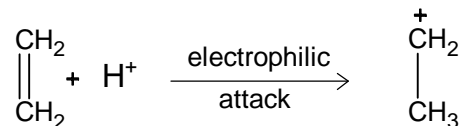
2nd stage : In the 2nd stage nucleophile attacks the carboniumion.

$$
\begin{array}{c}
\overset{+}{C}H_2 \\
\| \\
CH_3
\end{array}
+ \ X^- \quad \xrightarrow[\text{attack}]{\text{Nucleophilic}} \quad
\begin{array}{c}
CH_2\,X \\
| \\
CH_3
\end{array}
$$
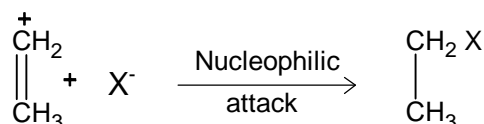
Nucleophilic addition reations :

Addition reactions initiated by nucleophiles are called nucleophilic addition reactions.

a)
$$
CH_3 - C = O + C\bar{N} \xrightarrow[\text{attack}]{\text{Nucleophilic}} CH_3 - \overset{CN}{\underset{H}{\overset{|}{C}}} - O^- \xrightarrow{\overset{+}{H}} CH_3 - \overset{CN}{\underset{H}{\overset{|}{C}}} - OH
$$

       H

    Acetaldehyde   Cyanohydrin

b)
$$
\begin{array}{c}
CH \\
\||| \\
CH
\end{array}
+ CN \xrightarrow[\text{attack}]{\text{Nucleophilic}}
\begin{array}{c}
\bar{C}H \\
\| \\
CHCN
\end{array}
\xrightarrow{\overset{+}{H}}
\begin{array}{c}
CH_2 \\
\| \\
CH_2CN
\end{array}
$$

    Acetylene   vinylcyanide

Mechanism :

$$HCN \rightarrow H^+ + CN^-$$
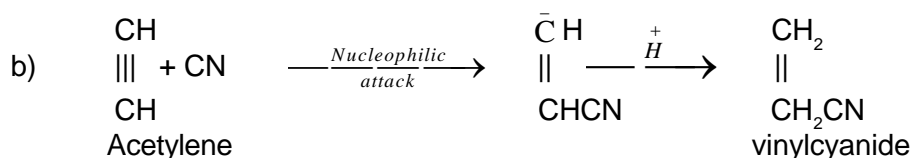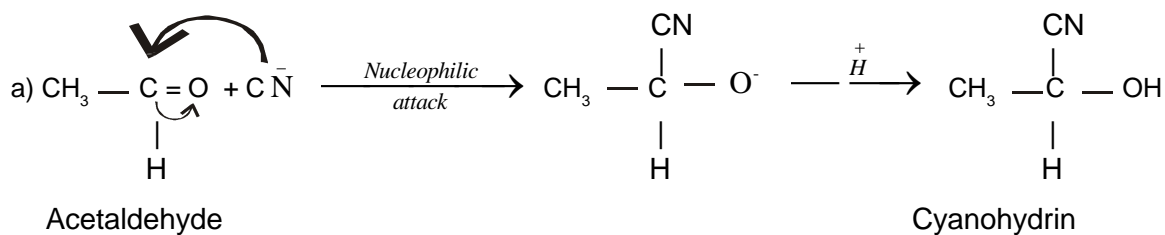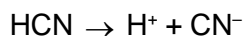
1st stage : In the first stage nucleophile attacks forming carbanion.

$$
\begin{array}{c}
CH \\
\||| \\
CH
\end{array}
+ \ \bar{C}N \quad \xrightarrow[\text{attack}]{\text{Nucleophilic}} \quad
\begin{array}{c}
\bar{C}H \\
\| \\
CHCN
\end{array}
$$
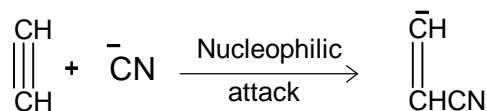
2nd stage : In the 2nd stage electrophile attacks the carbanion.

$$
\begin{array}{c}
\bar{C}H \\
\| \\
CH
\end{array}
+ \ H^+ \quad \xrightarrow[\text{attack}]{\text{electrophilic}} \quad
\begin{array}{c}
CH_2 \\
\| \\
CHCN
\end{array}
$$
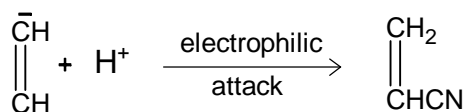
Free radical addition reactions :

Addition reactions involving free radicals are called free radical addition reactions.

Ex: a) $CH_3 CH = CH_2 + B\overset{\bullet}{r} \xrightarrow{\quad Peroxide \quad} CH_3 \overset{\bullet}{C} H CH_2 Br \xrightarrow{\quad HBr \quad} CH_3 CH_2 CH_2 Br$

    Propene   n-propylbroimide
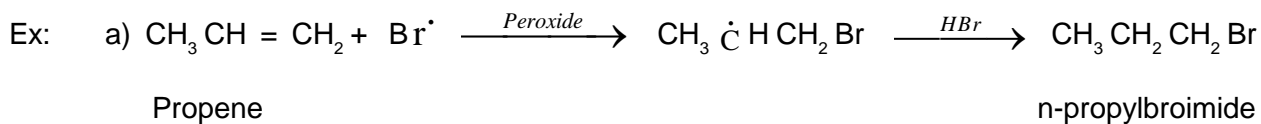
It is called Anti markownikov's rule. Here negative part of the reagent is added to the doubly bonded carbon containing more number of Hydrogen atoms.

b) $RO - OR \xrightarrow{\quad hv \quad} 2 R\overset{\bullet}{O} \xrightarrow{\quad HBr \quad} ROH + B\overset{\bullet}{r}$

Mechanism :

Here inductive effect is more predominent

$$HBr \xrightarrow{\quad hv \quad} Br^{\bullet}$$

$$CH_3CH = CH_2 + Br^{\bullet} \longrightarrow CH_3\overset{\bullet}{C}HCH_2Br$$

2° radical more stable

$\downarrow$

$$CH_3CH_2 CH_2 Br + Br^{\bullet}$$

n- Propyl bromide
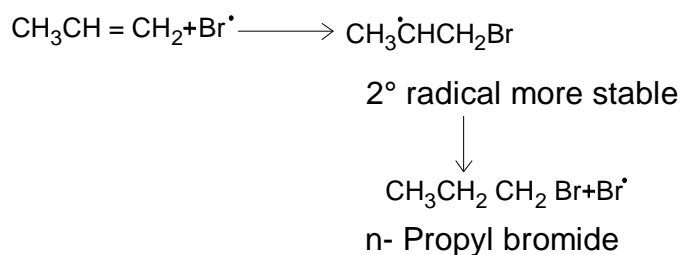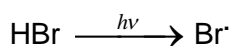
2.1.11 SUBUSTITUTION REACTIONS :

The reaction in which an atom or a group from a molecule is replaced by a different atom or group is called substitution reaction.

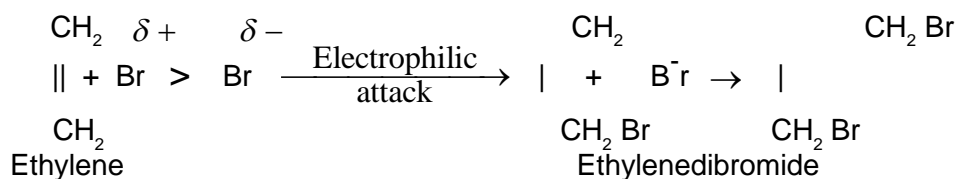Depending up on the nature of the attacking species substitution reactions are three types.

1) Electrophilic substitution reactions.

2) Nucleophilic substitution reactions.

3) Free radical substitution reactions.

Electrophilic substitution reactions : (SE)

Substitution reactions which involue the attack of electrophiles are called electrophilic substitution reactions.

These are more common in aromatic compounds.

Ex : a) Benzene $+ Cl_2$ $\xrightarrow[\text{dark}]{\text{Fe Cl}_3}$ Chlorobenzene

Benzene   Chlorination   Chlorobenzene

b) Benzene $+ H_2 SO_4$ (Conc) $\xrightarrow{\text{sulphonation}}$ SO_3H

Benzene Sulphonic acid

c) Benzene $+ HNO_3$ $\xrightarrow[\text{Nitration}]{H_2SO_4}$ NO_2

Nitrobenzene
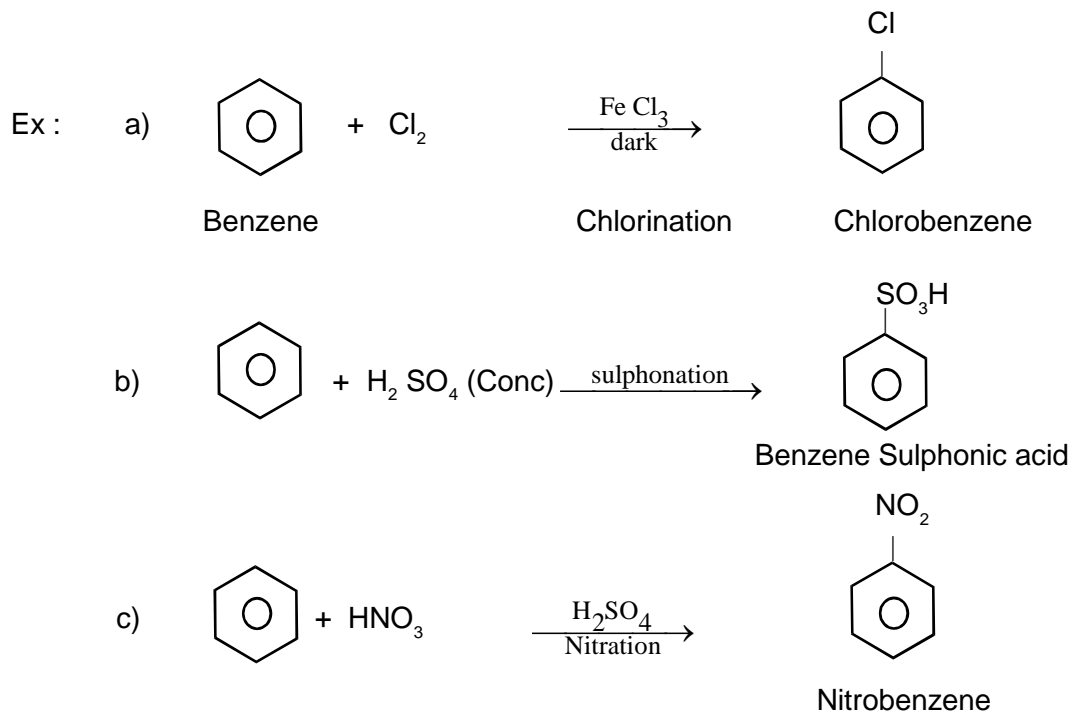
Mechanism :

i) Formation of carbonium ion
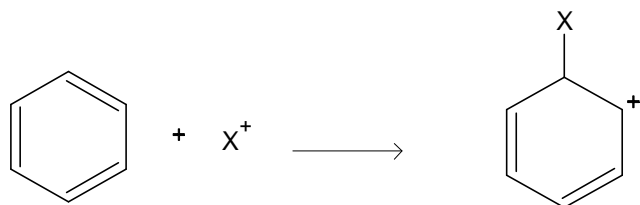
ii) Stability of carbonium ion
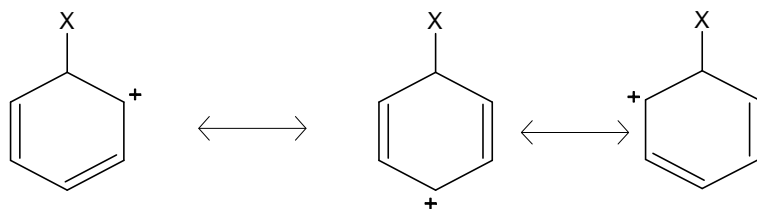
iii) Elimination of proton
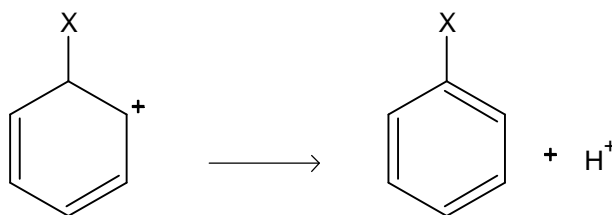
Nucleophilic substitution reactions : (SN)

Substitution reactions which involve the attack of nucleophiles are called nucleophilic substitution reactions.
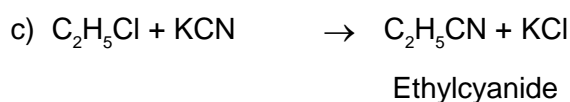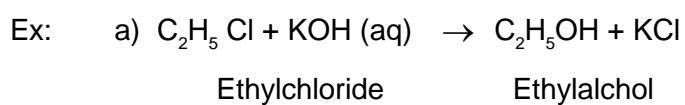
Ex: a) C_2H_5 Cl + KOH (aq) → C_2H_5OH + KCl

Ethylchloride   Ethylalchol

b) C_2H_5Cl + KCN   → $C_2H_5NH_2$ + HCl

Ethylamine

c) C_2H_5Cl + KCN   → C_2H_5CN + KCl

Ethylcyanide

Nucleophilic substitution reactions are classified as

a) SN^I reaction (Nucleophilic substitution unimolecular)

Nuclephilic substitution reactions in which rate of the reaction depends on the concentration of the reactant are called SN^I reactions.

$$\text{Rate } \alpha \text{ (reactant)}$$

Ex : t - Butylbronide $\xrightarrow{aq.KOH}$ t - Butanol + Br$^-$
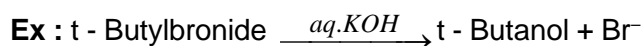
Mechanism :

It takes place in two stages.

1st stage : In the first stage carbonium ion is formed slowly.
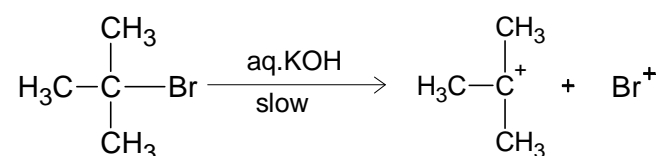
2nd stage : In the second stage the carbonium ion undergoes fast non - rate determining attack with the nucleophile.

$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{C}}} \; + \; \overset{-}{O}H \xrightarrow{\text{fast}} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$

Recemic mixture is obtained in SN^I mechanism.

b) **SN^2 reaction** (Nucleophilic substitution unimolecular)

Nuclephilic substitution reactions in which rate of the reaction depends on the concentration of the reactant are called SN^I reactions.

$$\text{Rate}\,\alpha \; (\text{ reactant}) \, (\text{ reagent})$$

Ex : 2- Bromo octane $\xrightarrow{aq.KOH}$ 2 - octanol
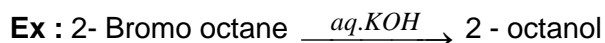
Mechanism :

In SN^2 reaction the attacking nucleophile forms bond simultaneously as bond of the leaving group breaks away.

2 - bromo octane   2 - Octanol
(-36.0°)   (-36.0°)
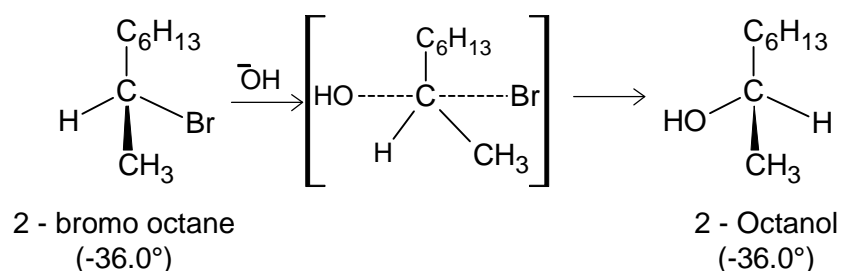
Here complete inversion of the molecule takes place. It is called walden inversion.

Free radical substitution reactions :

Substitution reactions which involve free radicals are called free radical substitution reactions.

Ex :   a) CH_4 + Cl_2 CH_3 Cl + HCl

                  $\xrightarrow{\text{light}}$

      Methane   Chloromethane

        CH_3 CH_2 Cl

b)

CH_3

$+$ Cl_2 $\xrightarrow{\quad heat \quad}$ CH_2Cl $+$ HCl

Toulene   Benzylchloride
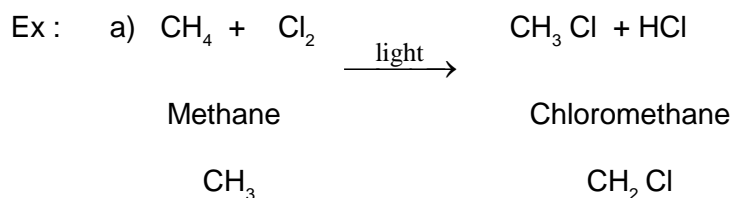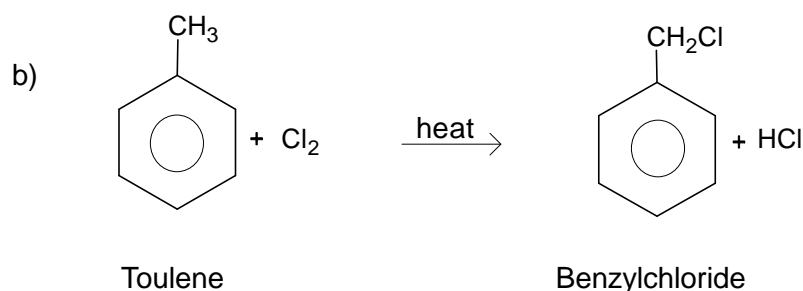
Mechanism :

The mecahnism involves three steps.

i) Inititation : In initiation free radicals are formed.
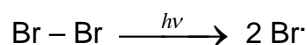
$$Br - Br \xrightarrow{\quad hv \quad} 2\ Br^{\cdot}$$

ii) Propagation : In propagation chain reaction takes place.

$$CH_3\ CH_3 + Br^{\cdot} \rightarrow CH_3\ CH^{\cdot}_2 + Br^{\cdot}$$

$$CH_3\ CH^{\cdot}_2 + Br - Br \rightarrow CH_3\ CH_2\ Br + Br^{\cdot}$$
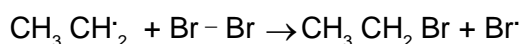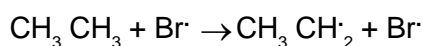
iii) Termination : In termination free radicals combine.

$$Br^{\cdot} + Br^{\cdot} \rightarrow Br - Br$$
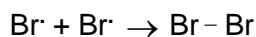
2.1.14 ELIMINATION REACTIONS :

The reaction in which two atoms or groups are eliminated to from a molecle of a multiple linkage is called elimination reaction.

Depending up on the relative positions of atoms or groups eliminaed, elimination reactions are classified as

        1) α - elimaination.

        2) β - elimaination.

        3) γ - elimaination

1) α -elimination : In α - elimination the two atoms or groups are eliminated from the same atom of the molecucle.

$$CHCl_3 \xrightarrow{\quad air \quad} \ddot{C}Cl_2 + HCl$$
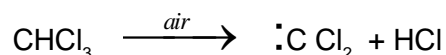
2) β -elimination : In β - elimination the two atoms or groups are eliminated from adjacent atoms of the molecule.

Ex: a) $H - CH_2 - CH_2 -OH \xrightarrow{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$

       Ethylalcohol   Ethylene

                       X
                       |

    b) $CH_3 CH_2 \overset{|}{C}H CH_3 \xrightarrow{Alc.KOH} CH_3 CH = CH CH_3 + HX$

       2-halobutane   2-butene
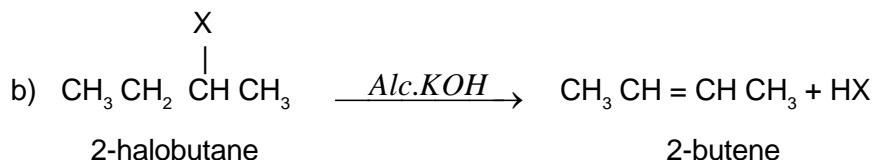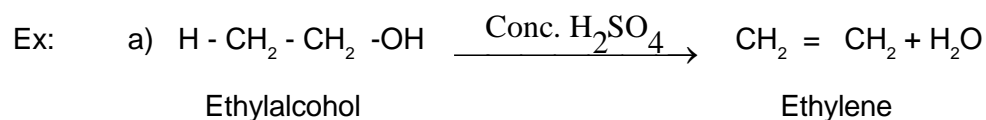
It is called saytzeff elimination. Here more stable alkene forms more.

3) γ -elimination : In γ - elimination the two atoms or groups are eliminated from α - and γ - positions of the moleucles.

                                  cyclopropane
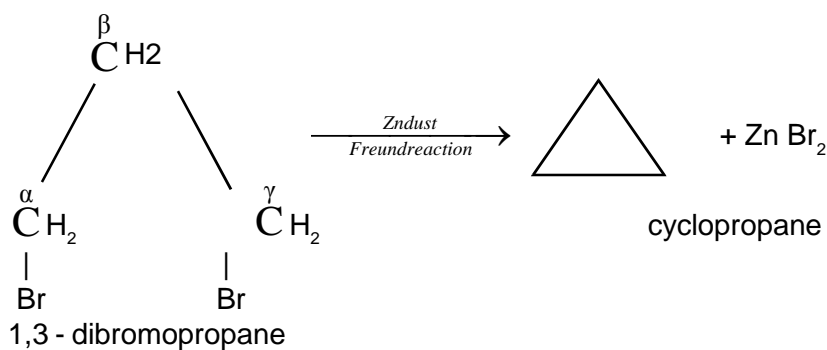
Based on mechanism Elimination reactions are classified as :

a) E^1 reaction : (Elimination Uni molecular)

Elimination reactions in which rate of the reaction depends on the concentration of the reactant only are called E^1 reactions.

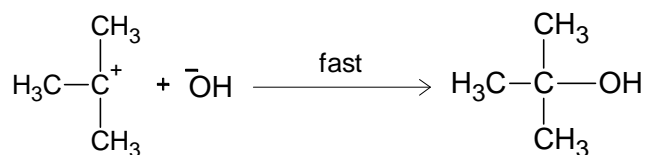$$\text{Rate} \, \alpha \, (\text{reactant})$$

    Ex :   Dehydration of alcohol.
Mechanism :

It takes place in two stages.

1st stage : In the first stage carbonium ion is formed slowly.

$$CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2\overset{+}{O}H_2 \xrightarrow{Slow} CH_3\overset{+}{C}H_2 + H_2O$$
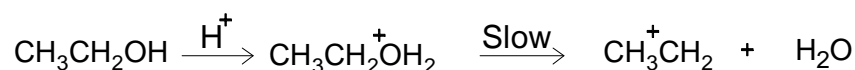
2nd stage : In the second stage the carbonium ion undergoes fast non - rate determining elimination of proton forming alkene.

$$CH_3\overset{+}{C}H_2 \xrightarrow{\text{fast}} H_2C{=}CH_2 + \overset{+}{H}$$
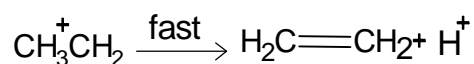
b) E² reaction : (Elimination bimolecular)

Elimination reactions in which rate of the reaction depends on the concentration of the reactant only are called E² reactions.

Rate α (reactant) (reagent)

Ex : Dehydro halogenation of Ethylbromide

Mechanism :

Here elimination of proton and nucleophile takes place simultaneously.

$$\overset{-}{O}H + CH_2{=}CH_2 + \overset{-}{Br}$$

$$H_2O + CH_2{=}CH_2 + \overset{-}{Br}$$
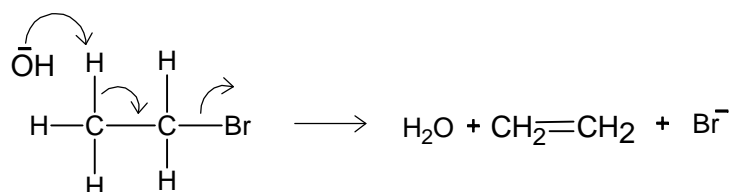
Model Questions :

1. What is hybridisation? What are the distinguishing features of Sp³ and Sp² orbitals. Explain with suitable examples.

2. Write notes on i) Sp³ hybridisation, ii) Sp² hybridisation and iii) Sp hybridisation.

3. Discuss orbital structure of methane and ethane.

4. Discuss orbital structure of Ethylene.

5. Discuss orbital structure of acetylene.

6. Describe homolytic and heterolytic fission of covalent bonds. How do these lead to the formation of carbonium ions, carbanions and free radicals ?

7. Explain the terms electrophiles and nucleophiles with suitable examples ?

8. Classify the following into electrophilic and nucleophilic reagents

    (a) H⁺ (b) Cl⁻ (c) $N\overset{+}{O_2}$ (d) $\overset{-}{O}H$ (e) H_2O (f) NH_3 (g) Br⁺ h) ROH

9. What is inductive effect ? Give an example

10. Unlike inductive effect electromeric effect is not a permanent polarization effect. Explain.

11. What are different types of organic reactions ? Explain with suitable examples.

12. Write notes on a) Mesomeric effect b) Hyperconjugation

13. Discuss the relative stability of primary, secondary and tertiary carbonium ions.

14. Distinguish SN^1 and SN^2 reactions.

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UNIT - II

Lesson -2

ALICYCLIC HYDROCARBONS

2.2.0 : Nomenclature - preparation by Freund method, dicarboxylic metal salts -properties - reactivity of cyclopropane and cyclobutane by comparing with Alkenes - Stability of cycloalkanes, Bayer strain Theroy, sachse Mohr Theroy, Pitzer strain Theory - Conformation structures of Cycloprapane, Cyclopentane and Cyclohexane.

2.2.1 : Nomenclature :

According to IUPAC system, these are named as cycloalkanes or cycloparaffins. Their names are derived by adding the prefix cyclo to the name of the corresponding open chain hydrocrabon.
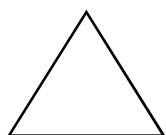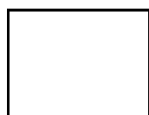
Cyclopropane   **Cyclobutane**   **Cyclopentane**   **Cyclohexane**
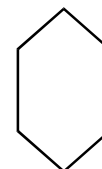
2.2.2 Preparation :

1. Freund Method : (Internal Wurtz reaction)

α, ω - dihaloalkanes react with sodium or Zinc forming Cycloalkanes.
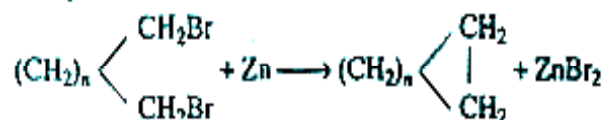
2.Dicarboxylic metal salts : (Wislicenus Method)

Calcium or Barium salts of 1,6 -or 1,7 - dicarboxylic acids on heating followed by reduction form   Cycloalkanes.
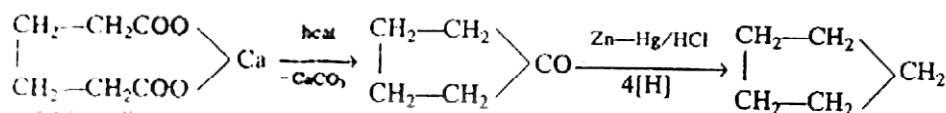
Calcium adipate
Cyclopentane

2.2.3 Properties :

1. Reactivity :

Cycloalkanes resemble alkanes in several chemical properties. For example, they do not react with acids, bases, oxidising agents and reducing agents. They undergo substitution reaction with halogens.

Cycloalkanes and cyclobutane form addition compounds with fission. Thus cycloalkanes behave as alkenes also.

2. Substitution :

Except cyclopropane, cycloalkanes react with halogens in the presence of light forming halocycloalkanes.

Cyclohexane   **Bromocyclohexane**

Cyclopentane   **Bromocyclopentane**
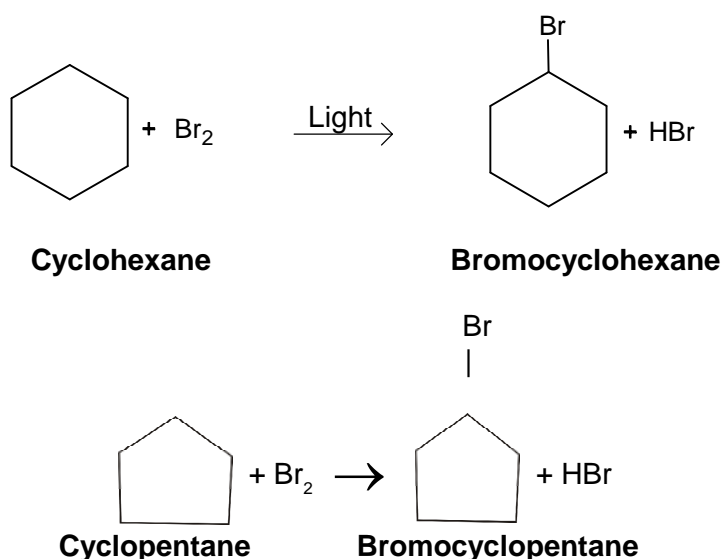
Addition with hydrogen :

Lower members of cyclo alkanes on addition with hydrogen form alkanes.

$+ H_2 \longrightarrow$ $CH_3\text{-}CH_2\text{-} CH_2$

Cyclopropane   **Propane**

$+ H_2 \longrightarrow$ $CH_3\text{-}CH_2\text{-} CH_2\text{-} CH_3$
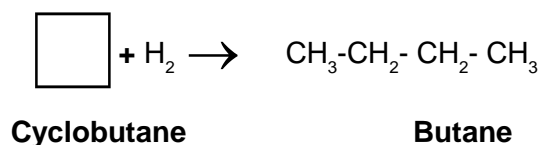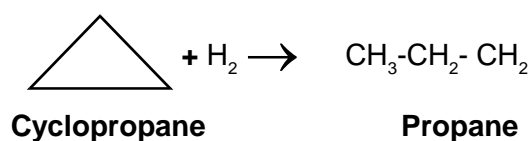
Cyclobutane   **Butane**

Additon with halogens :

Cyclopropane and cyclobutane on addition with bromine form dibromoalkanes.

 $+ Br_2 \longrightarrow$ Br $CH_2CH_2CH_2$ Br

1,3 - dibromopropane

 $+ Br_2 \longrightarrow$ Br $CH_2 CH_2 CH_2 CH_2$ Br

1,4 - dibromobutane
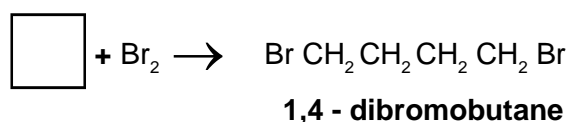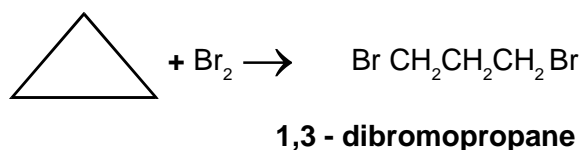
Addition with hydrogenhalides :

Cyclopropane and cyclobutane on addition with hydrogenbromide form bromoalkanes.

 $+ HBr \longrightarrow$ $CH_3CH_2CH_2$ Br

bromopropane

 $+ HBr \longrightarrow$ $CH_3 CH_2 CH_2 CH_2$ Br

bromobutane
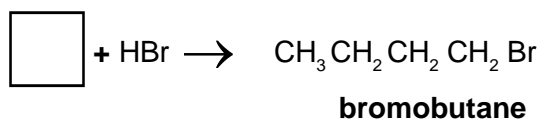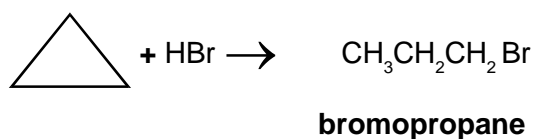
2.2.4 Bayer Strain Theory : (STABILITY OF CYCLOALKANES)

The ring opening or unstability in the case of three and four member compounds was explained by Bayer known as Bayer StrainTheory. The main postulations are

1. In a ring all carbon atoms lie in the same plane.

2. There is deviation or distortion from normal Tetrahedral angle.

3. The deviation from normal tetrahedral angle is called angle of strain.

4. Angle of strain depends on the size of the ring.

5. Angle of strain $= \dfrac{\text{Tetrahedral angle - distorted angle}}{2}$

Cycloalkane	Distorted angle	Angle of Strain
Cyclopropane	60°	$\dfrac{109°28' - 60°}{2} \rightarrow = 24°44'$
Cyclobutane	90°	$\dfrac{109°28' - 90°}{2} \rightarrow = 9°44'$
Cyclopentane	108°	$\dfrac{109°28' - 108°}{2} \rightarrow = 1°44'$
Cyclohexane	120°	$\dfrac{109°28' - 120°}{2} \rightarrow = 5°16'$

According to bayer strain Theory, Cyclopentane is more stable.

Defect : It was found that practically cyclohexane is more stable. So, Bayer strain theory is failed beyond cyclopentane.

2.2.5 Sachse Mohr Theory : (stability and conformations of cyclohexane)

To explain the stability of cycloalkanes beyond cyclopentane Sachse Mohr theory was introduced. The main postulations are.

1. Rings with Six or more carbon atoms are not planar but they are puckered.

2. These rings are called Strainless rings because the carbon atoms lie in different planes and normal Valency angle is retained.

3. The strainless conformations maintain normal tetrahedral bond angle of 109°28'.

Conformations of Cyclohexane :

4. The two extreme strainless multiplanar or puckered conformations of cyclohexane are the most stable chair form and the less stable boat form.

5. The twist - boat conformer is less stable than the chair form by about 5.5 K.cal/mole but is more stable than the boat form.

Chair form   Boat form   Twist- boat form
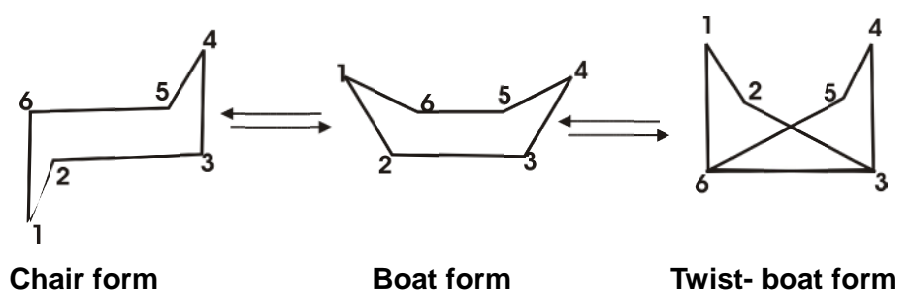
Conformations of cyclohexane :

6. The C-H bonds parallel to the axis of the ring are called axial bonds. They lie up or down to the ring carbon
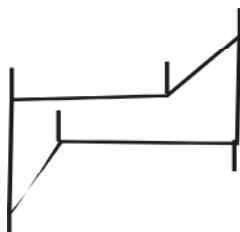
Axial Bonds

7. The C-H bonds making an angle of 109°28^{l} with the axis of the ring are called equitorial bonds. They lie in the plane of the ring carbons.
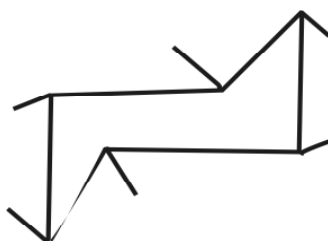
Equitorial bonds

8. Relative stability of chair and boat forms :

In chair form all the six C-H bonds of any two adjacent carbons are in skew position.

In boat form four C-H bonds of adjacent carbons are in skew position. The remaining two C-H bonds are eclipsed. These hydrogens are called flag pole hydrogens. They are present on C_1 and C_4.
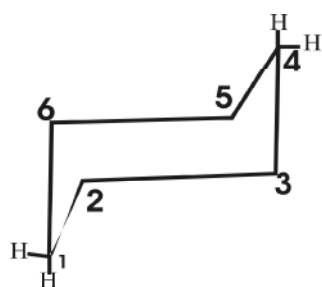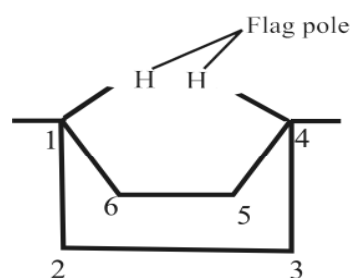
Chair form   **Boat form**

Hence chairform is more stable than boat form because electron repulsion is more in eclipsed hydrogens.

2.2.6 Pitzer Strain Therory : (Stability and Conformations of Cyclopentane)

1. In planar cyclopentane the angle of strain is almost neglisible. The distorted angle is 108° and it is practically free of strain.

2. In planar structure of cyclopentane all the 10 hydrogen atoms are eclipsed.

3. There is a strain because the hydrogen atoms can not take energitically preferable staggered conformation. This strain is called pitzerstrain.

4. Due to pitzer strain five membered ring is less stable than six membered ring.

5. Pitzerstrain is present in cyclopropane, cyclobutane and in medium size rings (8to11 membered).

6. In all cycloalkanes pitzer strain is operative .It can be relieved by non planar or pukered rings.

7. Conformations of cyclopentane :

The most important puckered structures of cyclopentane are envelope form and half chair form. This reduces the eclipsing and lowers the torsional strain.
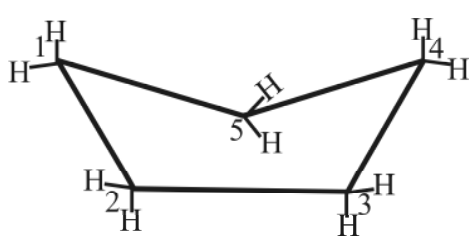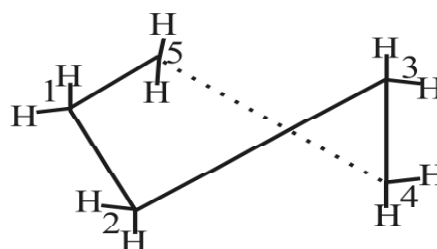
Envelope form   Half - Chair form

The puckered shape of cyclopentane is not fixed. It is dynamic. Electron diffraction studies showed that only four carbon atoms in cyclopentane are coplanar. The fifth carbon is out of plane.

2.2.7 Orbital picture of Angle Strain :(M.O.Theory)

 (stability and conformational structure of cyclopropane)

In cyclopropane the C-C-C bond angle is 60°.Thus the carbon atoms are not located in a position such that their Sp^3 orbitals point towards each other.
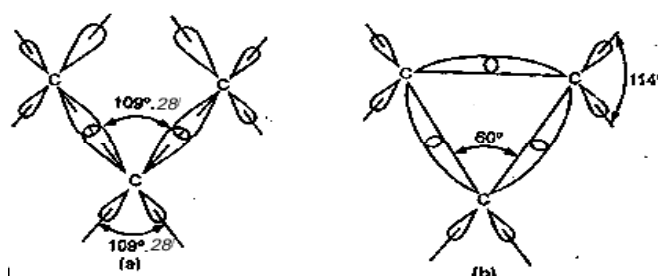
(a) Maximum overlap Sp^3 orbitals in open chain compounds.

(b) Poor overlap of Sp^3 orbitals in cyclopropane

Thus in cyclopropane, the overlap is less and C-C bonds formed are weak.

In short decrease in the stability of cyclopropane is due to poor overlap of atomic orbitals which is due to deviation in bond angle (angle strain) from 109°28$^|$ to 60°. The greater the deviation of the C-C-C bond angle from 109°28$^|$, greater will be the unstability.

Model Questions :

1. What are Cycloalkanes? How can cycloalkane be prepared? Explain it's activity with suitable reactions.

2. Give two methods of preparation and two reactions of cycloalkanes.

3. What is Bayer Strain Theory ? Explain.

4. What are the limitations of Bayer's Strain Theory ? How was it modified by sachse and Mohr?

5. Discuss the stability of cycloalkanes on the basis of molecular orbital theory.

6. Write notes on conformations of cyclohexane.

7. Cyclohexane is more stable than cyclopentane explain.

8. The carbon- carbon bonds in cyclopropane are weaker than those of propane. Explain this on the basis of molecular orbital theory.

9. What is pitzer strain ? Explain.

10. Describe general methods of preparation of cycloalkanes and write notes on their reactivity.

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UNIT - II

Lesson - 3

BENZENE AND ITS REACTIVITY

2.3.0 Concept of resonance, Resonance energy, Heat of hydrogenation, Heat of combustion of Benzene, mention of C-C bond lengths and orbital picture of Benzene. Concept of aromaticity - aromaticity (definiton), Huckel rule, application to Benzonoid (Benzene, Naphthalene) and Non-benzonoid compounds (cyclopentenyl cation, Cyclopentadienyl anion and tropylium cation) Reaction - General mechanism of electrophilic substitution, mechanism of nitration. Friedel Craft's alkylation and acylation. Orientation of aromatic substitution. Definition of ortho, para and meta directing gropus. Ring activating and deactivating groups like NO_2 and Phenolic). Orientation effect of (i). Amino, methoxy and methyl groups (ii) Carboxy, nitro, nitrile, carbonyl and sulfonic acid groups. (iii) Halogens (Explanation by taking minimum of one example from each type).

2.3.1 CONCEPT OF RESONANCE :

According to resonance theory benzene is regarded as a hybrid of the following canonical structures.

According to kekule each of the above structures should have independent existance. But according to resonance theory, the two structures have no independent existance but they contribute equally to the actual structure of benzene.

Resonance in benzene :

a) carbon - carbon bond length in benzene.

C - C (single) bond length is 1.54A°

C = C (double) bond length is 1.34A°

Carbon, carbon bond length in benzene is 1.39A°.

Thus it is in between that of a single bond (C-C) and a double bond (C=C).

b) Heat of hydrogenation :

Benzene has three double bonds. Heat of hydrogenation must be 85.8 K.cal. But heat of hydrogenation of benzene is 49.8 K.cal only. So, benzene has a resonance energy of 36K.cal/mole.
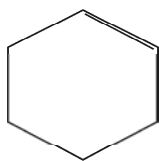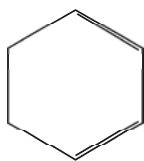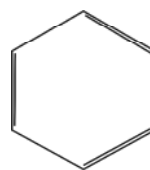
Cyclohexene	Cyclohex-1,3-diene	Benzene
ΔH obs. 28.6K.cal	(28.6x2) 57.2 K.cal	(28.6x3) 85.8 K.cal
ΔH cal. 28.6K.cal	55.4K.cal	49.8 K.cal

c) Heat of cobustion :

The calculated heat of combustion of benzene is 824.1K.cal. The actual heat of combustion of benzene is 789.1K.cal only. This suggests that benzene molecule is more stable by 35K.cal.

d) This peculiar behaviour of benzene is explained by valency bond theory or Resonance Theory. According to this theory benzene is the resonance hybrid of structures I and II.
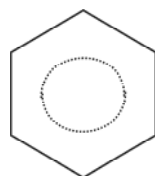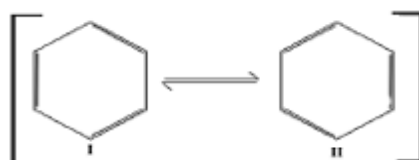
Resonance hybrid

Orbital picture of benzene : (molecular orbital theory)

CHO
|
CHO

In benzene the carbons are Sp2 hybridised. Bond angle is 120°. Symmetry is hexagonal. π electrons are delocalised forming an electron cloud above and below the plane of the ring.
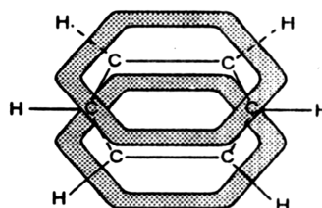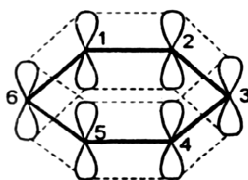
For convenience, benzene ring is generally represented as a regular hexagon containing a dotted line circle or a solid line circle.

(or)
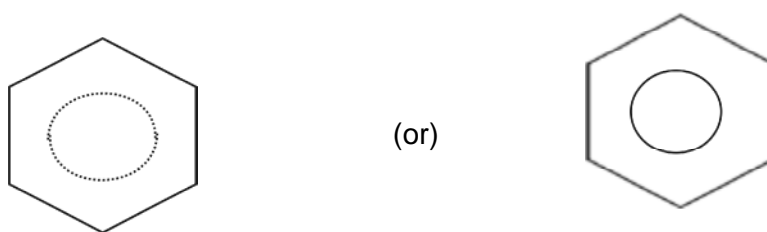
Representation of benzene ring

2.3.2 CONCEPT OF AROMATICITY

1. Definition :

The property of an unsaturated compound exhibiting unexpected stability and behaving as saturated compound is called aromaticity.

Ex. Benzene, Naphthalene.

2. Characteristic properties :

a) unusual stability

b) substitution rather than addition

c) Resistant to oxidation

3. Theoretical criteria : (Huckel (4n+2) rule)

The π clouds of molecules or ions containing (4n+2) π electrons show aromaticity where n=0,1,2,3....

Application to Benzonoid compounds :

1. Benzene
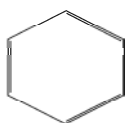
No.of π electrons = 6

$$= 4n+2 \text{ where } n = 1$$

$\therefore$ Benzene is aromatic

2. Naphthalene
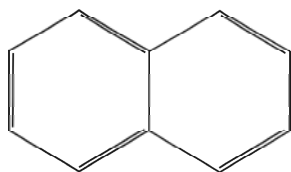
No.of π electrons = 10

= 4n+2 where n =2

∴ Naphthalene is aromatic.

3. Anthracene
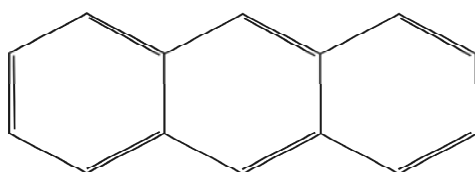
No.of π electrons = 14

= 4n+2 where n =3

∴ Anthracene is aromatic.

4. Phenanthrene
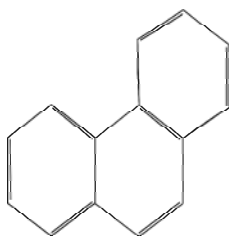
No.of π electrons = 14

= 4n+2 where n =3

∴ Phenanthrene is aromatic

Non-benzonoid compounds :

5. Cyclopentenyl cation:
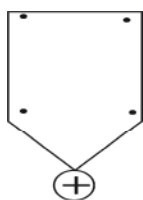
No.of π electrons = 4

$\neq 4n+2$

$\therefore$ Cyclopentenylcation is non-aromatic

6. Cyclopentadienyl anion :
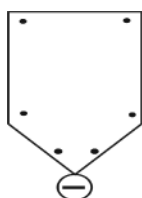
No.of π electrons = 6

= 4n+2 where n =1

$\therefore$ Cyclopentadienyl anion is aromatic

7. Tropylium cation : (cycloheptatrienyl cation)
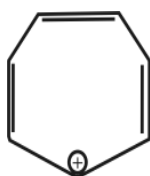
No.of π electrons = 6

= 4n+2 where n =1

$\therefore$ Tropylium cation is aromatic.

It may be noted that Huckel number 6 is the most common in aromatic system and hence the term aromatic sextet is commonly used for 6π electrons. Benzene is a perfect aromatic compound as it has 6π electrons over a flat hexagonal ring which has no angle strain at all in the molecule.

2.3.3 ELECTROPHILIC SUBSTITUTION :

The replacement of an atom or group attached to the carbon atom of the benzene ring by another atom or group is known as aromatic substitution.

Substitution reactions involving the attack of electrophiles are called electrophilic substitution reactions.

Ex : Benzene undergoes electrophilic substitution reactions.

Explanation : Due to the presence of the π electrons cloud above and below the plane of the ring benzene gets partially negative charge. It is easily attacked by electrophiles.

Thus aromatic compounds undergo electrophilic substitution reactions.

Mechanism : Aromatic electrophilic substitution proceeds through SE^2 mechanism.

Resonance of carbocation

Resonance hybrid

1. Nitration :
　　Formation of electrophile :

$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

Formation of carbocation :

　+ $NO_2^+ \longrightarrow$

　　Elimination of proton :

$\xrightarrow[+HSO_4^-]{}$ **+ H₂ SO₄**
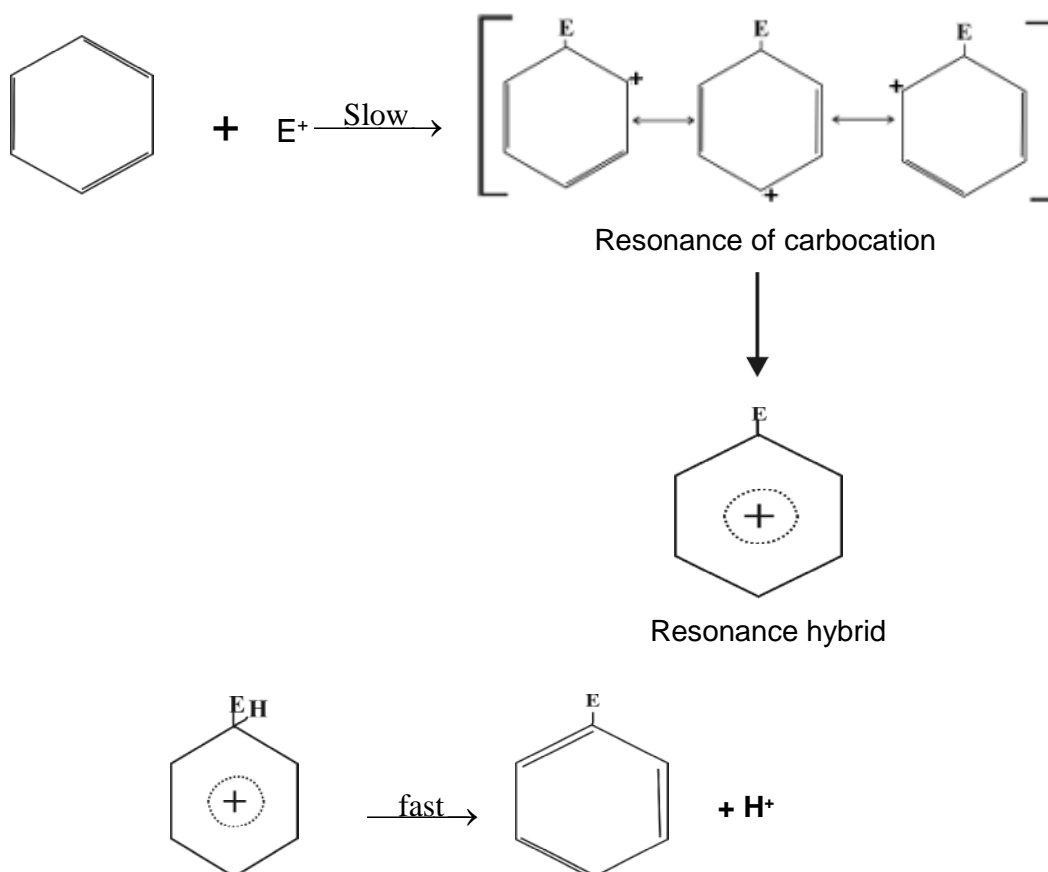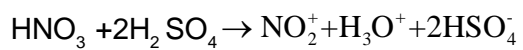
Nitrobenzene

2. Halogenation :
　　Formation of electrophile :
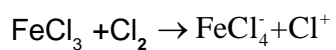
$FeCl_3 + Cl_2 \rightarrow FeCl_4^- + Cl^+$

Formation of carbocation :

　+ Cl⁺ $\longrightarrow$

Elimination of proton :

Chlorobenezene

3. **Friedel crafts Alkylation :**

Fromation of electrophile :

$$R - Cl + AlCl_3 \rightarrow R^+ + AlCl_4^-$$

Formation of carbocation :

Elimination of proton :

Alkylbenzene

4. Friedelcrafts Acylation :

Formation of electrophile :

R COCl +Al Cl$_3$ $\rightarrow$ $RCO^+ + AlCl_4^-$
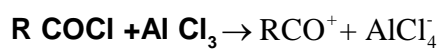
Formation of Carbocation :

Elimination of proton :

Acylbenzene

5. Sulphonation:

Formation of electrophile :

$2H_2SO_4 \rightarrow SO_3 + H_3O^+ + HSO_4^-$
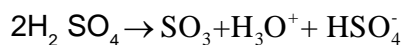
SO$_3$ is a neutral electrophile.

Formation of Carbocation :
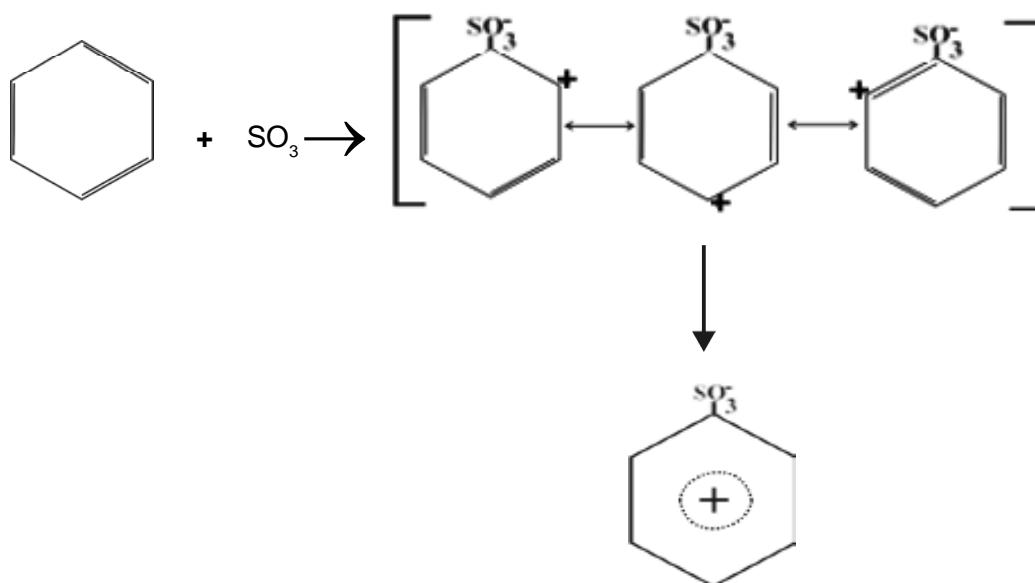
Elimination of proton :
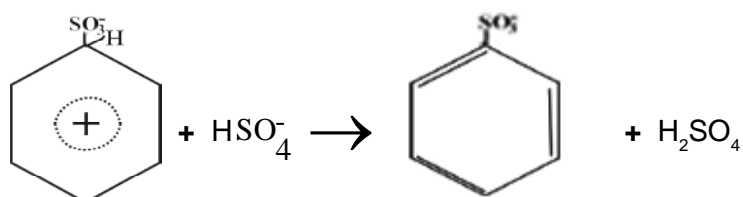
Reaction with hydroniumion :
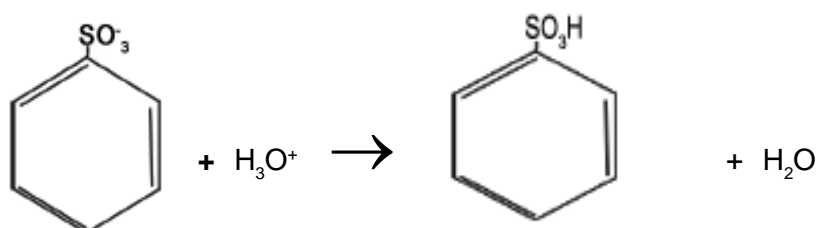
2.3.4 Orientation of Aromatic Substitution :

O-, m - and P - Postions :

In benzene adjacent positions are called ortho (1,2) alternate positions are called meta (1,3), Opposite positions are called para (1,4).
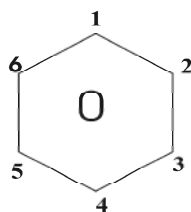
Orientation :

The influence of a group already present on the benzene nucleus towards the attacking group is called Orientation. This effect is called Orientation Effect.

Effect of electron releasing group (or) Ortho, Para orientation rule :

Electron releasing group activate ortho and para positions. So, the attacking electrophile is oriented to ortho and para positions. It is called ortho and para orientation rule.

R -, -ÖH, - N̈H$_2$, - Ẍ are electron relasing groups on benzene ring.

Ex : Phenol on nitration gives orthonitrophenol and paranitrophenol.

O-nitrophenol   P-nitophenol
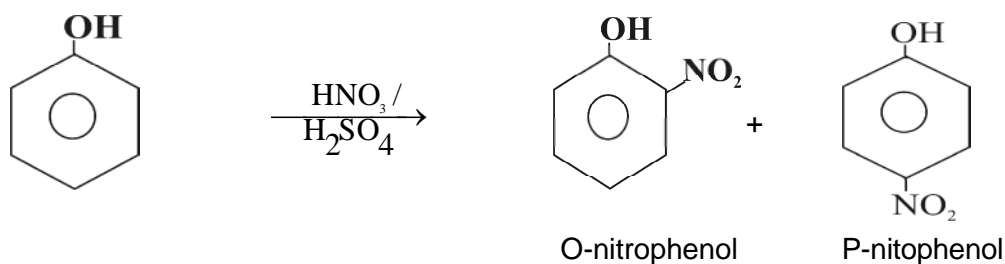
This is due to positive Mesomeric effect (+M).
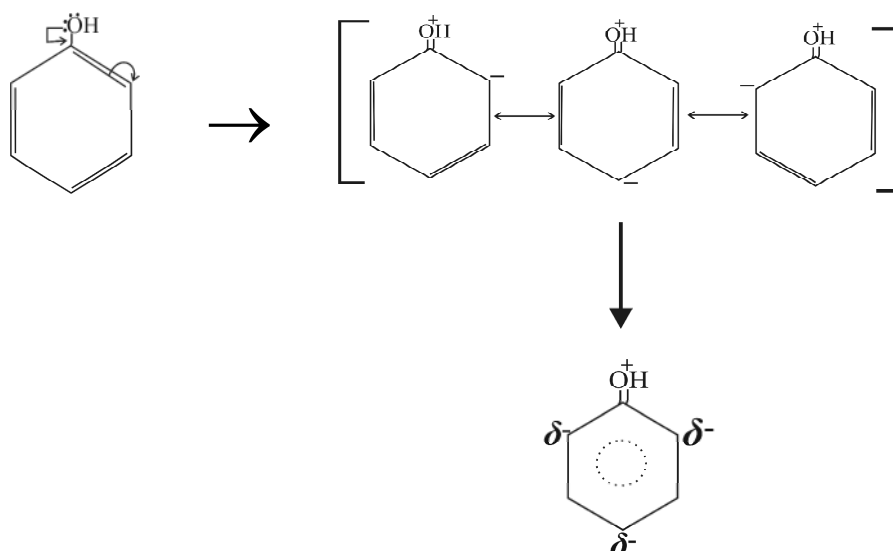
Mesomeric effect in O-, P- directing groups.

Here O- and P- Positions are activated. Hence these are activating groups

Electron withdrawing groups or meta -orientation rule :

Electron withdrawing group deactivates ortho and para positions. So, the attacking electrophile is oriented to meta position. It is called meta orientation rule.

Ex : Nitrobenzene on further nitration gives metadinitrobenzene.

m-dinitrobenzene
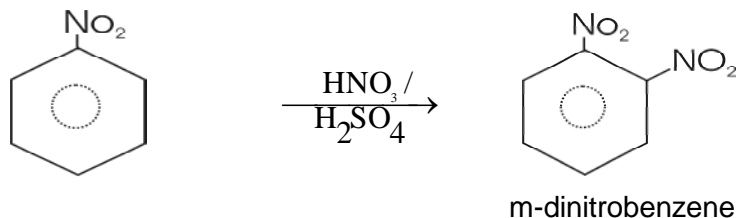
This is due to negative mesomeric effect (-M)
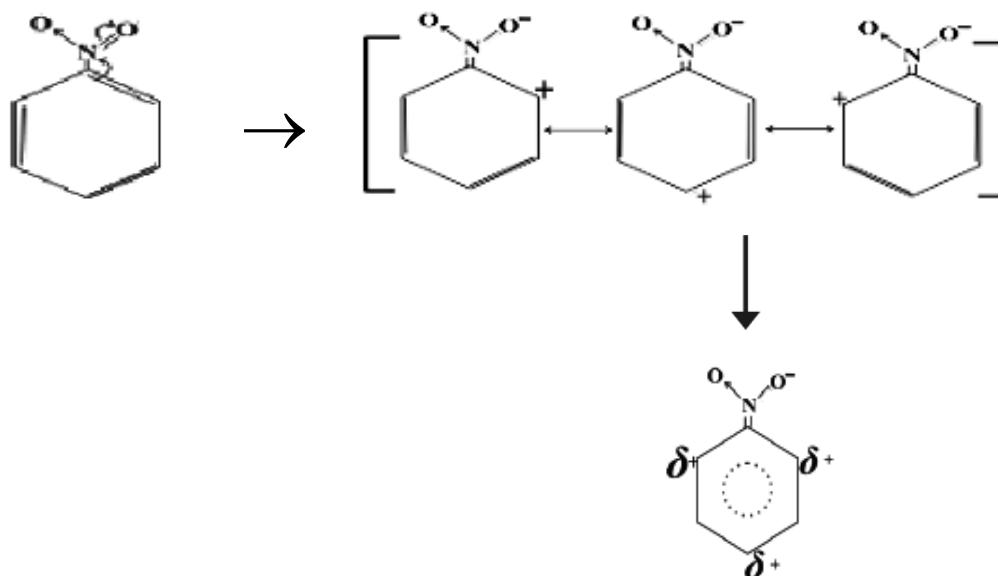
Mesomeric effect in m-directing groups.

Here O-and P-positions are deactivated. Hence these are deactivating groups.

2.3.5 ORIENTATION OF DIFFERENT GROUPS :

S.NO	Group	Electronic effects	Result	Oriention effect
1.	Amino (-NH$_2$)	+E, +M, -I	Strongly activating	O,P
2.	Methoxy (- $\ddot{\underset{\cdot\cdot}{O}}CH_3$)	+E, +M, -I	Strongly activating	O,P
3.	Methyl (-CH$_3$)	+I	weakly activating hyperconjugation	O,P
4.	Carboxyl (-COOH)	-E, -M, -I	Strongly deactivating	m
5.	Nitro (-NO$_2$)	-E, -M, -I	Strongly deactivating	m

6.	Nitrile (-CN)	-E, -M, -I	Strongly deactivating	m
7.	Carbonyl (>CO)	-E, -M, -I	Strongly deactivating	m
8.	Sulphonic acid (-SO$_3$H)	-E, -M, -I	Strongly deactivating	m
9.	Halogens (- $\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}$:)	+E, +M, -I	weakly deactivating	O,P

E   = electromeric effect

M   = Mesomeric effect

I   = Inductive effect

O,P = Ortho, Paradirecting

m   = metadirecting

The sum of mesomeric effect (M) and Electromeric effect (E) is called Tautomeric effect (T)

1   Amino (-NH$_2$) and Methoxy (-OCH$_3$) groups :

For Amino (-NH$_2$) and Methoxy (-OCH$_3$) groups the +T effect is more powerful than - I effect. Hence they are strongly activating groups orienting the attacking electrophile towards O-and P-Positions.
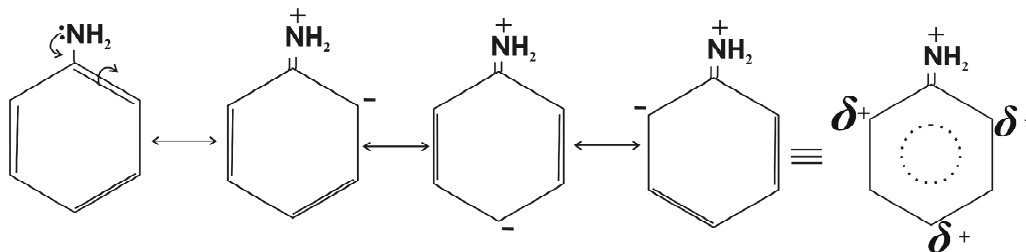
Mesomenic effect (+M) in O,P-dircting groups
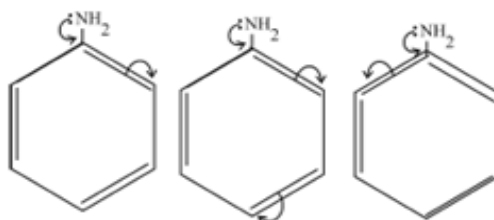
Electromeric effect (+ E)
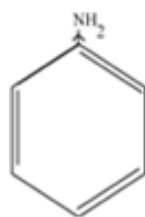
Inductive effect (-I)

Ex : 1. Aniline reacts with Bromine water forming 2,4,6- tribromoaniline.

2.

+ 3 Br$_2$ ⟶ + 3HBr
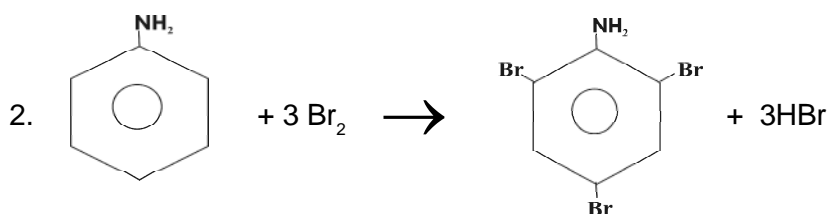
2. Methyl (-CH$_3$) group :

The O,P- directing effect of methyl group is due to inductive and hyperconjugation effects. Hyper conjugation effect is greatest in methyl group and lowest in t-butyl group.

  etc
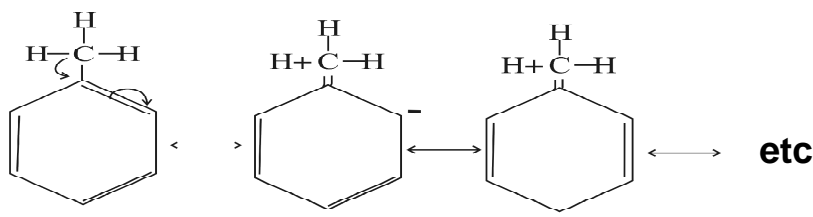
Hyper conjugation effect of Methyl group.

Inductive effect (+I)
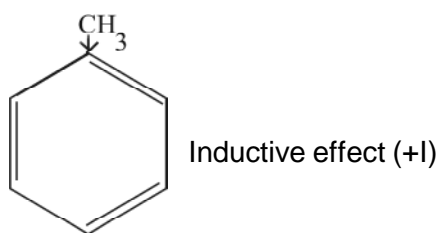
EX : Toulene on nitration with conc HNO$_3$ and Conc. H$_2$SO$_4$ at 60°c gives o-nitrotoulene and P- nitroloulene.

O-nitrotoulene   P-nitrotoulene
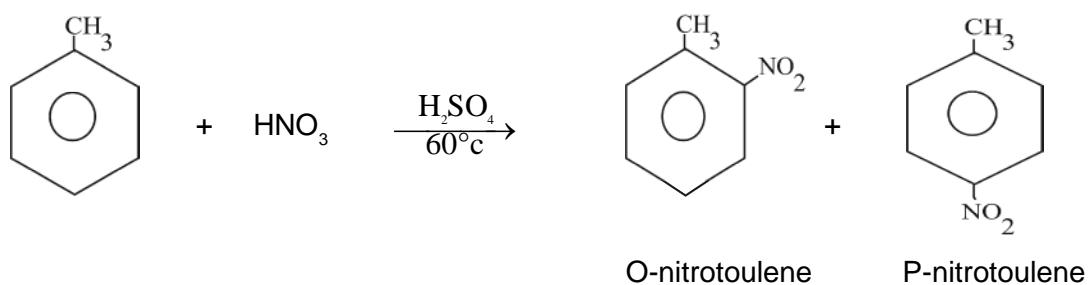
3. Carboxyl (-COOH), Nitro (-NO$_2$), Nitrile (-CN), Carbonyl (>CO) and Sulphonic acid (-SO$_3$H) groups :

Here the key atom of the substituent has a more electronegative atom linked by a multiple bond.

Carboxyl   Nitro   Nitrile   Carbonyl   Sulphonic acid
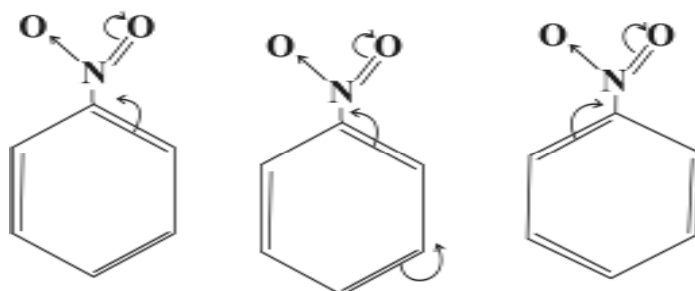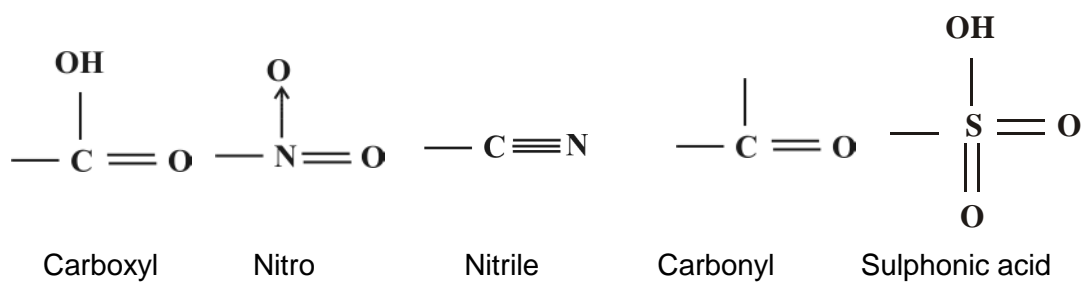
Electromenic effect (-E) of nitro group
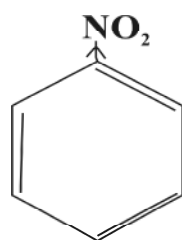
Inductive effect (- I)
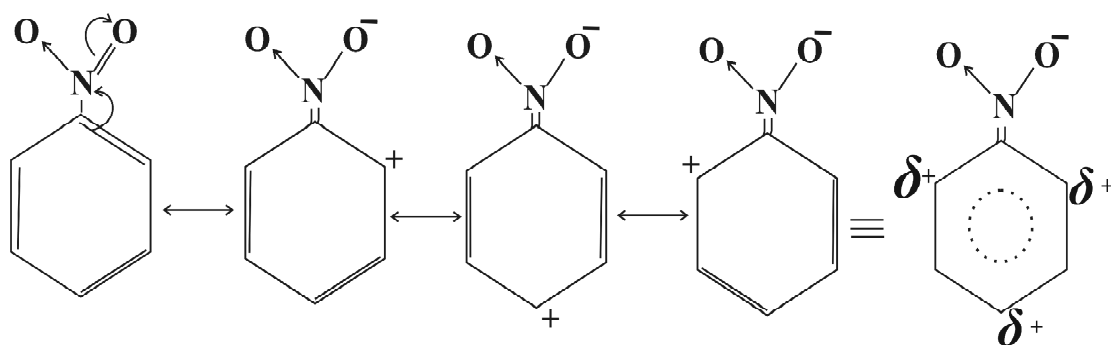
Mesomeric effect (-M) of nitro group

EX 1. Benzoic acid on nitration with Conc. HNO_3 and H_2SO_4 gives m-nitrobenzoic acid.
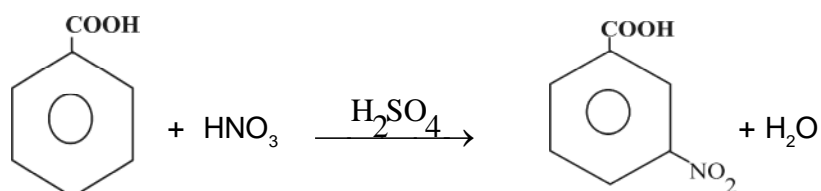
2. Nitrobenzene on further nitration with Conc.HNO_3 and Conc.H_2SO_4 gives m-dinitrobenzene.

Nitro-benzene   m-dinitrobenzene
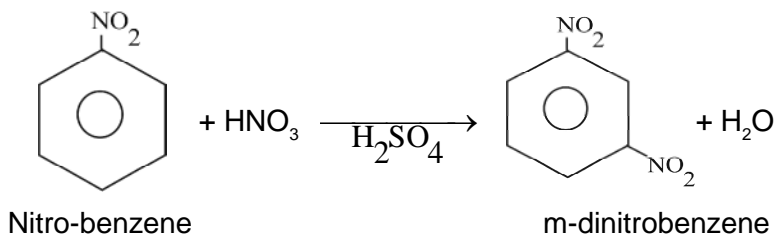
3. Benzaldehyde on nitration with Conc.HNO_3 and Conc.H_2SO_4 gives m-nitrobenzaldehydle.
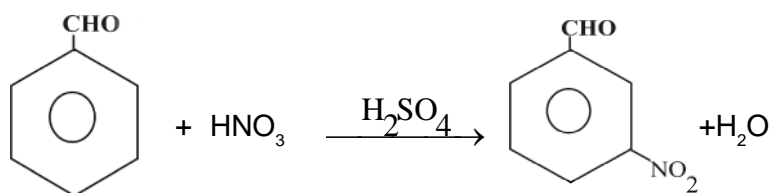
4. Acetophenone on nitration with Conc.HNO_3 and Conc.H_2SO_4 gives m-nitroacetophenone.
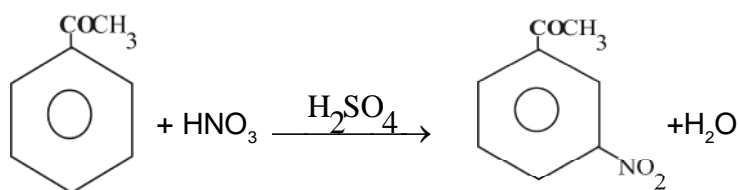
5. Benzene Sulphonic acid on nitration with Conc.HNO_3 and Conc.H_2SO_4 gives m-nitro benzene sulphonic acid.
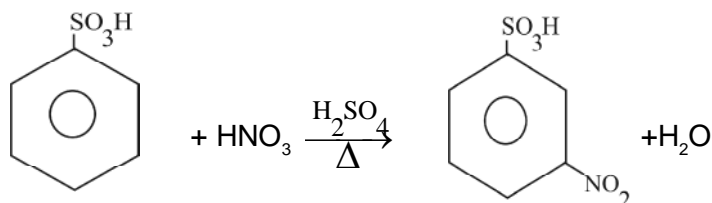
4. Halogen group (-X) :

Halogen group deactivates the ring due to strong inductive effect (-I). Here tautomeric effect is greater than inductive effect (+T>-I). Hence it is, O,P - directing and it is difficult to carry substitution in halobenzene than benzene because in benzene -I effect is absent.
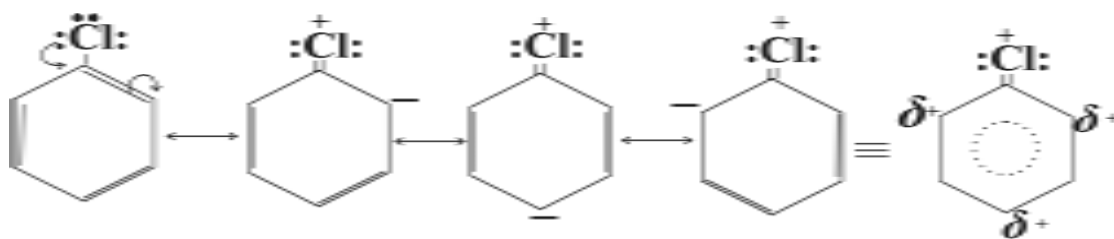
Mesomeric effect (+M) in chlorobenzene
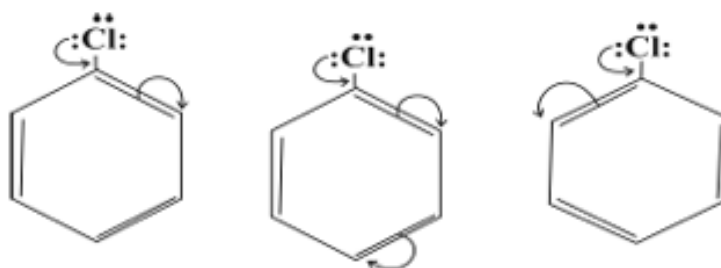
Electromeric effect (+E)
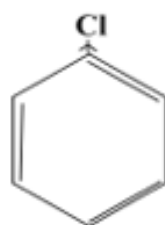
Inductive effect (-I)

Ex : Chlorobenzene on nitration with ConcHNO$_3$ and Conc.H$_2$SO$_4$ gives o- nitro chlorobenzene and P-nitrochloro benzene.
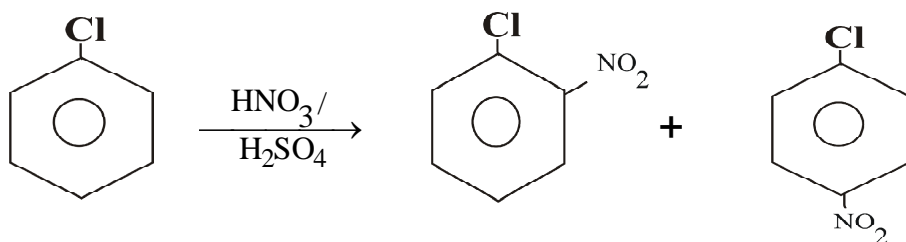
2.3.6 MODEL QUESTIONS :

1. Explain why benzene undergoes electrophilic substitution where as alkenes undergo addition.

2. Give general mechanism of electrophilic aromatic substitution. Explain with the two examples.

3. Discuss the structure of Benzene

4. Write notes on a) Heat of hydrogenation b) Orbital picture of Benzene c) Friedel crafts reaction

5. Explain aromaticity with Huckel 4n+2 rule.

6. Explain orientation in Benzene, reactivity and directing groups with examples.

7. Give the mechanism of Sulphonation of Benzene

8. Give the mechanism of nitration of Benzene

9. Apply Huckel 4n+2 rule to a) Anthracene b) Phenanthrene c) Cyclopentadienyl anion and d) Tropylium cation.

10. Give electronic interpretation of nitro and phenolic groups on benzene.

11. Discuss the directive influence of nitro, carbonyl, carboxy and sulphonic acid groups.

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UNIT - II

Lesson - 4

POLYNUCLEAR HYDROCARBONS

2.4.0 :

Structure of naphthalene and anthracene, (Molecualr orbital diagram and resonance energy) Any two methods of preparation of naphtalene and reactivity. Reactivity towards electrophilic substitution, nitration and sulfonation as examples.

2.4.1 Polynuclear hydrocarbons :

polynuclear hydrocarbons are compounds which contain two or more aromatic rings.

Ex :

Naphthalene   **Anthracene**
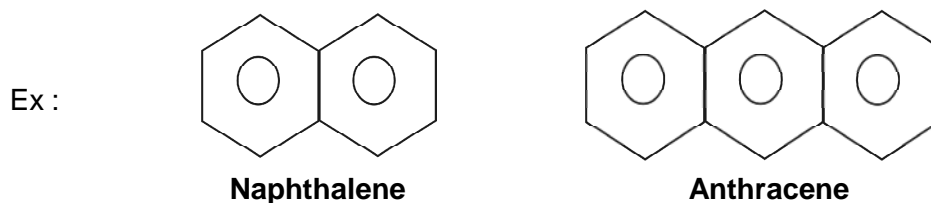
2.4.2 Naphthalene : (preparation and structure)

Manufacture : Middle oil fraction of coaltar on cooling gives naphthalene crystals. Crude naphthalene is seperated by centrifugation. It is melted and treated with conc. H_2SO_4 to remove basic impurities. It is washed and treated with aqueous alkali to remove acidic impurities. Finally it is purified by sublimation.

Structure:

1. Molecular formula is $C_{10}H_8$.

2. Naphthalene on nitration gives nitronaphthalene which on oxidation gives 3- nitrophthalic acid.
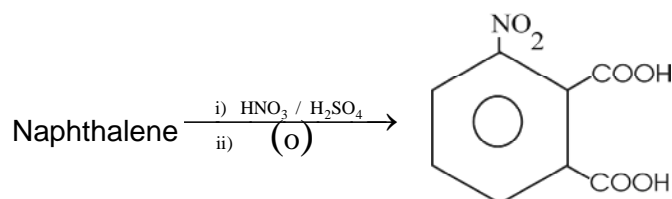
3. Nitronaphthalene on reduction gives aminonaphthalene which on oxidation gives phthalic acid.

Nitronaphthalene $\xrightarrow{\substack{\text{i) Reduction} \\ \text{ii) Oxidation}}}$
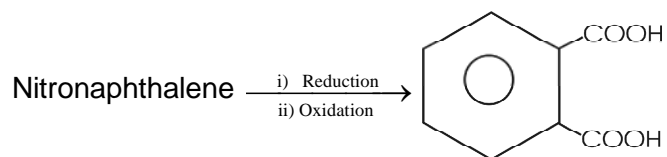
4. Hence in naphthalene the two benzene rings are fused in ortho-positions.
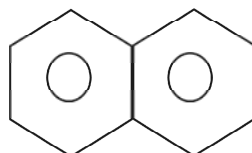
Napthalene

5. The above reactions are explained as :

3- nitrophthalic acid

reduction

(O)

Phthalic acid
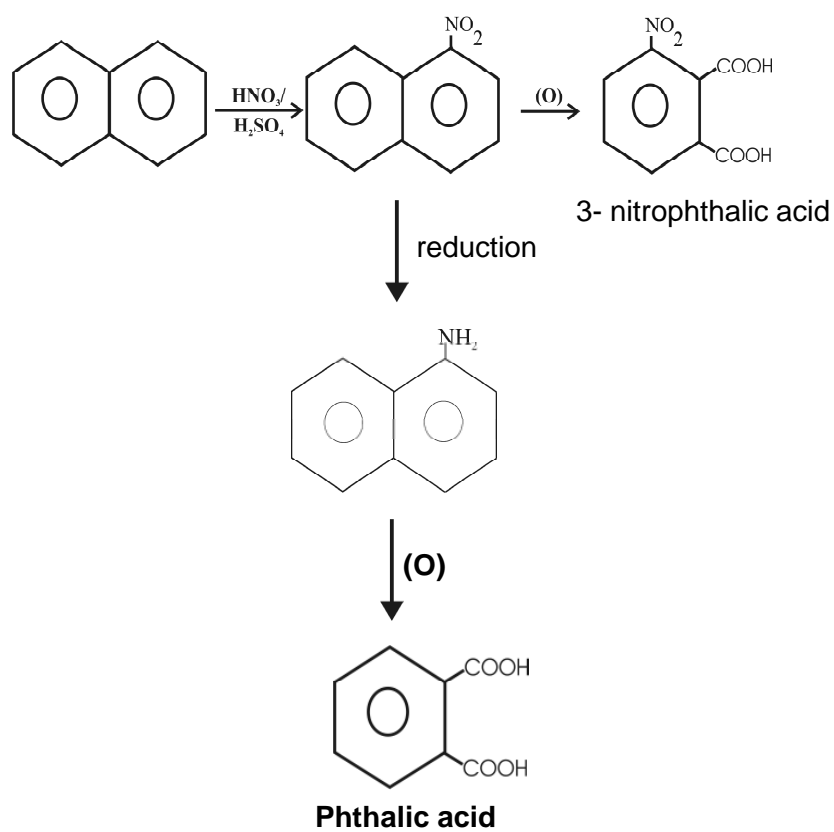
6. Resonance energy:

The resonance energy of naphthalene is 255KJ/ mole. This is slightly less than that of benzene (150KJ/mole). So naphthalene is relatively less aromatic than benzene. It is resonance hybrid of the following structures.

Resonance in naphthalene

Resonance hybrid
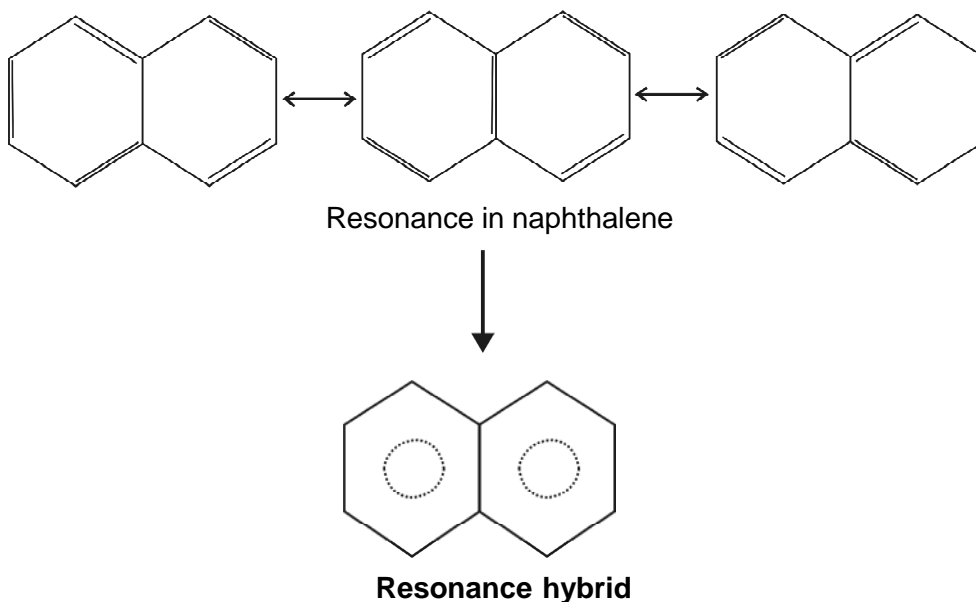
7. Molecularorbital diagram :

In Naphthalene each carbon atom is sp^2 hybridised. C- C bonds are formed by σ Sp^2 -Sp^2 overlapping and C-H bonds are formed by σ Sp^2 - S overlapping . All the ten carbons and eight hydrogens lie in the same plane. The 10π electrons are delocalised forming an electron cloud above and below the plane of the ring and satisfy Huckel $4n + 2$ rule when n= 2 .

Haworth synthesis :

Benzene + Succinic anhydride

$\xrightarrow{AlCl_3}$

$\xrightarrow[\text{HCl}]{\text{Zn Hg}}$

$\xrightarrow{\text{Conc. } H_2SO_4}$

$\xrightarrow[\text{HCl}]{\text{Zn Hg}}$ Tetralin

$\xrightarrow[\text{- 4H}]{\text{dehydrogenation}}$ Naphthalene
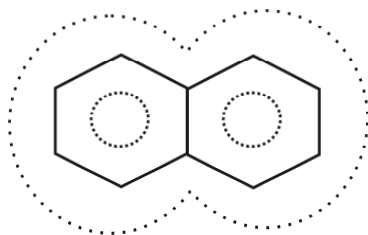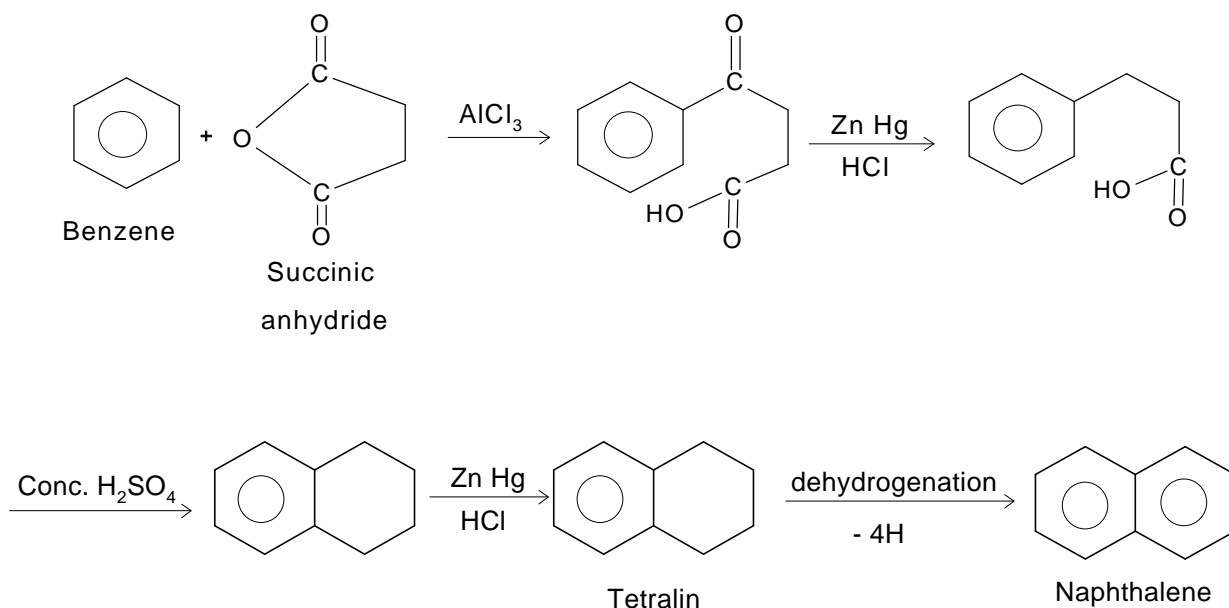
2.4.3 Electrophilic substitution in naphthalene:

Reactivity :

Napthalene resembles benzene in its chemical reactivity. It is more reactive and undergoes electrophilic. It is more reactive and undergoes electrophilic substitution reactions easily than benzene. It shows addition reactions also like alkenes.
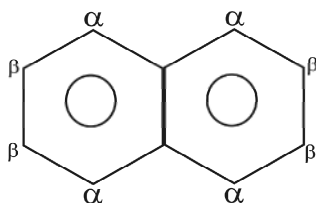
Two substitutions are possible in naphthalene, These are named as α - and β or 1- and 2-substitutions. Activation energy of α - isomer is less than that of β - isomer. So , at low temperature α - substitution occurs whre as at high temperature β - substitution takes place.

Ex: sulphonation :

α - napthol

β - napthol
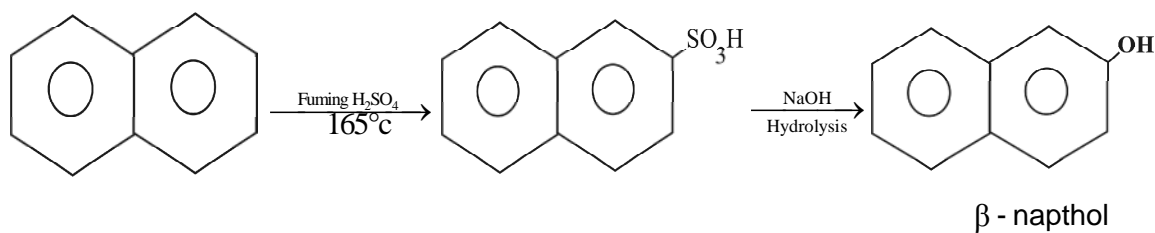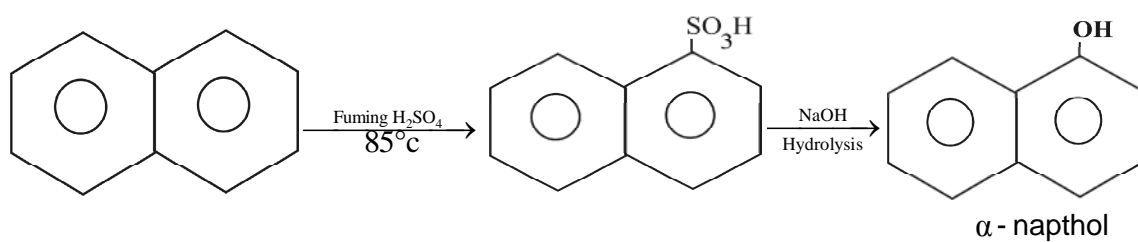
In naphthalene α - substituion is easy than β - substitution because two stable bezonoid resonance structures are possible in α - substituion where as only one stable benzonoid resonance is possible in β - substitution.

Stable (Benzonoid)   stable(Benzonoid)   Unstable
(non- benzonid)
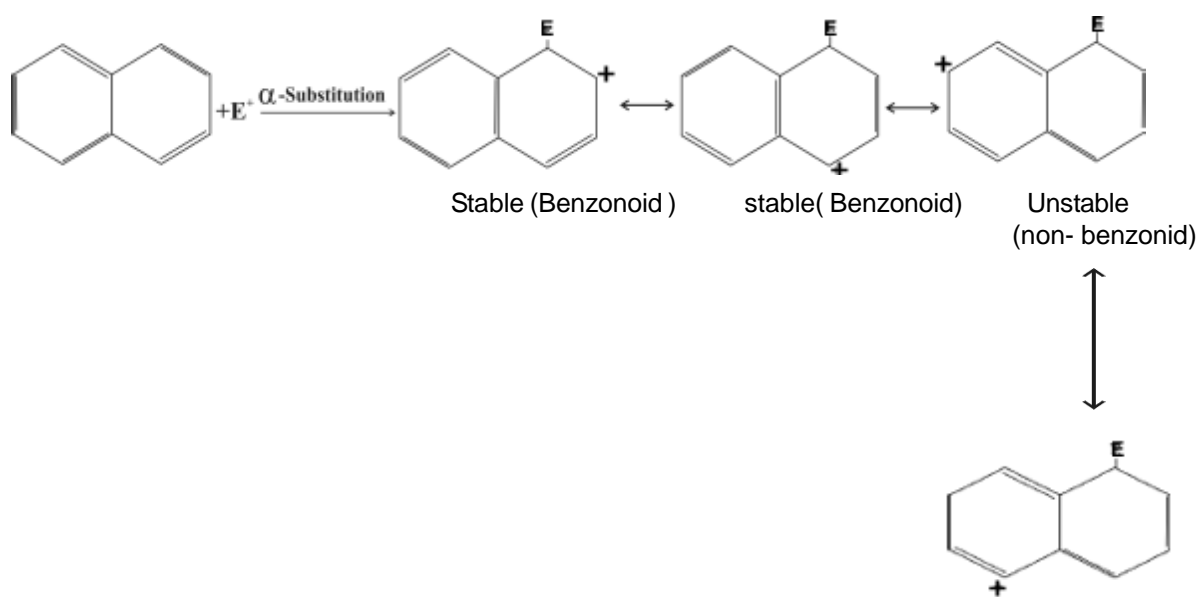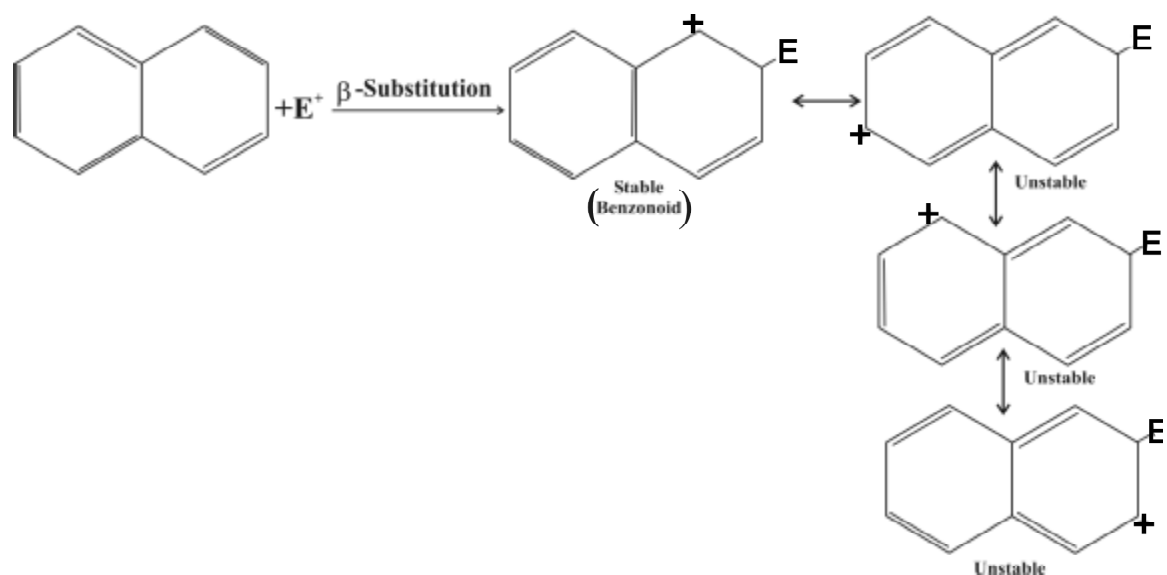
Ex :Nitration :

Naphthalene on nitration at low temperature gives α -nitro naphthalene. Since $-NO_2$ group deacivates the ring. Further nitration gives 1,8 - and 1,5- dinitro napthalene.
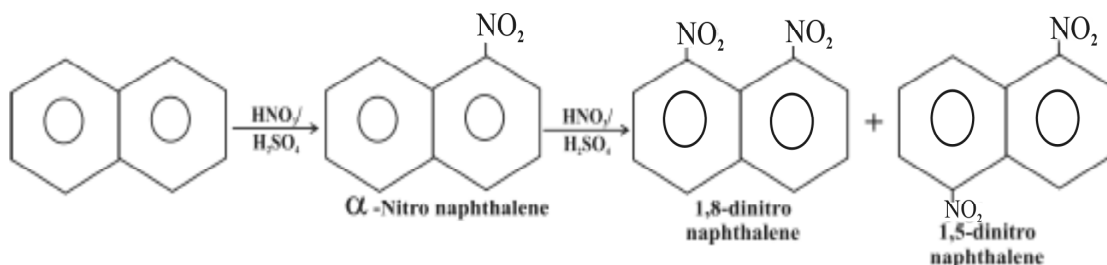
2.4.4 Anthracene : (preparation and structure)

Isolation : Anthracene crystallises out when anthracene oil fraction of coal tar is chilled. It is seperated by filtration and washed with solvent naphtha to remove phenanthrene. Then it is washed with pyridine to remove carbazole. This gives 50 % anthracene.pure anthracene is obtained by sublimation.

structure:

1.Molecular formula is $C_{14}H_{10.}$

2.It undergoes typical electrophilic aromatic substitution reactions such as nitration, sulphonation etc. This shows its relation to benzene and naphthalene.

3. $C_{14}H_{10}$ $\xrightarrow{Br_2}$ $C_{14}H_9$ Br $\xrightarrow[\text{fusion}]{\text{KOH}}$ $C_{14}H_9$ OH

    Anthracene   bromoanthracene   hydroxyanthracene

$\xrightarrow[\text{Oxidation}]{(O)}$

Phthalic acid   **O-benzoyl benzoic acid**
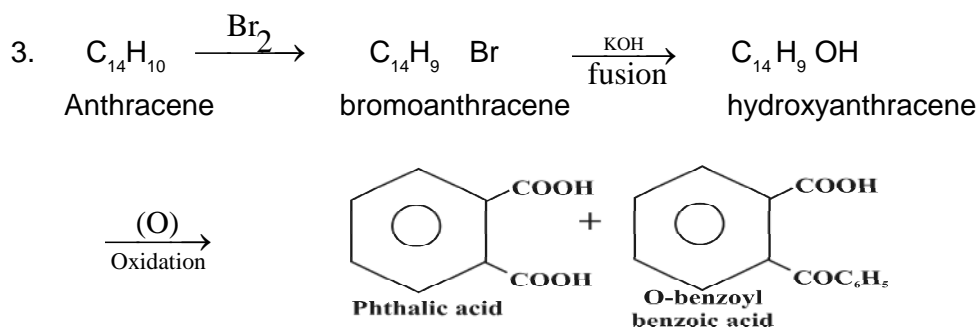
The formation of o- benzoyl benzoic acid indicates the skeleton structure of anthrancene as

4. $C_{14}H_{10}$ $\xrightarrow[V_2O_5,300°c]{(O)}$ Anthraquinone $\xrightarrow[\text{fusion}]{\text{KOH}}$ **2**
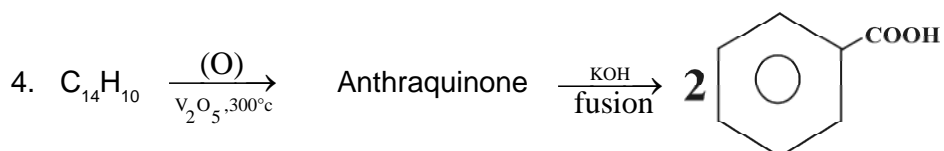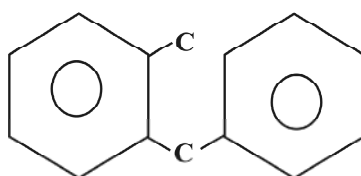
The formation of two molecules of benzoic acid indicates the presence of at least two benzene rings in anthracene

5.An thracene adds with seven molecules of hydrogen to form phenanthrene

$$C_{14}H_{10} + 7H_2 \quad \rightarrow \quad C_{14}H_{24}$$

    Anthracene   Phenanthrene
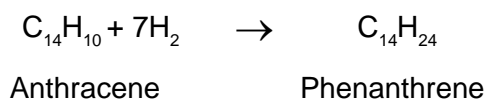
∴ It contains seven double bonds

6.Anthracene gives three monosubstituted and fifteen disubstituted isomers.

To explain this the structure of anthracene is written as
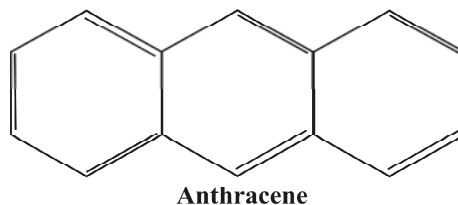
Anthracene

7.Resonance concept:

The resonance energy of Anthracene is 351 K.J/mole . This is 50 KJ more than the resonance energy of two benzene rings. Hence anthracene is more reactive than benzene. It is considered as the resonance hybrid of the following structures.

Resonance hybrid
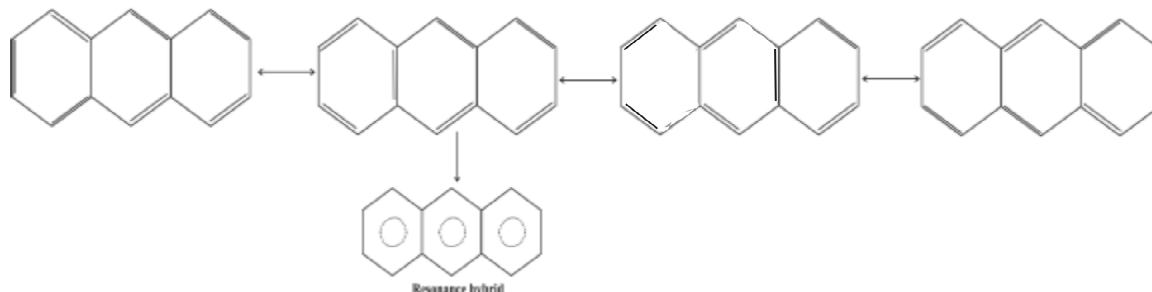
8. Molecular orbitial concept:

All the 14 carbons in anthrancene are sp^2 hybridised . C-C bonds are formed by σ Sp2-Sp2 overlapping and C-H bonds are formed by σ Sp2 -S overlapping . The fourteen carbons and ten hydrgens lie in one plane .The 14 π electrons in anthracene are delocalised forming an electron cloud above and below the plane of the ring and satisfy Huckel 4n+ 2rule when n=3
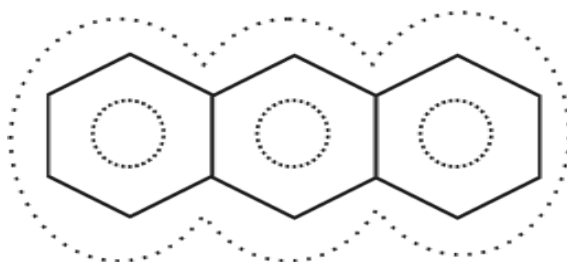
M.O.Picture of anthracene.

2.4.5 Electrophilic substitution in anthracene.
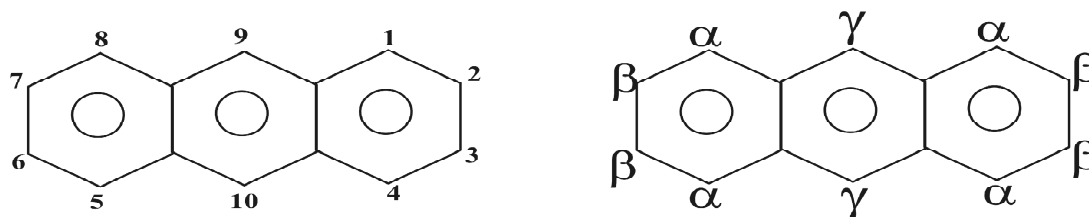
Anthracene has three kinds of carbon atoms.1,4,5 and 8 position are called α -, 2,3,6 and 7 positions are called β -, 9and 10 positions are called γ - . so,three isomers are possible in monosubstitution.

Attack at α -Carbon :

Contains naphthalene system
less favoured

Attack at β -Carbon :

Contains naphthalene system
less favoured

Attack at γ -Carbon :
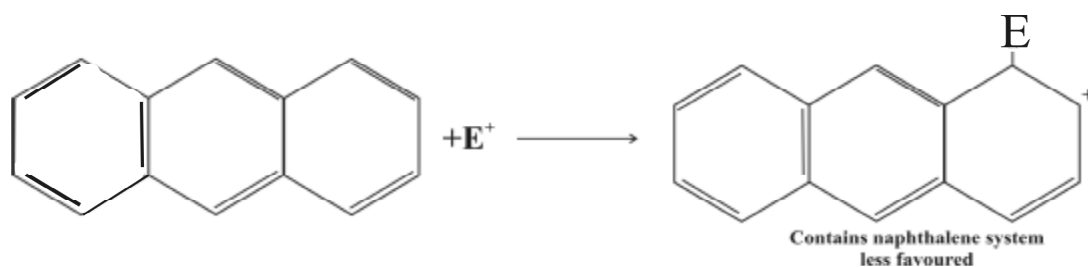
Contains two benzene rings
more favoured
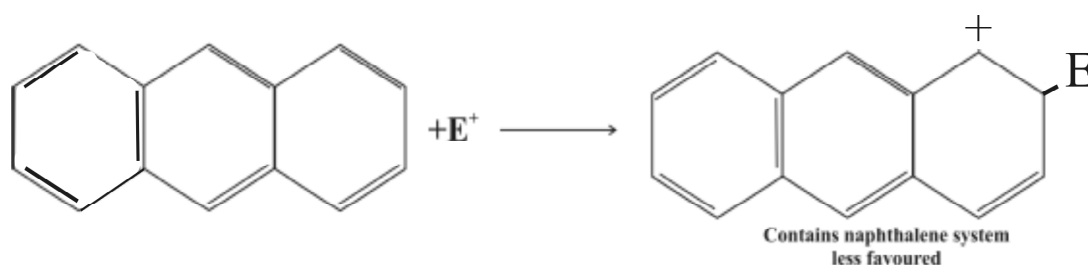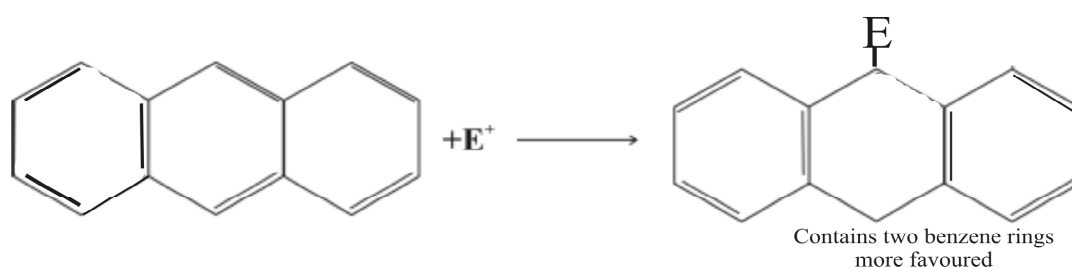
The carbonium ion intermediate with two benzene rings is more favoured because resonance energy of two benzene rings (302KJ) is more than that of naphthalene (252KJ). Thus attack at γ -carbon (9 and 10positions) is favoured.

Ex.: Nitration : Anthracene on nitration with conc.HNO_3 and acetic anhydride at room temperature gives 9- nitroanthracene and 9,10 - dinitroanthracene.

Anthracene   9-Nitroanthracene   9,10-dinitroanthracene
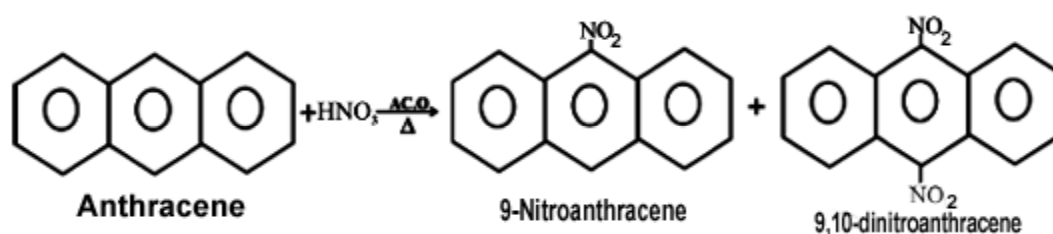
But substitution takes place at α - and β - carbons when the reaction is reversible.

Ex. Sulphonation : Anthracene on sulphonation with conc. H_2SO_4 gives a mixture of 1-anthracene sulphonic acid at low temperature and 2- anthracene sulphonic acid at high temperature.
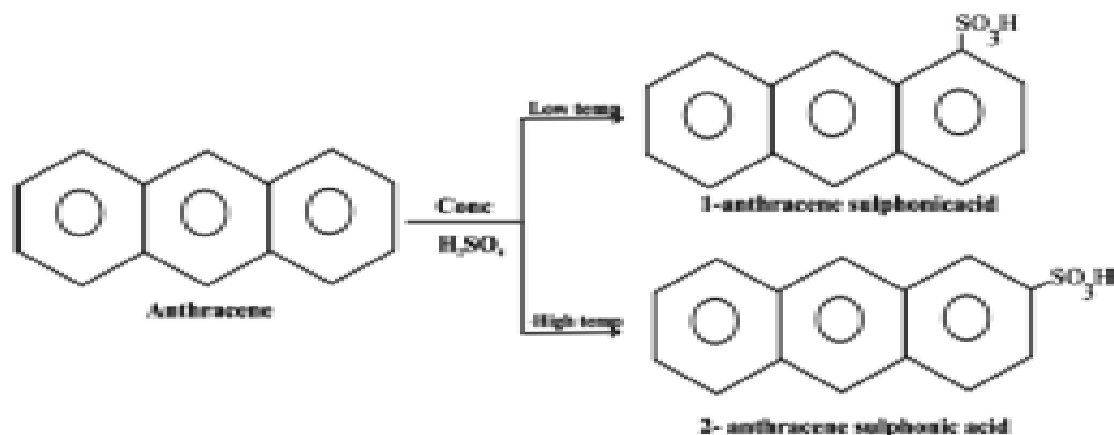
2.4.6 Modal Questions :

1. What are polynuclear hydrocarbons? Discuss the structure of naphthalene

2. In naphthalene α - substitution is easy than β - substitution why ?

3. Describe important reactions of naphthalene.

4. How do you synthesise α - naphthol and β - naphthol from naphthalene .

5. Explain stability and reactivity of naphthalene.

6. Discuss the structure of anthracene.

7. Describe the isolation and important reactions of anthracene.

8. Explain the stability and reactivity of anthracene.

9. Describe important reactions of anthracene.

10. Write molecular orbitals diagram and resonance in naphthalene.

11. Write resonance concept and molecular orbital concept of anthracene.

12. In anthracene substitution at 9- and 10 – positions take place. Explain.

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UNIT – III

Lesson – 1

LIQUID STATE

3.1.1 Depending on the nature and experimental conditions, we know that matter exists in three different forms namely solid, liquid and gaseous states. Liquid state is an intermediate state that exists between the gaseous and the solid states. The gas has neither a definite shape nor a definite volume. In the solid state there exists a strictly ordered arrangement of its atoms or ions or molecules which are fixed in position and have no translational motion. The molecules in solid state are in contact and possess a definite shape ad a definite volume. The liquid state is intermediate in character between the complete randomness of molecules characteristic of gases and the orderly arrangement of molecules typical of solids. IN a liquid the molecules are not as rigidly fixed as in solids and hence have some freedom of motion. So a liquid has a definite volume but not a definite shape. In terms of kinetic molecular model of the liquids the liquid is made of molecules that are closely packed and are in constant random motion. The inter molecular forces between the molecules of a liquid are stronger than those of gases and keep the molecules confined to a definite volume. The forces are not stronger enough to hold the molecules in fixed positions. In terms of these attractive forces it is possible to explain surface tension, viscosity, vapour pressure and heat of vapourization of liquids. Since the molecule in a liquid are in a state of random motion, most of the space in the liquid is occupied by its molecules leaving a small fraction of space for their free movement.

(a)   **(b)**

Fig 1.1   **Fig 1.2**

(c)
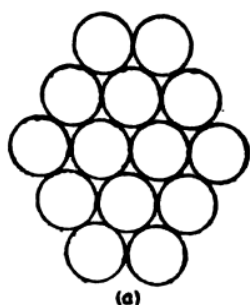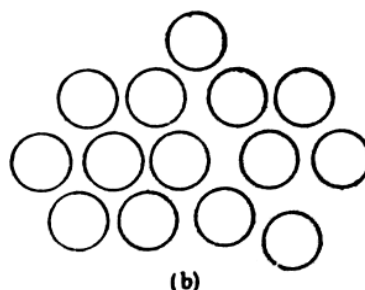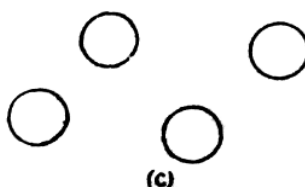
Fig 1.3
The relative spacing of molecules in

(a) Solids (b) Liquids and (c) Gases

This explains the incompressibility, higher density and show diffusion of liquids when compared to gases. The average kinetic energy of the molecules in a liquid is proportional to its absolute temperature.

Intermolecular Forces :

Most of the physical and chemical properties of substances i.e. gases, liquids and solids depends on intermolecular forces i.e how the molecules exert force on one another. The nature and magnitude of inter molecular forces present between the molecules decides most of the characteristic properties of the liquids.

These forces are some times known as cohesive or vanderwaals forces. These inter molecular attaractive forces are weak and are of two types namely vanderwaals attractive forces and (2) Hydrogen bond. The vanderwaals attractive forces are of three types.

Vanderwaals attractive forces :

1. Dipole - dipole attractions.

2. Dipole - induced dipole attractions.

3. Induced dipole - induced dipole attractions.

1. Dipole - dipole attractions :

Though polar molecules are neutral still they have permanent dipoles. certain covalent bonds are polar. Due to polarity of individual bonds, the entire molecule may have seperated centres of positive and negative charge. The molecule that possess polarity constitutes a dipole.

Dipole

Fig 1.4 Neutral and Polar Molecules

The vanderwaals forces that arise in these molecules are mainly due to electrical interaction between the positive pole of one molecule and negative pole of another molecule. Such type of interaction is known as dipole -dipole interaction. The magnitude of this type of interaction depends on the dipolemoment of the molecule. The polar molecules possess dipolemoment. Due to the dipole moment, the polar molecules tend to be oriented in an electrical field.
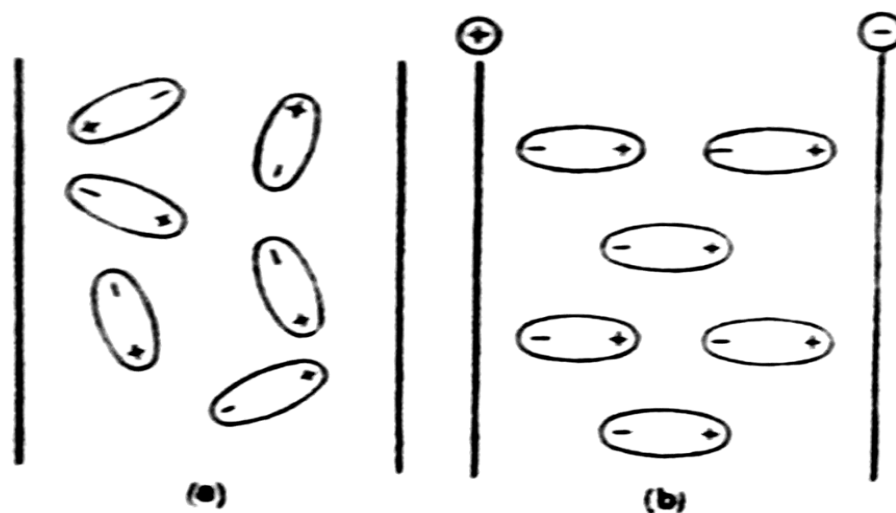
Fig 1.5 Orientation of polar molecules in an electric field
(a) Field off ; (b) Field on
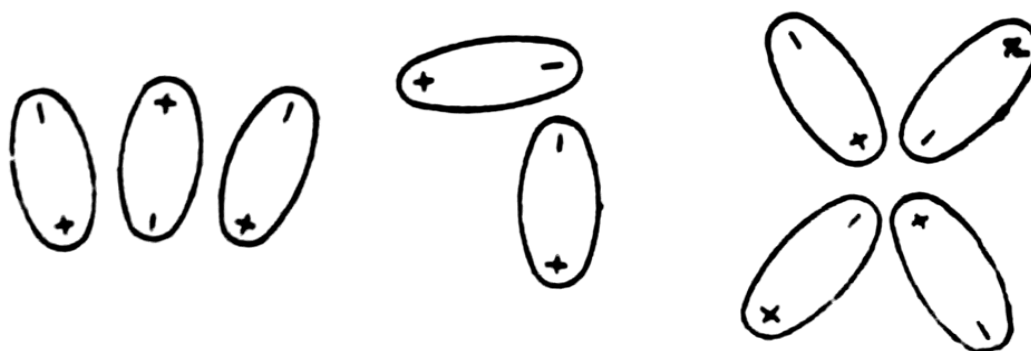
Fig 1.6 Dipole - Dipole attraction lead to the orientations

Greater the dipolemoment, greater is the dipole - dipole interaction. For example, NH_3 and H_2O have dipolemoments 1.49D and 1.85D respectively. The intermolecular forces of attractions are stronger in H_2O than in NH_3. Hence though both have nearly the same molecular weight, H_2O has higher m.pt and b.pt than NH3. The magnitude of dipole - dipole forces are smaller when compared to ion - ion attractions or ion - dipole attractions.

Gases like NH_3, SO_2, HF, HCl has permanent dipoles. Under similar conditions of temperature and pressure, the intermolecular distances are very large, the dipole - dipole forces among the gaseous molecules are very small. When there is increase in pressure or decrease of temperature the distance among the molecules gets decreased i.e. the molecules come closer as a result of it, the intermolecular forces of attraction increases and the gas changes into a liquid or solid.

2. Dipole - induced dipole attractions.

This type of interaction occurs in a mixture of polar and non- polar molecules. The polar molecule induce polarity in a non polar molecule by disturbing their electron system. The positive charge centres of the polar molecules attract the electron cloud of the neutral molecule as a result of which it gets displaced. Thus polarity is developed in the neutral molecules. The induced dipole undergoes interaction with the dipole of the polar molecule and hence the two molecules are attracted together.

3. Induced dipole - induced dipole attractions.

London forces:

In the case of non polar molecules there exists weak forces of attraction between them. These weak forces of attraction are called London forces. If a molecule is considered the electrons in it are constantly moving. If in a molecule the electrons are concentrated on one side than the other side, the molecule becomes momentarily a polar and it is called as instantaneous dipole. The negative side of instantaneous dipole repels the electrons of an adjacent molecule and as a result the second molecule becomes a dipole by induced polarity. This is called an induced dipole. The instantaneous dipole and the induced dipole molecules will attract each other. Since the electrons are keep moving , an instantaneous dipole may vanish the next moment and a new one is produced. This continuous process produces a weak attraction between molecules of a liquid. The moment attractions between the molecules of a liquid caused by instantaneous dipole and induced dipole attractions are called London forces. The strength of London forces depends up on no of electrons in a molecule and size of the molecule
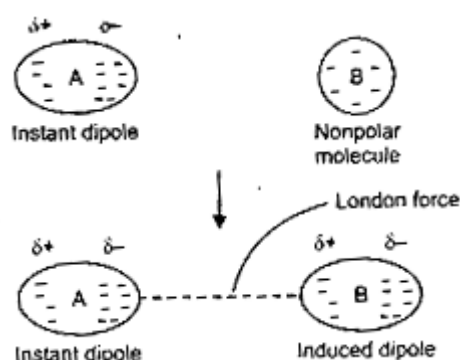
Fig 1.7 Explanation of London forces.

Hydrogen bonding :

Hydrogen bonding is a weak force of attraction between hydrogen of one molecule and electronegative element of another molecule. Whenever hydrogen is present between two electronegative elements it bonds with one electronegative element through covalent bond and with the other by weak force of attraction. This weak force of attraction is called hydrogen bonding. The electronegative elements, O, N and F involve in hydrogen bonding. Compounds having O-H, N-H and H-F bonds exhibit hydrogen bonding.

The hydrogen bonding in water molecule can be represented as follows

$$-\delta \quad +\delta \qquad -\delta \quad +\delta \qquad -\delta \quad +\delta$$

O —— H ·········· O —— H ·········· O —— H

| | |

H H H
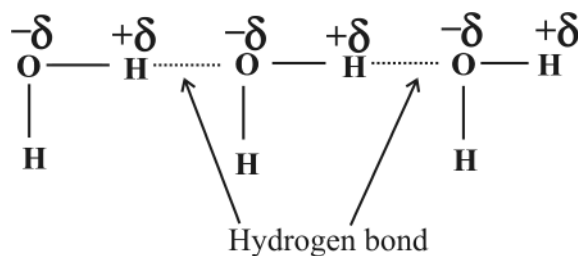
Hydrogen bond

In water O-H bond is highly polar .Due to greater electronegativity of oxygen, the electron pair in O-H bond shifts more close towards oxygen. So oxygen gets partial negative charge and hydrogen gets partial positive charge, same is the case with all O-H bonds in all water molecules. The positively charged H in one molecule is attracted by negatively charged O in another molecule and this force of attraction is hydrogen bond. The hydrogen bonding is the strongest of all inter molecular forces including the dipole –dipole attractions and London forces. Hydrogen bond is weaker than normal covalent bond but it is stronger than Vander waal's forces of attraction. A substance having hydrogen bonding will have high boiling point when compared to another substance having no hydrogen bonding with the same molecular weight. A substance having hydrogen bonding is soluble in another substance having hydrogen bonding. For example ethyl alcohol is soluble in water because of hydrogen bonding.

3.1.2. Structure of liquids :

In solids, there is a close packing of molecule or atoms or ions. The intermolecular forces are strong enough to hold them together. The ordered arrangement of the molecules or atoms or ions of a solid extends over a large distance and hence it is called as long range order. Hence, Solids exhibits both long range order and short range order.

In liquids, There is a little space between the molecules. This intermolecular space in a liquid contains molecular sized holes. The liquid is considered as a random congregation (union) of molecules and holes. The forces in liquids are stronger than those in gases. In terms of the arrangement of the constituents a liquid exhibits only a short range order. In gases, there is no possibility for any kind of ordered structure. In a gas, the molecules have complete random motion and the intermolecular forces are small and are effective only at short distances.

When a crystal melts, there is an increase in volume of about 10%. The molecules in the liquid state still remain in the vicinity of the other molecules surrounding them. The intermolecular forces tend to decrease with increase in the distance between the molecules. The short range forces exist while the long range forces are neglisible. The ordered arrangement in the crystal is not completely destroyed on melting.

Liquids may be regarded to have a structure similar to that of a crystal with a difference that the ordered arrangement extends over a short region instead of over the whole mass. The short range order in a liquid structure continuously changes because of the thermal motions.
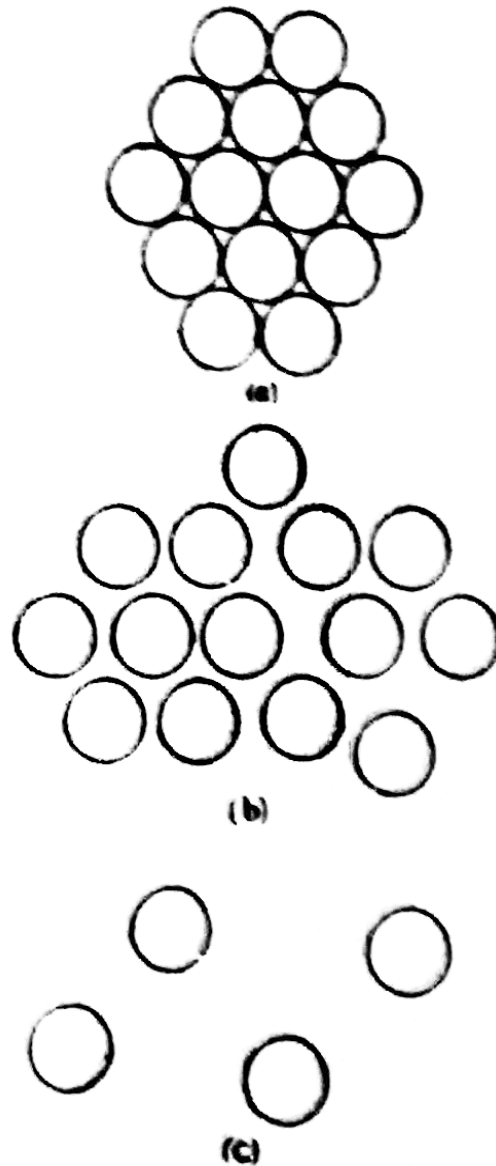
Fig 1.8 The relative spacing (artbitrary scale of molecules in

(a) solids (b) liquids (c)gases

3.1.3. STRUCTURAL DIFFERENCES BETWEEN SOLIDS, LIQUIDS AND GASES :

S.No.	Solids	Liquids	Gases
1.	The constituent particles are arranged in a perfect order. There is long range as well as short range order	There is only a short range order	There are neither Short range nor long range order.
2.	The constituent particles have neither translational nor rotational motion. They have vibrational motion.	They have some translational, rotational and vibrational motion	The constituent particles have large translational rotational and vibrational motion.
3.	Have rigidity and a definite volume	Have fluidity and have a definite volume but no definite shape.	Have neither definite volume nor definite shape.
4.	The X - ray diffraction patterns of solids are having well defined maxima.	Have only 1 or 2 well defined maxima.	Not having any maxima.
5.	Solids have high density.	Have density lower than that of solids and higher than that of gases.	Have low density.

3.1.4. Liquids Crystals : The mesomorphic state :

In solids state the inter molecular forces tend to hold the molecules in fixed positons. In some solids the constituent particles are arranged in regular positions. This regular arrangement of particles repeat three dimensionally. This leads to definite geometrical shape to the solid. Solids having definite geometrical shape are called Crystals.

When a solid is heated, the kinetic energy of the molecules increases, and it melts. In some cases, the molecules,or ionic clusters do not loose their identity beyond their melting point and yield viscous cloudy liquids at certain temperature called transtion temperature. If the temperature is increased beyond the transition temperature, the cloudiness disappears and a clear liquid is formed and this temperature is called melting point of the solid. So the temperature at which solid changes into turbid liquid is known as transition point and the second temperature at which turbid liquid changes into clear liquid is known as melting point. Between transition point and melting point the substance exhibits both the solid as well as liquid properties. Hence the cloudy liquid state is called mesomorphic state and the substance is called as liquid crystal. Thus the

liquid crystal state is intermediate between the liquid state and the solid state. The liquid crystals have a structure between that of a liquid and that of a crystalline solid. The liquid crystals have fluidity of liquid and optical properties of a solid. The liquid crystals are more like liquids in showing properties like mobility surface tension, viscosity etc.

There are many compounds that yield liquid crystals. organic molecules containing - OR, –COOR, – N = NO etc as terminal group form liquid crystals.

For example cholesteryl benzoate, $C_6H_5COOC_{27}H_{45}$, the first liquid crystal discovered, fuses sharply at 145°c to give a turbid crystal which on heating changes to a clear liquid at 178°c. The above change is reversed on cooling.

$$\text{Solid} \underset{\xleftarrow{\hspace{1cm}}}{\xrightarrow{145^0C}} \text{Liquid crystal} \underset{\xleftarrow{\hspace{1cm}}}{\xrightarrow{178^0C}} \text{Liquid}$$
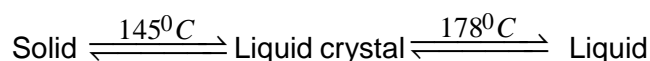
These turbid liquids show anisotropy. For example, they show double refraction, a behaviour normally exhibited by crystalline solids. But true liquids are isotropic.

The substances showing liquid crystal character are highly stable and do not decompose on heating.

Some other examples showing liquid crystal character :

Substance	Transition Point (°c)	Melting Point (°c)
Anisaldazine	165	180
Diethyl benzidine	115	120
P-Methoxy cinnamic acid	170	186
P- Azoxyanisole	116	135

3.1.5 Classification of Liquid crystals into Smectic and Nematic :

According to molecular arrangements, liquid crystals are classified into three types as Nematic liquid crystals, Smectic liquid crystals and chloesteric liquid crystals.

Nematic liquid crystals:

These liquid crystals have low viscosity and they flow readily. They are more turbid than the liquids. They have molecules parallel to each other like soda straws but they are free to slide or roll individually. Nematic liquid crystals can be shown as follows
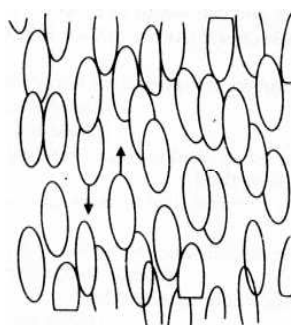
Fig 1.9 Nematic liquid crystal

P-azoxy anisole, p-azoxy phenolate, p-methoxy Cinnamic acid, dibenzal benzidine etc give nematic type of liquid crystals.

In an electric filed or magnetic field the Nematic liquid crystals get oriented in the same direction leading to change in their optical properties.

Compound	Transition Point (°c)	Melting Point (°c)
Anisaldazine	165	180
Dibenzal benzidine	234	260
P- Azoxy phenetole	137	167
P- Azoxyanisole	116	135
P-methoxy cinnamic acid	170	186

Smectic liquid crystals:

Smectic state is shown by common soaps at high temperatures and hence the name given as smectic state. The molecules in Smectic liquid crystals are also parallel but these are arranged in layers as shown below-
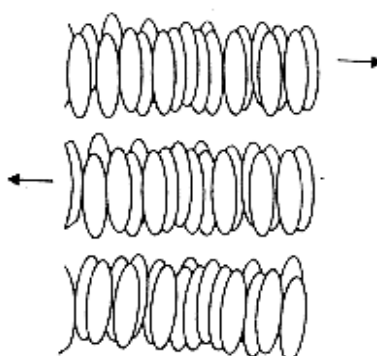
Fig 1.10 Smectic liquid crystal.

The smectic liquid crystals do not flow as normal liquids but they flow in layers. There will be weak forces between these layers and these layers can slide one over the other. The flow of smectic liquid crystals is non-Newtonian. The Smectic liquid crystals are used as lubricants. Ethyl p- azoxy benzoate, ethyl-p-azoxy cinnamate, n- octyl- p-azoxy cinnamate give smectic liquid crystals.

Compounds giving smectic type of liquid crystal :

Compound	Transition Point (°c)	Melting Point (°c)
n-octyl -p-azoxy cinnamate	94	175
Ethyl P- azoxy benzoate	114	121
Ethyl P- azoxy cinnamate	140	249

G. Friedel recognized only one type of smectics named as smetic A. Later on vorlander showed that there are different types of smectics identified by optical observation. They are referred as smectic ' A', Smectic B and Smectic 'C'.

Cholesteryl liquid crystals:

The skeleton of these crystals is similar to that of the cholesteryl, so they are named as cholesteryl liquid crystals .These liquid crystals have nematic behavior in addition to this they exhibit colour effects under polarized light. These liquid crystals are characterized by their high optical rotatory power. The plane of polarized light is rotated by few thousand times greater than their crystalline counter parts. In these liquid crystals the molecular axes are aligned and the molecules are arranged in layers. The molecules in successive layers are slightly rotated with respect the layers above and below so as to form a spiral structure. Cholesteryl benzoate is the first substance which was detected to have this property.

3.1.6. Differences between liquid crystal, Solid and liquid :

Liquids Crystal

S.No.	Solids	Smectic	Nematic	Liquid
1.	Orientation	Orientation	Orientation	No orientation
2.	Long chain molecules may be lined up as shown in 'a'. periodicity is observed.	Arrangement in equi spaced planes but no periodicity with in planes	No periodicity is seen.	No periodicity
3.	Anisotropic character.	The anisotropic properties such as double refraction can be easily understood	Lead to anisotropic character	Isotropic character. no scope for double refraction or any anisotropic behaviour
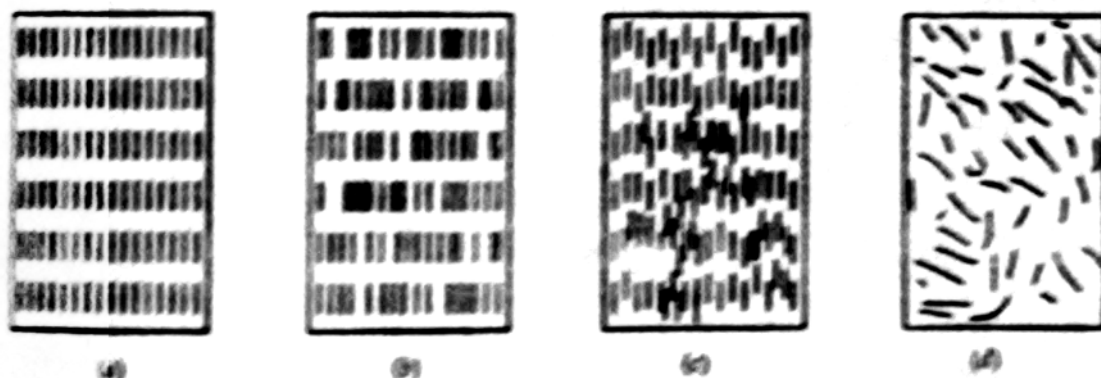
Fig 1.12 Possible degree of order in condensed states of long chain molecules :
   (a) Crystalline - Orientation and periodicity
   (b) Smetic - Orientation and arrangement in equispaced planes, but no periodicity within planes
   (c) Nematic - Orientation without periodicity,
   (d) Isotropic fluid - neither orientation nor periodicity

3.1.7 Application of liquid crystals as LCD devices :

Liquid crystals are used as displays in digital wrist watches, calculators and industrial products. Liquid crystals can be used to record, store and display images which can be projected on to a large screen. Colour allowed direct and active matrix liquid crystal displays are to be used as displays in several areas such as office automation equipment i.e laptop computers and communication equipment i.e television and tele conferencing systems portable and high definitions television (HDTV) and video games.

The two factors that make liquid crystals more useful for displays are lower power consumption and the clarity of display in the presence of bright light. The two modes, that are most widely used in liquid crystal displays are dynamic scattering and field effect. In dynamic scattering when no electric field is applied the liquid crystal cell is transparent. But the cell becomes opaques, on applying electric field to the liquid crystal. The field effect display utilizes the twisted nematic liquid crystals. The field effect display is widely used in watch and pocket calculator displays. In a liquid crystal watch that display hours and minutes, the quatz crystal controls the oscillating circuit. Ferroelectric liquid crystals such as the smectic 'C' is used for displays requiring a high information content.

When in a display smectic ' C' has two different molecular configurations, polarizers are kept such that one state is transparent while the other is opaque or dark. Since the smectic crystal is ferro electric, it reacts very quickly to electrical pulses.

In a filed - effect display device, the cell with the nematic liquid crystal is placed between two crossed polarizers. By changing the direction of the polarizers, the digit can be made to appear white on a balck background.

Another liquid - crystal technology is the polymer dispersed liquid - crystal display which operates on the principle of electrically controlled light scattering. The transparency of the display is switched from a white, opaque appearance to a clear, transparent appearance by applying an electric field. The polymer liquid - crystal display consists of a mixture of a liquid crystal and polymer sand witched between two pieces of conducting glass. Polymer dispersed liquid crystal displays are designed for the use as sun roofs in automobiles solar control in large office buildings and privacy windows.

3.1.8 Model Questions :

1. Explain different types of inter molecular forces of attraction.

2. Explain mesomorptic state of a substance.

3. What are liquid crystals? What are their characteristics?

4. Give the classification of liquid crystals.

5. Explain the differences between nematic and smectic liquid crystals?

6. What are cholesteryl liquid crystals? Give their importance ?

7. What are the applications of liquid crystals?

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UNIT – III

Lesson – 2

SOLID STATE

3:2:1 Matter exists in three states solid, liquid and gaseous states. In liquid and gaseous states the constituent particles continuously move and they have the ability to flow. In solid state the constituent particles are not free to move and they are held together by relatively strong chemical forces like ionic bond, covalent bond or by Vander waals forces of attraction. Solids are regid and they have definite shape.

Types of solids:

Solids can be broadly classified into two types as (a) crystalline solids and (b) amorphous solids.

A crystalline solid exists as small crystals. In a crystal the constituent particles are arranged in regular positions. This regular arrangement repeats three dimensionally and results in a definite geometrical shape to the crystal. NaCl and KCl are crystalline solids.

In an amorphous solid the constituent particles are not arranged in regular positions. They are arranged at random positions. They possess some mechanical properties like refractive index, rigidity etc., but do not occur in definite geometrical shape. Glass, rubber, plastic etc are amorphous solids.

Following are the important difference between crystalline solids and amorphous solids.

S.No	Crystalline Substances	Amorphous Substances
1.	Crystalline substances are true solids	Amorphous substances are not true solids.
2.	They have sharp melting points	They have no sharp melting points.
3.	Crystalline substances are anistropic. That is the physical properties such as refractive index, Coefficient of thermal expansion, elasticity etc.are different in different directions of the crystal.	These are isotropic. The physical properties are same in all directions.
4.	The constituent particles are present in an orderly manner.an orderly manner.	The constituent particles are not arranged in Under special conditions these substances may have crystalline Characteristics.

3:2:2 The law of constancy of interfacial angles:

The external shape of a crystal is called habit of the crystal. The plane surfaces of the crystal are called faces. The angle between two types of faces in a crystal is known as interfacial angle. According to the law of constancy of interfacial angles, the angles of intersection of two planes of a given crystal always remain constant at a given temperature. The habit of a crystal of a given compound depends on condition of crystallization. The extent of growth of a particular plane may vary. Different crystals of the same substances may not look alike .But the interfacial angels are always the same .Goniometer is used to measure interfacial angles. The following figure illustrates the law of constancy of interfacial angle.
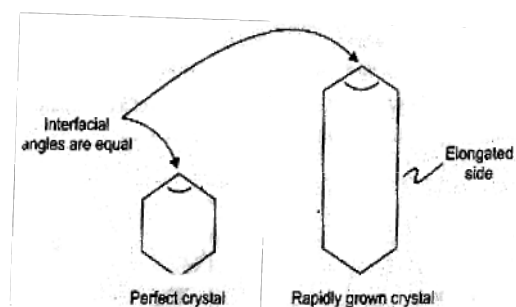
Fig 2.1 Interfacial angles are always the same

3:2:3 Symmetry of crystals:

The internal structure of a crystal is due to definite arrangement of its constituent particles. This arrangement repeats again and again in a definite space. That is a crystal is having symmetrical structure. The symmetry in crystals may be due to a plane, a line or a point. There are three types of symmetry elements associated with a crystal. They are called the elements of symmetry. They are (i) Plane of symmetry (ii) Axis of symmetry and (iii) Centre of symmetry

Plane of symmetry:

A crystal is said to have plane of symmetry if an imaginary plane passing through the centre can devide it into two equal parts, each of which is the exact mirror image of the other.

A rectangular plane devide a cube into two halfs. There can be three such planes.Therefore a cube has three rectangular planes of symmetry. They can be represented as follows
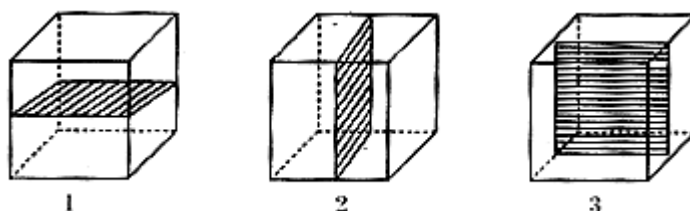
Fig 2.2

A rectangular plane passing through diagonal edges of a cube divide it into two halfs . There can be six such planes, Hence a cube has six diagonal planes of symmetry . They can be represented as follows.
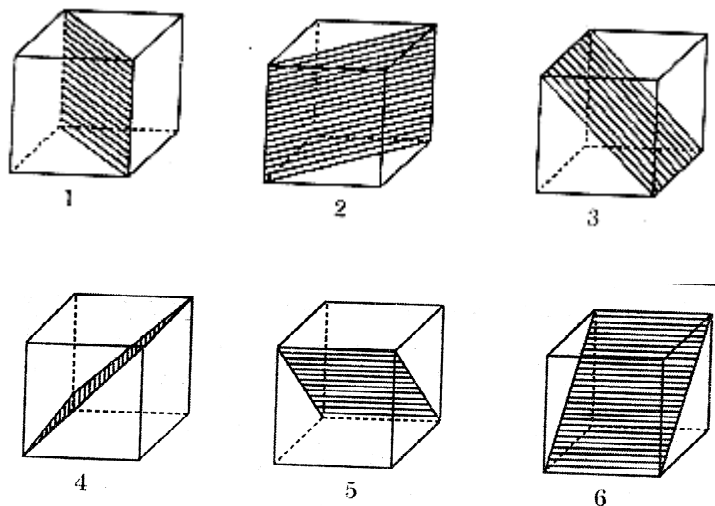
Fig 2.3 Six diagonal planes of Symmetry

Thus a cubic crystal has 9 planes of symmetry.

Axis of symmetry:

An axis of symmetry of a crystal is an imaginary line drawn passing through the centre about which the crystal may be rotated such that it presents exactly the same appearence more than once in the course of one complete revolution.

If the same appearance is repeated after a rotation of 180° the axis is said to be two fold symmetry or diad axis .If the same appearence is repeated for every 120° , it is three fold symmetry or triad axis. Similarly if the same appearence is repeated for every 90° , it is four fold symmetry and for every 60° it is six fold symmetry and so on.

In a cubic crystal there is an axis passing through the centre and perpendicular to the opposite sides. This is four fold symmetry. There are three such axis of symmetry. They can be represented as follows
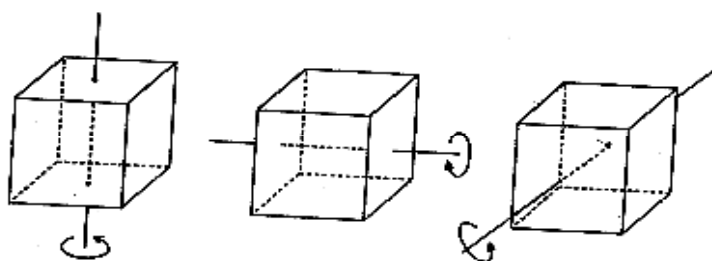
Fig : 2.4. Four -fold or a tetrad axis.

In a cubic crystal there is another axis of symmetry passing through the centre and diagonal corners. This is three fold axis. That is for every 120° rotation there is similar appearance. There are four such axis for a cubic crystal. They can be represented as follows.
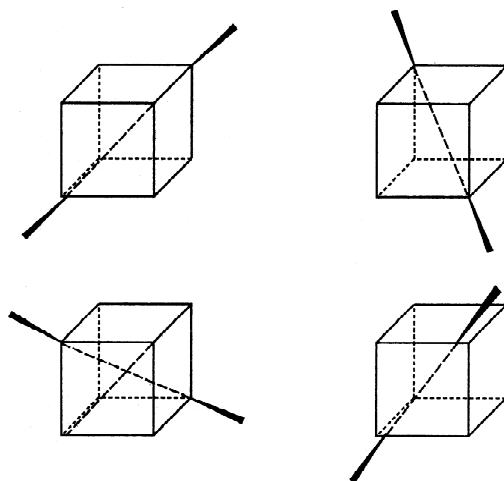
Fig 2.5. Three fold axis.

In the same way in a cubic crystal there is one more axis of symmetry passing through the centre and mid points of diagonal edges. This is a two fold axis. That is the same appearance is there for a rotation of 180° . There are six such axis of symmetry. It can be represented as follows.
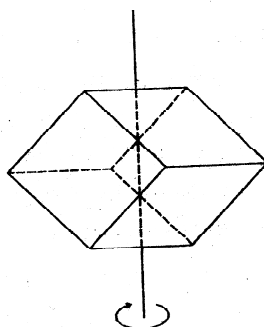
Fig 2.6 Two fold axis of symmetry.

Thus for a cubic crystal three are three four fold axis , four three fold axis and six two fold axis of symmetry. Total there are thirteen axis of symmetry

Centre of symmetry:

Centre of symmetry is a point at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distances on either side. In a cubic crystal the centre of symmetry is the centre of gravity. A crystal may have a number of planes of symmetry or axis of

symmetry but it can have only one centre of symmetry. For many crystals there is no centre of symmetry as the planes grow unsymmetrically.
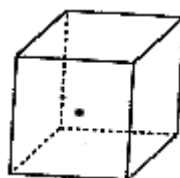
Fig 2.7

Thus for a cubic crystal total elements of symmetry are 9+13+1=23.

3:2:4 Law of Rational Indices :

The crystal lattice consists of unit cells arranged in parallel planes. Thus each crystal plane lies parallel to the crystal face as also to the unit cell face. Consider three mutually perpendicular axis so that all faces of the crystal will either intercept these axis at definite distance from the origin or be parallel to some of the axes in which case the intercepts are at infinity. Law of rational indices states that "the intercept of any face of crystal along the crystallographic axis are either equal to the unit cell intercepts or some simple whole number multiples of them."

Let the three axis OX, OY and OZ represent crystallographic axis with O as origin. ABC is the unit cell which cuts the crystallographic axis at A, B, and C respectively. The Unit cell makes the intercepts   OA = a, OB = b and OC = c. The lengths a, b and c many or many not be equal but their ratio is constant. The ratios of unit intercepts are called axial ratios. Let K L M is the face of the crystal understudy. The intercepts of the face under study may be OK = k, OL = l and OM = m. The intercepts of the face can be expressed as integral multiples of a, b and c respectively.

OA = a
OB = b
OC = c

OH = h
OK = k
OL = l
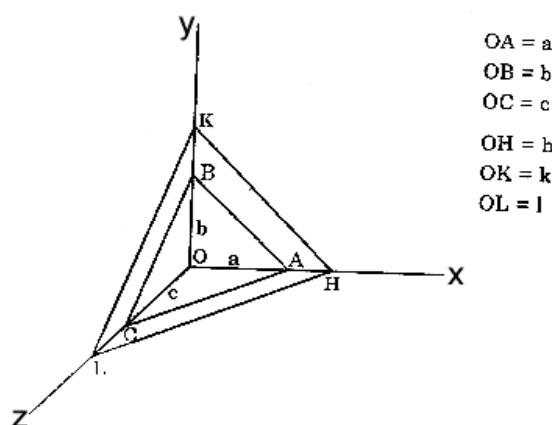
Fig 2.8 Law of rotational indices.

Let K = 2a, l = 2b and m = 3c. The coefficients of a,b,c for the intercepts of the face under consideration are called Weiss indices. Therefore the Weiss indices for the face will be (2, 2, 3). The reciprocals of Weiss indices are (1/2, 1/2, 1/3) .The whole number ratio of these is (3, 3, 2) or

3:3:2. These numbers are called Miller indices. The plane KLM is designated as (3, 3, 2) plane. If a plane cuts only two axis and the third is parallel to the axis, then the Weiss indices for that parallel axis is infinity and its Miller index will be Zero.

Weiss and Miller indices of some crystal planes are given below.

Intercepts of face Under consideration	Weiss indices	Reciprocals	Miller Indices
a, 2b, αc	1; 2; α	$\frac{1}{1};\frac{1}{2};0$	2,1,0
2a,3b,2c	2,3,2	$\frac{1}{2};\frac{1}{3};\frac{1}{2}$	3,2,3
a, αb, αc	1,α,α	1,0,0	1,0,0

3:2:5 Space Lattice and Unit Cell:

The constituent particles in crystals are highly ordered which is evident from their geometrical shapes, smooth surfaces and specific interfacial angles. The particles in crystals are arranged in regular patterns and extend in all directions. The overall arrangement of particles in a crystal is called space lattice. The positions occupied by the particles in the crystal lattice are called lattice points. The crystal may be considered as being made up of a large number of basic units. The simple basic unit or the building block of the crystal lattice is called the unit cell. The unit cell of a crystal is the smallest portion of the space lattice of the crystal, representing the crystal as a whole .The crystal is the repetetion of the unit cell in an orderly three dimensional fashion. The shape and dimensions of the unit cell determines the external appearance of the crystal. X- ray diffraction studies provide the details of unit cell. The edge lengths of unit cell along the x,y and z axis are represented by a, b and c respectively. The angles between xy, yz and zx are represented by α,β and γ respectively.
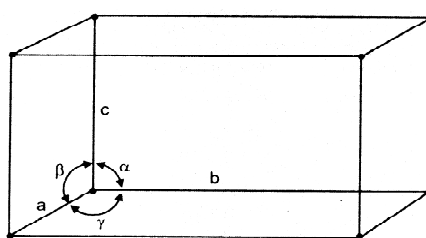
Fig 2.9 Illustration of parameters of a unit cell.

Depending on the shape of unit cell seven crystal systems are possible. They are cubic, tetragonal, orthorhombic, rhombohedral, Hexagonal, monoclinic and triclinic systems. They can be represented as follows.

Cubic

Tetragonal

Orthorhombic

Rhombohedral

Hexagonal

Monoclinic

Triclinic
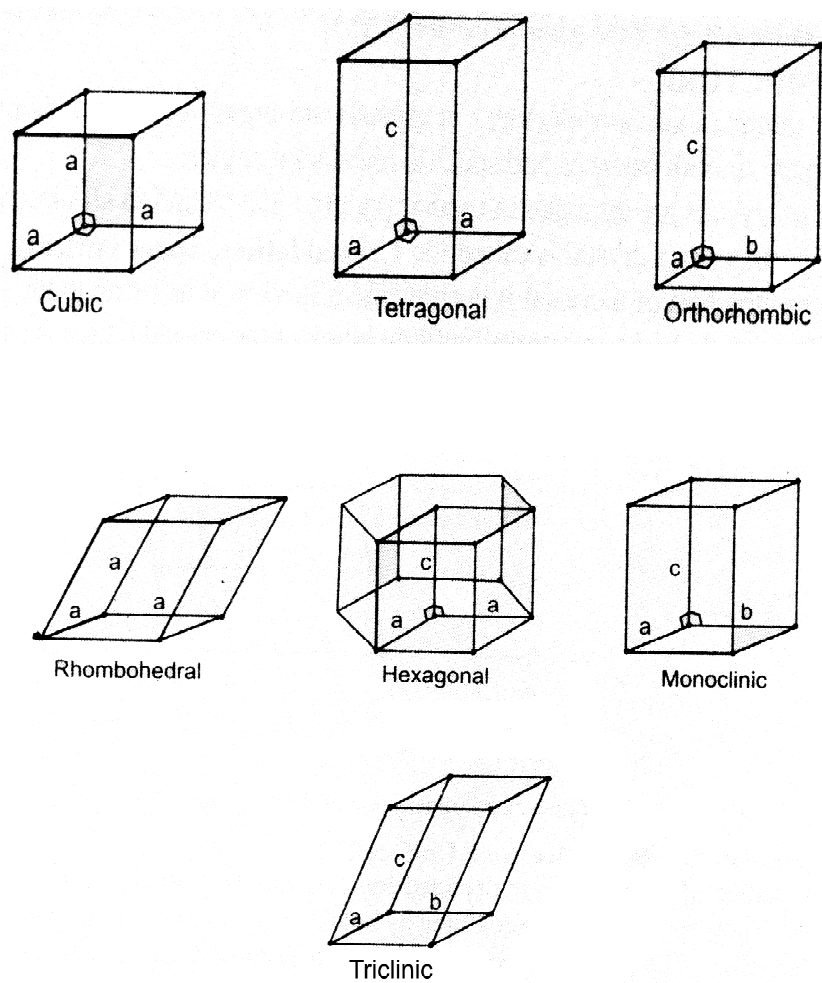
Fig 2.10 The primitive unit cells for the seven crystal systems. Where two or more of the axes are equal, the same letter is shown in each.
Right angles (90°) are shown as7.
The heavy line indicates the hexagonal unit cell.

The characteristics of crystal systems and some examples are given below

Table 2.1 : The seven unit cells

Crystal system	Relative axial length	Angles	Examples
Cubic (isometric)	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Na^+Cl^-, Cs^+Cl^-, $Ca^{2+}(F^-)_2$, $Ca^{2+}O^{2-}$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	$(K^+)_2\ PtCl_6^{2-}$, $Pb^{2+}\ WO_4^{2-}$, $NH_4^+\ Br^-$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	$(K^+)_2SO_4^{2-}$, $K^+NO_3^-$, $Ba^{2+}SO_4^{2-}$, $Ca^{2+}\ CO_3^{2-}$ (aragonite)
Rhombohedral (trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$Ca^{2+}CO_3^{2-}$ (calcite), $Na^+NO_3^-$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120$	AgI, SiC, HgS

In the various unit cells, there are three kinds of lattice points. The simplest unit cell having the lattice points at the corners is called as primitive unit cell (p). The unit cell with lattice points in each face in addition to at the corners is called face - centred unit cell (F) and that having one point at the centre in addition to at the corners is called body centred unit cell. Each unit cell is characterized not only by the symmetry and the primitive face centred or body centred nature of the unit cell but also by the type of axis and their inclination with respect to each other. The number of atoms belonging to unit cell is also known as lattice sites and is denoted by z. The number of atoms in the crystal is called coordination number for that lattice. In a simple cubic lattice each particle is surrounded by 6 other particles and hence the coordination number of a simple cubic lattice is 6.

As discussed earlier the positions of similar particles in a regular three dimensional network is called space lattice. Thus is sodium chloride crystal the position of sodium ions constitute the space lattice of Na^+ ions. Similarly the network of Cl^- ions spacing is called space lattice of Cl^- ions. The interpenetration of the space lattices of Na^+ and Cl^- ions is the crystal lattice of Nacl.

In NaCl crystal, the space lattice $Na^+$of ions is similar to that of it Cl^- ions. In all crystal lattices it need not be like this but each point in the lattice has exactly the same environment as any other point representing the same atom or ion.

According to geometric arguments there can be fourteen simple lattices. They are called Bravis lattices. Thus similar points can be arranged in regular three dimensional order only in fourteen possible ways. They can be represented as follows

SIMPLE
OR PRIMITIVE   BODY CENTRED   FACE CENTRED

CUBIC SPACE LATTICES

SIMPLE
OR PRIMITIVE   BODY CENTRED   END CENTRED   FACE CENTRED

ORTHORHOMBIC SPACES LATTICES

SIMPLE   BODY CENTRED   SIMPLE   END CENTRED

TETRAGONAL   MONOCLINIC

TRICLINIC   HEXAGONAL   RHOMBOHEDRAL
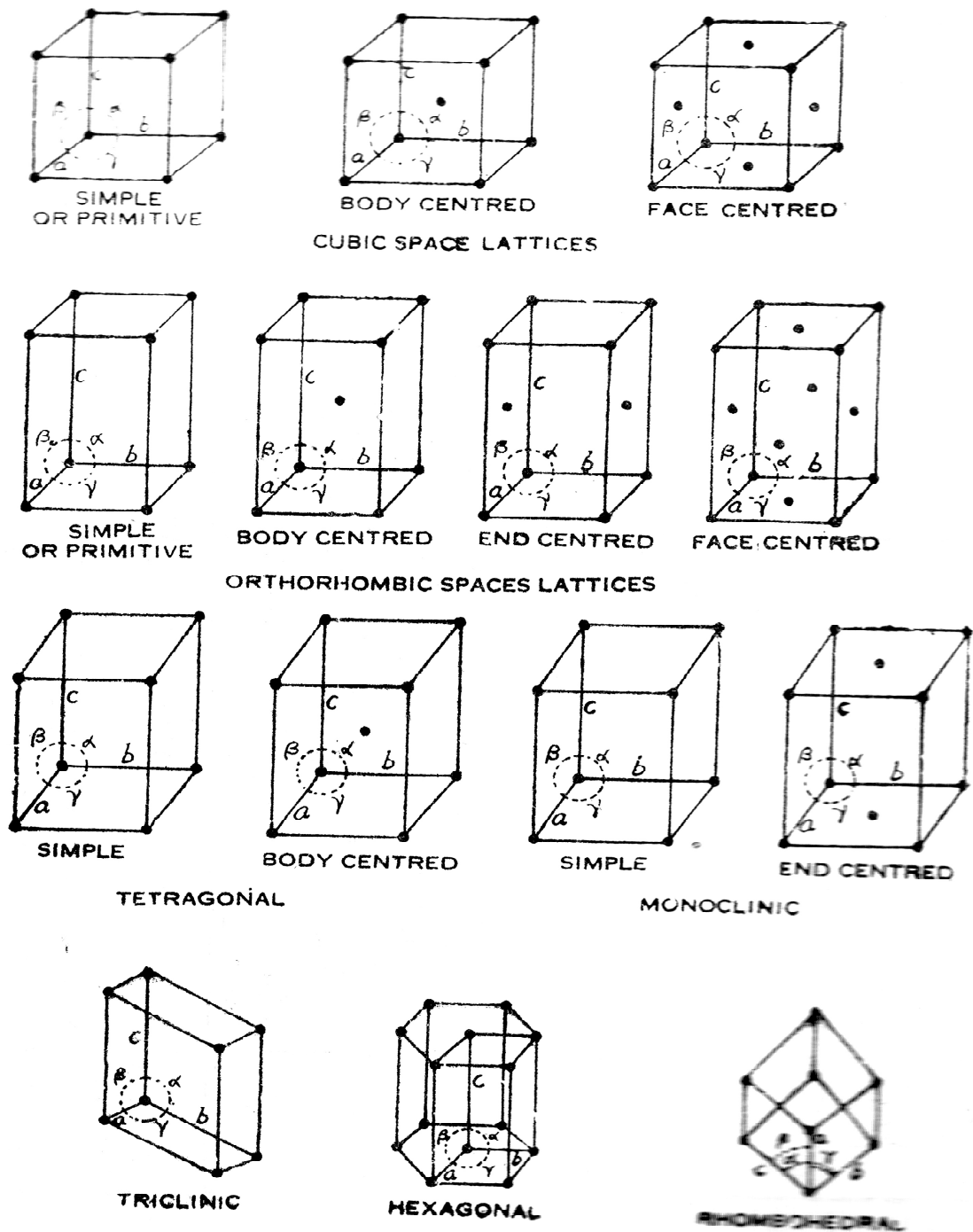
Fig 2.11 The fourteen lattices.

3:2:6 X-Ray Diffraction by Crystals:

The crystal lattice is considered to be made up of regular layers or planes of atoms of equal distance apart. Thus wave length of x-rays is comparable to the inter atomic distances. Lane suggested that crystal can act as grating to x-rays. When a beam of x-rays is allowed to fall on a crystal, a large number of images of different intensities are formed. If the diffracted waves are in the same phase, they reinforce each other and a series of bright spots are produced on a photographic plate placed in their path. If the diffracted waves are out of phase dark spots are caused on the photographic plate. From the x-ray studies it is possible to study the crystal structure.

Bragg's equation:

W.L. Bragg and W.H.Bragg studied the diffraction of x-ray by sodium chloride crystal. They obtained the relation between the wave length of x-rays, the interplanar distance in the crystal and the angle of reflection. This equation is called Bragg equation. They showed that the x-ray diffracted from atoms in a crystal obey the laws of reflection. The two rays reflected by successive planes will be in phase if the extra distance traveled by the second ray is an integral multiple of wave lengths.
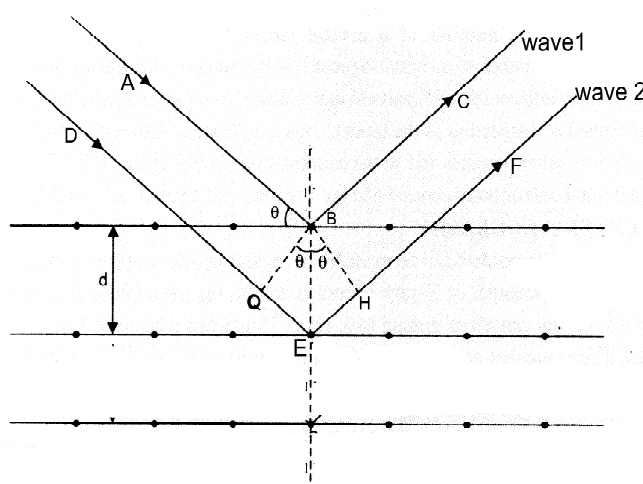
Fig 2.12 Reflection of X-rays from two different planes of a crystal.

Two waves AB and DE are incident on identical lattice planes 1 and 2 respectively at an angle θ. They are reflecting along B C and EF respectively .The wave 2 travels a greater distance than the wave 1 Draw perpendiculars from B on DE and EF as BG and BH respectively.

The path difference between the two waves is (GE + EH). The reflected waves BC and HF must be in phase so that the waves reinforce each other . This is possible when the path difference is wave length (λ) or integral multiple of it, that is nλ .

$\therefore GE + EH = n \lambda$

Δ^{les} BGE and BEH are similar triangles

GE = d sin θ and EH = d sin θ.

$\therefore 2d \sin\theta = n \lambda$

This equation is known as Bragg's equation. From this equation if θ, n and λ are known d can be calculated (or) if d is known, the crystal may be used to determine the wave length of X-rays.

The measurement of diffraction angle θ, required for Bragg's equation can be done by (i) The rotating crystal method and (ii) The powder method.

(i) The rotating crystal method

The apparatus will be as shown in the figure.
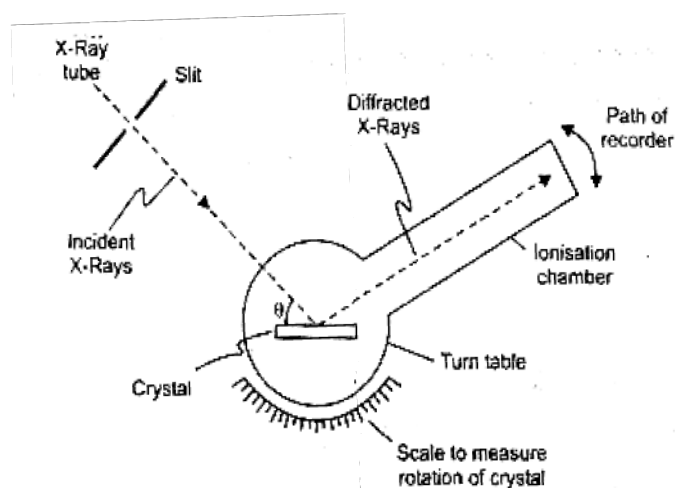
Fig 2.13 Rotating crystal method to determine the angle of diffraction 'θ'

A beam of X- rays of known wave length falls on the face of the crystal mounted on a graduated turn table. The diffracted rays are allowed to pass into the ionization chamber of the recorder. In this chamber air ionises and a current flows between the chamber wall and an electrode inserted in it which is connected to an electrometer. The electrometer reading is proportional to the intensity of X-rays . As the recorder along with the crystal is rotated, the angles of maximum intensity are noted on the scale. Thus values of θ for n = 1,2,3 etc are used to calculate the distance between the lattice planes parallel to the face of the crystal.

(ii) The powder method :

This is more advantageous method when compared to rotating crystal method. The rotating crystal method can be used only if a single undistorted crystal is available. That problem is not there in this method. In this method the crystalline material is taken in a capillary tube and it is placed in the camera containing a film strip.
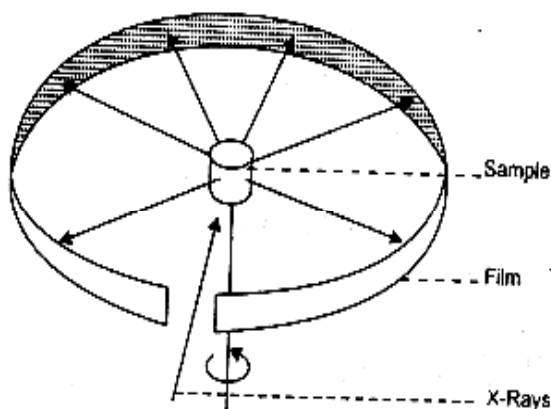
Fig 2.14 The powder method

The Sample is rotated by means of a motor. The x-rays pass through the gap between the ends of the film. The powdered sample contain small crystals with all orientations. Some of these will reflect X- rays from each lattice plane at the same time. The refelected X- rays make an angle 2θ with the original direction. Hence on the photo are obtained lines of constant θ. From the geometry of the camera θ can be calculated for different crystal planes.

3:2:7 Structure of Nacl:

A stable crystal is formed as a result of opposing effects of coulombic interactions between ions of opposite charge and repulsion between completely filled shells of electrons. Nacl, Kcl, Na2SO4, KNO3 etc are examples of ionic crystals. The number of ions surrounding an oppositely charged ion in the crystal lattice is called coordination number. The coordination number depends on the ratio of radii of ions

Ratio of $\left(\dfrac{r_c}{r_a}\right)$	Coordination Number
> 0.73	8
0.41 - 0.73	6
0.22 - 0.41	4

The crystal lattice of NaCl can be represented as follows.
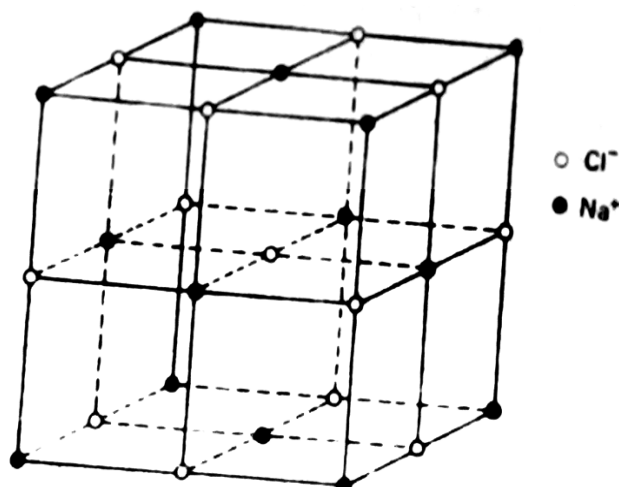
Fig 2.15

In the lattice of NaCl, each sodium ion is surrounded by six chloride ions and in turn each chloride ion is surrounded by six sodium ions. The coordination number of NaCl crystal lattice is 6. The structure is reffered to as (6:6) coordination. In this cubic system the planes can be passed through the atoms having Miller indices (100), (110), (111) and the relating spacings for the unit cell of a face centred cubic lattice are

$$d_{100} : d_{110} : d_{111} = \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}}$$

$$= 1 : 0.707 : 1.154 \quad \text{............... (i)}$$

These values agree with those calculated for a face centred cubic lattice.

In the case of NaCl the first order reflection from (100), (110), (111) faces using K line from palladium anticathode are 5.9° ; 8.4° and 5.2° respectively.

From Braggs equation n $\lambda = 2d \, Sin \, \theta$

$$d = \frac{n\lambda}{2 Sin\theta}$$

$$d_{100} : d_{110} : d_{111} = \frac{1}{\sin 5.9^0} : \frac{1}{\sin 8.4^0} : \frac{1}{\sin 5.2^0}$$

$$= 9.731 : 0.844 : 11.04$$

$$= 1 : 0.704 : 1.136 \quad \text{.............. (ii)}$$

The above ratio is almost identical with the ratio required in the case of a face - centred cubic lattice as shown in (i)

Structure of KCl :

The structure of KCl is isomorphous with NaCl. Discrepancy is observed in the x-ray results that can be explained as follows. The scattering power of an atom or ion is governed by the number of extranuclear electrons. Since K^+ and Cl^- posses same number of electrons their scattering powers will be almost equal, the first order reflections from (III) planes are extinguished due to destructive interference and the X - rays record a lattice of small simple cubes.

On analysis of first order spectrum from (100), (110), (111) planes of potassium chloride give that it is required for a simple cubic.

$$d_{100} : d_{110} : d_{111} \quad = \quad 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$$

lattice .
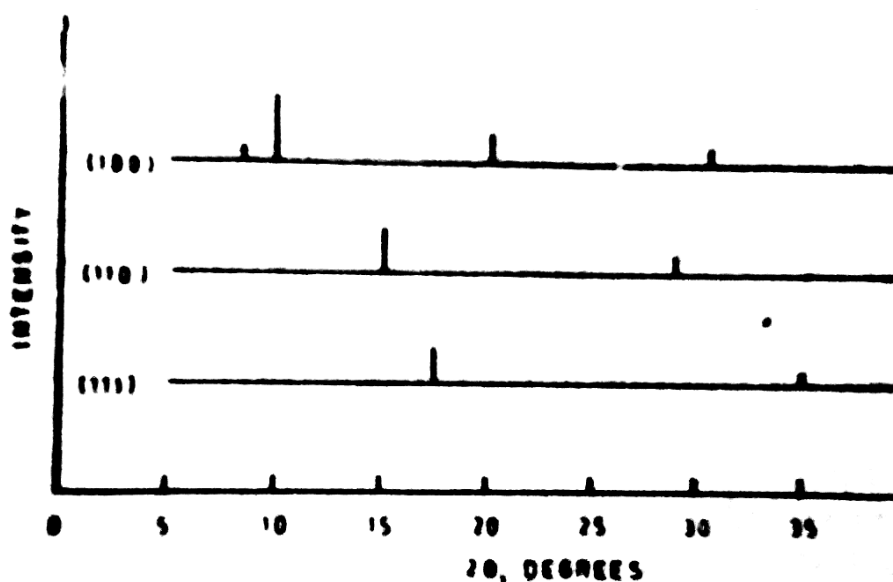
Fig 2.16 Intensity vs 2θ plot for X - ray results of potassium chloride crystal.

3.2.8 Model Questions :

1. What is crystallography? Distingnish between crystalline and amorphous substances.

2. Write a note on(a) plane of symmetry (b) axis of symmetry and (c) centre of symmetry.

3. Explain the terms.

   (a) unit cell (b) space lattice

4. Explain weiss indices and Miller indices with examples.

5. Give the classification of crystals.

6. Derive Bragg's equation for diffraction by crystals.

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UNIT – III

Lesson – 3

DEFECTS IN CRYSTALS

3:3:0 Classification of crystals :

On the basis of nature of forces, that hold the particles together in a crystal lattice, crystal are classified into four types namely (i) ionic crystals (ii) Covalent crystals (iii) Molecular crystals and (iv) Metallic crystals.

Ionic crystals :

In ionic crystals the lattice points are occupied by ions. In the crystal the oppositely charged ions are held together by ionic bonds. A stable crystal is formed as a result of opposing effects of columbic interactions between ions of opposite charge and repulsion between filled shells of electrons. NaCl, KCl, Na_2SO_4, KNO_3 etc are examples of ionic crystals. The number of ions surrounding an oppositely charged ion in the crystal lattice is called coordination number. The coordination number depends on the ratio of radii of ions.

Ratio of $\left(\dfrac{\gamma_c}{\gamma_a}\right)$	coordination no.
>0.73	8
0.41-o.73	6
0.22 -0.41	4

The crystal lattice of NaCl can be represented as follows ;
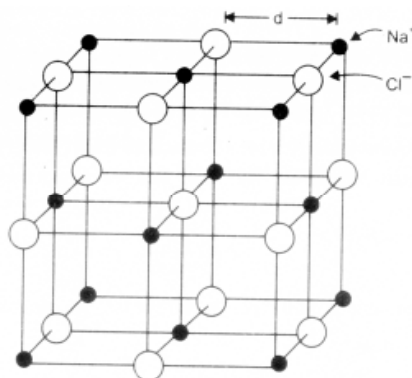
Fig 3.1 Sodium chloride crystal lattice d =2.814 A°.

In face centered cubic lattice (f.c.c) the coordination number is 6. Sulphides of Mg, Ba, Mn, and Pb, Oxides of Mg, Ca, Sr, Ba etc have face centered cubic lattice.

In body centered cubic lattice (b.c.c) the coordination number is 8. caesium chloride, caesium bromide, alkali metals, Ca, Ba, V etc have body centered cubic lattice.

Ionic compounds will have the following characteristics :

1. Typical ionic solids are hard and rigid with high melting points.

2. Ionic solids are brittle. They can be shattered easily by hammering

3. Ionic solids are non conducting because the ions are not free to more.

4. In molten or aqueous state they are good conductors of electricity.

5. The vapour pressure of ionic crystals is low at room temperature.

Covalent crystals :

In covalent crystals the lattice positions are occupied by atoms. These atoms share electrons with the neighboring atoms and are bonded by covalent bonds. The covalent crystals will have giant inter locking structure. Such solids are called net work covalent solids or simply covalent solids. The classical example of covalent crystal is diamond. Its structure can be represented as follows.
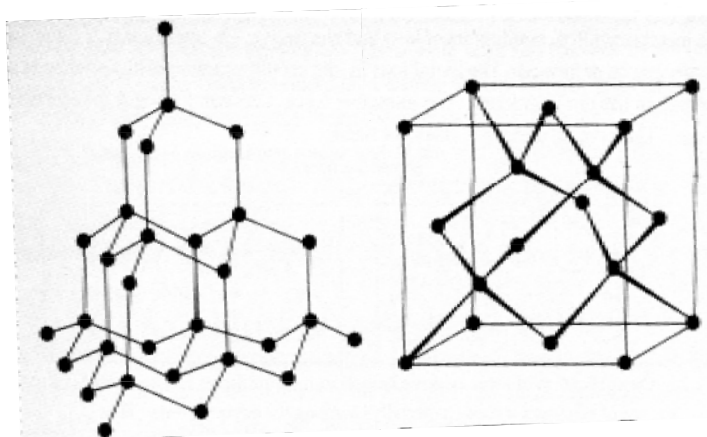
Fig 3.2 Crystal structure of diamond.

In diamond each carbon is surrounded by four other carbon atoms arranged towards the corners of a tetrahedron. Diamond is the hardest substance known with an extremely high melting point. Silicon carbide, germanium arsenite are other examples of covalent crystals. These are non conductors of electricity with high melting point.

Molecular crystals :

In molecular crystal the lattice positions are occupied by molecules. In these crystals the atoms of the lattice are attracted by Vander waal's forces which are weak. They will have low melting and low boiling points. Most organic substances are molecular solids. Argon, ice, iodine, solid CO_2 (dry ice), solid CCl_4 are example of molecular crystals.

Metallic Crystals :

Metals are generally solids. In metallic crystals the lattice positions are occupied by positive metal ions surrounded by mobile electrons through out the crystal. The mobile electrons in the crystal structure make metals excellent conductors of heat and electricity. The individual atoms in a metallic crystal lattice can be thought of as hard spheres. The spherical atoms are packed together in the lattice very efficiently in geometrical arrangements so as to have minimum interspaces.

Most of the metals have hexagonal close packing, cubic close packed structure or body centered cubic lattice.

The hexagonal close packing structure of metal crystals will be as shown below.
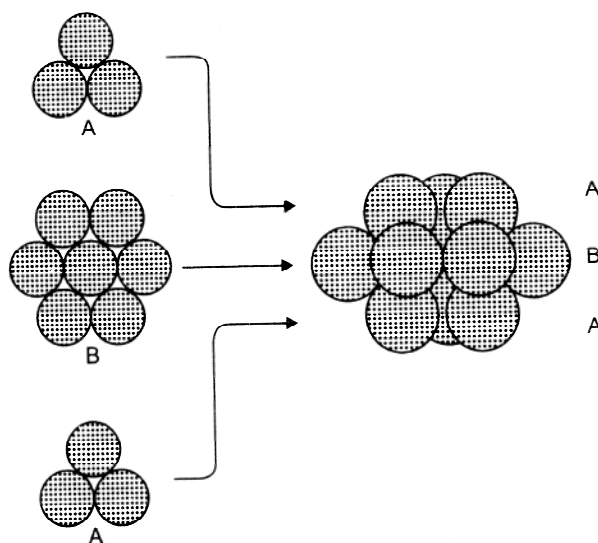
Fig 3.3 Hexagonal close - packing

Be, Mg, Zn, Cd, Be, Co etc have hexagonal close packing. The cubic close packed structure in metallic crystals will be as shown below.
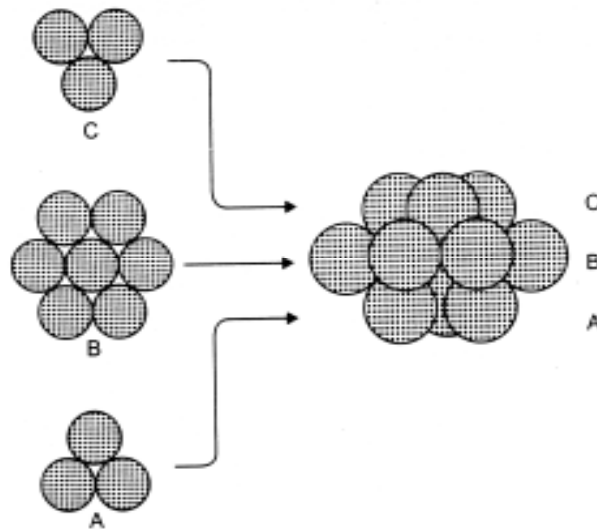
Fig 3.4 Cubic close -packing

Metals like Ag, Au, Ca, Co, Cu, Ni etc have cubic close packed structure.

About $\frac{1}{3}$ of the metals have body centered cubic structure. The body centered cubic structure will be as shown below.
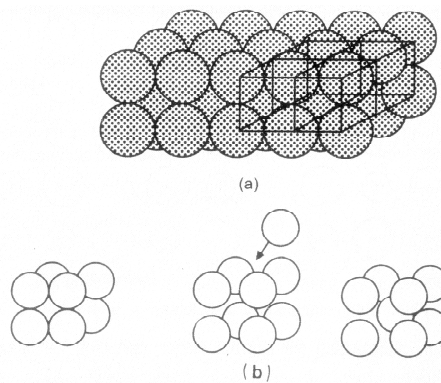
Fig 3.5 (a) Layers of non- close sphere stacked one on the other. (b) Fifth atom when inserted in a simple cubic structure forms a body - centred cubic pattern.

Metals is general are malleable and ductile.

3:3:1 Defects in Crystals :

A crystal is said to be perfect in which all the atoms or ions are lined up in a precise geometric pattern. In other words, when all the atoms or ions in a crystal are arranged in a regular fashion, then the structure is called ideal or perfect structure. No crystal structure is perfect. Crystal with perfect lattices are very rare. Most of the crystals in practice shows some deviations or imperfections which are called defects. The term defect may be defined as the deviation from regularity in the arrangement of the atoms, ions and molecules constituting a crystal. Defects in crystals mainly changes the physical properties like electrical conductivity and diffusion and sometimes even the chemical properties to a lesser extent. There are two types of defects namely (a) point defects or stoichiometric defects and (b) Non - stoichiometric defects.

3:3:2 Stoichiometric defects :

In stoichiometric compounds, the number of different types of atoms or ions are present exactly in the ratios indicated by their chemical formulae.

In stoichiometric compounds two types of defects are observed namely (i) schottky defect and (ii) Frenkel defect.

i. Schottky defect :

Some times a lattice position may be left vacant if no particle is present in the lattice position, it is called vacancy defect. In ionic crystals, the overall electrical neutrality is to be maintained. In ionic crystals, if a positive ion and negative ion are absent there are two vacancies. Hence, a schottky defect consists of a pair of holes in the crystal lattice.

In ionic crystals if the sizes of anions and cations are same and having high coordination numbers schottky defect is favoured. In Nacl, Cscl, KCl and KBr, this schottky defect is observed.
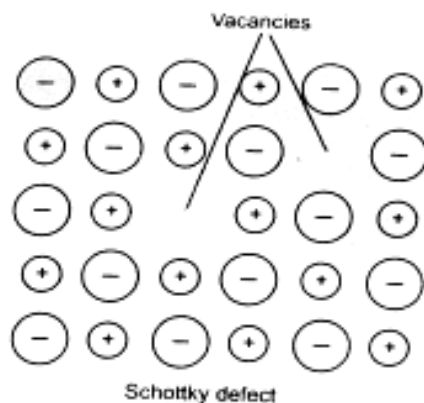
Fig 3.6

ii. Frenkel defect :

In some crystals an ion is shifted from normal position to occupy a position in the space between the lattice sites called interstecial position. Such defect is called interstecial defect or Frenkel defect arises due to a vacancy at a cation site. In ionic crystals if one ion is smaller than the other ion Frenkel defect is favoured. Frenkel defect occurs in compounds having low coordination number, ions having different sizes and having highly polarising cation and an easily polarizable anion. This type of defect leads to an increase in the dielectric constant of the medium. Examples of Frenkel defect are Zns ; Ag Br and Ag I.
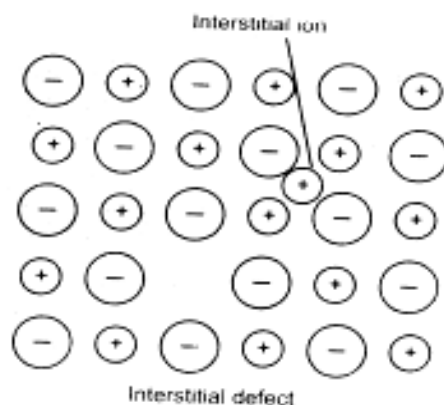
Fig 3.7

3:3:3 Non - Stoichiometric defects :

Non - Stoichiometric compounds are known to exist over a range of chemical composition. Non - stoichiometric compounds are those in which the number of positive and negative ions are not in the ratio indicated by their perfect chemical formulae. Oxides and sulphides of the transition elements are examples for non- stoichiometric compounds. Thus in FeO ; Fe S or Cu S the ratio of Fe ; O ; Fe ; S or Cu : S differs from that indicated by their ideal or perfect chemical formulal. If the ratio of ions is not exactly 1:1 there must be either excess of metal ions or a deficiency of metal ions. For example in Fe O the ratio of positive and negative ions is 0.94 : 1. Electrical neutrality can be maintained either by having extra electrons in the structure or changing the charge on some of the metal ions. This makes the structure irregular.

1) Metal excess defect :

When excess of metal ions are present, then it is termed as metal excess defect and it arises in two ways.

a) Anion Vacancies :
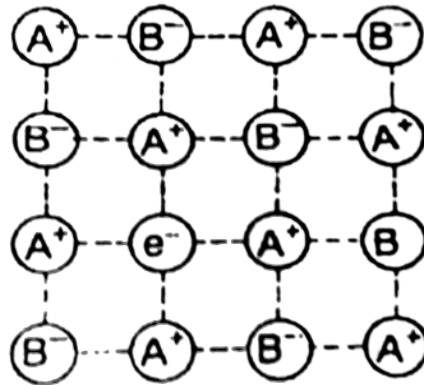
Fig 3.8 Metal excess defect because of absent anion

The defect involves the removal of anion (non - metal) there by causing an increase in the cation (metal) concentration. The electrons associated with the anions are trapped in the lattice, there by maintaining the electrically neutral character. This defect is found in crystals which are found to have schottky defects. For example when NaCl is treated with sodium, vapour form of NaCl is obtained which has excess of sodium ions. Other examples are KCl and LiH.

b) Extra cation occupying the interstecial sites :

The defect involves the presence of an extra positive ion occupying an interstecial position. Electrical neutrality is maintained by an electron which is also present in an interstecial position. This defect is just like Frenkel defect and is much more common than the anion vacancies defect. This defect is found in crystals which are expected to have Frenkel defects. Examples are ZnO, CdO, Fe_2O_3 and Cr_2O_3.
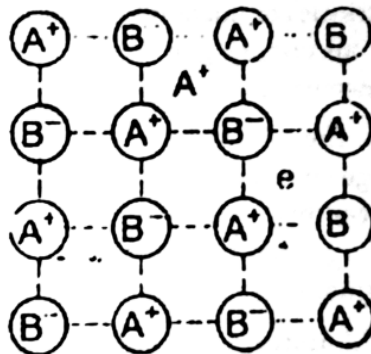
Fig 3. 9 Metal excess defect caused by interstitial cations

2) Metal deficiency defect :

The metal deficiency defect arises in two ways.

a) Cation Vacancies :

If a positive ion is missing from its lattice site, the charge can be balanced or electrical neutrality is maintained by an adjuscent metal ion having an extra positive charge. Examples of this type of defect are FeO ; Ni O ; Fe S and Ti O.
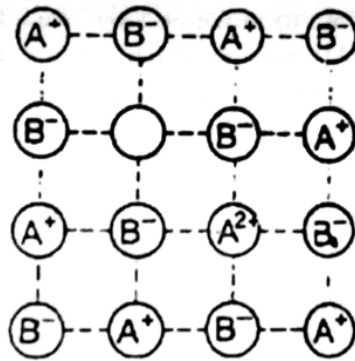
Fig 3.10 Metal deficiency caused by missing positive ion

b) Extra cation occupying the interstecial sites :

This defect involves the presence of an extra anion in an interstecial position. The electrial neutrality is maintained by an extracharge on a cation.

No example of crystals possessing this defect is known at present. In some crystals, the regular lattice sites are occupied by foreign atoms or ions. The defect is called substitutional impurity defect since foreign particle is substituted for normal lattice particle and interstecial impurity if foreign particles are trapped in vacant intersteciol spaces.
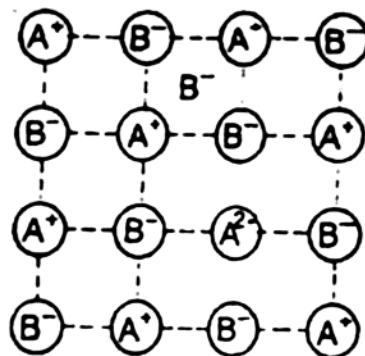
3.11 Metal excess defect caused by interstitial negative ions

3:3:4 Band theory of Semi conductors :

The band theory of metals explain the differences between conductors, insulators and semiconductors. The basic difference between conductors, insulators and semi-conductors, , lies in the number of free electrons present in the material.

The theory takes into account that all the electrons of all atoms in the metallic crystal belong to the crystal as a whole. The energy levels of electrons in an atom are quantized. When two atomic orbitals combine, two molecular orbitals are formed. The molecular orbitals formed of lower energy is called bonding molecular orbital and that of higher energy is called antibonding molecular orbital and thus the valency electrons prefer to occupy the bonding molecular orbital.

In general in a metallic crystal, n atomic orbitals may combine to form n/2 bonding molecular orbitals and n/2 antibonding molecular orbitals. With the increase in the number atoms, the spacing between the energy levels of the various orbitals decreases and thus the energy levels of the orbitals are very close to each other. In other words, the energy difference between the various molecular orbitals will be very small which yields the formation of energy bands.
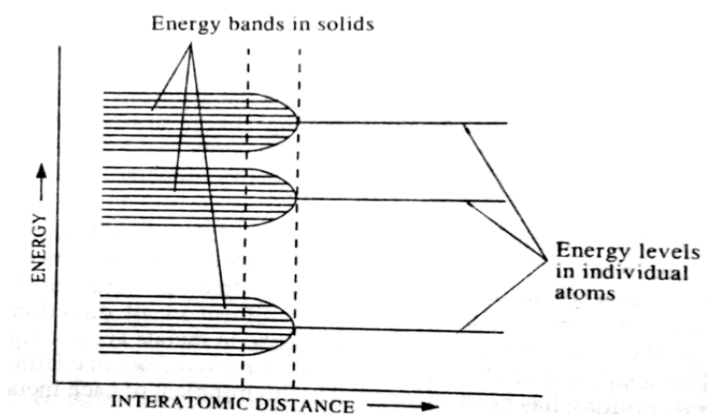
Fig 3.12 Formation of energy bands in a solid

Thus when compared to the energy gap (E_g) between the bands, the energy difference between the energy levels with in a band is very small. The difference in energy between the valence band (V.B) and the conduction band (C.B) is called the energy gap (E_g).

Conductors :

In a conductor (a metal) the valence band is full of electrons while the conduction band is partially filled. Only a small amount of energy is enough to allow electrons to move within the conduction band some rising to a higher energy level and others returning to a lower energy level.

Insulator :

In an insulator, the valence band is full and the energy gap is large. Thus it takes a large amount of energy to make an electron jump the energy gap.
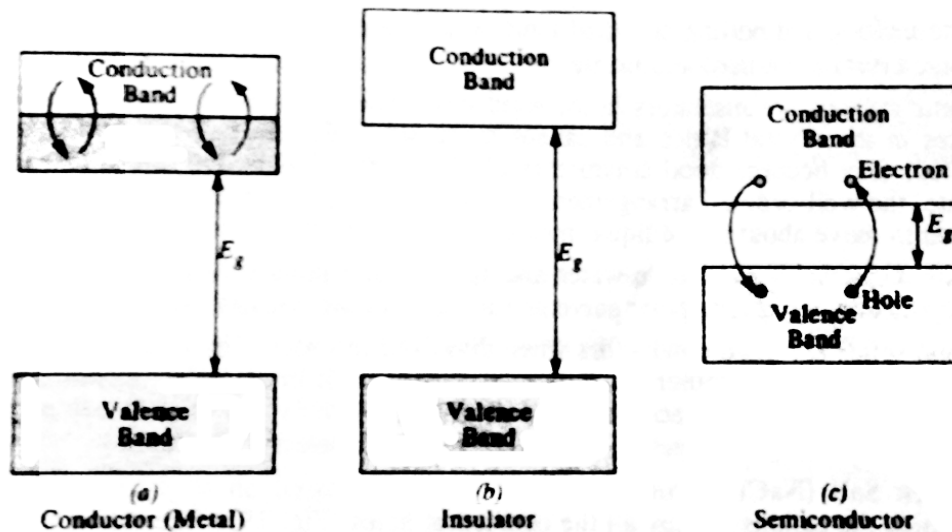
Fig 3.13 Energy band diagrams of (a) conductor (b) insulator (c) semiconductor

3:3:5 Semi conductors :

Metals are good conductors of electricity while elements like silicon, germanium are non conductors at room temperature. However these elements exhibit conductance due to presence of impurities like arsenic and boron. The resulting materials are called semi conductors.

A semiconductor can be defined as an electronic conductor with electrical conductivity in the range 10^{-7} to 10^{-4} ohm^{-1} m^{-1}. Semi conductors can be classified as intrinsic semi conductors and extrinsic semi conductors.

Intrinsic Semi Conductors :

The electrical conductivity of a pure semi conductor crystal is referred to as intrinsic conductivity. The pure elements like Si, Ge etc have four valence electrons. In these elements the valency electrons can readily cross the energy gap between valence bond and conduction band since the energy gap is small and it is about l ev. At room temperature they exhibit low electrical conductivity. When the temperature is raised the electrons migrate to conduction band leave a positive hole. Under the influence of applied electric field electrons in the conduction bond move to anode and the positively charged holes move towards cathode. Thus in an intrinsic semi conductor there is simultaneous movement of conduction band electrons and valence band holes in the opposite direction. The no. of electrons and holes are equal in number and they are charge carriers in intrinsic semi conductors.

Extrinsic Semi conductors :

The conductance of intrinsic semi conductors is improved by adding small quantities of impurities called doping agents. The conductance of silicon and germanium can be increased to a large extent by the addition of small amount of impurties like P,As or Sb. The addition of these impurities results in the decrease in the energy gap and allow more number of electrons to jump

from valency band to conduction band. Depending on the nature of doping agent the extrinsic semi conductors are divided into two types as n-type conductors and p-type conductors.

n-type Semi conductors :

Semi conductors which exhibit conductivity due to the flow of excess negative electrons are called n-type semi conductors. For example when a small quantity of doping agent like p, As or Sb is added to a pure intrinsic semi conductor like Si, Ge a negatively charged semi conductor called n-type semi conductor is obtained.

The doping agent forms four covalent bonds with surrounding atoms of intrinsic semi conductor leaving one electron vacant and loosely bound to itself. On applying external electrical field this loosely bounded electron can readily be promoted to conduction band. Thus the conductance increases due to movement of excess electrons with out leaving positive holes in the valency band. So these are n-type semi conductors.

p-type Semi conductors :

Semi conductors which exhibit conductivity due to the positive holes are called p- type semi conductors. For example when a small quantity of doping agents like B or Al is added to an intrinsic semi conductor like Si, Ge, a positively charged semi conductor called P-type semi conductor is obtained.

The doping agent forms three covalent bonds with surrounding three atoms of the intrinsic semi conductor (say Ge) leaving a surrounding Ge atom with incomplete bonding. This gives raise to a positive hole. This positive hole conducts electricity when an external electric field is applied. During this conduction, a hole travels to an adjacent atom by taking an electron and forming a covalent bond and by breaking a covalent bond in the adjacent atom forming a new hole. In this way the holes in a p-type semi conductor conduct electricity. The n-type and p-type semi conductors with As and B atoms are shown below.
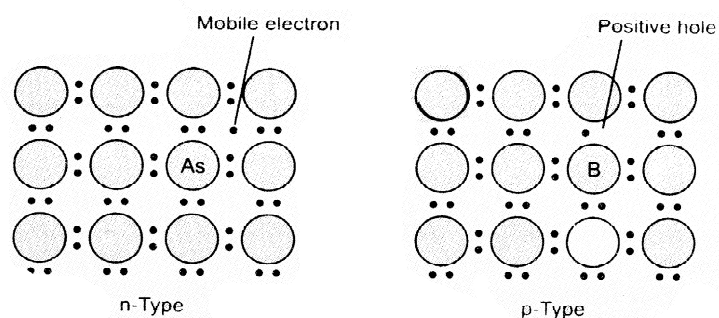
Fig .3.14 Semi conductors derived from silicon. n-type semiconductor has As atom impurity and a mobile electron; P-type conductor has B atom and positive hole. n-type semi conductors are more in conduction capacity than p-type semi conductors.

3.3.6 Uses of semi conductors :

1. Semi conductors are used as rectifiers in converting A.C current to D.C current.

2. Semi conductors are used as detectors for radiation in photo cells.

3. The combination of n and p –semi conductors are used in transistors.

4. They are responsible for the development of integrated circuits , micro processors etc. used in computors and electronic equipment.

3.3.7 Model Questions :

1. Discuss Scholtky defect and Frenkel defect.

2. Explain the impurity defects.

3. What are semi conductors? How are they classified. Explain.

4. What are semi conductors? Explain p - and n-type of semi conductors.

5. Mention the uses of semi conductors?

6. Explain metal excess defect.

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UNIT – III

Lesson – 4

SOLUTIONS

3:4:1 :

A solution is defined as a homogeneous mixture of two or more substances. The substance present in larger proportion is called as solvent while the substance present in smaller amounts is called as solute. A solution may exist in three states namely gaseous state, liquid state and solid state. Depending upon the physical state of solute and solvent, nine types of solutions are possible, out of which solid in liquid, liquid in liquid and gas in liquid type of solutions are more significant.

Reasons for a substance to dissolve :

Every system exhibits two types of tendencies :

(i) The system always tends to move towards decrease in energy and

(ii) To move towards increased disorderliness or randomness.

Solution exhibits a state of greater randomness. Randomness favours solution. So, randomness always trying to increase the solubility while energy trying to decrease it. Temperature always increases randomness and hence solubility increases with rise in temperature.

Solutions of liquids in liquids :

Solutions containing only two liquids are known as binary liquid solutions. Depending upon their solubility in one another the binary liquid solutions are classified into three types.

(i) The two liquids are completely soluble in all proportions.

Examples : Benzene and toluene , Water and alcohol.

(ii) Partially miscible binary liquid solutions : The two liquids are soluble in one another only to a limited extent.

Examples : Phenol and water ; Nicotine and water.

(iii) The two liquids do not mix with each other and hence form separate layers.

Examples : Carbon tetrachloride and water ; Aniline and water ;
Carbon disulphide and water

Completely miscible liquids :

Completely miscible liquids are further classified into two types of solutions namely ideal and non - ideal solutions.

Ideal solutions :

A solution in which the molecules attract one another with equal force irrespective of their nature is known as an ideal solution.

Raoult's law is obeyed perfectly by ideal solutions.

For example in an ideal solution of two liquids A and B, the forces of attraction between A and A, B and B and A and B molecules are same.

Liquid Mixtures : Examples of ideal solutions :

Benzene and toluene , carbon tetrachloride and silicon tetrachloride, Ethylene chloride and ethylene bromide, n - Hexane and n - Heptane.

In an ideal solution

i) Total volume of the solution = Volume of one liquid and volume of another liquid i.e. no volume change occurs when the two liquids are mixed.

ii) No heat is evolved or absorbed on mixing the two liquids.

So, thermodynamically in an ideal solution, no volume change and no enthalpy change occurs, when the two liquids are mixed.

iii) Ideal solutions obey Raoult's law exactly. It is proved by a straight line graph obtained by plotting vapour pressure versus mole fraction of components.

3:4:2 Raoult's law :

Raoult gave an empirical relation between the relative lowering of vapour pressure and the concentration of the solute present in the solution. This is known as Raoult's law.

Relative lowering of vapour pressure = $\dfrac{P^0 - P}{P^0}$

Where
$P° $ = Vapour pressure of the solvent
P = Vapour pressure of the solution
$P° - P$ = Lowering of vapour pressure

$\dfrac{P^0 - P}{P^0}$ = Relative lowering of vapour pressure.

According to Raoult's law the relative lowering of the vapour pressure of a dilute solution is equal to the mole fraction of the non - volalite solute present in the solution.

Mathematically, Raoult's law can be expressed as

$$\frac{P^0 - P}{P^0} = \frac{n}{n+N}$$

Where ;

n = number of moles of solute

N = number of moles of solvent.

Derivation of Raoult's law :

The vapour pressure of the solution is determined by the number of molecules of the solvent present at any time in the surface which is proportional to the mole fraction.

$$\frac{P^0 - P}{P^0} = \frac{n}{n+N} \quad \text{............. (i)}$$

Consider a solution obtained by dissolving 'n' moles of a non - volatile solute in ' N ' moles of a volatile solvent.

Mole fraction of the solvent $X_1 = \dfrac{N}{N+n}$ .... (ii)

Mole fraction of the solute, $X_2 = \dfrac{n}{N+n}$ ....(iii)

Since the solute is non - volalile it has neglisible vapour pressure and the vapour pressure of the solution is equal to the vapour pressure of the solvent.

According to Raoult's law, the vapour pressure of a solvent in an ideal solution (P) is equal to its mole fraction (x1) multiplied by the vapour pressure of the solvent (P°)

$$P = X_1 P° \text{............. (iv)}$$

Since $X_1 + X_2 = 1$

$\therefore X_1 = 1 - X_2$

Substituting the value of X_1 in equation (iv) we get.

$P = (1 - X_2)P°$ (or) $\dfrac{P}{P^0} = 1 - X_2$

or $X_2 = 1 - \dfrac{P}{P^0}$

On substituting the value of mole fraction of the solute (x_2) from equation (iii) in the above equation we get

$$\frac{P^0 - P}{P^0} = \frac{n}{n+N} \ .$$

Limitations of Raoult's law :

1. Raoult's law is applicable only to very dilute solutions which shows ideal behaviour.

2. It is applicable only to solutions containing non volalile solutes only.

3. It does not applicable to solutions which dissociate.

$$AB \rightarrow A^+ + B^-$$

or to solutions which associate

$$2A \rightarrow A_2$$
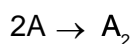
Hence, Raoult's law is applicable only to very dilute solutions containing non - volatile and non - electrolytic solutes which exist as simple molecules.

3:4:3 Solubility of gases in liquids :

All gases are soluble in water as well as other solvents to a certain extent. The solubility of the gas in a liquid depends upon the pressure, temperature, the nature of the gas and the nature of the solvent. At a given pressure, the solubility of a gas decreases with rise in temperature.

Henry's law :

The solubilities of solids in liquids are almost independent of pressure. But the solubilities of gases in liquids vary considerably with pressure.

The effect of pressure on the solubility of a gas in a given solvent was discovered by william Henry.

William Henry, found a simple relation between the pressure and solubility of a gas. He found that the solubility of a gas at a given temperature increases directly as the pressure. This relation is known as Henry's law and may be stated that at constant temperature, the mass of a gas dissolved per unit volume of a solvent is proportional to the pressure of the gas.

$$m \propto P$$

or $\qquad m = KP$

Where

m = mass of a gas dissolved per unit volume of a solvent.

P = Pressure of the gas

K = Proportionality constant.

Gases obey Henry's law provided :

i.   The temperature is not too low

ii. Pressure is not too high

iii. The gas does not dissociate or enter into chemical combination with the solvent and the gas should not be highly soluble. For example, Henry's law is valid in case of solubility of ammonia in benzene since it is sparingly soluble but in case of solubility of ammonia in water Henry's law is not valid since it enters into chemical combination with water.

$$NH_3 + H_2O \rightarrow NH_4OH \rightleftharpoons NH^+_4 + OH^-$$
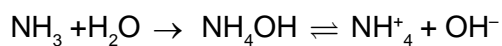
Henry's law may be stated in another form considering the volume of the gas dissolved instead of the mass.

" The volume of the gas dissolved in a solvent at a given temperature is independent of the pressure".

If Henry's law is valid, the graph obtained should be a straight line, when solubility of a gas is plotted against pressure at constant temperature.

Variation of solubility of agas with pressure.
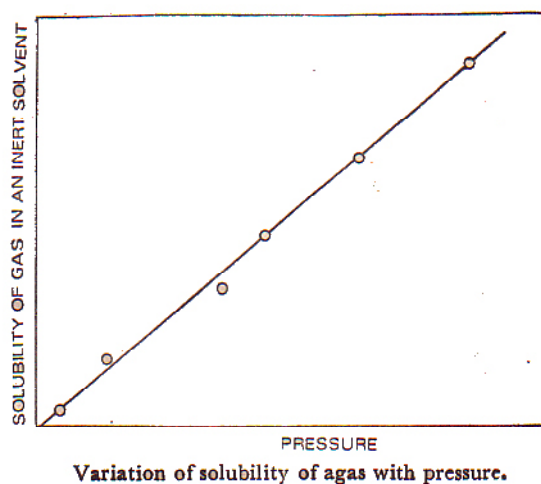
Fig 4.1

3:4:4 Non - ideal solutions : Vapour pressures on Non - ideal solutions:

The solutions which does not obey Raoult's law are known as real or non - ideal solutions. In non - ideal solutions, the molecular inter actions between the two components i.e. A - B are either higher or lower than the molecular interactions between the individual components i.e. A–A or B–B.

The vapour pressure of a solution is given by Raolult's law, Only few solutions obey Raolut's law over the entire range of composition. Most of the solutions show positive or negative deviations from the ideal behaviour in their vapour pressure.

In case of ideal solutions, the graphs of vapour pressure versus composition (mole fraction) are straight lines while in the case of non - ideal solutions the graphs are curved lines. Depending upon these curves, the non - ideal solutions are divided into three types namely.

i. Solutions that show small positive deviations from Raoult's law.

ii. Solutions that show large positive deviations and

iii. Solutions that show large negative deviations.

(i) Solutions that show small positive deviations from Raoult's law :-

The vapour pressure composition graphs of these solutions show small positive deviation. For any mole fraction the total vapour pressure of the solution as well as the partial vapour pressure of each component are very slightly more than that expected from Raoult's law for ideal solutions.
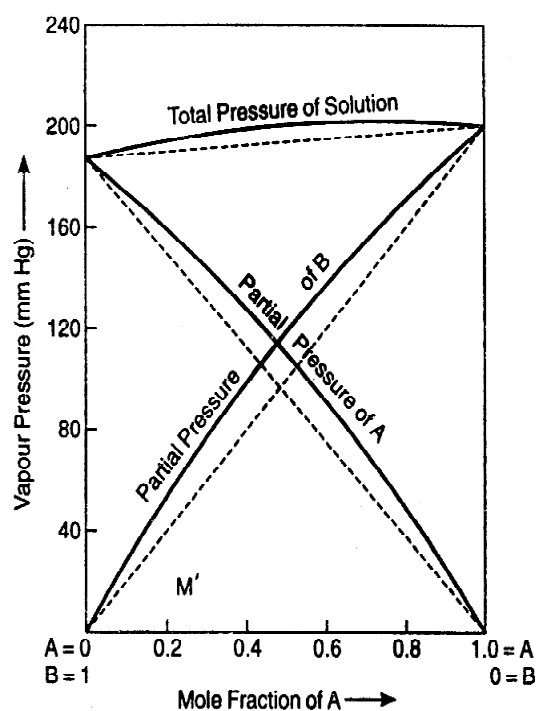
**Fig4.2 : Vapour pressure - Composition plots for real
Solution showing small positive deviation.
The dotted lines represent ideal behaviour.**

(ii) Solutions that show large positive deviations :-

In these solution salso, the total vapour pressure of the solution and, the partial vapour pressure of each component are greater or maximum than that calculated from the Raoult's law.
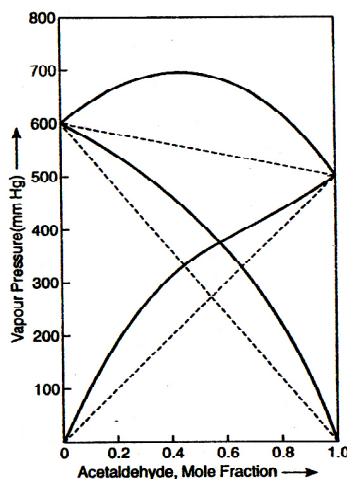
**Fig4.3 Vapour pressure composition plots for real
Solution showing large positive deviation.
The dotted lines represent ideal behaviour.**

The tendency for the molecules to escape from the solution is more than that from the pure liquids, In other words, the inter molecular attractions between A - B are weaker than A-A or B-B attractions, Formation of this type of solution is accompanied by an increase in volume and absorption of heat.

Examples : Water and ethanol ; acetaldehyde - carbon disulplide, Benzene and Cyclohexane etc.

iii) Solutions that show large negative deviations :

In these solutions the total vapour pressure of the solution is less than that calculated from the Raoult's law and hence show negative deviation. Here, the tendency for the molecules to escape from the solution is less than that from the pure components, It indicates that the intermolecular attractions between molecules of liquid pair A-B are stronger than either A-A or B-B attractions. Formation of this type of solutions is accompanied by decrease in volume and evolution of heat. Examples : Water and nitric acid ; Acetone and chloroform ; Pyridine and acetic acid etc.
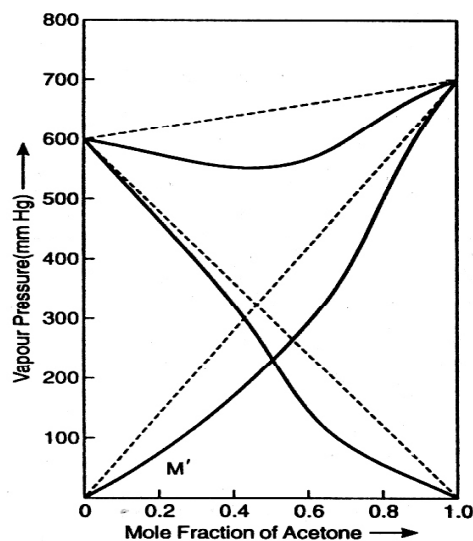
**Fig 4.4 Vapour pressure composition plots for non - ideal
Solution showing negative deviation.
The dotted lines represent ideal behaviou**

3:4:5 Vapour pressure - Composition and Vapour pressure - temperature curves of completely miscible binary solutions :

In order to determine the composition of the system, two variables i.e pressure and temperature must be known. consider a binary mixture consisting of two liquids A and B which are completely miscible with each other. On heating under constant pressure i.e suppose under atmospheric pressure the binary mixture start boiling at temperature at which its total vapour pressure becomes equal to the atmospheric pressure. If 'P' is the atmospheric pressure then the condition for boiling is that $P = P_A + P_B$ where P_A and P_B are the patrial pressures of the two liquids A and B. Solutions of different compositions have different vapour pressures and hence, they boil at different temperatures. Thus, as the boiling point and vapour pressure of a liquid are inversely related, a solution of higher vapour pressure will boil at a lower temperature and vice versa. From this it is possible to draw boiling temperature composition graphs from the corresponding vapour pressure - composition diagrams. The following are the three types of mixtures.

In Type I, the vapour pressure changes continuously with composition of the mixture (Figi).

In Type II, the vapour pressure shows a maximum in its vapour pressure composition curve. (Fig ii)

In Type III, the vapour pressure shows a minimum in its vapour pressure composition curve (Fig iii).

Type I : In this type the vapour pressure of pure ' A ' is the lowest and that of pure ' B ' is the highest and hence the boilling point of A will be highest and that of ' B ' the lowest. Since the vapour pressure of the mixtures of A and B lie in between the extreme values, their boiling points also lie in between. (6iv) At a given temperature, the vapour phase will be richer in the more volatile component 'B',

the composition of the vapour phase will be always richer in ' B' than that of the liquid phase Hence the vapour composition curve will lie above the liquid composition curve.

Type II : In type II, the vapour pressure curve shows a maximum for a certain composition 'C' as in (Fig ii) the solution of that composition will boil at the lowest temperature which gives rise to a minimum in the boiling point curve (Fig V)

Type III : In type III, the vapour pressure curve shows a minimum for a certain composition ' D' as in (Fig iii) the solution of that composition boil at the highest temperature which shows a maximum in the boiling point curve (Fig VI).
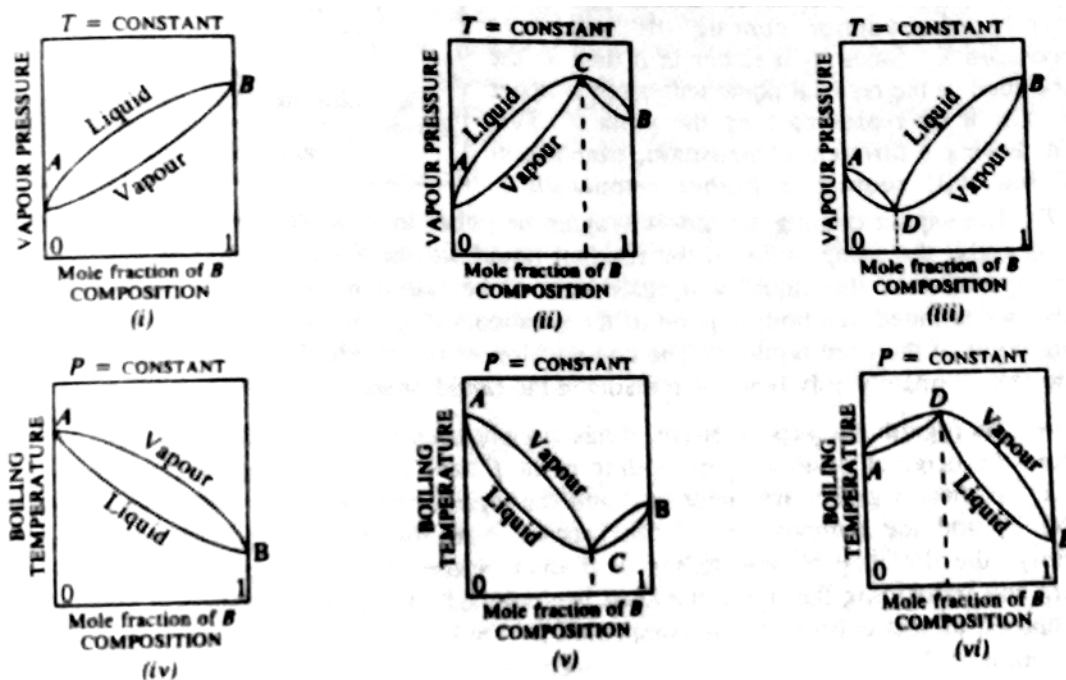
Fig 4.5 Vapour pressure - Compostion and Boiling point - Composition curves of completelymiscible binary solutions

3.4.6 Azeotropes mixtures :

Completely miscible liquids are divided into azeotropic mixtures (two types) and Zeotropic mixtures, A mixture of two or more liquids which boils at a constant temperature with out change in composition is known as azeotropic mixture. But azeotropic mixtures can not be regarded as compounds because the boiling point and composition of an azeotrope change with the pressure while the composition of a compound remain unchanged with temperature and pressure.

3.4.6.1 Azeotropes – HCl-H$_2$O; Ethanol- water systems :

The study of the vapour pressures of completely miscible liquids mixtures are of great help in the separation of liquids by fractional distillation. plotting the vapour pressures of these mixtures of completely miscible liquids against composition has revealed that the mixtures of completely miscible liquids are of three types –

  i)   Maximum boiling point azeotropic solutions

  ii) Minimum boiling point azeotropic solutions and

  iii) Zeotropic mixtures.

i) Maximum boiling point azeotropic solutions :

The vapour pressure curve of this first type of solutions exhibit minimum vapour pressure at a particular composition and thus a maximum boiling point. In a mixture of two liquids X and Y in which X is a more volatile component. On adding more and more of component 'Y', the vapour pressure of the mixture decreases and the point 'D' where the vapour pressure is minimum and thus boiling point is maximum. The mixture will boil at constant temperature and distil over completely without any change in its composition.

Complete separation of this type of solutions into its components is impossible. Such type of liquid mixtures which distil unchanged in composition at a constant temperature and show a maximum boiling point are called as maximum boiling point azeotropic solutions.
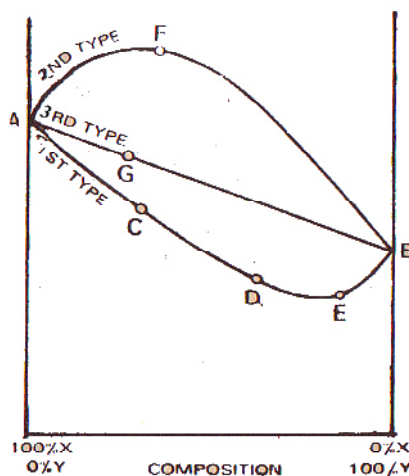
Fig 4.6 Vapour Pressure of Liquids

Example : HCl – H$_2$O system.

Hydrochloric acid form a constant boiling mixture at 110°c containing 20.24% of hydrochloric acid.

ii) Minimum boiling point azeotropic solutions

The vapour pressure curve of this type of solutions of completely miscible liquid mixtures show maximum vapour pressure at point F and hence lowest boiling point. Such type of solutions show a constant boiling point until one of the component has been completely exhausted. After that the temperature rises and the other component will pass over. It is not possible to separate these solutions also into its components completely by fractional distillation. At the most, it is possible to separate it into a constant boiling mixture and one of the components in pure state.

Such liquid mixtures which distil without change in composition at a constant temperature are called minimum boiling point azeotropic solutions.

Example :

Ethanol or Ethyl alchol and water system. Ethanol – water mixture containing 95.59% alcohol boils at the minimum temperature of 78.13°c. Thus it is very difficult to get pure alcohol by distillation. How ever, by adding benzene, it is possible to convert it into low boiling benzene – water mixture and on distillation, pure alcohol may be left behind.

iii) Zeotropic mixtures.

The liquid mixtures which distil with a change in composition are called zeotropic mixtures. The vapour pressure of this type of mixtures always lie between the vapour pressure of pure components and hence the vapour pressure composition curve is a straight line. This type of miscible liquid mixtures can be separated completely into its components by fractional distillation.

Examples : Methyl alcohol – water mixture.

3.4.7 Theory of fractional distillation :

The vapour pressure composition curves of completely miscible liquid mixtures are helpful in separation of the liquid mixtures by fractional distillation. Complete separation by fractional distillation is possible only in case of third type of solution i.e. in Zeotropic mixtures.

When a binary liquid mixture consisting of x and y components is heated, then the component having higher vapour pressure will boil at a lower temperature. To understand the process of fractional distillation it is necessary to have an idea of the composition of the vapour phase and that of liquid mixture at different boiling temperatures. For this purpose the temperature - composition curves are important. When we plot the boiling point of liquid mixture against its composition, and the composition of the vapour in contact with it, two separate curves for each type of solution are obtained. The curves obtained for third type of solutions are shown below.
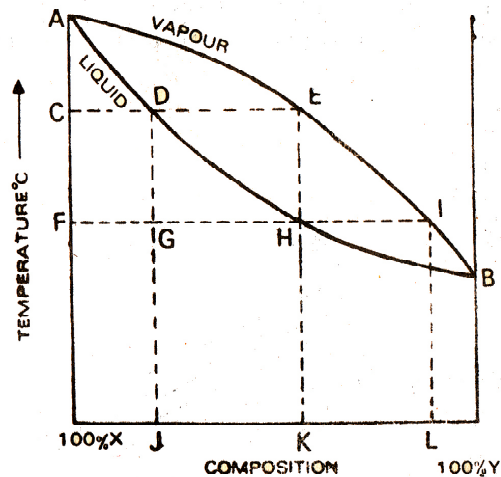
**Fig 4.7 Curves showing the composition of vapour and
liquid at various boiling temperatures.**

AEB and ADB are the temperature composition curves obtained for the vapour and liquid respectively. The composition of liquid mixture is represented by 'J' at temperature 'C' and that of vapour in equilibrium by K. The more volatile component 'Y' is present in greater proportion in the vapour than in the liquid mixture. Thus the distillate, richer in 'x' if it is subjected again to distillation, it will boil at 'F' and the fresh distillate will have the composition 'L'. Now the proportion of 'Y' in the second distillate is greater than in the first one. By repeating the process of distillation in this way, 'Y' can be obtained, almost in pure state.

In first type of solutions, (Maximum boiling point azeeotropic Solutions) a boiling mixture indicated by 'Y' has its vapour, poor in 'Y' than the liquid mixture and there is gradual rise in boiling point till the maximum point 'C' is reached where the liquid mixture and vapour have the same composition. Here, the distillation proceeds without change of composition.
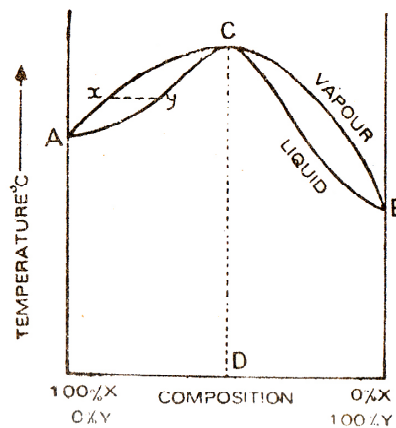
Boiling point curves
for 1st type of solutions.

Fig 4.8

In second type of solutions, (Minimum boiling point azeotropic solutions) a boiling mixture indicated by the point 'X'. In vapour the amount of 'Y' is in higher amount and there is gradual fall in boiling point till it reaches the minimum point 'C' Where the vapour and liquid mixtures have the same composition here, the mixture boils with out any change in composition.
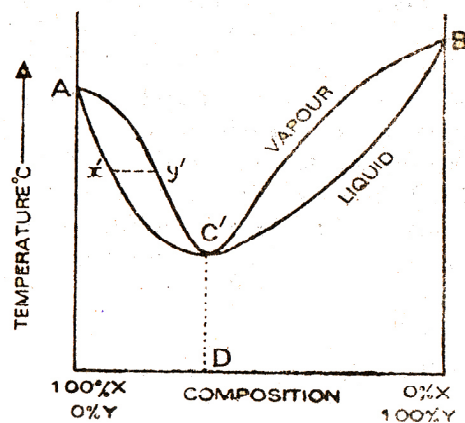
Boiling Point Curves
for 2nd type of solutions.

Fig 4.9

So, the above two types of solutions, can not be completely separated by fractional distillation.

Fractional distillation :

Fractionating columns are used in order to decrease the number of distillations and so increase the efficiency of the process of fractional distillation. It is a long tube provided with obstruction to the passage of vapour going upwards and that of the liquid coming downwards. The liquid mixture which is to be fractionated is taken in a distillation flask fitted with a fractionating column, a thermometer and a condenser.

–Fractional distillation.

Bell and
plate type frac-
tionating column.
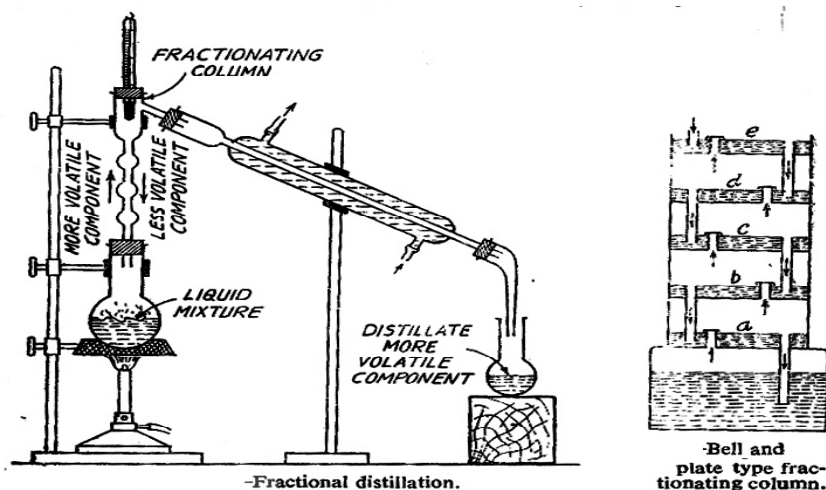
Fig 4. 10

The flask is heated from below. The liquid vapourises and the vapours rise into the fractionating column where some of the vapours condense and start flowing down.

For industrial purposes a fractionating tower is employed which is divided into several compartments by means of trays that are set one above the other. At the centre of each tray, there is a hole which is covered by a bubble cap. Each tray has an over flow pipe which joins it with the tray present below it. The fractionating column is fitted in the neck of the distillation flask so that the vapours of the liquid being heated passes up through it. The temperature falls in the fractionating column as the vapours pass from bottom to the top. The hot vapours that enter the column get condensed in the lower part and when heating is continued more vapours travel upwards and boil the liquid already condensed. Thus the liquid condensed in the lowest part is distilled on to the upper part. A sort of condensation and distillation goes on along the height of the column which results in the increase of the proportion of the volatile component in the out going vapours. There exists an equilibrium between the liquid and vapour, at every point in the column vapours of the low boiling liquid escape at the top and are condensed while the high boiling liquid collects at the bottom.

3.4.8 Partially miscible liquids :

A large number of liquids which dissolve in one another, only to a limited extent are called as partially miscible liquids. Their solubility in one another is limited. For example, ether dissolves about 1.2% water and water dissolves about 6.5% ether. When equal volumes of ether and water are shaken, two separate layers are formed one of which is a saturated solution of ether in water and the other layer is a saturated solution of water in ether. These two solutions which are in equilibrium are known as conjugate liquids and the partially miscible liquids systems are divided into three types basing on their critical solution temperatures.

i) Partially miscible liquids having upper critical solution temperature **Eg :** Phenol – water system

ii) Partially miscible liquids with lower CST, **Eg :** Triethyl amine – water system and

iii) Partially miscible liquids having upper as well as lower CST, **Eg :** Nicotine water system.

The temperature at which the two partially miscible liquids become completely miscible is called the critical solution temperature (CST) or consolute temperature of the system. Critical solution temperature is very much influenced by the presence of impurities. When the critical solution temperature is lower than the room temperature, it is known as lower critical solution temperature while if it is higher than the room temperature, it is known as upper critical solution temperature.

i) Phenol - water - system with upper CST :

Phenol and water are partially miscible at ordinary temperature. On shaking these two liquids, two saturated solutions of different compositions are formed i.e. one is phenol in water and the other is water in phenol. Such solutions of different composition coexisting with one another are called conjugate solutions. Their mutual solubility in one another increases with rise in temperature and hence the concentration of phenol in water and water in phenol goes on increases with rise of temperature and finally at a certain temperature, the two conjugate solutions merge into one another to form one layer of homogenous solutions. This temperature at which the two

conjugate solutions merge into one another to form a single layer is called critical solution temperature (CST) or upper consolute temperature. This temperature for phenol water system.

% By Weight of phenol

Phenol-Water System
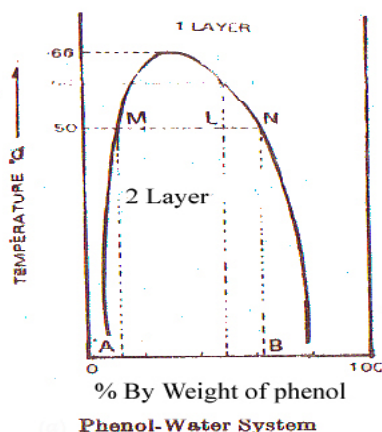
Fig .4.11

Corresponds to 66°c and the composition of phenol as 33%. Above this critical solution temperature and outside the curve, the phenol and water are completely miscible and the system is homogeneous. But , below this curve, the complete miscibility depends upon the composition of the mixture. It is clear from the graph that at a temperature below 50°c, a mixtures of 90% phenol and 10% water (Point M) or 5% phenol and 95% water (Point N) will lie outside the curve and hence the above composition is completely miscible. At 50°c, a mixture of equal proportions (50%each) of phenol and water form two layers whose compositions are given by A and B. The critical solution temperature is very much influenced by the presence of impurities. Hence the critical solution temperature is used for testing the purity of phenol and other substances.

ii) Triethyl amine – water system - systems with lower CST :

In triethyl amine – water system the mutual solubilities of the two components increases with decrease in temperature. The two liquids are completely miscible at 18.5°c. This temperature is called lower critical solution temperature or lower consolute temperature. Below 18.5°c temperature, the two liquids are completely miscible to form one layer but above this temperature the two liquids form two different layers.

WEIGHT PERCENT TRIETHYL AMINE

Triethyl amine-water system.
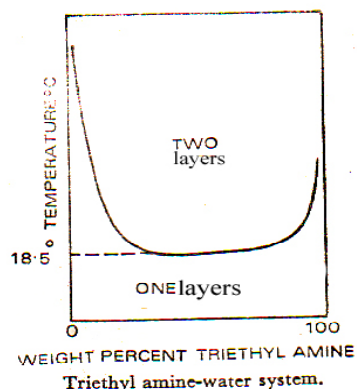
Fig 4.12

iii) Nicotine water systems with upper as well as lower CST :

Some partially miscible liquid systems, for example Nicotine water system, appear to be as a combination of the above two types. These liquids are completely miscible above certain critical temperature and below certain critical temperature. They show both upper as well as lower consolute temperature. Thus the system has two critical solution temperatures or consolute temperatures upper 208°c and the lower 61°c . Above 208°c and below 61°c the two liquids are miscible in all proportions. In other wards, between these two limiting temperatures the two liquids are partially miscible. Increase of pressure on the system raises the value of lower critical solution temperature and decreases the values of the upper critical solution temperature and finally they become one at a particular pressure.
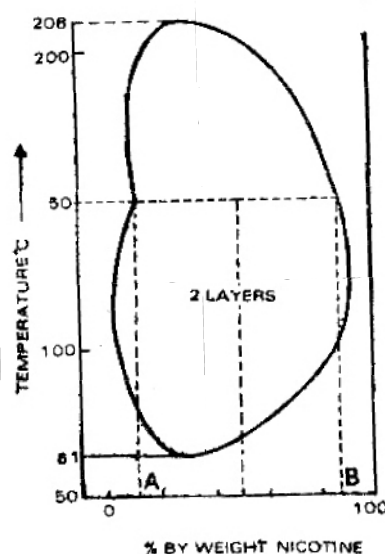
4.13 Nicotine and water system.

3:4:9 Effect of impurity on consolute temperature :

The critical solution temperature or consolute temperature is very much influenced by even traces of impurities present in the system. The amount of impurity present in a system can be known by studying the variation of its critical solution temperature. This method of testing any sample of compound is called " Crismer" test.

Example : If a small amount of naphtalene (0.1M) is added to the phenol - water system, the critical solution temperature rises by 20°c.

If general, if the impurity is soluble in one of the liquids only, the critical solution temperature or consolute temperature rises, other wise it decreases.

3.4.10 Immiscible liquids :

Liquid pairs such as water ether ; water – benzene ; water – carbon tetrachloride and water – Cyclohexane do not mix with each other. Hence they are known as immiscible liquids or non- miscible liquids. In such liquid mixtures, each liquid exerts its own vapour pressure independent of the other. The total vapour pressure of the in the liquid mixture.

$$P = P_A + P_B$$

Where P_A and P_B are the individual vapour pressures of the liquids A and B respectively.

Any mixture of two immiscible liquids boil at a temperature lower than that at which any pure liquid of the mixture boils.

The relative proportion of the two liquids in the distillate can be calculated, considering the fact that the number of moles of each liquid present in the vapour phase is proportional to its vapour pressure. If n_A and n_B are the number of moles of the two liquids A and B

Then

$$\frac{P_A}{P_B} = \frac{n_A}{n_B}$$

$$= \frac{W_A/M_A}{W_B/M_B}$$

$$\frac{W_A}{W_B} = \frac{P_A}{P_B} \times \frac{M_A}{M_B}$$

W_A and W_B represent the actual weights and MA and MB are the molecular weights of the liquids A and B respectively.

Thus the weights of the liquids in the distillate are in the ratio of their vapour pressures and molecular weights.

3.4.11 Steam distillation :

Steam distillation is a process of distillation carried out in a current of steam. It is used in the purification of organic compounds having high boiling points. These compounds should be immiscible in water. The process of steam distillation is done in preference to ordinary distillation

        i)   for the purification of organic liquids when it is difficult to remove impurities by other methods and

        ii)   when the given impure liquid decomposes at higher temperatures.

When a mixture of water and a high boiling liquid is heated in a current of steam, the mixture boils at a lower temperature than the boiling point of the organic liquid.
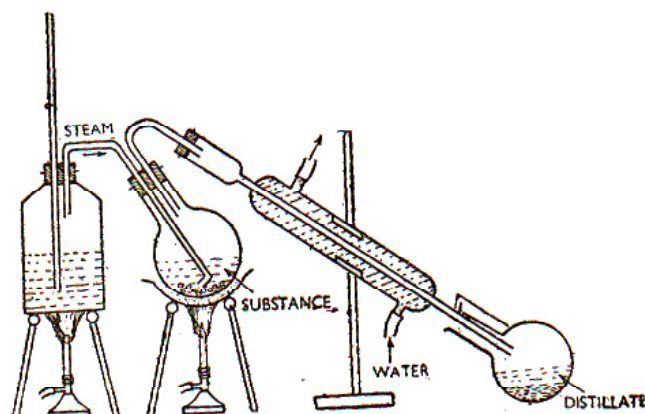
Fig 4.14 Steam distillation

Steam distillation is used in the purification of organic compounds having high boiling points. The mixture to be distilled is placed in a round bottomed flask and steam is passed into it from a metallic can in which steam is produced by boiling water. The flask which is heated on a sand bath is connected to a water condenser which has a receiver placed below its lower end. Water and organic liquid collected in the receiver form two separate layers which can be separated by means of a separating funnel. The organic liquid is then dried and redistilled. The ratio of distilling liquids is given by the relation.

$$\frac{\text{Organic substance}}{\text{Water}} = \frac{P_o}{P_W} \times \frac{M_o}{18}$$

Where P_O and P_W are the vapour pressures of organic substance and water; M_O – molecular weight of organic substance and 18- molecular weight of water.

3.4.12 Problems :

1)   A mixture of nitrobenzene and water boils at 99°c at one atmospheric pressure. The vapour pressure of water at that temperature is 733 m.m. calculate the proportion of water in nitrobenzene in the distillate at the boiling point.

Ans : Molecular weight of nitrobenzene = 123

Vapour Pressure of water (P_W) = 733m.m.

Vapour Pressure of nitrobenzene (PNB) = 760 – 733 = 27 mm

$$\frac{\text{Weight of } C_6H_5NO_2}{\text{Weight of } H_2O} = \frac{P_A . M_A}{P_B . M_B}$$

$$\frac{W C_6H_5NO_2}{W H_2O} = \frac{27 \times 123}{733 \times 18} = \frac{1}{3.97} \text{ or } 4:1$$

2)   The vapour pressures of water and aniline at 98.5°c are 717m.m and 43m.m respectively. The molecular weights of water and aniline are 18 and 93. Calculate the relative weights of the two liquids in the distillate.

Ans : $\dfrac{\text{Weight of aniline } (W_A)}{\text{Weight of water } (W_B)} = \dfrac{P_A \cdot M_A}{P_B \cdot M_B}$

$$\dfrac{(W_A)}{(W_B)} = \dfrac{43 \times 93}{717 \times 18} = 0.3098$$

3)   When a mixture of nitro benzene and water is distilled at a pressure of 732m.m at 98.2°c, the distillate contains 18.8 gm of nitrobenzene per 100 gm of water. Vapour pressure of water at 98.2°c is 712 m.m. Calculate the molecular weight of nitrobenzene.

Ans : Vapour pressure of nitrobenzene = 732 – 712 = 20m.m

Vapour Pressure of water = 712 m.m

$$\dfrac{(W_A)}{(W_B)} = \dfrac{P_A \cdot M_A}{P_B \cdot M_B}$$

$$\dfrac{W_{N.B}}{W_w} = \dfrac{P_A \cdot M_A}{P_B \cdot M_B}$$

$$\dfrac{18.8}{100} = \dfrac{20 \times M_A}{712 \times 18}$$

$$M_A = \dfrac{18.8 \times 712 \times 18}{2000} = 120.5$$

Molecular weight of nitrobenzene = 120.5

3.4.13 Model Questions :

1)   State and explain Henry's law. Show that the volume of a gas absorbed by a given volume of solvent is independent of pressure.

2)   State and explain Raoult's law and Henry's law.

3)   What are ideal and non- ideal solutions? Show that in an ideal solution, the volume of mixing and the enthalpy of mixing is zero.

4)   what are azeotropic mixtures ? Explain with one example

5)   Draw a labeled temperature composition diagram for the nicotine water system and discuss the variation of mutual solubility of nicotine and water with temperature.

6)   Define the term critical solution temperature. Explain upper consolute temperature and lower consolute temperature with one example each.

7)   What do you understand by positive and negative deviations from Raoult's law. Explain with suitable examples.

8) Explain the principle underlying the process of steam distillation.

9) Discuss the principle of fractional distillation of a miscible liquid pair.

10) Explain the terms consolute temperature and conjugate solution. Discuss the variation of mutual solubility of Phenol – water.

11) A mixture of chloro benzene and water which are immiscible boils at 90.30°c at an external pressure of 740m.m.The vapour pressure of pure water at 90.3°c is 630.1m.m. Calculate the weight composition of the distillate.

12) A mixture of Chlorobenzene and water distills at 90°c and at 734.4m.m pressure. At 90°c, the vapour pressure of water is 506m.m. Calculate the ratio of weight of chlorobenzene to water collected in the distillate.

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UNIT – III

Lesson – 5

NERNST DISTRIBUTION LAW

3:5:1 :

     If we take two immiscible solvents in a beaker, they form separate layers. When a solute, which is soluble in both solvents is added, it distributes itself between the two layers in such a way that at a given temperature, the ratio of its molar cocentration in the two layers was constant, irrespective of the amount of solute.

     For example (i) When iodine is added to a beaker containing water and an organic solvent such as carbon disulphide or carbon tetrachloride it distributes itself between the two layers. In other words at constant temperature.

$$\frac{\text{Concentration of iodine in carbon disulphide } (C_1)}{\text{Concentration of iodine in water } (C_2)} = K$$

$$\frac{C_1}{C_2} = K$$

Where K is termed as distribution or partition coefficient.
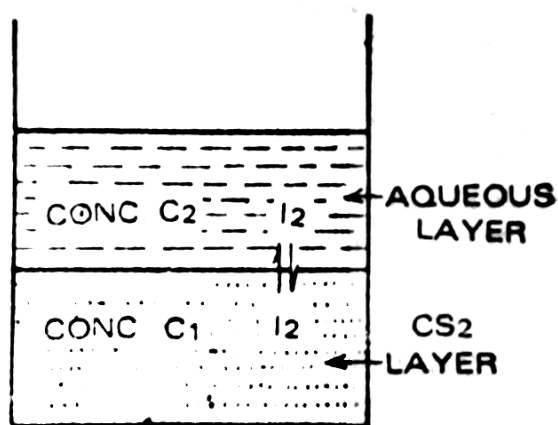
Fig 5.1 Distribution of iodine between water and carbon disulphide

i) Distribution of Succinic acid between organic solvent ether and water explains the constancy of the concentrations in each layer.

Concentration of acid in ether (C₁)	Concentration of acid in water (C₂)	$\dfrac{C_1}{C_2}$
0.0046	0.024	0.191
0.013	0.069	0.188
0.022	0.119	0.185
0.031	0.164	0.189

ii) Distribution of iodine between carbon tetrachloride and water.

Concentration of iodine in CCl_4 (C₁)	Concentration of iodine in water (C₂)	$\dfrac{C_1}{C_2}$
0.02	2.35×10^{-4}	85.1
0.04	4.69×10^{-4}	85.2
0.06	7.03×10^{-4}	86.0
0.08	9.30×10^{-4}	86.0
0.10	11.4×10^{-4}	87.5

M. Berthelot (1872) and Nernst (1891) studied the distribution of several solutes between different pairs of solvents. Nernst gave a generalization known as Nernst's distribution law or simply distribution law or partition law, which may be stated as follows.

When a solute with similar molecular form distributes itself between two immisible solvents, at a given temperature, exists a constant ratio of distribution between the two solvents.

Thus $\dfrac{C_1}{C_2}$ = K

Where

C_1 = Concentration of solute in organic layer

C_2 = Concentration of solute in aqueous solvent

K = Distribtion Coefficient or partition coefficient

3:5:2 Conditions for the validity of distribution law :

The essential conditions to be satisfied for the application of the Nernst's distribution law are :

1) Mutual immiscibility of the two solvents.

2) Constant temperature. The temperature should be maintained constant through out the experiment.

3) Same molecular state. The molecular state of the solute is the same in the two solvents.

4) Dilute solutions. solutions should be dilute.

Deviations from distribution law :

Due to the change in the molecular state of the solute :

As pointed out the Nernst, the ration $\dfrac{C_1}{C_2}$ is constant only if the solute molecules exists in simple form . $\dfrac{C_1}{C_2}$ is not constant, if the solute undergoes association or dissociation in one of the solvents. In such cases, distribution law is applicable only to the part of solute that is present as simple molecules.

a) When the solute undergoes association in one of the solvents :

Suppose a solute 'X' is present as simple molecules in solvent ' A' and ' n ' molecules of 'X' associates to form ' Xn' molecules in solvent ' B ' . On assuming the presence of ' X ' also as simple molecules in solvent 'B', then the equilibrium that exists in the two solvents are as follows.
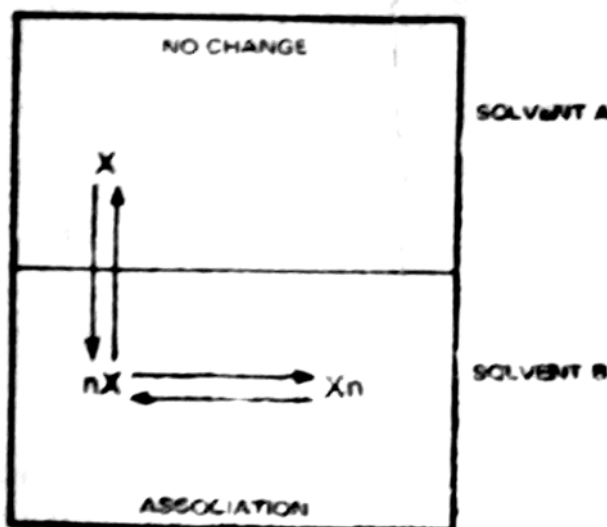
Fig 5.2 Distribution diagram when the solute is associated in one solvent

Let   concentration of X in solvent ' A ' $= C_1$

concentration of Xn in solvent ' B ' $= C_2$

concentration of X in solvent ' B ' $= C_3$

Applying distribution law to the equilibrium

X in solvent ' A ' $\rightleftharpoons$ X in solvent ' B '

We know that

$$\frac{C_1}{C_3} = K \text{ .... (i)}$$

Applying the law of mass action to the chemical equilibrium

n X $\rightleftharpoons$ Xn
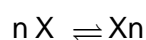
We know that

$$\frac{(X)^n}{[X_n]} = Kc \text{ (or) } \frac{C_3^n}{C_2} = Kc \text{ .... (ii)}$$

Taking n^{th} root on both sides

$$\frac{C_3}{\sqrt{C_2}} = n\sqrt{Kc}$$

Dividing equation (i) by (iii)

$$\frac{C_3}{n\sqrt{C_2}} = \frac{K_D}{n\sqrt{Kc}} = K$$

Thus when association occurs in one of the solvents, the distribution equation is modified as

$$\frac{C_3}{n\sqrt{C_2}} = K$$

Example :

Distribution of benzoic acid between water and benzene. The solute, benzoic acid exists mainly as dimer ($C_6H_5COOH)_2$ in benzene and in simple form in water.

Benzoic acid

C water	**C** benzene	$\dfrac{C_w}{C_b}$	$\dfrac{C_w}{\sqrt{C_b}}$
0.15	0.24	0.062	0.096
0.19	0.41	0.048	0.096
0.29	0.97	0.030	0.093

Problem : When benzoic acid was shaken with mixtures of benzene and water at constant temperature, the following results were obtained.

Conc of acid in benzene (C_1)	0.24	0.55	0.93
Conc of acid in water (C_2)	0.015	0.022	0.029

Comment on the results.

Sol : Calculating the ratio C_1/C_2 for each case

$$\frac{0.24}{0.015} = 16 \qquad \frac{0.55}{0.022} = 25 \qquad \frac{0.93}{0.029} = 32$$

Thus the distribution coefficient is not constant. There fore benzoio acid does not exist as single molecule in both solvents.

By calculating gives

$$\frac{\sqrt{0.24}}{0.015} = 32.6 \qquad \frac{\sqrt{0.55}}{0.022} = 33.7 \qquad \frac{\sqrt{0.93}}{0.029} = 33.2$$

The constant value of partition coefficient suggests that benzoic acid is associated into DOUBLE MOLECULES in the benzene.

b) When the solute undergoes dissociation in one of the solvents :

Suppose a solute 'X' is present as simple molecules in solvent ' A' and dissociates into A+B in solvent 'B', then the equilibrium that exists in the two solvents are as follows.
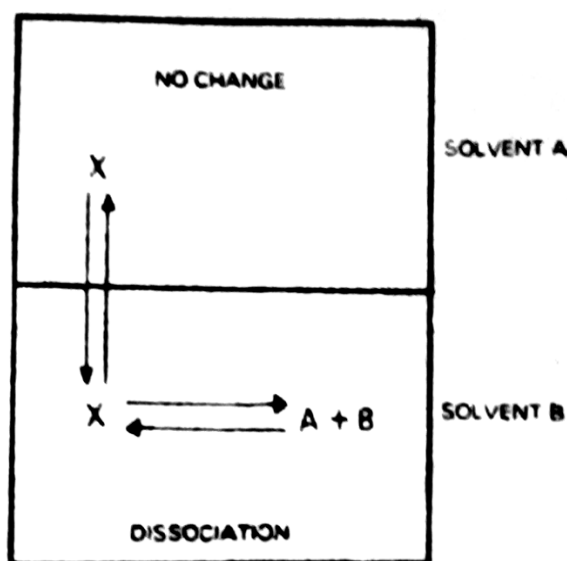
Fig 5.3 Distribution diagram when dissociation occurs in one solvent

Let concentration of X in solvent ' A ' = C_1

concentration of X (both dissociated and undissociated) in solvent ' B ' = C_2

If the degree of dissociation in solvent ' B ' is X, then

$$X \rightleftharpoons A + B$$
$$(1 - x) \quad x \quad x$$
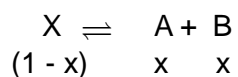
Hence the concentration of undissociated molecules in solvent ' B ' = C_2 (1- x)

On applying distribution law to simple molecules in the two solvents, we get modified distribution law equation when there is dissociation in one of the solvents.

$$\frac{C_1}{C_2(1-x)} = K$$

Example :

Distribution of a weak acid i.e succinic acid or oxalic acid between ether and water.

3:5:3 Applications of distribution law :

1) Determination of association of a solute :

When a solute associates in one of the solvents in which its concentration is C_2 and exists as simple molecules in another solvent where its concentration is C_1, then

$$\frac{C_3}{n\sqrt{C_2}}$$

Where n = Number of simple molecules which combine to form an associated molecule.

By studying the distribution of acetic acid and benzoic acid between benzene and water, it is possible to show that these substances exist in benzene as double molecules or dimers, the value of ' n' being 2.

2) Determination of dissociation of a solute :

When a solute ' x ' is dissociated in one of the solvents in which its concentration is say C_2 and exists as simple molecules in another solvent.

Where the concentration of it is C_1, then

$$\frac{C_1}{C_2(1-x)} = K$$

Where x is the degree of dissociation of a solute.

Since K is constant, the degree of dissociation (x) of a solute can be calculated at any concentration, provided its value is known at one concentration.

3) Solvent extraction :

Solvent extraction is the process used for the separation of organic substances from aqueous solutions in the laboratory as well as in industry.

The process of extraction is more efficient if the solvent is used in a number of small portions than used all in a single operation. The process is called multiple extraction.

It is possible to derive a general formula which enables the calculation of the amount left unextracted after a given number of operations. Let 'V' ml of a solution containing W gram of a solute be repeatedly extracted with ' V' ml of another solvent which is immisible with the first. Let W_1 be the weight of solute remained unextracted at the end of the first operation. Then the distribution coefficient K is

$$\frac{\dfrac{w_1}{V}}{\dfrac{w-w_1}{V}} = K \ (\text{ or })$$

$$w_1 = w \frac{Kv}{K_V + v}$$

Similarly at the end of second operation, the amount w_2 that remained unextracted is given by

$$w_2 = w_1 \frac{Kv}{K_V + v}$$

$$= w\left(\frac{Kv}{K_V + v}\right)^2$$

The amount remained unextracted at the end of n operations, Wn will be given by

$$w_n = w\left(\frac{Kv}{K_V + v}\right)^n$$

The efficiency of extraction increases by increasing the number of extractions using only a small amount of the extracting solvent each time.

Similarly, in the washing of precipitates the efficiency increases when we use a small quantity of water at a time and to repeat the process a number of times.

4) Desilverization of lead by Parke's process :

The principle of solvent extraction applies in the desilverization of lead by parkes process. Molten zinc is added to molten argentiferous lead (lead containing silver) which is heated to 800°c. Molten zinc and molten lead forms two immiscible layers and silver is distributed between them. The solute, silver is more soluble in zinc than in lead, the partition coefficient being of the order 300 at 800°C. On cooling the Zinc layer, Zinc - silver alloy separates out. The Zinc - silver alloy is then distilled in a retort. Zinc passes over leaving silver behind. The process is repeated to recover almost the entire amount of silver.

5) Partition chromatography :

This is a method of separating a mixture of small amounts of organic materials. A paste of the mixture is applied at the top of a column of silica soaked in water. Another solvent i.e. hexane which is immiscible is allowed to flow down the column. Each component of the mixture is partitioned between water, the stationary liquid phase and hexane, the mobile liquid phase. The various components of the mixture are extracted by hexane in order of their distribution coefficients.

6) Study of complex ions

Deducing the formula of a complex ion , (I_3^-).

Iodine is added to a solution of KI and the reaction mixture is shaken with benzene.

a) Knowing the concentration of iodine in benzene and the value of K, the concentration of iodine in aqueous layer can be calculated.

b) The total concentration of iodine, $(I_2)+(I^-)$ in water layer is found by titrating against sodium thiosulphate knowing I_2 from first step (a), (I_3^-) can be calculated.

c) The initial concentration of KI taken is represented by the equilibrium concentrations $(I^-) + (I_3^-)$ knowing (I_3^-) (I^-) K can be calculated.

Substituting the values of concentrations in the law of mass action equation of the reaction in water.

$$\frac{\left[I_3^-\right]}{\left[I_2\right]\left[I^-\right]} = K$$

If the value of K comes out to be constant for different concentrations of iodine, it confirms that the formula I_3^- which is assumed is correct.

3.5.7 Model Questions :

1. State distribution law. What are its limitations ?

2. State and explain Nernst's distribution law. How it is modified when the solute undergoes.

   (i) association

   (ii) dissociation in one of the liquids.

3. State and explain distribution law. Under what conditions is the law valid?

4. State and explain Nernst's distribution law. Mention any three of its applications.

5. Explain how the extraction of a solute from its solution can be made efficiently.

6. Discuss the statement " Multistep extraction is more economical than a single - step extraction.

3.5.6 Problems :

1. In the distribution of a solute between water (C1) and chloroform (C2) the following results were obtained. Calculate the molecular state of the solute in chloroform with the help of these data.

C_1	0.0160	0.0237
C_2	0.3380	0.7530

   Ans : Uni molecular

2. The following data were obtained at 298 k for the distribution of I_2 between H_2O and CCl_4.

$[I_2]H_2O$ (mol d_m^{-3}) x 10^4	2.35	4.69	7.03	9.30
$[I_2]CCl_4$ (mol d_m^{-3}) x 10^2	2.00	4.00	6.00	8.00

Verify that the data obey Nernst distribution law and calculate KD in favour of CCl_4

Ans : 85.5

3. The following data were obtained at 25°c for the distribution of a weak organic acid between water and benzene.

Conc in H_2O (g/dm³)	1.50	1.95	2.89
Conc in C_6H_6 (g/dm³)	14.20	41.20	96.50

Assuming that the acid is not dissociated in H_2O, determine the molecular complexity of the acid in benzene.

Ans : Dimer

4. The solubility of a solute is three times as high in ether as in water. Compare the amounts extracted from 100 ml of aqueous solution by (a) 100 ml of ether in one step and (b) two successive extractions each with 50ml of ether.

Ans : (a) 75%, ; (b) 84%

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UNIT-IV

Lesson - 1

ATOMIC STRUCTURE AND ELEMENTARY QUANTUM MECHANICS

4:1:0 **Black Body Radiation, planck's Radiation law, photo electric effect, compton effect, De Broglies Hypothesis, Heisenberg's uncertainity principle, Postulates of quantum mechanics. Schrodinger's wave equation for H-atom. Separation of variables, Radial and angular functions hydrogen like wave functions quantum numbers and their importance.**

4.1.1 Black body Radiation :

Plank's quantum theory of radiation is introduced to explain black body radiation.

Black body : A black body is one which absorbs and again emits all radiations falling on it.
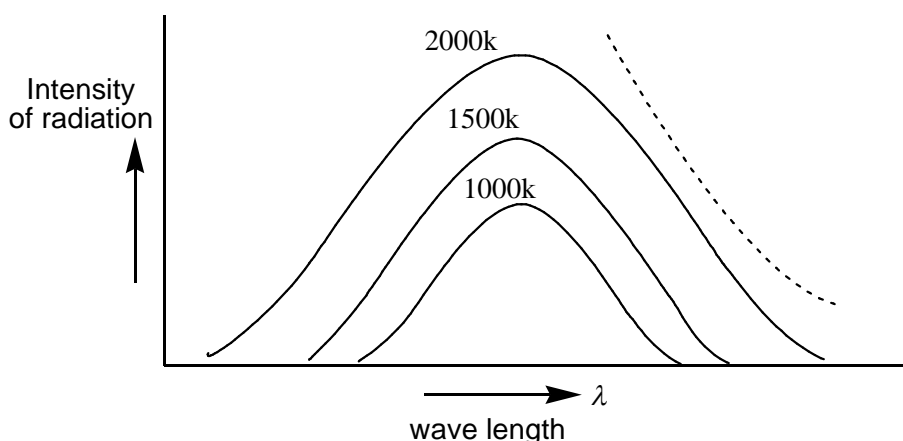

Fig 4.1

When emission of radiation is continuous the graph must be as shown by the dotted line. But it is not so, plank proposed that emission of radiation is discontinuous.

(i)   The main postulations are energy is absorbed or emitted by a body, not continuously but discountinuously.

(ii)   Emission of radiation is due to vibration of electrons.

(iii)   Energy is absorbed or emitted in small packets called quanta.

(iv)   Energy of quanta is E = h υ

Where h = planck's constant

(v)   Emitted radiation is propagated as waves.

4:1:2 Plank's radiation Law :

On the basis of quantum theory plank derived a formula for energy distribution in thermal spectrum. It is called Plank's radiation law.

According to plank, a black body consists of molecular dimensions which act as simple harmonic oscillators. These oscillators exchange energy with its surroundings in discrete values i.e, $0, 1h\upsilon, 2h\upsilon, 3h\upsilon \ldots\ldots$

Based on this theory, planck obtained an expression for the energy density of black radiation

$$E\lambda = \frac{8\pi hc}{\lambda^5 [\frac{hc}{e^{\lambda kt-1}}]}$$

This equation account for the black body radiation curves of all wavelengths obtained at different temperatures.

4:1:3 PHOTO ELECTRIC EFFECT :

"When an electromagnetic radiation of critical or threshold frequency falls up on a metallic surface, it causes the ejection of electrons from its surface. This Phenomenon is called Photo-electric effect.
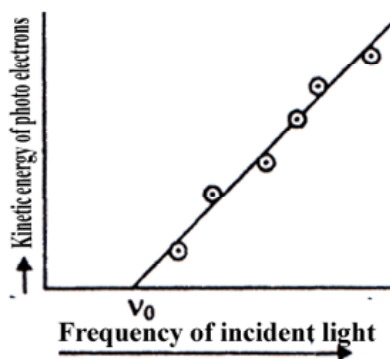
Laws of photoelectric Emission :

Fig 4.2 : Plot K.E of photo electrons versus frequeny

1. The K.E. of ejected photoelectrons is directly proportional to the frequency of incident light.

2. Increase in intensity of the incident light increases the number of ejected electrons.

3. No electrons are ejected from the metal unless the frequency of light used is greater than certain value. It is called critical or threshold frequency.

4. Electrons are ejicted even in high vacuum

5. Ejection of electrons is a spontaneous process.

Explanation of photoelectric effect by planck's quantum theory of radiations:

Einstein utilised quantum theory to explain photoelectric effect.

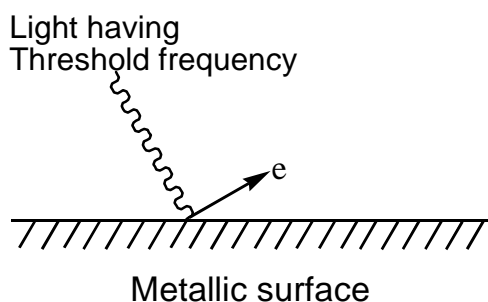Light having
Threshold frequency

e

Metallic surface

Fig 4.3

When Photon strikes the metal surface.

1. a part of its energy is used to eject the electron from the metal atom. It is called binding energy.

2. The remaining part of its energy is given to the ejected electron as kinetic energy.

Thus,

Total energy = Binding energy + K.E of the ejected electron.

$$h\upsilon = h\upsilon_0 + 1/2\ mv^2$$

$$1/2\ mv^2 = h\upsilon - h\upsilon_0$$

$$= h(\upsilon - \upsilon_0)$$

a) If $\upsilon > \upsilon_0$ the excess energy $h\upsilon - h\upsilon_0$ is transferred as K.E. and electron is ejected.

b) If $\upsilon < \upsilon_0$ no electron is ejected what ever the intensity of the radiation may be.

4:1:4 COMPTON EFFECT :

The phenomenon in which the wave length of the radiation scattered by an element is greater than that of incident radiation is called compton effect.
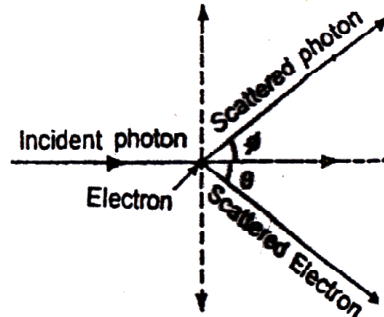

Fig 4.4 : Schematic representation of Compton effect

In order to explain this effect the following assumptions are made.

1. a free electron is always present in all scattering materials

2. The free electron is supposed to be at rest.

3. The collision between the electron and photon is elastic

4. a free electron can be knocked out only by a definite amount of energy called threshold energy.

5. The energy of incident photon is supposed to be greater than that of the threshold energy.

6. The beam of photon is monochromatic. So, it consists of single wave length and frequency.

7. for particles in electron the following mass - energy relation holds good.

$$E = mc^2$$

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$$

Where ,

m_o = Rest mass of electron

m = mass of electron moving with velocity v.

C = Velocity of light

Importance :

1) This effect provides additional support to the quantum theory of light .

2) This effect helps in the deduction of uncertainity principle

3) This effect helps in the interpretation of hydrogen spectrum.

4:1:5 Derivation of De-Broglie equation :

Debroglie stated that all material objects have duel character ie wave as well as particle nature.

According to quantum theory $E = h\nu = \dfrac{hc}{\lambda}$

According to Einstain $E = mc^2$

$$mc^2 = \frac{hc}{\lambda}$$

$$\lambda = \frac{h}{mc} = \frac{h}{p}$$

Where ,

h = planks constant

m = mass

c = velocity of light

p = momentum of photon

1. For microbodies like electron, m is low λ is high.
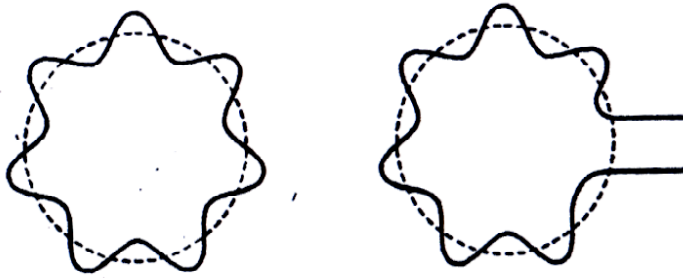
$\therefore$ Wave nature is predominent. So, Debroglie proposed wave nature for electron.

2. For macro bodies like cricket ball m is high. λ is low

$\therefore$ particle nature is predominent.

Significance :

Debroglie developed new model of atom based on this concept. According to him, in orbits electron behaves as standing or stationary wave and it is in phase.

(a) Electron wave in phase　　　(b) Electron wave out of phase

Fig 4.5 : Electron Wave in a circular path

For the wave to remain continually in phase the cicumference of the orbit (2 π r) should be integral multiple of wave length λ

2 π r = nλ

Substituting the value of $\lambda = \dfrac{h}{mv}$

$\therefore$ mvr $= \dfrac{nh}{2\pi}$ ...... (vi)

So, Debroglic waves can be used to explain Bohr model.

Applications :

1. Debroglie concept has led to the development of electron microscope.

2. The concept supported Bohr's postulate that the electron moves in stationary orbits.

4:1:6 Heisenberg's principle :

Principle :

In an atom both the position and momentum of electron can not be determined accurately simultaneously

$$\Delta x . \Delta p \geq \dfrac{h}{4\pi}$$

where

Δ x = uncertainity in position

Δ p = uncertainity in momentum

Explanation :

When light is passed into the atom, electron absorbs light and its energy increases. As energy increases velocity increases and position changes.
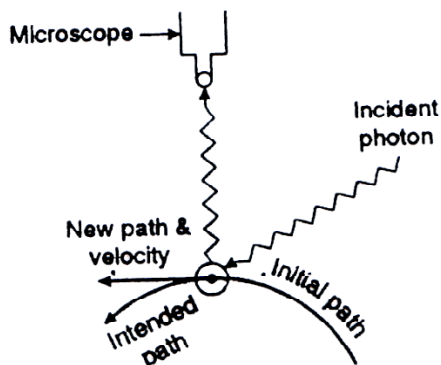

Fig 4.6: Change in direction and momentum of an electorn by the impact of a photon of light

Case (i) : When position is determined accurately, $\Delta x = 0$

$$\Delta p = \frac{h}{4\pi \times \Delta x}$$

$$= \frac{h}{4\pi \times 0}$$
$$= \alpha$$

$\therefore$ Uncertainity in momentum is infinity

Case (ii) : When position is determined accurately, $\Delta p = 0$

$$\Delta x = \frac{h}{4\pi \times \Delta p}$$

$$= \frac{h}{4\pi \times 0}$$
$$= \alpha$$

$\therefore$ Uncertainity in momentum is infinity.

4.1.7 Postulates of quantum mechanics :

Quantum mechanics deals with the motion of microscopic bodies which are of atomic or molecular dimensions.

The following are the postulates of quantum mechanics to derive schrodinger equation.

1. The state of the system is defined by wave function φ .

2. For every independent state of the system, function of the coordinates can be written which is continuous, finite and single valued.

3. For a system moving in one direction i.e x - axis wave function will be φ (x). Function φ (x) = sinx. It is continuous, for every value of φ it is finite and gives one value.

4. **Operator :** It is a mathematical symbol or expression which tells us to do something.

   Ex : In the expression $\sqrt{4}$, the square root symbool ($\sqrt{}$) is an operator which tells that we have to take the square root of 4.

5. In quantum mechanics there are certain mathematical operators for the measureble or observable quantities.

Observable quantity	Operator
(a) Position	(a) x
(b) Linear momentum along x - axis	(b) $\dfrac{h}{2\pi i}\dfrac{\delta}{\delta x}(i=\sqrt{-1})$
(c) Sum of the squares of linear momentum along x, y and z - axis.	(c) $-\dfrac{h^2}{4\pi i}-v^2(\bar{v}^2=\dfrac{\delta^2}{\delta x^2}+\dfrac{\delta^2}{\delta y^2}+\dfrac{\delta^2}{\delta z^2})$ (The laplacian operator)
(d) Total energy H = P.E + K.E	(d) $\dfrac{-h}{8\pi m}\bar{v}^2+V(x,y,z)$

6. **Eigen values :** Schordinger wave equation is a second order equation. It has several solutions but many of them have no significance. Only for certain definite values of the total energy, the solution have significance. These values are known as eigen values.

7. $\hat{A} \varphi = a\varphi$

Where φ = well behaved function of the system

$\hat{A}$ = suitable operator for observable property.

The given state is called eigen state of the system because φ and a are eigen function and eigen value respectively.

8. Schrodinger wave equation is time dependent. The dependence of the wave function

can be represented as $\dfrac{ih}{2\pi} \cdot \dfrac{\delta \psi}{\delta t} = \hat{H} \varphi$ where $\hat{H}$ is Hamiltonian operator.

4:1:8 Schrodinger Wave equation :

In order to provide sense and meaning to the probability approach, schrodinger derived an equation, known after his name, schrodinger's wave equation .

Since the electron has wave nature the classical wave equation of a particle can be applied. So, along the x- axis.

$\varphi = A \; \mathrm{Sin} \; 2\pi \dfrac{x}{\lambda}$

Where ,

$\varphi =$ Wave function representing the amplitude of the wave.

A = Maximum value of φ (a constant)

X = displacement in a given direction.

and λ = Wave length

Differentiating the above equation twice with respect to 'x'

$\dfrac{d\varphi}{dx} = A \; \dfrac{2\pi}{\lambda} \cos 2\pi \dfrac{x}{\lambda}$

$\dfrac{d^2\varphi}{dx^2} = -\dfrac{4\pi^2}{\lambda^2} A \; \mathrm{Sin} \; 2\pi \dfrac{x}{\lambda} = -\dfrac{4\pi^2}{\lambda^2} . \varphi$ $\left(\because \varphi = A \; \mathrm{Sin} \; 2\pi \dfrac{x}{\lambda} \right)$

or $\dfrac{1}{\lambda^2} = -\dfrac{d^2\varphi}{dx^2} \times \dfrac{1}{4\pi^2 \psi}$ ....(1)

From the de Broglie's equation we know that

$\lambda = \dfrac{h}{mu}$

or $\dfrac{1}{\lambda^2} = \dfrac{m^2 u^2}{h^2}$ .....(2)

From equations (1) and (2)

$$\dfrac{m^2 u^2}{h^2} = -\dfrac{d^2\varphi}{dx^2} \times \dfrac{1}{4\pi^2\psi}$$

$$m^2 u^2 = -\dfrac{h^2}{4\pi^2\varphi} \times \dfrac{d^2\varphi}{dx^2}$$

or $\dfrac{1}{2} m u^2 = -\dfrac{h^2}{8\pi^2\varphi m} \times \dfrac{d^2\varphi}{dx^2}$

$\therefore KE = -\dfrac{h^2}{8\pi^2\varphi m} \times \dfrac{d^2\varphi}{dx^2}$

$$\dfrac{d^2\varphi}{dx^2} = -KE\dfrac{8\pi^2\varphi m}{h^2}$$

$$\dfrac{d^2\varphi}{dx^2} + \dfrac{8\pi^2\varphi m}{h^2} KE.\varphi = 0 \text{--------(3)}$$

But total energy E = k.E + PE

$$KE = E - PE$$

$$\dfrac{d^2\varphi}{dx^2} + \dfrac{8\pi^2\varphi m}{h^2} KE.\varphi = 0$$

This eqⁿ represents wave motion of electron along x - axis. Considering the electron moving along x,y and z - axis, we get

$$\dfrac{d^2\varphi}{dx^2} + \dfrac{d^2\varphi}{dy^2} + \dfrac{d^2\varphi}{dz^2} + \dfrac{8\pi^2 m}{h^2}(E - P.E)\varphi = o$$

This eqⁿ is called schrodinger eqⁿ

since $\dfrac{d^2}{dx^2} + \dfrac{d^2}{dy^2} + \dfrac{d^2}{dz^2} = \nabla^2$ (The laplacian operator)

$\nabla^2\psi + \dfrac{8\pi^2 m}{h^2}$ (E-P.E) $\psi = 0$

Schrodinger wave eqⁿ for hydrogen atom :

Hydrogen atom has nuclear charge +e. Charge on the electron is – e and potential energy of electron is $-\dfrac{e^2}{r}$ where r is the radius of the orbital and for H atom Z = 1.

Substituting P.E. value in schrodinger eqn we get.

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}\ (E + \frac{e^2}{r})\ \psi = 0$$

It is the schrodinger wave eqⁿ for hydrogen atom.

4:1.9 Significance of 'ψ' :

(i) ψ' is a wave function which is solution to schrodinger waver eqⁿ

(ii) It represents amplitude of wave and describes how amplitude varies with distance and direction.

(iii) For electron wave, it represents intensity of electron at any point.

(iv) It represents the probability of finding electron at different regions in space of specific energy.

(v) It leads to the idea of orbital.

4:1:10 Hydrogen like wave functions - Radial and Angular wave function :

Schradinger wave equation for Hydrogen atom is

$$\frac{d^2\varphi}{dx^2} + \frac{d^2\varphi}{dy^2} + \frac{d^2\varphi}{dz^2} + \frac{8\pi^2 m}{h^2}(E + \frac{e^2}{r})\varphi = o$$

It can be solved by substituting polar co - ordinates (r, $\theta\, and\, \phi$) in place of cartesian coordinates (x, y and z).

In order to evaluate φ (r, $\theta\, and\, \phi$) the function is written as

φ (r, $\theta\, and\, \phi$) = R (r) $\ominus(\theta)\, \Phi(\phi)$

Where :
i) R(r) is a function of r, which depends on the quantum numbers n and l but independant of polar coordinates θ and ϕ .

ii) $\ominus(\theta)$ is a function of θ, which depends on the quantum numbers l and m but independant of polar coordinates r and ϕ .

ii) $\Phi(\phi)$ is a function of ϕ , which depends only on the quantum numbers m but independant of polar coordinates r and θ .

The above Eq n of φ can be written as

φ = Rnl. lm. m

= Rnl. Aml

This splits the wave functions into two parts which can be solved seperately

a. Radial wave function

b. Angular wave function

c. Radial wave function

Radial Probability distribution curves :

It was found that neither Rnl nor R^2nl can be directly related with the probability of findin electron at a point distance R from the nucleus. So, radial probability distribution of electron is obtained by drawing graph between radial probability and distance r. These graphs are called radial probability distribution curves.

The probability of finding electron at different distances from the nucleus is given by radial probability distribution curves.

The probability of finding electron at a distance r from the nucleus plotted for 1s, 2s, 2p, 3s, 3p and 3d- orbitals of the hydrogen atom is given below.

(a) 1S- orbital

(b)   2S- orbital

(c) 3 S- orbital

(d)   2.P- orbital

(e)   3P- orbital

(f)   3d- orbital
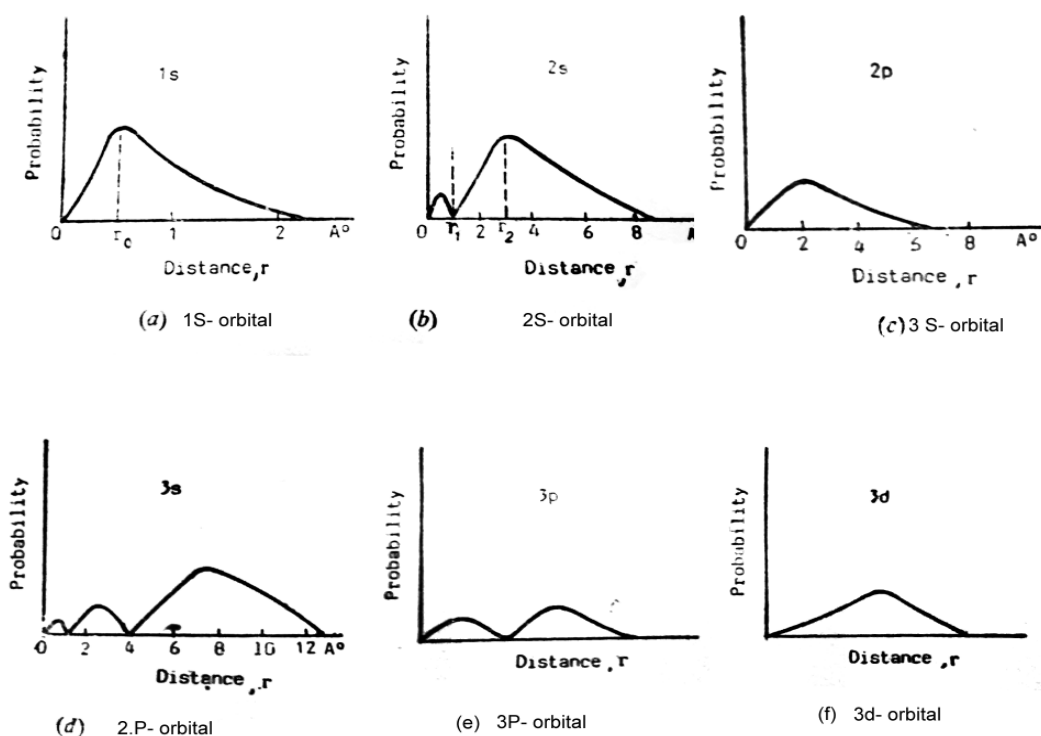
Fig 4.7

1. In each diagram, the peak gives distance between the nucleus and maximum probability of finding electron.

Ex : The distance of maximum probability of finding 1s electron is 0.529A°.

2. No. of peaks for s - orbital is equal to n value.

Ex : No. of peaks is 1 for 1s, 2 for 2s and 3 for 3s.

3. Number of peaks for p - orbital is equal to (n-1) value and soon.

Angular wave function :

The function A ml ie $\ominus(\theta)\,\Phi(\phi) = \ominus lm.\,\Phi m$ is known as angular wave function. It depends on the quantum numbers m and l. It gives shape of the orbital.

The probability of finding electron in a perticular direction w.r.t. nucleus is given by angular probability distribution.

Shape of orbital :

Angular wave function is $\ominus lm.\,\Phi m$

For S - orbital, l = 0 , m = 0

$$\therefore\ \ominus_{00}.\,\Phi_0 = \frac{1}{\sqrt{2}}.\frac{1}{\sqrt{2\pi}} = \frac{1}{2\pi}$$

It is independant of θ and ϕ . So, S - orbital is symmetrical in all directions. Hence it is spherical.

Similarly P - orbitals are dumb - bell, d- orbitals are double dumbell and f- orbitals are four fold dumbbell.

S - orbital :
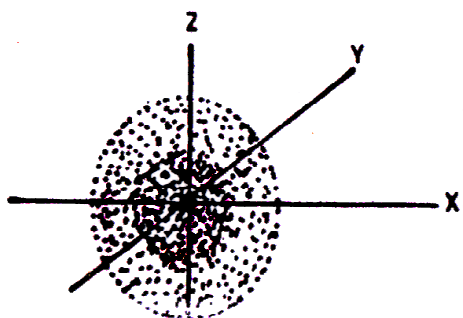
Fig 4.8 : Electron charge cloud

The angular probability distribution diagram for S - orbital is spherical. The length of the line OP is same in all direction. The S electron has no preferred direction. There is equal chance of finding S electron in all directions w.r.t the nucleus.

P - orbital :

There are Three P - orbitals, They are Pxy, Pxz and Pyz shape is dumb bell.
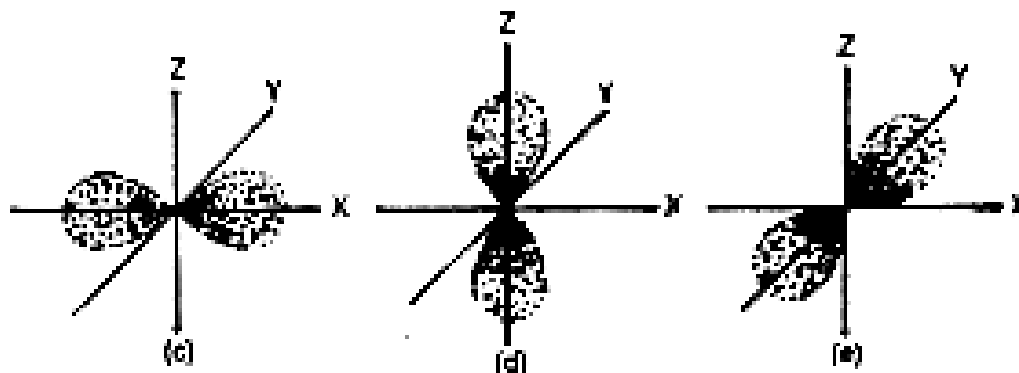
Fig 4.9 : Shapes of 1s and 2p orbitals.

The angular probability distribution diagram for P - orbital is dumb- bell. These diagrams are self descriptive. For example the diagram for Px - orbital represents that the most probable direction for the electron is along the x - axis. There is no probability of finding electron at right angles to the x - axis which is the nodal plane. In the absence of external field the three orbitals have same energy. So, they are triply degenerate.

d - orbital :

There are five d - orbitals, They are dxy, dxz , dyz, dx^2-y^2 and dz^2 shape is dumb bell.
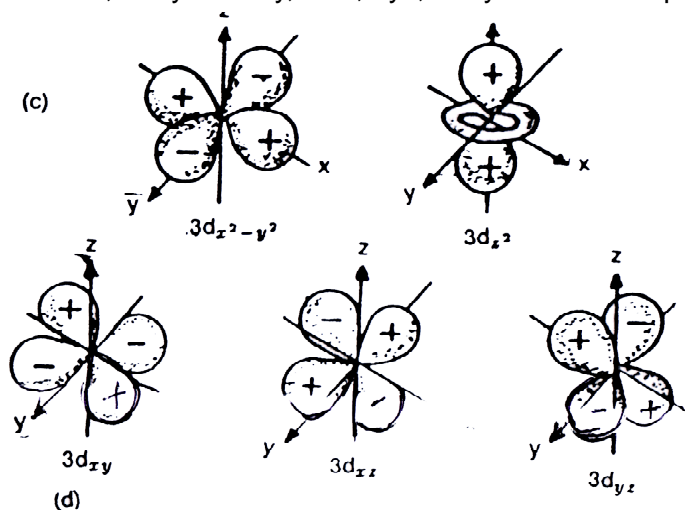
Fig 1.10 Shapes of d-orbitals

Fig 4.10

The angular distribution diagrams of d - orbitals are quite complicated. They are dxy, dyz, dx^2-y^2 and dz^2. In the absence of external field the five orbitals have same energy. So they are five fold degenerate.

f - orbital :

There are seven f - orbitals, They have more complicated geometrical shapes of four fold dumbbell.

The angular distribution diagrams of f - orbitals are much more complicated.

4:1:11 Quantum numbers and their importance :

Quantum numbers are index numbers used to know the position of electron in an atom.

There are four quantum numbers.

  1. Principal quantum number

  2. Azimuthal quantum number

  3. Magnetic quantum number

  4. Spin quantum number

1. Principal quantum number :

Bohr introduced principal quantum number. It is represented by n.

Values : It takes values from 1 to n.

  n = 1 1st orbit or k - shell

  n = 2 2nd orbit or L - shell

  n = 3 3rd orbit or M - shell

Importance : It gives radius of the orbit or main energy level. It gives energy or electron.

2. Azimuthal quantum number :

Sommerfeld introduced Azimuthal quantum number. It is represented by l.

Values : It takes values from 0 to (n-1)

  n = 1   l = 0(s)

  n = 2   l = 0(s)

       = 1(p)

  n = 3   l = 0(s)

       = 1(p)

       = 2(d)

$$n = 4 \qquad l = 0(s)$$
$$= 1(p)$$
$$= 2(d)$$
$$= 3(f)$$

S = Spherical

p = dumb - bell

d = double dumb - bell

f = fourfold dumb - bell

Importance : It gives shapes of the orbital. It gives the number of sub - shells or sub energy levels in an orbit or main energy level.

3. Magnetic quantum number :

Lande introduced magnetic quantum number. It is represented by 'm'.

Values : It takes values from - l through 0 to + l

$$l = 0 \qquad m = 0$$
$$l = 1 \qquad m = -1, 0, +1$$
$$l = 2 \qquad m = -2, -1, 0, +1, +2$$

Importance : It gives orientation of electron in space. It gives the number of orbitals present in a sub - shell or sub - energy level.

4. Spin quantum number :

ullen e and goudschmidt introduced spin quantum number. It is represented by 'ms'.

Values : It takes values $+\dfrac{1}{2}(\uparrow)$ and $-\dfrac{1}{2}(\downarrow)$

$+\dfrac{1}{2}$ represents clockwise spin of electron. $-\dfrac{1}{2}$ represents anti clockwise spin of electron.
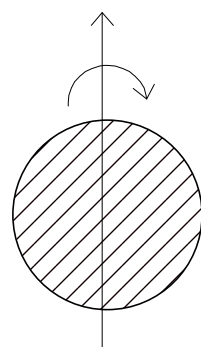
Clock wise spin
of electron
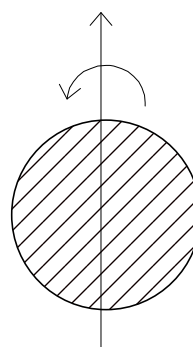
anti Clock wise spin
of electron

Fig 4.11

Importance : It gives spin of electron around its own axis.

4.1.12 Model Questions:

1. What is black.body radiation.?

2. What is a black body ?

3. Explain planck's radiation law

4. what doyou understand by Heisenberg's uncertainity principle?

5. Derive de Broglie relation.

6. Explain the concept of probability from Heisenberg's uncertainity principle

7. Write down the schrodinger equation for hydgrogen atom.

8. Discuss the significanxce of ψ and ψ^2

9. Explain Radial and angular wave functions for H atom.

10. What is a radial probability distribution ? Draw the radial probability distribution curves for 1s, 2s , 3s, 2p, 3p and 3d orbitals.

11. What is the shape of "d" orbital ? Explain its shapes.

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CHEMICAL BONDING

4:2:0 **Valence bond theory, hybridization, VB theory as applied to ClF$_3$, BrF$_5$,Ni(CO)$_4$, XeF$_2$, Dipole moment - orientation of dipoles in an electric field, dipole moment, induced dipole moment, dipole moment and structure of molecules. Molecular orbital theory - LCAO method, construction of M.O. diagrams for homo - nuclear and heteronuclear diatomic molecules (N$_2$, O$_2$, HCl, CO and NO). Comparision of VB and MO theories.**

4.2.1 VALENCE BOND THEORY :

Valence bond theory is introduced to explain the formation of covalent bond.

Bond formation : Covalent bond is formed by the overlapping of atomic orbitals containing single electrons with opposite spin.
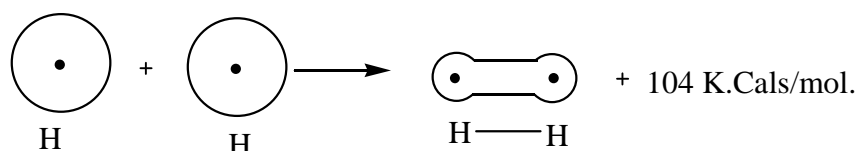
Bond strength : As overlapping increases bond strength increases. Strong bonds are formed by the overlapping of orbitals containing same energy.

Bond direction :

(i)   Covalent bonds formed by the overlapping of spherical and symmetrical atomic orbitals are non - directional othus are directional.

(ii)   The direction of covalent bond is the direction of molecular orbital concentrated.

Bond Energy : The amount of energy released due to the overlapping of atomic orbitals forming molecular orbital is called bond dissociation energy.

Formation of σ bonds :

Sigma bonds are formed by the face to face overlapping of orbitals. Here overlapping is more so, the bond is strong.
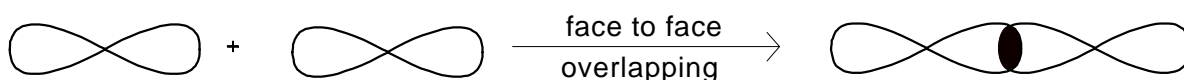
Pi bonds :

π Bonds are formed by the side wise overlapping of orbitals. Here overlapping is less. So, the bond is weak.

side wise
overlapping
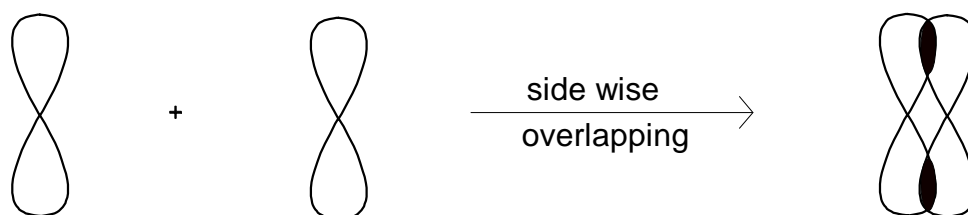
4:2:2 HYBRIDISATION :

S.No.	Element	At.No.	Electronic configuration
1	Be	4	$1s^2\ 2s^2$
2	B	5	$1s^2\ 2s^2\ 2Px^1$
3	C	6	$1s^2\ 2s^2\ 2Px^1 2Py^1$

According to these configurations covalency of Beryllium is Zero, Boron is one and carbon is two. But actually Be forms two, B three and C four covalent bonds. So, in the excited state one 2s electron enters into 2P- orbitals.

S.No.	Element	At.No.	E.C. in the excited state
1	Be	4	$1s^2\ 2s^1\ 2Px^1$
2	B	5	$1s^2\ 2s^1\ 2Px^1\ 2Py^1$
3	C	6	$1s^2\ 2s^1\ 2Px^1\ 2Py^1 2Pz^1$

According these configurations one bond must differ from the other bonds. But all bonds are found to be identical. To explain this the theory of Hybridisation is intoduced.

Hybridisation :

In an atom valence orbitals of same energy level combine forming an equal number of new identical orbitals. This process is called hybridisation. The new orbitals are called hybrid orbitals.

SP^3 Hybridisation :

In SP^3 hybridisation one S - orbital and three P - orbitals combine forming four identical orbitals.

Ex : Methane.

	2S	2P
Outer E. C. in Ground state	↑↓	↑ ↑
Outer E. C. in excited state	↑	↑ ↑ ↑

SP^3 hybridisation

Structure of CH$_4$:

H

C

H　　H

H

σ SP^3 - S
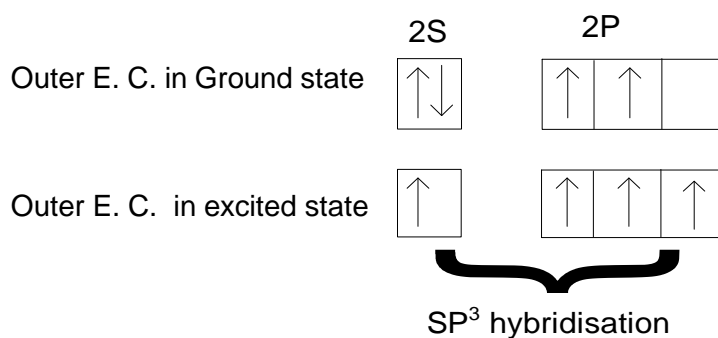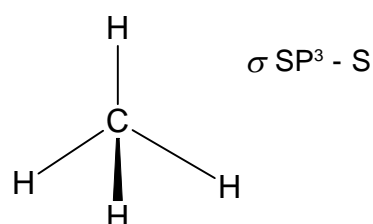
SP^2 Hybridisation :

In SP^2 hybridisation one S - orbital and two P - orbitals combine forming three identical orbitals.
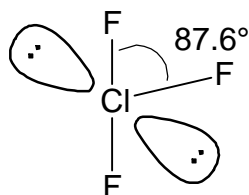
Ex : Boron trifluoride

	2S	2P
Outer E. C. in Ground state	↑↓	↑
Outer E. C. in excited state	↑	↑ ↑

SP^2 hybridisation

Structure of BF$_3$:

F

B

F　　F

σ SP^2 - P

Shape - Trigonal　　Bond angle - 120°
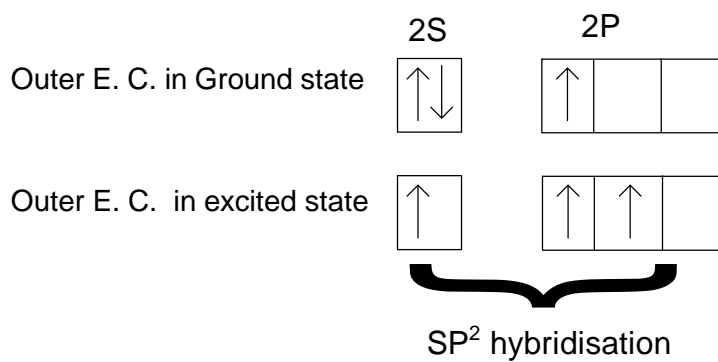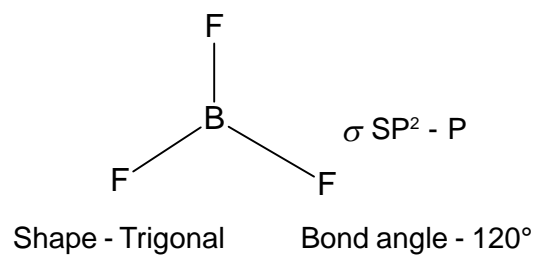
SP Hybridisation :

In SP hybridisation one S - orbital and two P - orbitals combine forming three identical orbitals.

Ex : Beryllium chloride

	2S	2P
Outer E. C. of Be in Ground state	↑↓	▯ ▯ ▯
Outer E. C. of Be in excited state	↑	↑ ▯ ▯

SP hybridisation

Structure of BeCl$_2$:

$$\sigma \text{ SP - P}$$
$$\text{Cl} \text{———} \text{Be} \text{———} \text{Cl}$$

Shape - Linear   Bond angle - 180°
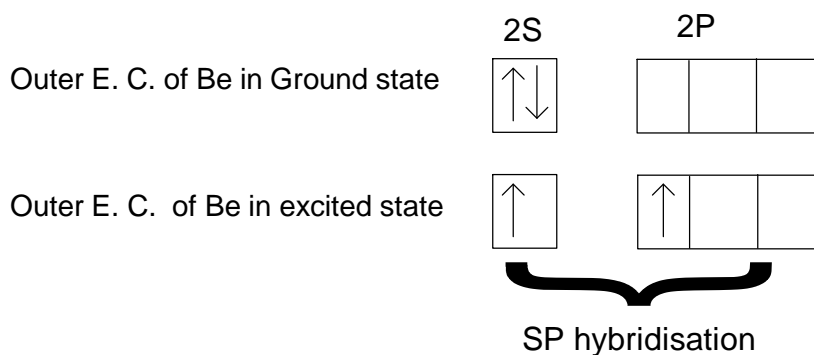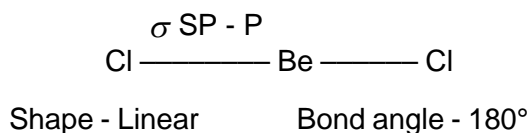
4:2:3 APPLICATION OF VALENCE BOND THEORY :

(i) Formation of Cl F$_3$ molecule :

	3S	3P	3d
Outer E. C. of Cl in Ground state	↑↓	↑↓ ↑↓ ↑	▯ ▯ ▯ ▯ ▯
Outer E. C. of Cl in excited state	↑↓	↑↓ ↑ ↑	↑ ▯ ▯ ▯ ▯

SP^{3}d hybridisation
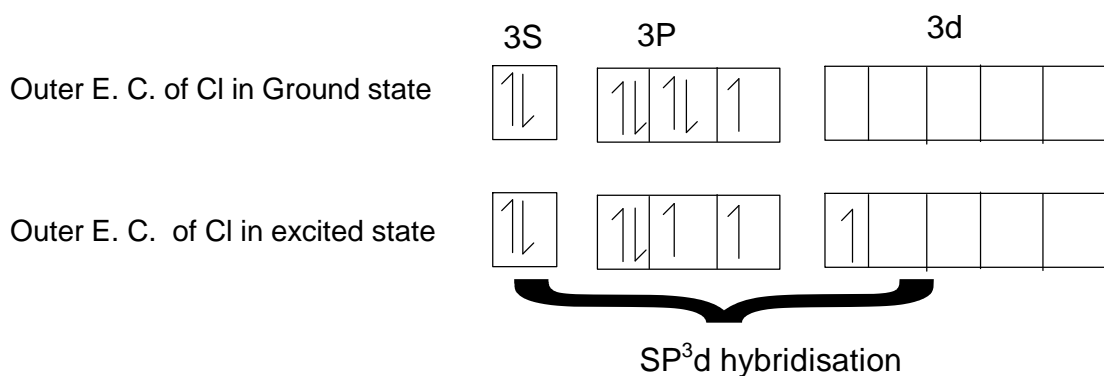
Structure of ClF$_3$:

Shape : The expected geometry is trigonal bipyramidal. FClF is 90°

But due to the repulsion between lp- lp and lp - bp there is distortion. The actual shape of the molecule is ' T' and bond angle is 87.6°.

(ii) Formation of Br F$_5$ molecule :

Outer E. C. of Br in Ground state

Outer E. C. of Br in excited state

SP^3d^2 hybridisation
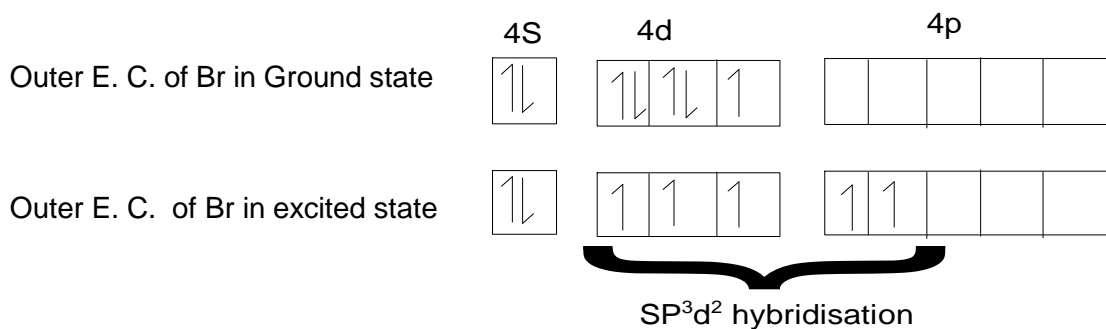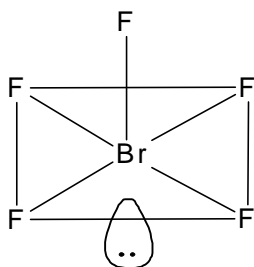
Structure of BrF$_5$:

Shape : The expected geometry is octaheial. But due to the repulsion between lp-lp and lp-bP there is distortion. The actual shape of the molecule is square planar.

(iii) Formation of Ni(CO)$_4$ molecule :

Outer E. C. of Ni atom in Ground state

Outer E. C. of Ni atom in excited state

SP^3 hybridisation

Ni (CO)$_4$

CO   CO CO CO
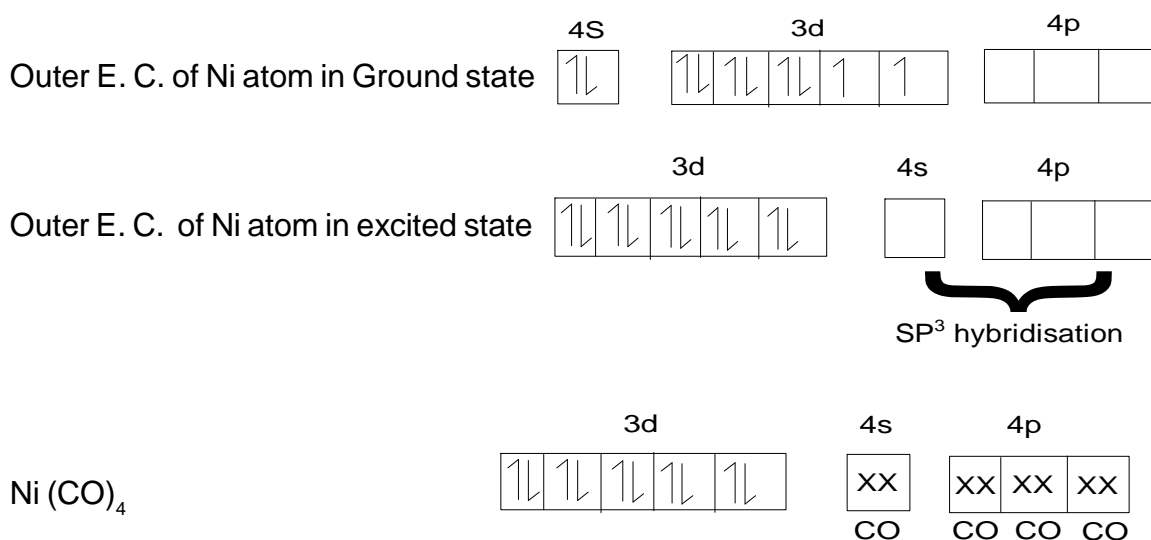
Structure of BrF$_5$:
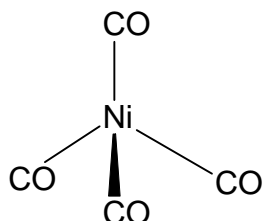
According to this structure the molecule is diamagnetic which is in agreement with the experimental results.

Shape : The expected geometry is tetrahedial. But the actual shape is Octahedial.

If we consider SP2 hybridisation then also the molecule is diamagnetic. The expected structure is square planar but not octahedial.

Here the magnetic property is unable to give true structure. This is the limitation of valence bond theory.

(i) Formation of Xe F$_2$ molecule :

SP^3d hybridisation
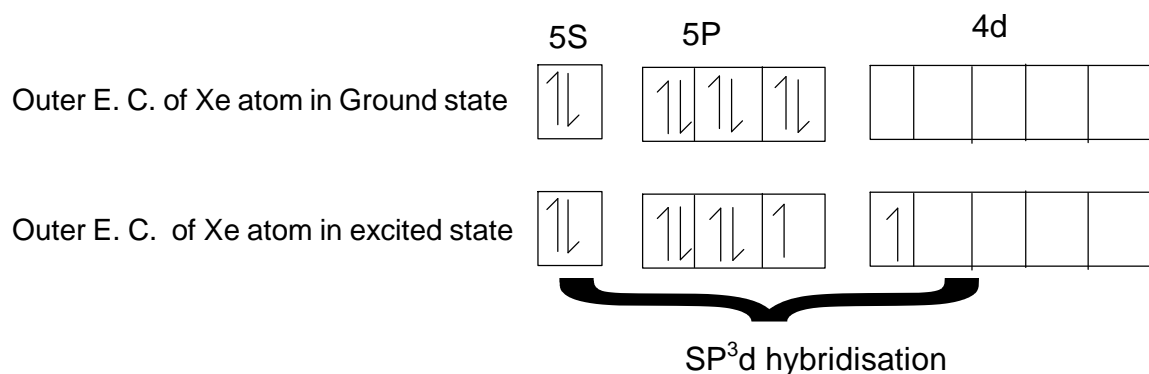
Structure of Xe F$_2$:
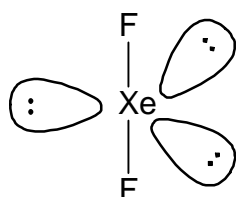
Shape : The expected geometry is trigonal bipyramidal.

But due to the repulsion between lp- lp and lp - bp there is distortion. The actual structure is linear. Bond angle is 180°.

4:2:4 DIPOLEMOMENT :

Dipolemoment is defined as the product of magnitude of charge and distance between the charges.

$\mu = \boldsymbol{q}.\ r$

Where, $\mu.$ = dipolemoment

q = magnitude of charge

r - distance between the charges.

Units : It is a vector quantity, it is expressed in Debye units.

1 Debye = 10^{-18} esu.

Explanation : If a bond is formed between two atoms of different electronegativity values, negative charge is accumulated on a more electronegative atom and positive charge is accumulated on a more electropositive atom. Then the bond constitutes an electric dipole of equal positive and negative charge ±q, separated by a distance r. A dipole is characterized by its dipolemoment. It is a vector qr and direction is the line joining the negative to the positive charge.

If a polyatomic molecule contains two or more dipoles in different bonds, the net dipolemoment of the molecule is the resultant of vector addition of the individual bond moments.

Importance :

Dipole moments provide.

i) an insight into the geometric structure of the molecule.

ii) the extent to which a bond is polarized.

4:2:5 ORIENTATION OF DIPOLES IN AN ELECTRIC FIELD :

Molecules are made up of protons. Neutrons and electrons. When they are placed between two charged parallel plates, the electric field causes separation of positive and negative charges. Thus an electric field always induce dipoles whether the molecules contain dipoles or not in the begining. The electric field is said to polarize the dielectric.

Dielectric constant :

When dielectric is introduced between the plates of a capacitor, the capacitance is increased called dielectric constant.

$$c = \in c_o$$

Where,

C_O = capacitance with vacuum

C = capacitance with dielectric

$\in$ = dielectric constant.

The dipolemoment perunit volume is called dielectric polarization.   It is represented by *P*.

4:2:6. INDUCED DIPOLEMOMENT :

An electric field acting on a dielectric causes polarization in two ways.

i) Induction effect

ii) Orientation effect

Thus polarization is the sum of two terms, $P = P_d + P_o$. P_d is the orientation polarization caused by the preferential alinement of permanent dipoles in the direction of the electric field. P_o is the induced or distortion polarization caused by the separation of positive and negative charges due to the action of electric field on the dielectric.
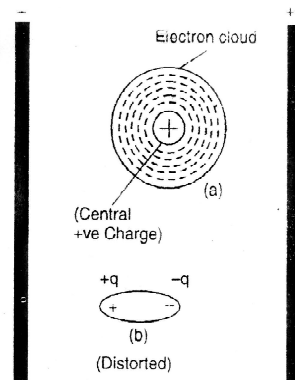
Fig. 2.1.

The polarized state of the molecule exists as Ion as it is in between the electrically charged plates. When once the charged plates are removed, the molecule gets initial state. So, it is called induced polarization.

The magnitude of induced dipolemoment is proportional to the strength of the field acting on it.

$\mu i \alpha\ F$

$\mu.i = \alpha\ F$

Where μi = magnitude of induced dipolemoment.

F = Field strength

α = proportionality constant called polarisability.

According to clausius and Mosotti equation .

$$Pi = \left(\frac{D-1}{D+2}\right)\frac{M}{p} = \frac{4}{3}\pi N\alpha$$

Where, Pi = induced polarization.

M = Mol. Wt.

P= density

N - Avogadro number

D = Electric distortion.

4.2.7. DIPOLEMOMENTS AND STRUCTURE OF MOLECULES :

Dipolemoments provide two kinds of information about molecular structure.

1. The extent to which a bond is permanently polarized.

2. An insight into the geometry of the molecules

Ex : 1. Carbondioxide :

$$\overset{\longleftarrow\quad\longrightarrow}{O = C = O}$$
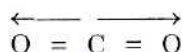
Carbondioxide has no dipolemoment, despite the difference in electro negativity between carbon and oxygen. So, the molecule is linear. The dipolemoments due to C - 0 bonds exactly cancel each other by vector addition.

2. Water molecule :
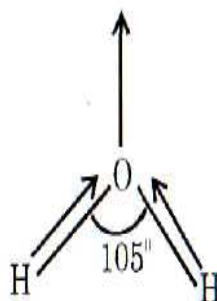
Water has dipolemoment 1.85 d. It must have a triangular structure. Each O — H bond has a moment of 1.60 d. So, the bond angle must be 105° such that resultant dipolemoment is 1.85d.

3. Benzene and it's derivatives :

I
μ = 0

II
1.7 d

III Cl
0

IV
O ˙˙

V
OH
1.4 d

IV OH
1.64 d
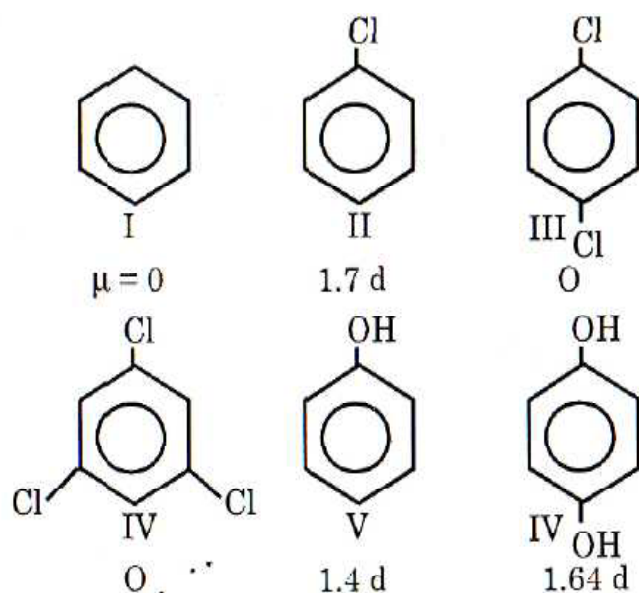
Benzene (I) P – dichloro bezene (III), Trichloro benzene (IV) have zero dipolemoments. So, benzene is planar and C-Cl bonds are in the plane of the ring, there by the moments due to C-Cl bonds cancel each other by vector addition.

P-dihydroxy benzene (VI) has dipolemoment 1.64d. This shows that O - H bonds are not in the plane of the ring. They are directed at an angle to the ring, thus providing a net dipole moment.

4. Ethyl chloride and chlorobenzene :

$CH_3 CH_2 – Cl$
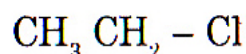
μ = 2.05 d

I
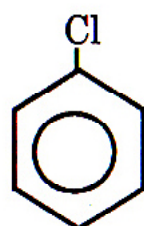
1.70d

II

Chlorobenzene (II) has less dipolemoment than ethyl chloride(I). This is due to resonance in chlorobenzene which decreases negative charge on the aromatic chlorine.
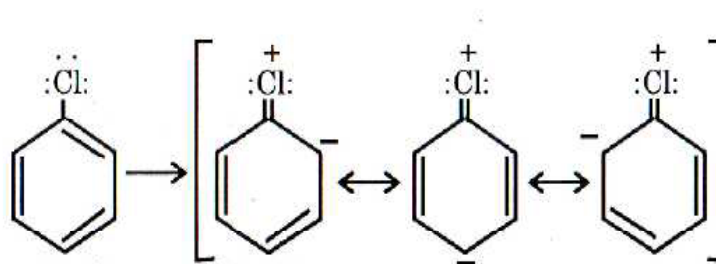
5. Hydrogen chloride :
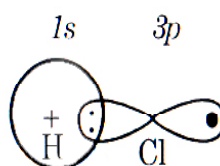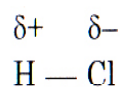
Internuclear distance in HCl = 1.26A°

Dipolemoment should be μ = 1.26 X 4.8 = 6.05 d

But HC1 has dipolemoment of 1.30 d only. This shows that the pair of electrons in the non-bonding *sp* hybrid orbital are not symmetrically disposed. This makes substantial contribution in decreasing the dipolemoment. Thus HC1 was proposed the following model rejecting the older model.
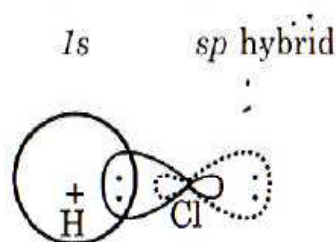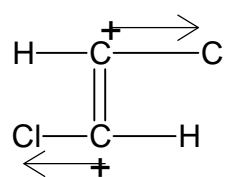

6. Differenciation of cis and trans - isomers :

This cis isomer of a symmetrical alkene has a definite dipolemoment while the trans isomer has zero dipolemoment.

Ex :1) 1,2 - dichloro ethylene.
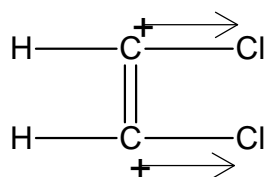
cis 1,2 - dichloro ethylene
μ = 1.9D

Trans 1,2 - dichloro ethylene
μ = 0D.

Ex :2) 2 -butene.
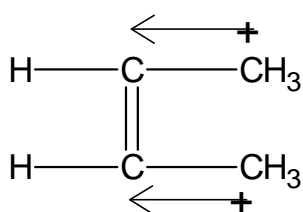
cis - 2 - butene
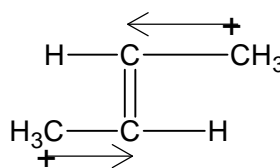
Trans -2 - butene μ = 0.

In symmetrical trans isomer the effect produced by one half of the molecule is cancelled by other half of the molecule.

4:2:8 MOLECULAR ORBITAL THEORY - LCAO METHOD:

Molecular orbital theory is introduced to explain bond formation and magnetic properties of molecules. According to this theory wave function representing molecular orbital is obtained by LCAO method ie. Linear combination of atomic orbitals.

LCAO method : It is simply addition or substraction of wave functions of atomic orbitals. By LCAO method

We get -

1. Bonding molecular orbitals.

2. Anti Bonding molecular orbitals.

3. Non - Bonding molecular orbitals.

1. Bonding molecular orbitals :

Formation : Bonding molecular orbital (ψ_g) is formed When signs of the adjacent lobes are same.
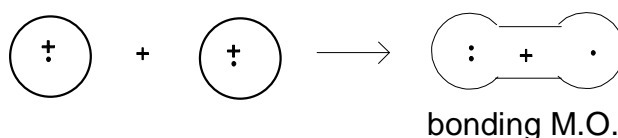
bonding M.O.

M.O. is obtained by the addition of wave functions of the atomic orbitals.

Consider two atoms of wave functions ψ_1 and ψ_2

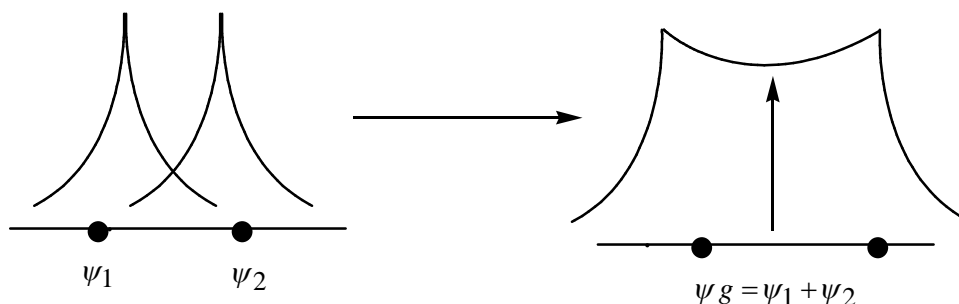$$\psi_g = N[\psi_1 + \psi_2]$$

Where   N = normalising constant

ψ_g = Bonding M.O.

' g' stands for gerade (even) symmetry.
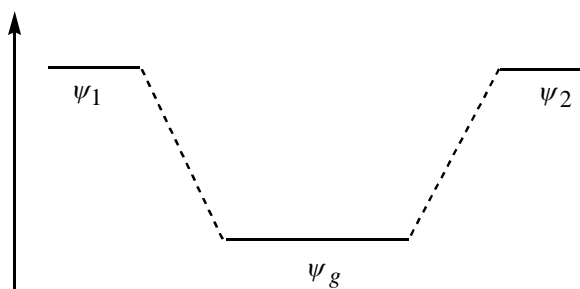
addition of atomic orbitals forming bonding M.O.

Here two waves are in phase a resultant wave is formed high electrondensity.

ψ_1 ψ_2 $\psi g = \psi_1 + \psi_2$

Electron density : Increase of electron density in bonding M.O. is known by squaring the equation.

$$\psi^2_g = [\psi_1 + \psi_2]^2$$
$$= \psi^2_1 + \psi^2_2 + 2\psi_1\psi_2$$

Energy change : Energy of the bonding M.O is less than that of the atomic orbitals.
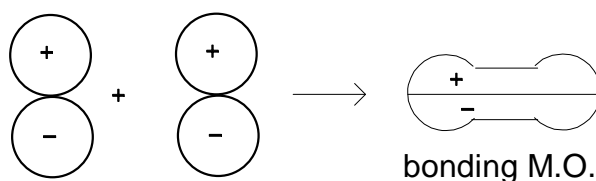
Formation of σ bonding M.O's :

σ is the Greek equivalent of S. It is used for M.O. in which electron density is cylindrically symmetrical around the internuclear axis.
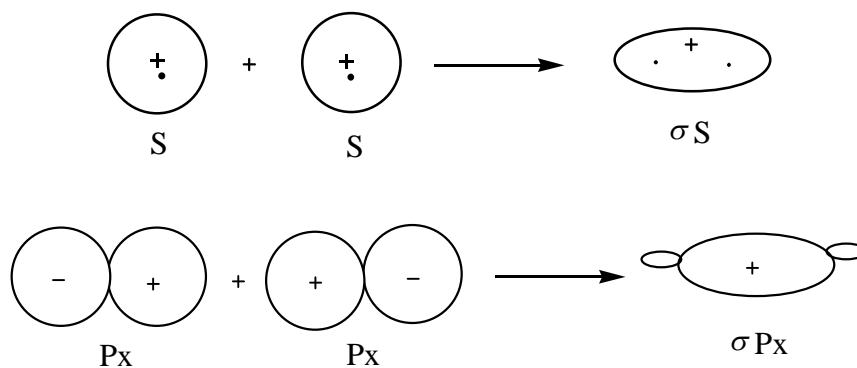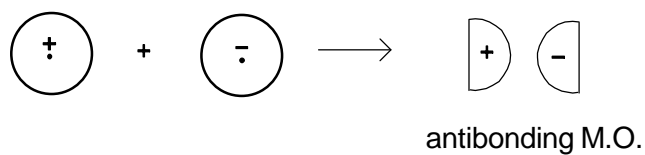

Formation of π bonding M.O's :

π is the Greek equivalent of P. It is used for M.O. in which electron density is present on either density is present on either side of the intunuclear axis.

bonding M.O.

2. Anti Bonding molecular orbitals :

Formation : Anti bonding M.O (ψ_U) is formed when signs the adjucent lobes are different

antibonding M.O.

M.O. is obtained by the substraction of wave functions of the atomic orbitals.

Consider two atoms of wave functions ψ_1 and ψ_2
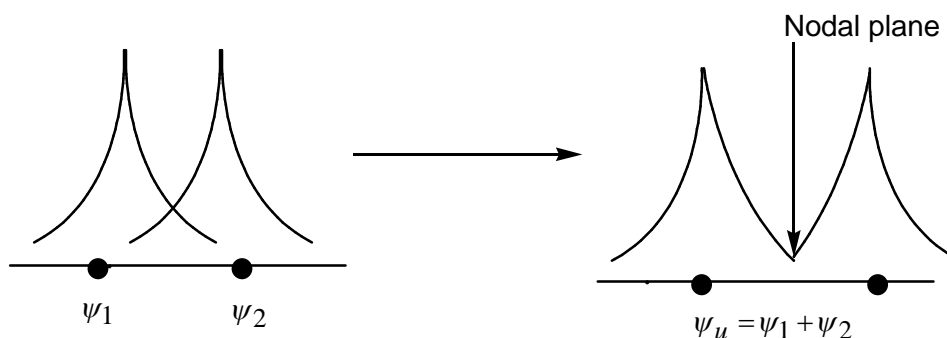
$$\psi_u = N[\psi_1 - \psi_2]$$

Where N = normalising constant

ψ_U = anti Bonding M.O.
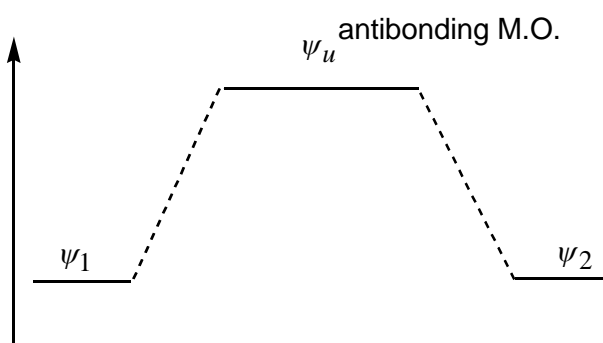
' U' stands for Ungerade (uneven) symmetry.

Here two waves are out of phase. So, they cancel each other

Electron density : Increase of electron density in bonding M.O. is known by squaring the equation.
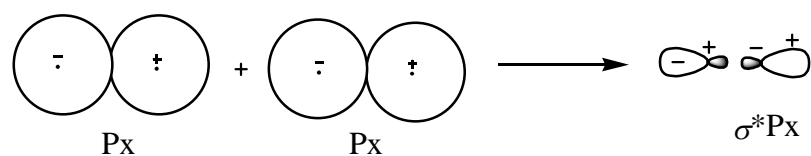
$$\psi^2_u = [\psi_1 + \psi_2]^2$$
$$= \psi^2_1 + \psi^2_2 - 2\psi_1\psi_2$$

Energy change : Energy of the bonding M.O is less than that of the atomic orbitals.

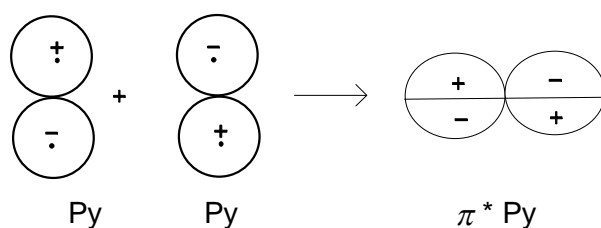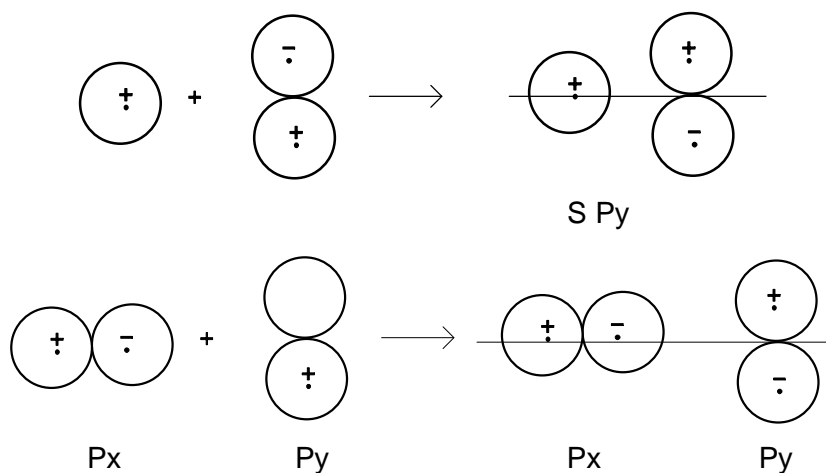**Formation of σ * bonding M.O's :**

In σ * antibonding M.O combination of atomic orbitals take place along Major axis.

$$Px \qquad Px \qquad \qquad \sigma^*Px$$

Formation of π * bonding M.O's :

In π * antibonding M.O. Combination of atomic orbitals take place along parallel axis.

$$Py \qquad Py \qquad \pi * Py$$

3. Non - Bonding molecular orbitals :

Formation : Orbitals which make no contribution to the binding energy of the molecule are called non - bonding orbitals.

$$S\ Py$$

$$Px \qquad Py \qquad \qquad Px \qquad Py$$

Explanation : Here stabilisation due to the formation of bonding M.O. is can called by the formation of antibonding M.O.

4:2:9 BOND ORDER :

Bond order = $\dfrac{1}{2}$ [No. of $\bar{e}$ in bonding M.O's − no. of $\bar{e}$ in antibonding M.O's]

Importance :

1. The value of bond order gives stability of the molecule and nature of the bond.

2. Zero or less than Zero value indicates that the molecule does not exist Ex : He_2

2. The free electron is supposed to be at rest.

3. $+ \dfrac{1}{2}$ Value indicates that the molecule exists but it is unstable Ex : H_2^+

4. 1,2 and 3 values indicate that the molecule is stable and the two atoms are held together by single double and triple bonds respectively.

Ex : H – O, O = O, N= N

4:2:10 CONSTRUCTION OF M.O DIAGRAMS OF HOMO NUCLEAR DIATOMIC MOLECULES :

(I) Nitrogen molecule :

At No. of Nitrogen atom is 7.

E.C. of Nirogen atom is $1S^2\ 2S^2\ 2P^3$

Nitrogen atom has 5 outer electrons.
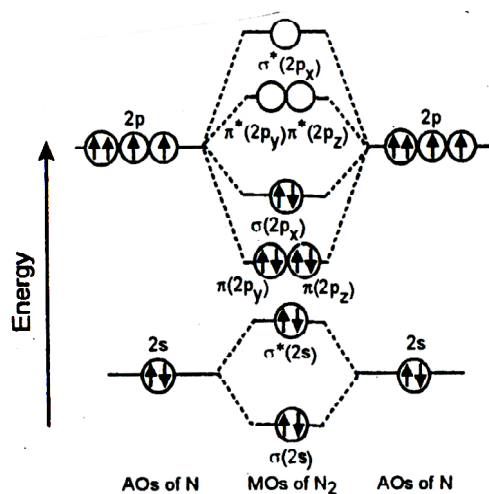
Nirogen molecule contains 10 outer electrons.

M.O configuration of N_2 molecules is KK $\sigma\ 2S^2\ \sigma\ {}^*2S^2\ \pi\ 2Py^2\ \pi\ 2Pz^2\ \sigma\ 2Px^2$

Since there are no unpaired electrons N_2 Molecule is diamagnetic

Bond order $= \dfrac{1}{2}\ [\ Nb - Na\ ]$

$= \dfrac{1}{2}\ [\ 8 - 2\ ] = 3$

So, N_2 Molecule contains a triple bond (one σ and two π bonds)

Molecular orbital energy level diagram of N_2 molecule.

(II) Oxygen molecule :

At No. of Nitrogen atom is 8.

E.C. of Nirogen atom is $1S^2 \, 2S^2 \, 2P^4$

Oxygen atom has 6 outer electrons.
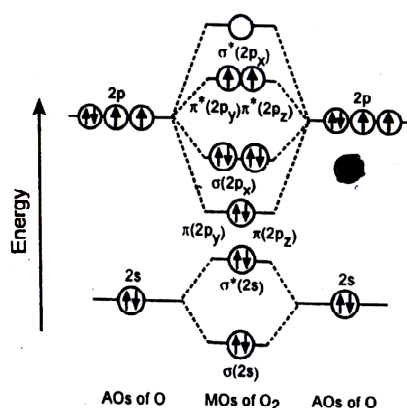
O_2 molecule contains 12 outer electrons.

M.O configuration of O_2 molecules is KK $\sigma \, 2S^2 \, \sigma \, *2S^2 \, \pi \, 2Py^2 \, \pi \, 2Pz^2 \, \sigma \, 2Px^2 \, \pi \, *2Py^1 \, \pi \, *2Pz^1$

Since there are no unpaired electrons O_2 Molecule is Paramagnetic.

Bond order $= \dfrac{1}{2} [\, Nb - Na \,]$

$= \dfrac{1}{2} [\, 8 - 4 \,] = 2$

So, O_2 Molecule contains a double bond (one σ and one π bonds)

Molecular orbital energy level diagram of O_2 Molecule

4:2.11 M.O. ENERGY DIAGRAM OF HETERO NUCLEAR DIATOMIC MOLECULES :

(I) HCl molecule :

At No. of Hydrogen atom is 1.

E.C. of Hydrogen atom is $1S^1$

At No. of Chlorine atom is 1.

E.C. of Chlorine atom is $1S^2\ 2S^2\ 2P^6 3S^2\ 3P^5$

M.O E.C of HCl molecules is $1S^2\ 2S^2\ 2P^6\ 3S^2\ 3Px^2\ 3Py^2\ \sigma\ SP^2$
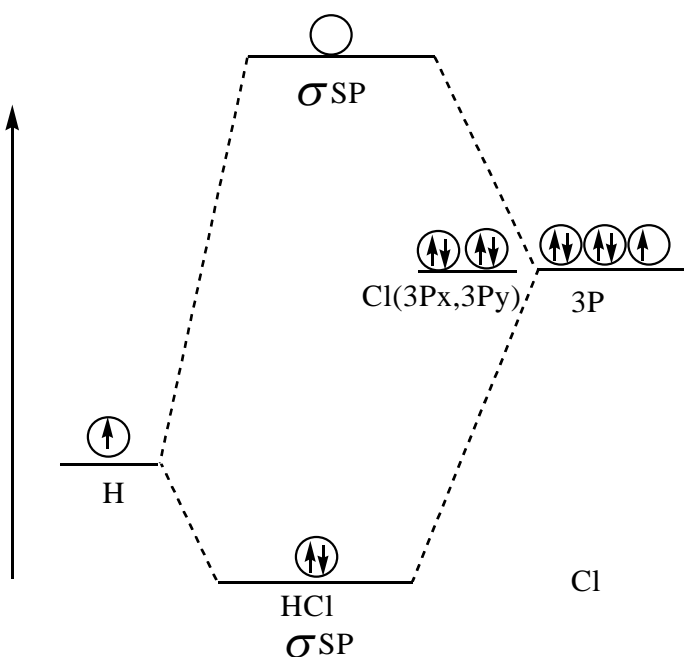
Since there are no unpaired electrons Cl_2 Molecule is diamagnetic

Bond order $= \dfrac{1}{2}\,[\,Nb - Na\,]$

$= \dfrac{1}{2}\,[\,2 - 0\,] = 1$

It contains one σ

The molecular orbital formed by H(1S) and Cl (3P) orbitals is not symmetrical. So, the bond formed is polar.

σ SP

Cl(3Px,3Py)

3P

H

HCl

σ SP

Cl

Molecular orbital energy level diagram of HCl Molecule

(II) CO molecule :

At No. of Carbon atom is 6.

E.C. of Carbon atom is $1S^1 2S^2 2P^2$

Carbon atom his four outer electrons

At No. of Oxygen atom is 8.

E.C. of Chlorine atom is $1S^2 2S^2 2P^4$

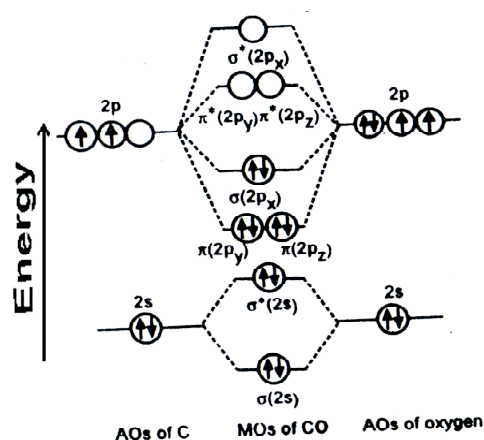Oxygen atom has six outer electrons

CO molecule has 10 outer electrons.

M.O configuration of CO molecules is KK $\sigma 2S^2 \; \sigma^* 2S^2 \; \pi 2Py^2 \; \pi 2Pz^2 \; \sigma 2Px^2$

Since there are no unpaired electrons CO Molecule is diamagnetic

Bond order $= \dfrac{1}{2}$ [Nb – Na]

$= \dfrac{1}{2}$ [8 – 2] = 3

So, CO Molecule contains a triple bond (one σ and two π bonds)

Molecular orbital energy level diagram of CO Molecule

(III) NO molecule :

At No. of Carbon atom is 7.

E.C. of Carbon atom is $1S^2 2S^2 2P^3$

Nitrogen atom has 5 outer electrons

At No. of Oxygen atom is 8.

E.C. of oxygen atom is $1S^2 2S^2 2P^4$

Oxygen atom has 6 outer electrons

NO molecule has 11 outer electrons.

M.O configuration of NO molecules is KK $\sigma 2S^2 \sigma^*2S^2 \pi 2Py^2 \pi 2Pz^2 \sigma 2Px^2 \pi^*2Py^1$

Since there is one unpaired electrons NO Molecule is paramagnetic

Bond order $= \dfrac{1}{2} [\, Nb - Na \,]$

$= \dfrac{1}{2} [\, 8 - 3 \,] = 2.5$

The bond order of 2.5 is inagreement with the bond length of No (114 Pm) which is less than that of single bond and more than that of double bond.
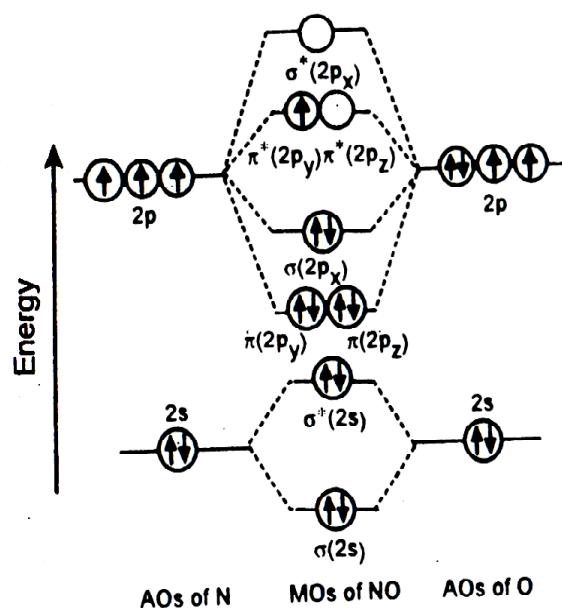
Molecular orbital energy level diagram of NO Molecule

4:2:12 COMPARISON OF VALANCE BOND AND MOLECULAR ORBITAL THEORIES :

A) common features :

In both theories :

i) a covalent bond is formed by sharing of bonding electron density by both the nuclei

ii) there occurs concentration of electron density between the two nuclei

iii) an orbital whether atomic or molecular can not have more than two electrons.

iv) orbitals whether atomic or molecular are filled up in the order of increasing energy

v) Both the methods explained directional nature of the covalent bond.

DISTINCTION :

	V.B. THEORY		M.O THEORY
1	In V.B. Theory atoms do not lose their identity	1	In M.O. thoery atoms losetheir identity
2	This theory rejects ionic structures like A^+B^-	2	This theory accepts ionic structures.
3	It does not readily explain para magnetism	3	It readily explains paramagnetism
4	According to V.B. Theory an electron moves in the field of one nucleus only	4	According to M.O Theory an electron moves in the field of more than one nucles
5	In this theory resonance and hybridisation play an important role	5	In this theory resonance and hybridisation donot play anyrole

4.2.13 Model Questions:

1. What is meant by hybridisation ? On the basis of the concept of hybridisation discuss the shape of CH_4, BF_3 and $BeCl_2$ molecules.

2. Basing on the concept of valence bond theory explain the shapes of ClF_3, BrF_5 and $Ni(CO)_4$ molecules.

3. What is meant by dipolemoment ? Explain how the dipolemoment can give an idea about the structure of molecules with two examples.

4. What are molecular orbitals ? How does it differ from atomic orbitals? What are bonding and antibonding molecular orbitals?

5. What is meant by bond order ? Discuss about the energies of different molecular orbitals.

6. Discuss briefly the molecular orbitals theory. Explain with the help of M.O. theory, the paramagnetic character of oxygen and diamagnetic character of nitrogen.

7. Draw the molecular orbital diagram of NO molecule and discuss its structure.

8. Draw the molecular orbital energy level diagram of CO molecule and calculate bond order.

9. Discuss the formation of oxygen molecule on the basis of molecular orbital theory.

10. Discuss briefly the molecular orbital theory. How does it differ from valence bond theory?

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Principal;
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UNIT - IV

Lesson - 3

STEREO CHEMISTRY OF CARBON COMPOUNDS

4.3.1. Molecular Representations :

Wedge, Fischer, Newman and Saw - horse formula. Isomerism - definition of homomers and isomers. Classification of isomers - constitutional and stereoisomers, definition and examples. Constitutional isomers - Chain, functional, positional isomers and metamerism. Stereoisomers - enantiomers and diastereomers, definitions and examples. Conformational and configurational isomerism, definiton. Conformational isomerism of ethane and n- butane.

Enantiomers :

Optical activity - wave nature of light, plane polarised light, interaction with molecules, optical rotation and specific rotation. chiral molecules - definition and criteria - absence of plane, centre and Sn axis of symmetry. Asymmetric and disymmetric molecules - examples of asymmetric molecules (Glyceraldehyde, Lactic acid, Alanine) and disymmetric molecules (trans -1-2- dichloro cyclopropane). Chiral centres - definition, molecules with similar chiral carbons (Tartaric acid), defintion of mesomers, molecules with dissimilar Chiral carbons (2, 3 - dibrompentane). Numbers of enantiomers and mesomers - calculation. D,L and R,S configuration of asymmetric and disymmetric molecules. cahn- Ingold - prelog rules. Recemic mixture, Recimisation and Resolution techniques.

Diastereomers :

Definition, geometrical isomerism with reference to alkenes - cis, trans and E, Z - Configuration.

4.3.2 MOLECULAR REPRESENTATIONS :

### Dashed - Wedged Representation :

Dashed - Wedged representations illustrate the structures of molecules in three dimensions. Drawing the structures of three dimensional molecules on a two dimensional paper is difficult. For example a Tetra hedron should look three dimensional. So, a short hand notation is used to simplify three dimensional drawings known as Dashed - Wedged line drawings.

In this representation Dashed lines (are used to) show the bonds that go backward, away from the reader.

Thick lines are used to show the bonds that come forward, towards the reader.
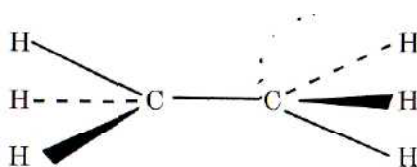
Straight lines are used to show the bonds in the plane of the paper.

Ex : 1. Methane molecule :
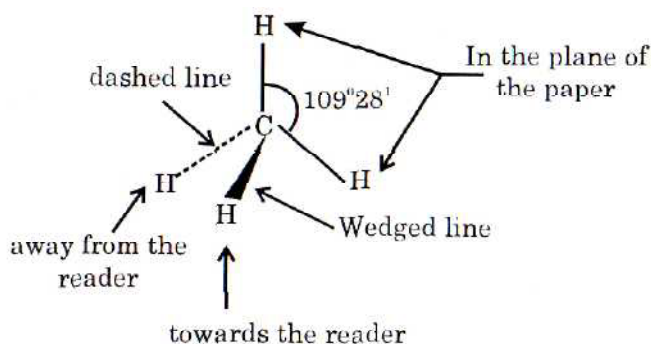
Three - dimensional molecule Methane (CH_4)

2. Ethane molecule :

Three dimensional structure of Ethane (C_2H_6). As the number of chiral carbons in a molecule increases, it becomes difficult to draw the structures in three dimension.

Fischer projection :

The Fischer projection is a standard way to project the three dimensional configuration of each chiral carbon in a molecule. The Fischer projection can be written in the following way.

Ex : 1. Lactic acid CH3. CHOH. COOH.

COOH
|
C - - - - - - CH₃   ≡
HO   H
S – Lactic acid
Three dimensional
projection

COOH
|
HO —|— H
|
CH₃
S – Lactic acid
Fischer projection
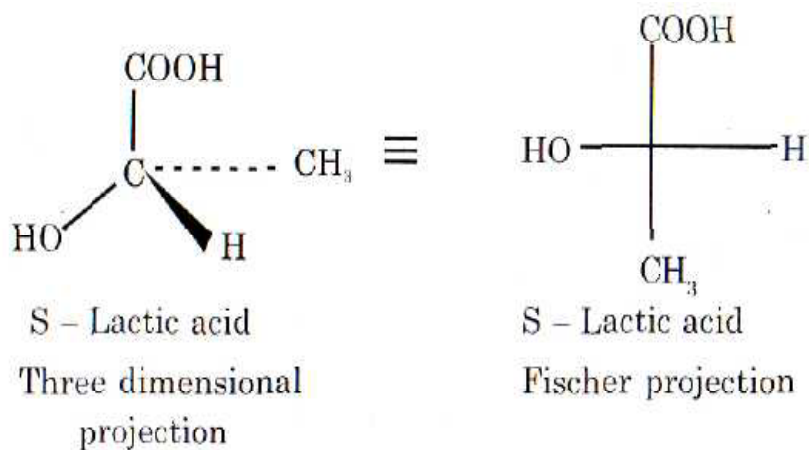
1. The molecule is written with its main carbon chain vertical and C_1 is at top.

2. The structure is flattend at chiral carbon to a plane surface.

3. The horizontal line at the chiral carbon represent bonds that project forward.

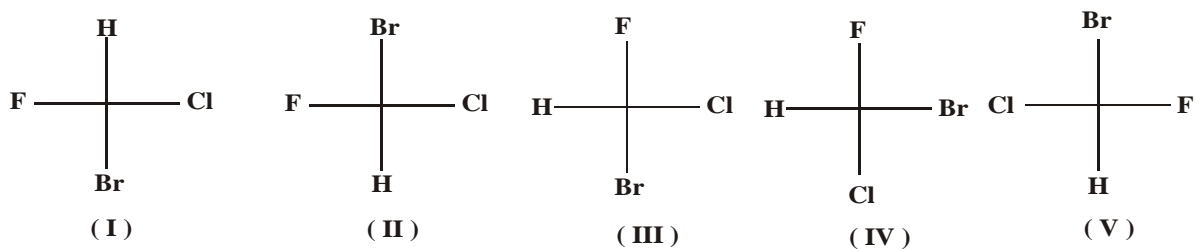4. The vertical line at chiral centre represent bonds that project backward.

Thus the Fischer projection of S - Lactic acid indicates.

COOH
|
HO — C — H
|
CH₃
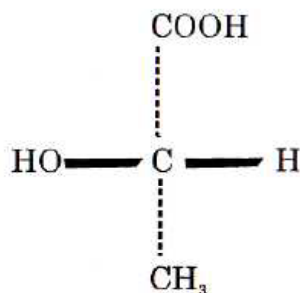
Illustraton :

If two structural formula differ by odd number of interchanges, they are enantiomers. If by even number they are identical.

Ex :

H
|
F —|— Cl
|
Br
(I)

Br
|
F —|— Cl
|
H
(II)

F
|
H —|— Cl
|
Br
(III)

F
|
H —|— Br
|
Cl
(IV)

Br
|
Cl —|— F
|
H
(V)

Relation of structures (II) to (v) W.r.t. (I)

Structure	Sequence of interchange	No.of interchanges	Relationship w.r.t. (I)
II)	H, Br	1(odd)	enantiomer
III)	H, F	1(odd)	enantiomer
IV)	H,F ; Br, Cl	2(even)	identical
V)	H, Br ; Cl, F	2(even)	identical
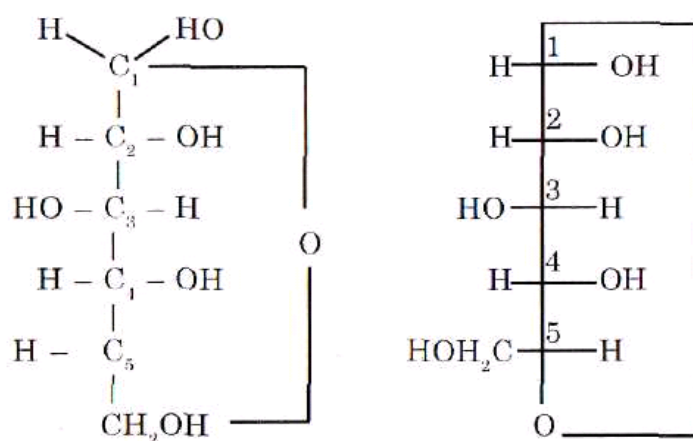
Common Fischer projection   Modified Fischer projection

Advantage : It can not only be drawn quickly, but it facilitates comparision of Stereo isomers easy.

NEWMAN PROJECTION :

Newman projections are useful for drawing conformations.

1. The front carbon is represented by three equally spaced lines coming together in 'Y' shape. These three lines represent three bonds.
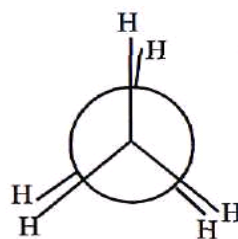
carbon nearer to the eye
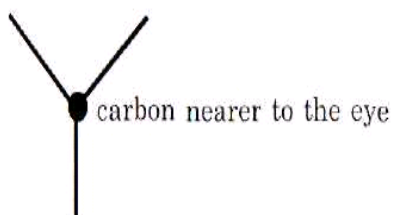
2. The back carbon is represented by a circle with three equally spaced radial extensions. These three radial extensions represent three bonds.

carbon far from the eye

Ex : 1. Ethane molecule

Three dimensional
projection formula

Newman projection formula.
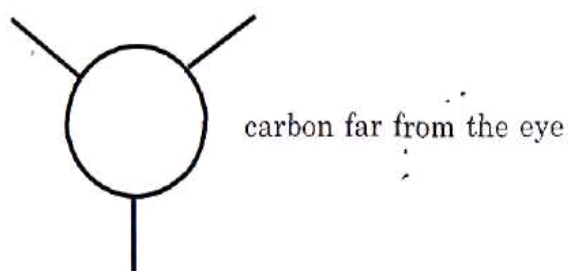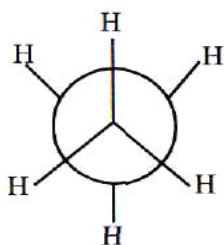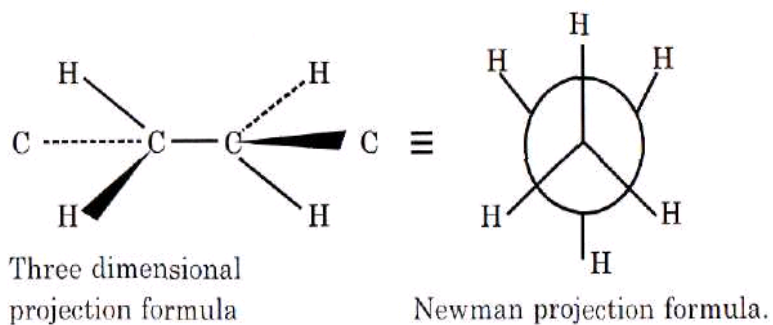
Staggend form of ethane
These are also called
Anti forms. More stable.

Eclipsed form the Ethane
These are also called
Synforms. These are less stable.

SAWHORSE FORMULA :

Sawhorse formula is used to specify conformation like Newman projection.

In Sawhorse representation the C - C bond is viewed side ways where as in Newman projection the C - C bond is along the line of vision. In Sawhorse representation C - C bond can be seen while in Newman projection the C - C bond can not be seen.

Ex. Ethane molecule

Newman projection   Sawhorse model

Eclipsed form of Ethane

Newman projection   Sawhorse model

Staggered form of Ethane
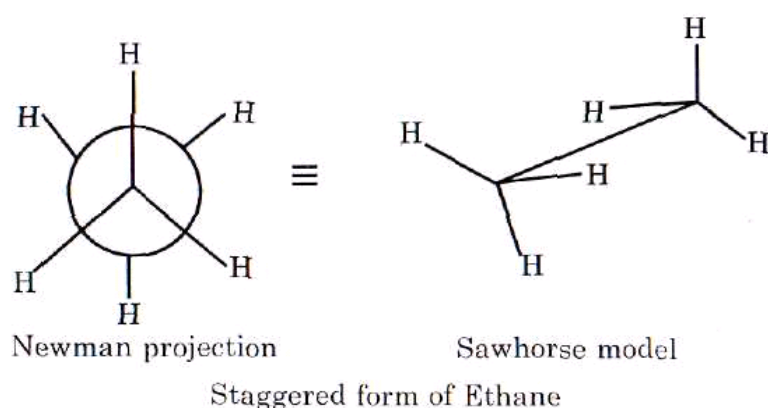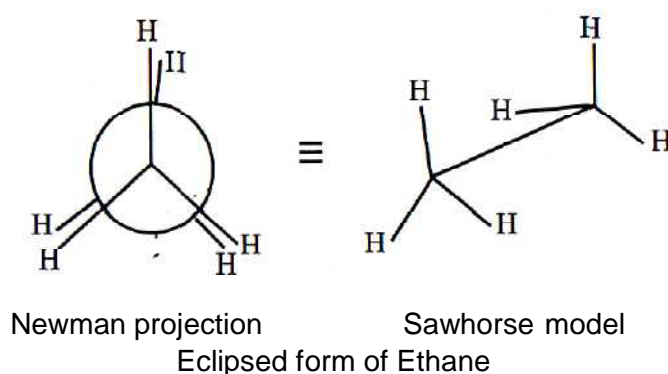
4.3.3. ISOMERISM

The phenomenon of different compounds having same molecular formula is called isomerism.

Isomers :

Isomers are different compounds having same molecular formula.

Ex : Glucose and Fructose. They are having same molecular formula $C_6H_{12}O_6$.

Homomers :

Homomers are the identical representations of the same compound. The molecular models of these representations are superimposable.

At different times two molecules of the same compound occupy same position in space. They are identical and called Homomers.
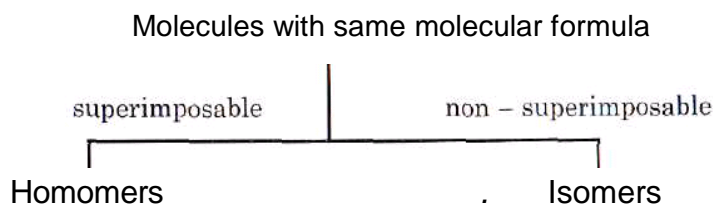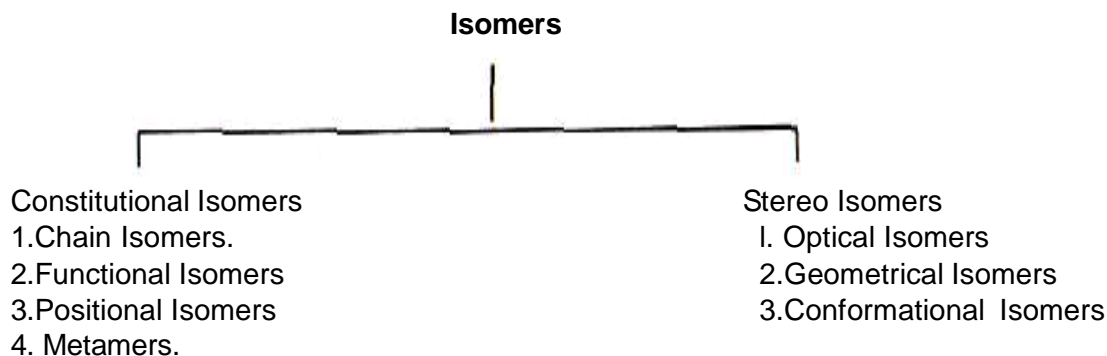
Ex : Lactic acid $CH_3CHOHCOOH$.
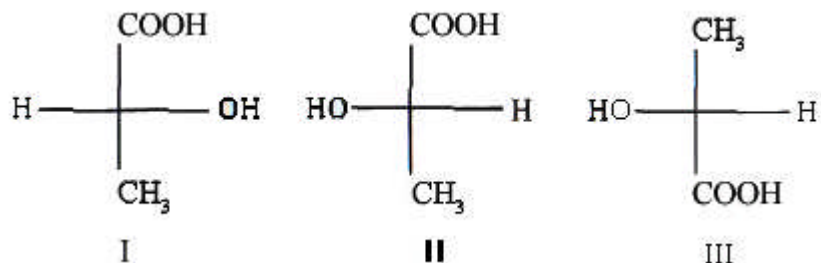
Structures I and II are Isomers. Structure II -is the mirror image of structure I. They are not super imposable called Enantiomers.

Structures I and III are same. They are Homomers. When structure I is rotated by 180°. structure III is obtained.

Classification :

Molecules with same molecular formula

superimposable	non – superimposable
Homomers	Isomers

CLASSIFICATION OF ISOMERS

Isomers

| Constitutional Isomers	Stereo Isomers
1.Chain Isomers.	I. Optical Isomers
2.Functional Isomers	2.Geometrical Isomers
3.Positional Isomers	3.Conformational Isomers
4. Metamers.	

4.3.3.1. Isomers are two types.

1. Constitutional Isomers   2. Stereo Isomers.

1. Constitutional Isomers :

Isomers with different constitutions are called constitutional Isomers, This phenomenon is called structural Isomerism.
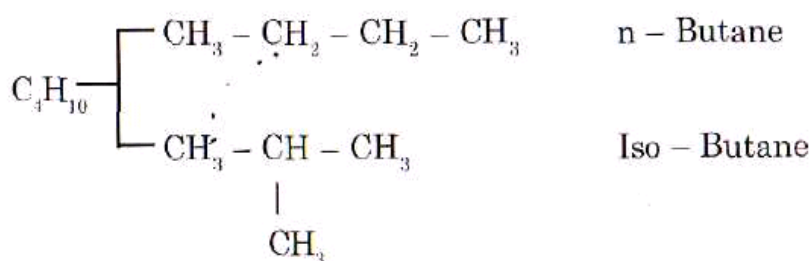
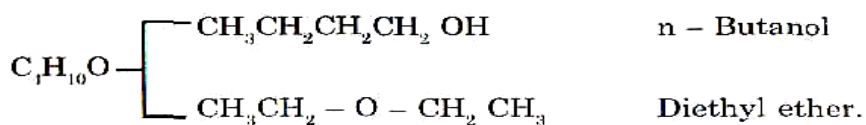**Ex :** Methyl Cyclopropane and Cyclobutane.
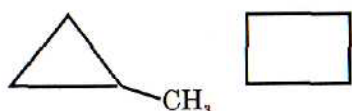
Chain Isomers :

Isomers which differ in carbon chains are called chain Isomers. Such phenomenon is called chain Isomerism.

Ex : Butane C_4H_{10}

$$C_4H_{10} \begin{cases} CH_3 - CH_2 - CH_2 - CH_3 & n - Butane \\ \\ CH_3 - CH - CH_3 & Iso - Butane \\ \qquad\quad | \\ \qquad\quad CH_3 \end{cases}$$
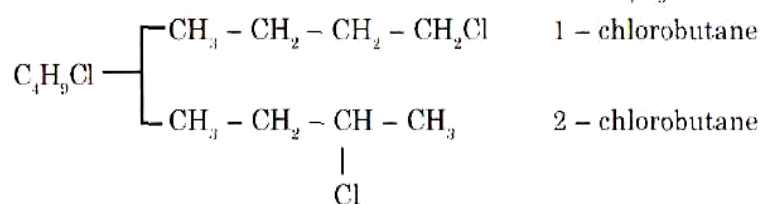
Functional Isomers :

Isomers which differ in the nature of the functional group are called Functional Isomers. Such phenomenon is called Functional Isomerism.

$$C_4H_{10}O \begin{cases} CH_3CH_2CH_2CH_2\,OH & n - Butanol \\ \\ CH_3CH_2 - O - CH_2\,CH_3 & Diethyl\ ether. \end{cases}$$
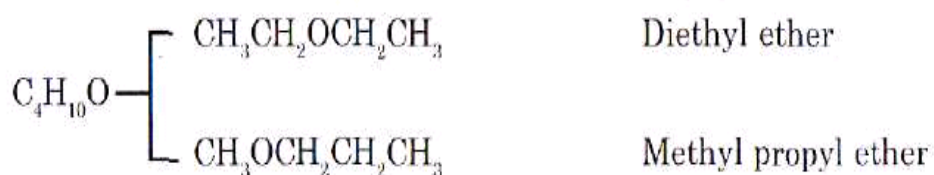
Positional Isomers :

Isomers which differ in the position of an atom or group are called positional Isomers. Such phenomenon is called position Isomerism. **Ex :** Chloro – Butane C_4H_9Cl

$$C_4H_9Cl \begin{cases} CH_3 - CH_2 - CH_2 - CH_2Cl & 1 - chlorobutane \\ \\ CH_3 - CH_2 - CH - CH_3 & 2 - chlorobutane \\ \qquad\qquad\qquad | \\ \qquad\qquad\qquad Cl \end{cases}$$

Metamers :

Isomers which differ in the distribution of carbon atoms on either side of the functional group are called Metamers.Such Phenomenon is called Metamerism **Ex :** $C_4H_{10}O$

$$C_4H_{10}O \begin{cases} CH_3CH_2OCH_2CH_3 & \text{Diethyl ether} \\ CH_3OCH_2CH_2CH_3 & \text{Methyl propyl ether} \end{cases}$$

4.3.3.2. Stereo Isomers :

Isomers with same constitution which differ in special arrangement of atoms or groups are called Stereo Isomers.This phenomenon is called Stereo isomerism.

They are two types

1. Enantiomers   2. Diastereomers.

Enantiomers :

Isomers which are mirror images and non -super imposable are called Enantiomers.

COOH   COOH
 | |
 C   C
H   CH₃   OH | HO   CH₃   H
*d*– lactic acid | *l*– lactic acid
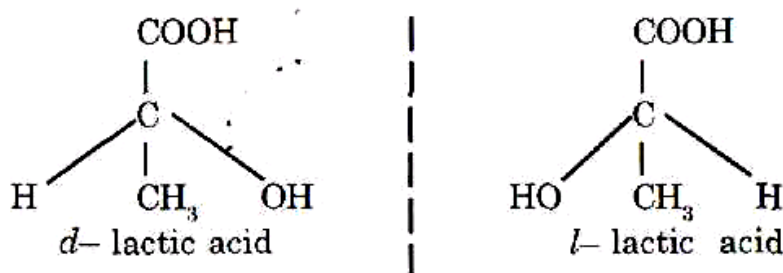
d- lactic acid rotates the plane of polarized light to right. It is a dextro isomer. *l*- lactic acid rotates the plane of polarized light, to left. It is a leavo isomer. These two are mirror images and non -super imposable. Hence they are enantiomers.

Diastereomers :

Optical Isomers which are not enantiomers are called Diastereo Isomers.   They are not mirror images.

Ex : Cis - 2 - butene and trans - 2 - butene

Cis – 2 – butene   trans – 2 – butene
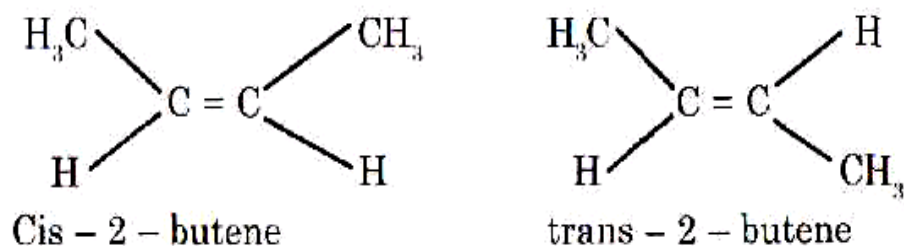
Conformational and configurational Isomerism :

i) **Conformational Isomerism** :

The formation of different easily interconvertible structures by rotation about a single bond is called conformational Isomerism. Such compounds are called conformations or conformers. These are non - super imposable. A single conformation can not be physically separated because the energy required for rotation about a single bond is neglisible and different conformers are easily interconvertible.

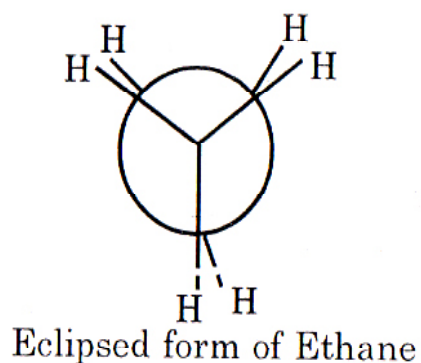**1) Ex :** Conformers of Ethane

Staggered form:

In staggered form the atoms on the two carbons are as far as possible.   These are also called Anti forms. They are more stable.
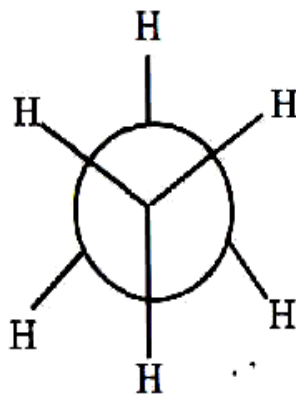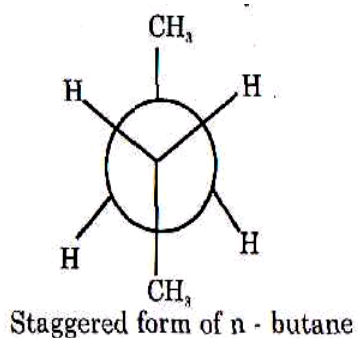

Staggered form of Ethane

Eclipsed form :

In Eclipsed form atoms on the two carbons are as close as possible. These are also called synforms. They are less stable.

Eclipsed form of Ethane

Skew forms :

The infinite number of conformers existing between staggered and Eclipsed forms are called Skew forms.

2. Conformers of n - Butane :   Staggered form :

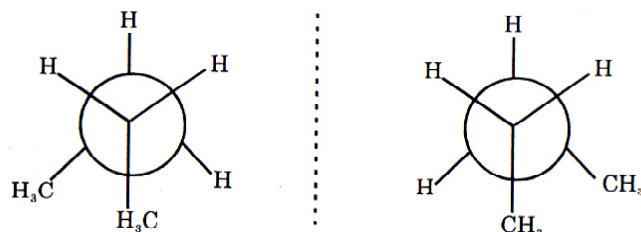In staggered form of n- Butane the Methyls are at an angle of 180°.

Staggered form of n - butane

Eclipsed form : In Eclipsed form of n-butane the Methyls are at an angle of 0°**.**

Eclipsed form of n - butane
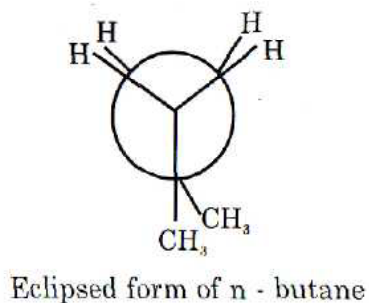
Gouche forms : Partially staggered forms :

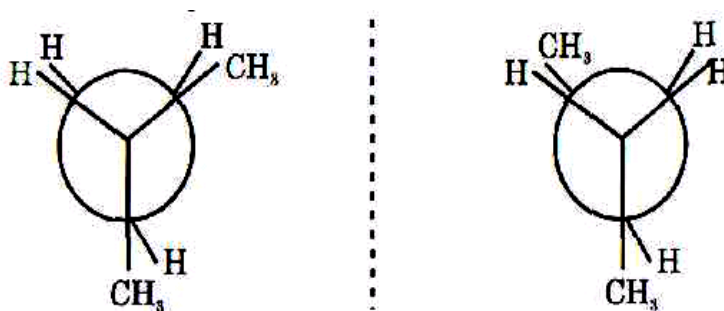In partially staggered forms, the Methyls are at an angle of 60°.

Partially staggered forms of n – butane.
These are mirror images. enantiomers.

Partially Eclipsed forms :

In partially Eclipsed forms the Methyls are at an angle of 120°.


ii) Configurational isomerism :

The formation of different non - interconvertible structures by rotation about a single bond is called configurational Isomerism. Such compounds are called configurational isomers. They are non - super imposable.

A single configuration can be physically separated because they are non - interconvertible.

Ex : 1. Configurational Isomers of Bromochlorofluoro Methane. CHBrFCl :

$$Cl \qquad\qquad Cl$$
$$|\qquad\qquad\quad |$$
$$F - C - Br \qquad Br - C - F$$
$$|\qquad\qquad\quad |$$
$$H \qquad\qquad H$$
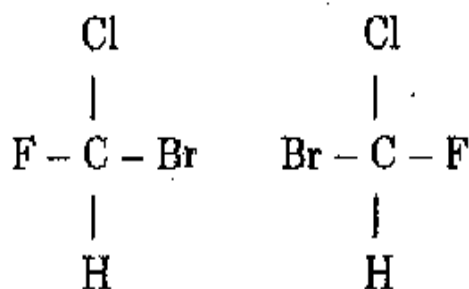
2. Configurational Isomers of Lactic acid (CH_3CHOH COOH) :
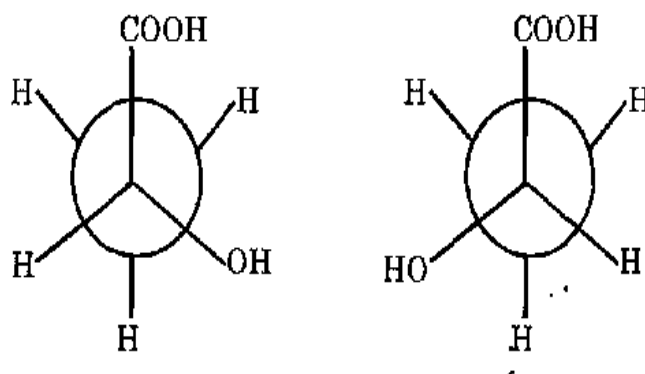
4.3.4. OPTICAL ACTIVITY :

The phenomenon of rotating the plane of polarized light is called optical activity. The compounds exhibiting this property are called optically active compounds.

The compounds which have similar physical and chemical properties and differ only in their optical activity are called optical isomers. This phenomenon is called optical Isomerism.

Ex : Lactic acid, Tartaric acid.

Condition for optical activity:

The necessary and only sufficient, condition for a molecule to show optical activity is that the geometrical structure of the molecule should not super impose on its mirror image.

Wave nature of light:

Light is propagated in all directions in the form of waves. It is an electromagnetic radiation. It is associated with electric and magnetic fields.

The vertical component of the wave E indicates change in the strength of the electric field. The horizontal component of the wave H indicates change in the strength of the magnetic field.

Plane polarized light :

An ordinary light vibrates in all planes at right angles to the plane of propagation.

Ordinary light
Vibrating in all
directions

Nicolprism
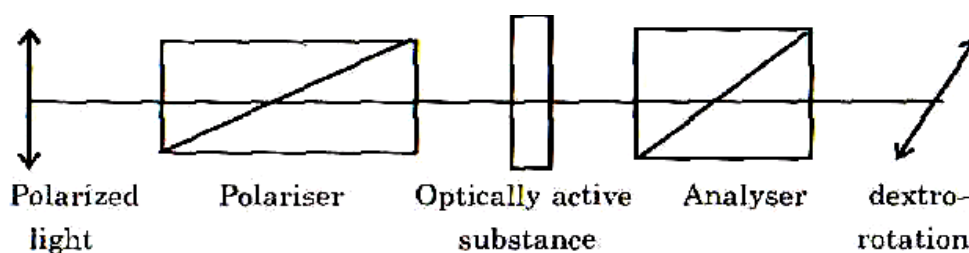
Plane polarized light
vibrating in one
direction only.
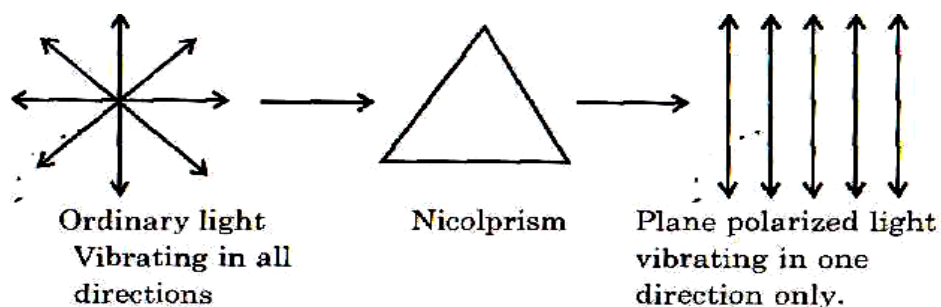
When light is passed through a NiCol prism, the emergent beam vibrates only in one direction. This type of light, which vibrates only in one plane, is called polarized light.

Interaction with molecules:

A plane polarized light consists of a right handed and a left handed circularly polarized light. Therefore it represents a chiral environment. Because of opposite chiralities, the rays establish diastereomeric relationship with any particular enantiomer and interact differently. As a result the plane of polarization is rotated either towards right (clock wise) or towards left (anti-clock wise) by a certain angle.

4.3.4.1. OPTICAL ROTATION : Dextro- rotatory :

Substances which rotate the plane of polarized light to right are called dextro rotatory. It is indicated by d or (+).

Polarized
light

Polariser

Optically active
substance

Analyser

dextro–
rotation

Leavo- rotatory :

Substances which rotate the plane of polarized light to left are called leavorotatory. It is indicated by / or (-).

Polarized light   Polariser   Optically active substance   Analyser   leavo– rotation
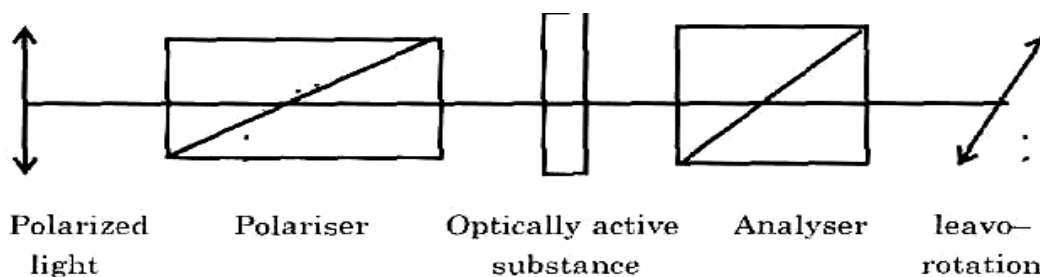
4.3.4.2. On the basis of optical activity organic compounds are divided into three types.

1. Dextro - rotatory : It rotates the plane polarized light to right (dextro = right), d or (+) form

    Ex : *d*— Tartaric acid.

2. Leavo - rotatory : It rotates the plane of polarized light to left, (leavo = left). It is 1 or (-) form.

    Ex : *l* - Tantaric acid.

3.Optically inactive : The compounds do not rotate the plane polarized light in any direction.

    Ex : Meso - tartaric acid

4.3.4.3.Factors Effecting Optical rotation :

    The magnitude of optical rotation depends upon the following factors.

      1.   Nature of the substance.

      2.   Concentration of the solution

      3.   Length of the tube containing the solution.

      4.   Nature of the solvent

      5.   Temperature of the solution

      6.   Wave length of the light used.

4.3.4.4. Specific rotation :

    Specific rotation is defined as the observed rotation when polarized light is passed through 1 decimeter of the solution having concentration of 1 gram per milli litre.

Specific rotation $\left[\alpha\right]_D^{t°c} = \dfrac{\alpha}{lc}$

Where,

α = Observed rotation

l = Length of the solution in decimeters. (1 decimeter = l0cmsj

C = No. of'grams of substance in 1 ml of the solution

D = The Sodium D line corresponding to 589 $m\mu$ wave length

t = Temperature.

The sign (+) attached with the angle of rotation indicates rotation towards right and (-) sign indicates rotation towards left.

Ex : $[\alpha]_D$ of α - glucose is +112°.

4.3.5. CHIRALITY :

On studying several optically active organic compounds it was found that chiral carbon or chirality is responsible for optical activity.

Chirality :

Chirality is the property of a molecule being non - super imposable on its mirror image.

Chiral Carbon :

A carbon atom having four different monovalent atoms or groups is called asymmetric carbon.

In Greek, cheir = hand. Chirality means handedness. The term chiral or chirality is used to a molecule whose mirror image is non - super imposable. It is responsible for optical activity.

Chirality was proposed by Kelvin. It largely displaced the earlier term dissymetric and still earlier term asymmetric. However on account of their popularity they are still used.

Explanation :

The left hand of a person looks similar to his right hand. But the left hand gloue does not fit to his right hand. The relation between two hands is that they are non - super imposable mirror images of each other. Molecules having left hand and right hand forms are called chiral molecules. They are optically active.
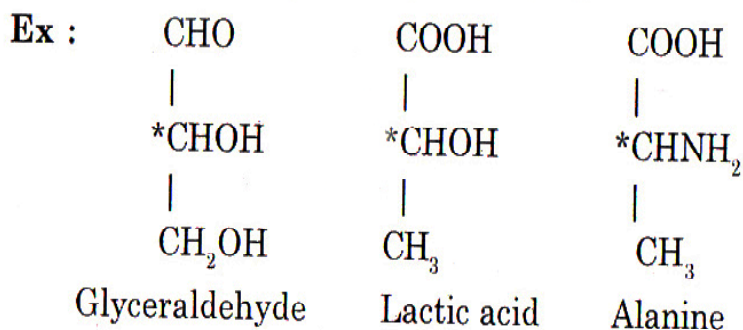
Ex : Lactic acid .

COOH | COOH

C | C

H CH₃ OH | HO CH₃ H

Lactic acid
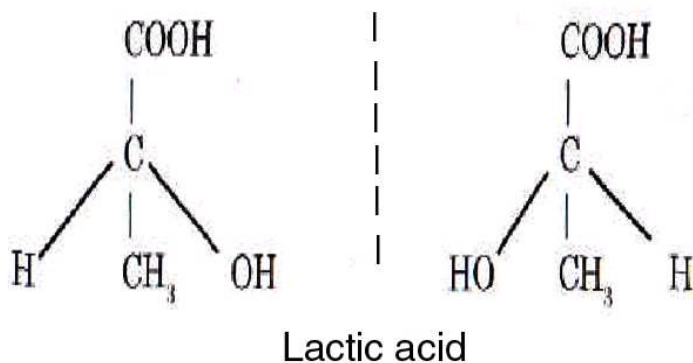
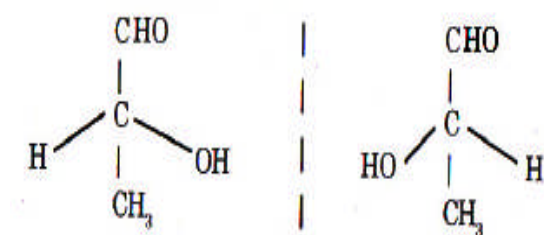These are non - super imposable mirror images. Chiral and optically active.

4.3.5.1. Asymmetric Molecules : A molecule is said to be asymmetric if it has no elements of symmetry except C_1 symmetry.

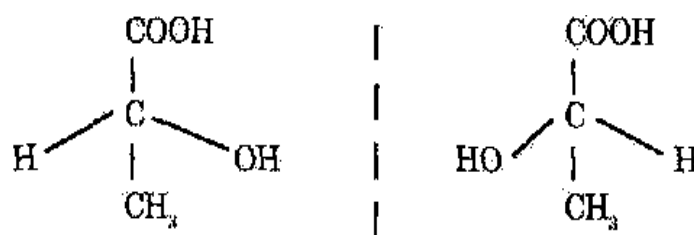Asymmetric molecule does not possess either of the following elements of symmetry.

1. Plane of symmetry.

2. Centre of symmetry.

3. Alternating axis of symmetry.

4. Simple axis of symmetry except C_1.

Ex :

CHO

|

*CHOH

|

CH_2OH

Glyceraldehyde

COOH

|

*CHOH

|

CH_3
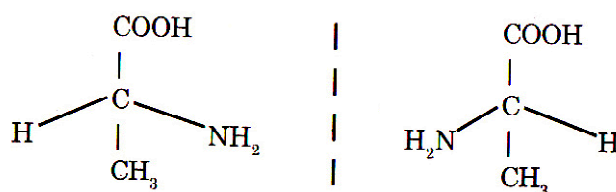
Lactic acid

COOH

|

$*CHNH_2$

|

CH_3

Alanine

Each molecule has two non - super imposable mirror image structures.   They are chiral and optically active.

non - super imposable mirror images of Glyceraldehyde

non - super imposable mirror images of Lactic acid.
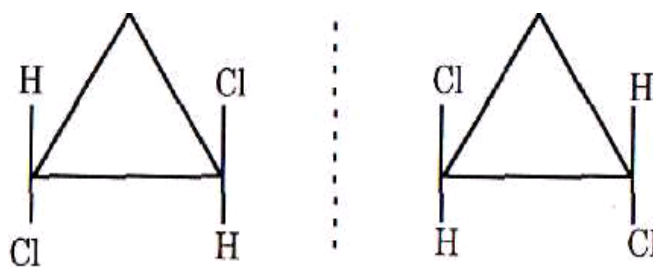

non – super imposable mirror images of Alanine.

All molecules contain an infinity number of C_1 axes.

4.3.5.2. Disymmetric molecules : A molecule is said to be dissymmetric if it has no element of symmetry except simple axis of symmetry.

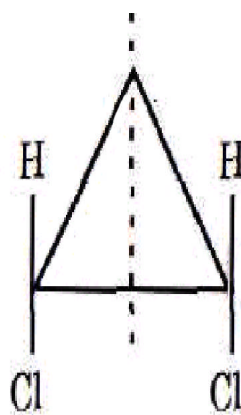A disymmetric molecule does not possess either of the following elements of symmetry.

    1. Plane of symmetry.

    2. Centre of symmetry

    3. Alternating axis of symmetry.

Ex : 1. Trans 1. 2- dichloro cyclopropane.

non – super imposable mirror images of trans 1,2- dichloro cyclopropane

2. Cis - 1,2 - dichloro cyclopropane :

Cis – 1,2- dichloro cyclopropane has plane or symmetry, it is a Meso compound.

One fold alternating axis of symmetry corresponds to plane of symmetry. Two fold alternating axis of symmetry corresponds to centre of symmetry. So, a molecule that lacks alternating axis of symmetry is called disymmetric. These are usually optically active.

Symmetry designations

Term	Alternating axis	Simple axis	Optical activity
Symmetric	Present	May or may not be present	Inactive
Disymmetric	Absent	May or may not be present	Usually active
Asymmetric	Absent	Absent	Usually active

4.4.6. CHIRAL CENTRE :

A carbon atom containing four different monovalent atoms or groups is called chiral carbon or chiral centre.

Ex : Lactic acid

$$\begin{array}{c} COOH \\ | \\ {}^*C \\ H \diagup \ | \ \diagdown OH \\ CH_3 \end{array}$$
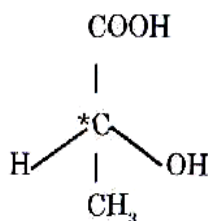
Explanation :

The term chiral is used to compounds whose mirror images are non - super imposable.

If a molecule has only one chiral centre, it is always chiral. But molecules having two or more chiral centres may be chiral or achiral.

Thus the presence of chiral centre is not the criterion of chirality. The only thing is that the molecule as a whole should be chiral.

4.3.6.1. Compounds containing similar chiral carbons :

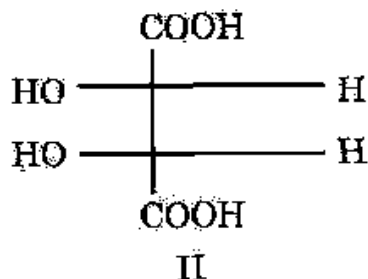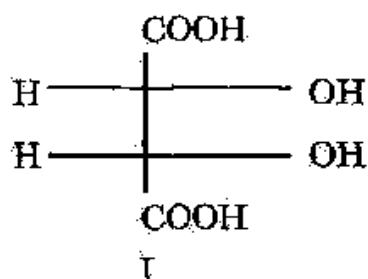The no.of optical isomers in a molecule containing 'n' number of similar chiral carbon atoms is always less than 2^n.

Ex : Tartaric acid COOH $(CHOH)_2$ COOH.

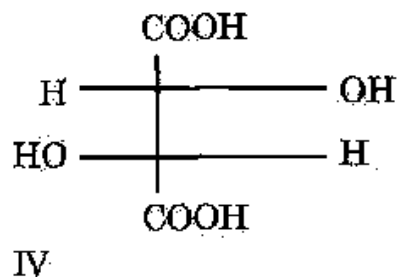$$\begin{array}{c} COOH \\ | \\ *CHOH \\ | \\ *CHOH \\ | \\ COOH \end{array}$$
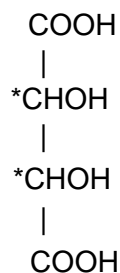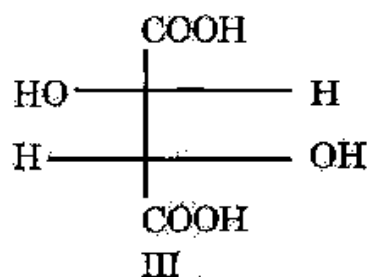
No. of chiral carbons = 2

No. of possible optical isomers = $2^n = 2^2 = 4$

But Tartaric acid has only three Isomers because it contains two similar chiral carbons.

Mirror images are super imposable

Mirror images are non - super imposable

Enantiomers :

Stereo Isomers which are mirror images of each other and non-super imposable are called enantiomers. They are optically active. Structures III and IV are mirror images of each other and optically active. They are non-super imposable. They are enantiomers. They are not interconvertible by rotation about carbon - carbon bond.

Mesomers :

Stereo isomers which are optically inactive due to internal compensation are called Mesoisomers. They can not be separated into two optically active forms. In these molecules the rotation of upper half of the molecule is cancelled by the rotation of lower half of the molecule.

Structures I and II are mirror images of each other and optically inactive due to internal compensation. When one of these Isomers {I or II) is rotated through 180° with the plane of the paper, the second one is obtained. Hence these structures are identical.

Thus Tartaric acid has three Isomers only.
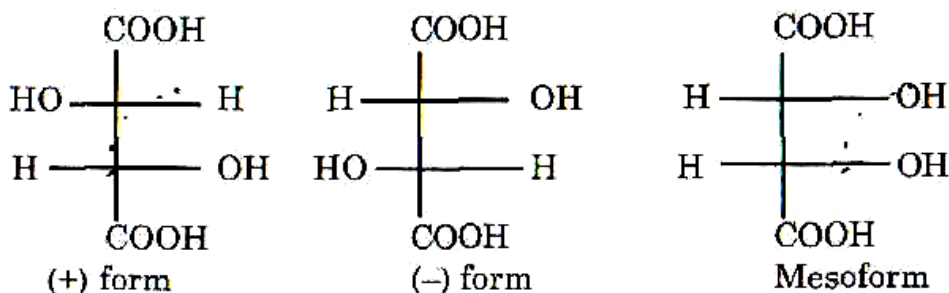
Recemic modification :

The mixture containing equimolar quantities of dextro and leavo forms is called Recemic mixture. Equimolar quantities of structures III and IV form a recemic mixture. Tt is optically inactive. It shows zero rotation. It can be separated into two optically active forms.

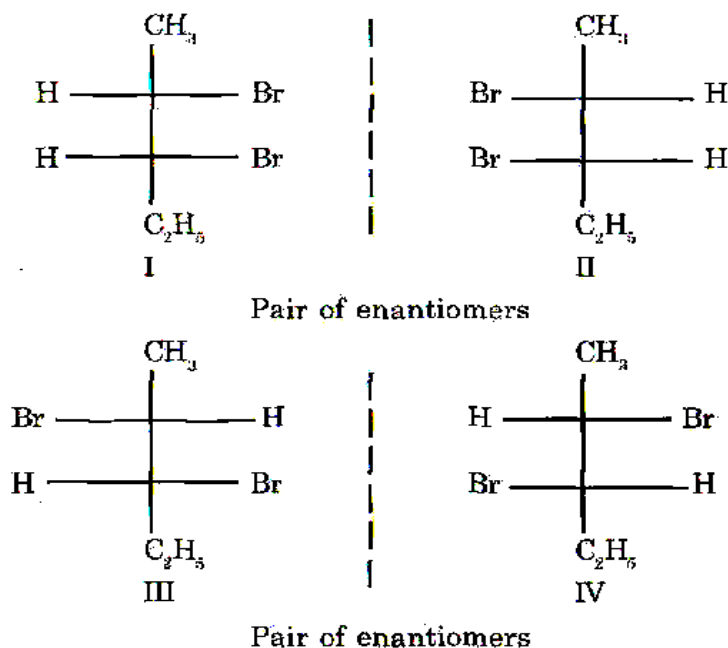**4.3.6.2. Compounds containing dissimilar chiral carbon atoms:**

The no. of optical isomers in a molecule containing different chiral carbon atoms is given by 2^n. There will be 2^{n-1} pairs of enantiomers and same number of Racemic modifications.

Ex : 2, 3 - dibromo pentane CH_3, CHBr CHBr C_2H_5.

It has two dissimilar chiral carbon atoms.

No. of optically active Isomers = $2^n = 2^2 = 4$

No. of enantiomeric pairs = $2^{n-1} = 2^{2-1} = 2$

$$
\begin{array}{ccc}
& CH_3 & \\
H & \!\!-\!\!\!\!\mid\!\!\!\!-\!\! & Br \\
H & \!\!-\!\!\!\!\mid\!\!\!\!-\!\! & Br \\
& C_2H_5 & \\
& I &
\end{array}
\qquad
\begin{array}{ccc}
& CH_3 & \\
Br & \!\!-\!\!\!\!\mid\!\!\!\!-\!\! & H \\
Br & \!\!-\!\!\!\!\mid\!\!\!\!-\!\! & H \\
& C_2H_5 & \\
& II &
\end{array}
$$

Pair of enantiomers

$$
\begin{array}{ccc}
& CH_3 & \\
Br & \!\!-\!\!\!\!\mid\!\!\!\!-\!\! & H \\
H & \!\!-\!\!\!\!\mid\!\!\!\!-\!\! & Br \\
& C_2H_5 & \\
& III &
\end{array}
\qquad
\begin{array}{ccc}
& CH_3 & \\
H & \!\!-\!\!\!\!\mid\!\!\!\!-\!\! & Br \\
Br & \!\!-\!\!\!\!\mid\!\!\!\!-\!\! & H \\
& C_2H_5 & \\
& IV &
\end{array}
$$

Pair of enantiomers

Enantiomers :

Stereo Isomers which are non - super imposable mirror images of each other and optically active are called enantiomers. Structures I and II (or) III and IV are two pairs of enantiomers.,

Diastereo Isomers :

Stereo isomers which are not mirror images of each other are called diastereo isomers.

Structures I and 111 are not mirror images of each other. They are optically active.   So, they are diastereo isomers.

Similarly structures II and III (or) II and IV (or) I and IV are also diastereo isomers.

Recemic modifications :

The mixtures containing equimolar quantities of dextro and leavo forms are called recemic mixtures. They are optically inactive. They show zero rotation separated into two optically active forms.

Mixtures of equimolar quantities of I and II (or) III and IV form two different Recemic modifications.

4.3.7. DL - Configuration (Or) Relative configuration :

Fischer arbitrarily proposed the following configuration for dextro (+) - Glyceraldehyde it is named it as D - glyceraldehyde.

CHO

H   OH

CH_2OH
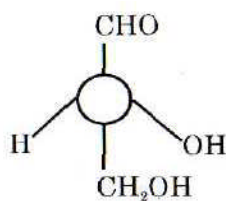
D(+) glyceraldehyde.

All Isomers prepared from or converted into D- glyceraldehyde are named as D - Isomers whether they are dextro or leavo rotatory.

Fischer arbitrarily proposed the following configuration for leavo (-) - glyceraldehyde it is named it as L - glyceraldehyde.
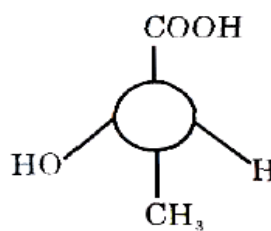
CHO

HO   H

CH_2OH
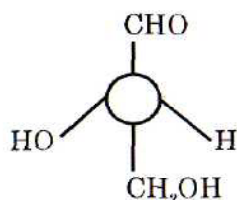
L(-) glyceraldehyde

All Isomers prepared from or converted into L-glyceraldehyde are named as L - Isomers whether they are dextro or leavo rotatory.
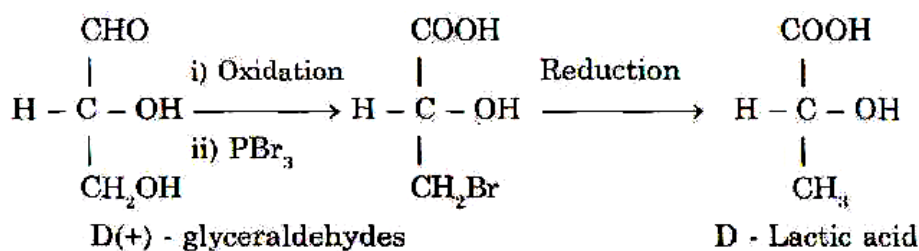
Ex : Lactic acid

COOH   COOH

H   OH   HO   H

CH_3 CH_3
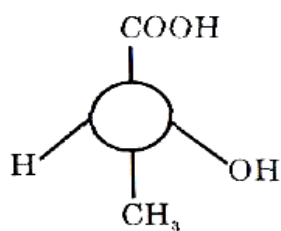
D- Lactic acid   L- Lactic acid

Lactic acid obtained from D(+)- glyceraldehyde was assigned D - configuration.

$$
\begin{array}{ccc}
\text{CHO} & \text{COOH} & \text{COOH} \\
| & | & | \\
\text{H} - \text{C} - \text{OH} & \text{H} - \text{C} - \text{OH} & \text{H} - \text{C} - \text{OH} \\
| & | & | \\
\text{CH}_2\text{OH} & \text{CH}_2\text{Br} & \text{CH}_3 \\
\end{array}
$$

CHO — i) Oxidation / ii) PBr$_3$ → COOH — Reduction → COOH

D(+) - glyceraldehydes　　　　　　　　　　　D - Lactic acid

Similarly Lactic acid obtained from L (-) - glycer aldehyde was assigned L - configuration.

Defects :   1. It is only a relative configuration.

2. The basic defect is that some times the same molecule may be related to both D and L series.

3. It is cumbersome to apply it to complicated molecules.

4.3.8. ABSOLUTE CONFIGURATION OR R, S - CONFIGURATION :

R. S- configuration is an unambiguous system devised by Cahn, Ingold and Prelog. It is based on the actual three -dimensional formula.

Sequence rules :

The order of priority of atoms or groups directly attached to the asymmetric centre is given by the sequence rules.

1. The atom of highest atomic number gets highest priority and that of lowest atomic number gets lowest priority.

Ex : I > Br > Cl > F >. O > N > C > H.

2. If two atoms attached to the asymmetric centre have same atomic number, then priority is given by comparing next atom in the group.

Ex : $CH_3 CH_2 > CH_3$

3. A doubly bonded atom attached to the asymmetric centre is considered as two such atoms attached.

Ex : $> C = O > - CH_2 OH$

4. A triply bonded atom attached to the asymmetric centre is considered as three such atoms attached.

$$-C \equiv N > >C = O$$
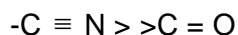
In $C \equiv N$, carbon is considered as attached to three Nitrogen atoms where as in $>C = O$. carbon is considered as attached to two oxygen atoms.
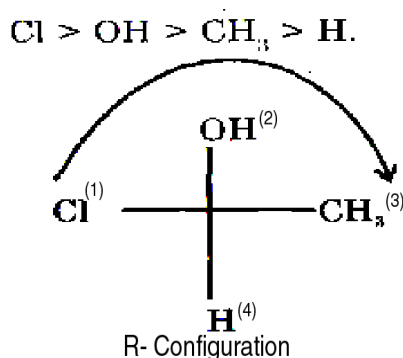
Assignment of configuration :

Configuration of the molecule is represented by the projection formula such that least priority atom or group must present, on the lower vertical position .
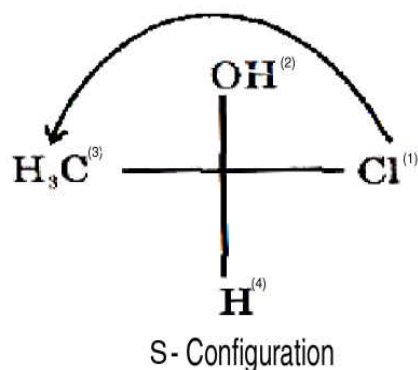
R - Configuration :

If decreasing order of priority is clock-wise, then the molecule is assigned R - configuration (Rectus = right)

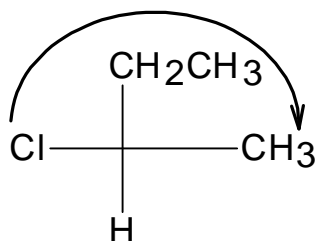Ex : 1-chloro ethanol. Priority order of the atoms is

$$Cl > OH > CH_3 > H.$$

R- Configuration

S - configuration :

If decreasing order of priority is anti clock wise, then the molecule is assigned S - configuration (Sinister = left).
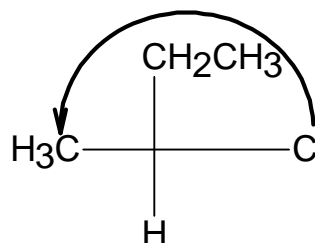

S- Configuration

Here lowest priority atom - H is present, on the lower vertical position.

Ex : 2. 2 - chloro butane.

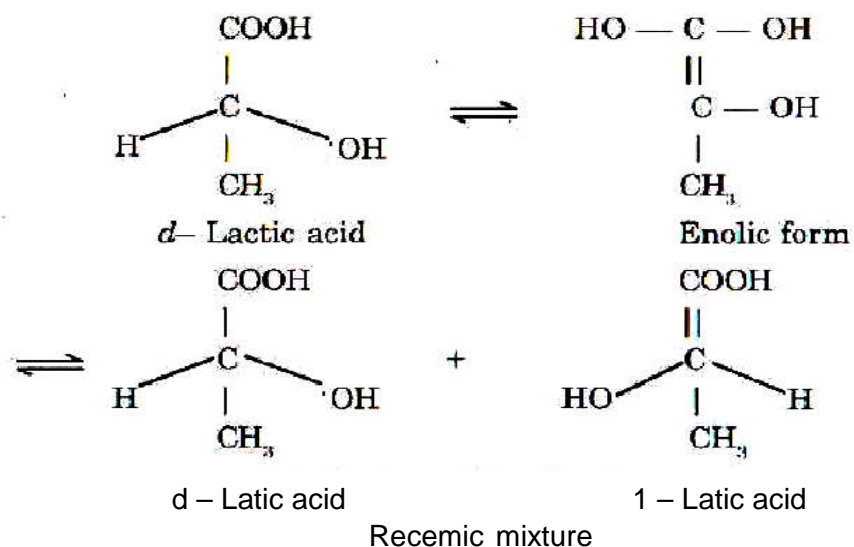R - 2 - Chlorobutane   S - 2 - Chlorobutane

4.3.9. Recemisation :

The process of conversion of an optically active compound into a recemic mixture is called recemisation.

Ex : Lactic acid undergoes recemisation in the presence of a base.

d – Latic acid   1 – Latic acid

Recemic mixture
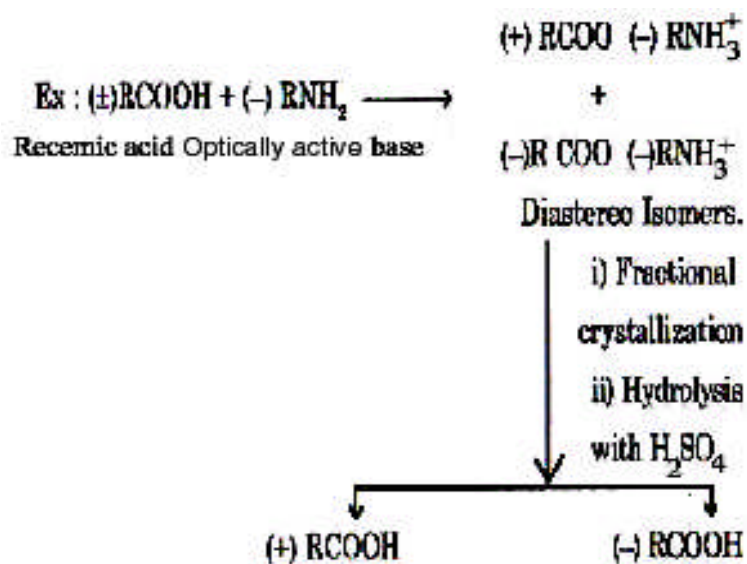
4.3.9.1. Resolution :

The process of separation-of a recemic mixture into *d-* and *l-* forms is called Resolution.

Resolution of Recemic acids :

Resolution of recemic acids is carried with the help of optically active bases such as Brucine and Strychnine.

Resolution of Recemic bases :

Resolution of recemic bases is carried out with the help of optically active acids such as Camphor and Menthol derivatives.

Ex : $(\pm)RCOOH + (-)\, RNH_2 \longrightarrow$
Recemic acid   Optically active base

$(+)\, RCOO\ (-)\, RNH_3^+$
+
$(-)R\, COO\ (-)RNH_3^+$
Diastereo Isomers.

i) Fractional crystallization
ii) Hydrolysis with H_2SO_4

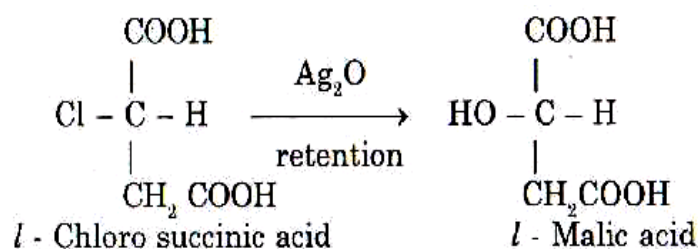$(+)\, RCOOH$ $(-)\, RCOOH$

4.3.9.2. Retention :

The process in which attacking groups takes the position of the leaving group is called retention.

In these reactions there is no change in configuration.

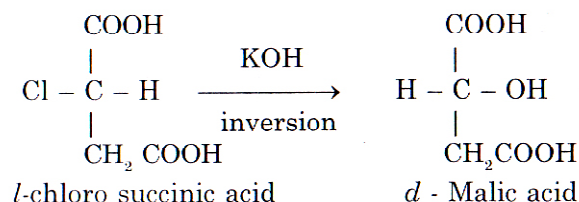Ex : L- Chlorosuccinic acid undergoes retention on hydrolysis with mild reagents like Ag_2O.

$$
\begin{array}{ccc}
COOH & & COOH \\
| & Ag_2O & | \\
Cl - C - H & \xrightarrow{\quad\quad} & HO - C - H \\
| & retention & | \\
CH_2\,COOH & & CH_2COOH \\
l \text{ - Chloro succinic acid} & & l \text{ - Malic acid}
\end{array}
$$

4.3.9.3. Inversion:

The process in which attacking group takes any position other than that of the leaving group is called inversion. In these reactions there is change in configuration.

Walden inversion :

The conversion of *d-* form of an optically active compound into *l-* form and vice versa is called Walden inversion.

Ex : *l-* Chloro succinic acid undergoes inversion on hydrolysis with strong reagents like KOH.
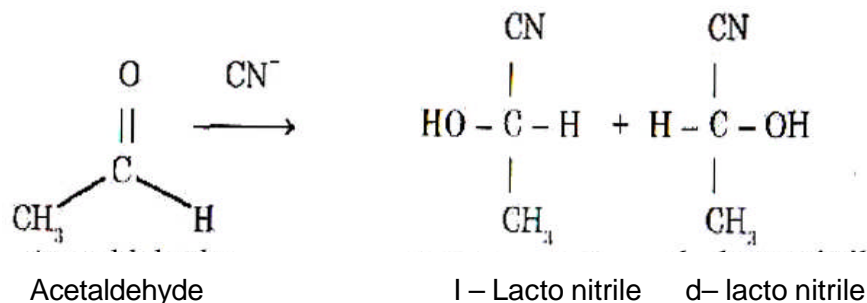
$$
\begin{array}{ccc}
\text{COOH} & & \text{COOH} \\
| & \xrightarrow[\text{inversion}]{\text{KOH}} & | \\
\text{Cl} - \text{C} - \text{H} & & \text{H} - \text{C} - \text{OH} \\
| & & | \\
\text{CH}_2\,\text{COOH} & & \text{CH}_2\text{COOH} \\
l\text{-chloro succinic acid} & & d\text{ - Malic acid}
\end{array}
$$

4.3.10. Recemic mixtures :

The mixture containing an equimolar quantities of dextro and leavo forms is called Recemic mixture. It. shows zero rotation. It can be resolved into two optically active forms.

By synthesis :

The synthesis of chiral compounds from symmetrical compounds in the absence of optically active agent always produce a recemic mixture.

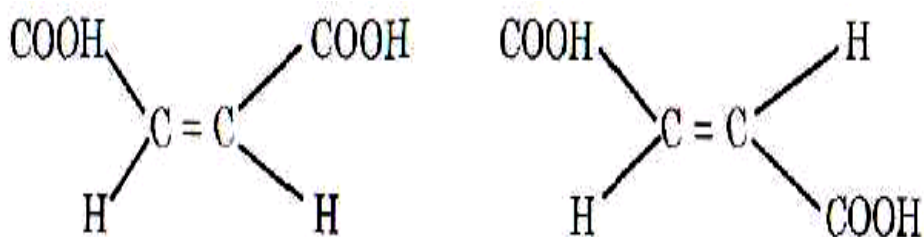Ex : The formation of lacto nitrile from Acetaldehyde always produce a recemic mixture.

$$
\begin{array}{ccc}
\text{O} \quad \text{CN}^- & & \text{CN} \qquad\qquad \text{CN} \\
|| \quad \longrightarrow & & | \qquad\qquad\quad | \\
\text{C} & & \text{HO} - \text{C} - \text{H} \;+\; \text{H} - \text{C} - \text{OH} \\
\text{CH}_3 \quad\quad \text{H} & & | \qquad\qquad\quad | \\
& & \text{CH}_3 \qquad\qquad \text{CH}_3
\end{array}
$$

| Acetaldehyde | l – Lacto nitrile   d– lacto nitrile |

4.3.11. Geometrical Isomerism :

1. Isomerism due to hindered rotation of a double bond is called Geometrical Isomerism.
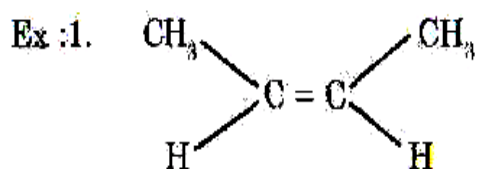
Ex : 2 - Butene
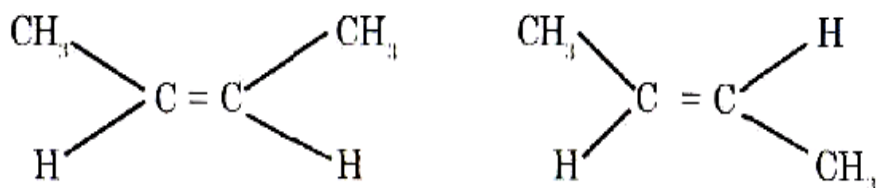
Geometrical Isomers of 2-Butene

2. Maleic acid and fumaric acid :

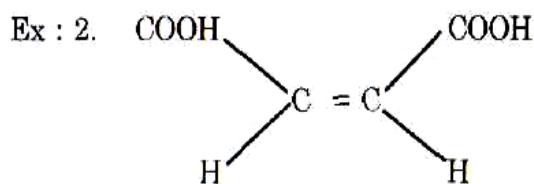|	
Maleic acid	Fumaric acid
less stable	more stable

These Isomers can be separated.

Cis, trans - Configuration :

Cis - Isomers :

In Cis - Isomers similar atoms or groups are present on the same side of the double bond.

Cis -2- Butene
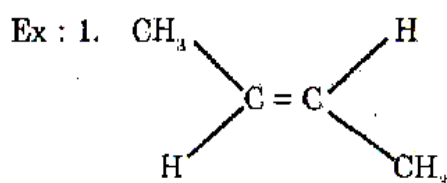
In Cis -2 - butene the two Methyl groups are present on the same side of the double bond. It is Cis - Configuration.

Ex : 2.

Cis- Isomer
Maleic acid

In Maleic acid the two - COOH groups are present on the same side of the double bond. Hence it is Cis- configuration.

Trans - configuration : In Trans - Isomers similar atoms or groups are present on the opposite sides of the double bond.

Ex : 1.

Trans - 2- butene

In Trans - 2 - butene the two Methyl groups are present on the opposite sides of the double bond. It is trans configuration.

Ex : 2.
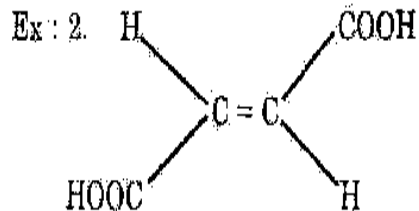
Trans - Isomer
Fumaric acid

In Fumaric acid the two carboxylic acids groups are present on the opposite sides of the double bond. It is trans - configuration.

Stability : Cis —Isomers are less stable while Trans -Isomers are more stable.

Ex : At room temperature in the presence of HC1 less stable Maleic acid converts into more stable Fumaric acid.

Maleic acid
less stable

Fumaric acid
more stable
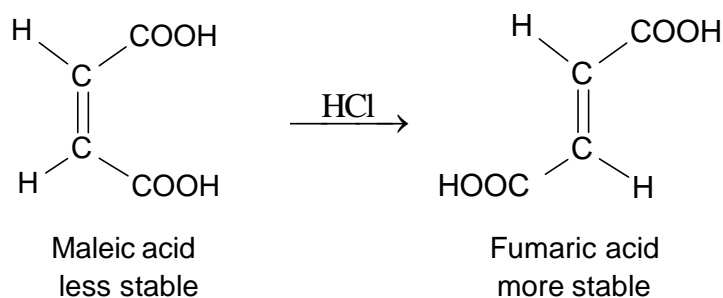
Dipolemoments :

Cis - Isomers are unsymmetrical.   They show definite dipolemoment.
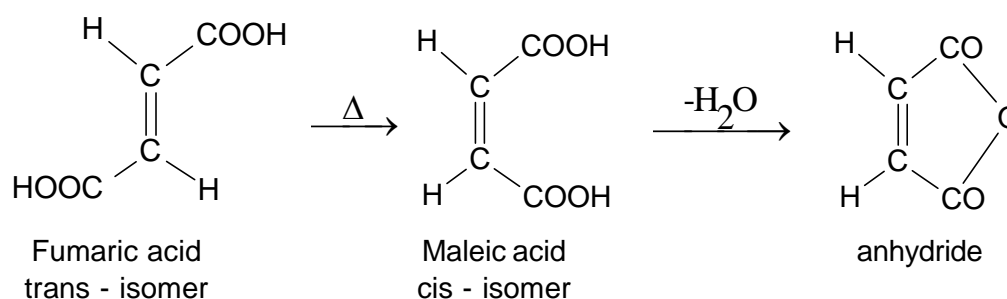
Trans - Isomers are symmetrical. ∴ They show zero dipolemoment.

Dehydration :

In Maleic acid both the -COOH groups are on the same side.   It easily forms anhydride.

Maleic acid

Maleic anhydride

On heating Fumaric acid converts into Maleic acid and forms anhydride.

Fumaric acid
trans - isomer

Maleic acid
cis - isomer

anhydride

Defect :

Cis, trans- nomenclature is failed when Alkenes have no identical substituents on the ends of the double bond.

Ex : 1 - bromo - 1 - chloro propene
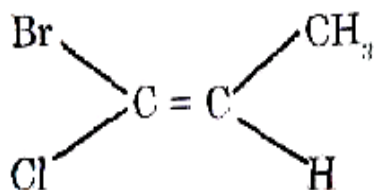
4.3.12. E, Z - **Configuration** :

To solve the problem of compounds containing no identical substituents on the ends of the double bond. E, Z - configuration is introduced.

In E, Z - nomenclature the order of priority of atoms or groups attached directly to the double bonded carbon atoms is given by sequence rules. For this Cahn - Ingold - Prelog convention for chiral carbon atoms is used.

Sequence rules :

1. The atom of highest atomic number gets highest priority and that of the lowest atomic number gets lowest priority.

Ex : 1 > Br > Cl > F > O > N > C > H.

2. If two atoms attached to the double bonded carbon atom have same atomic number, then priority is given by comparing next atom in the group.
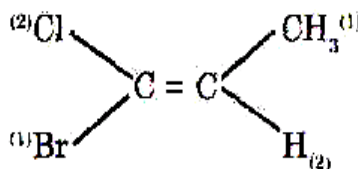
Ex : $CH_3 CH_2- > CH_3-$

E - Isomer :

In E - Isomer the two atoms or groups of highest priority are on the opposite sides of the double bond.

In German, E = Entegen means opposite.

Ex : 1 - bromo - 1- chloro propene

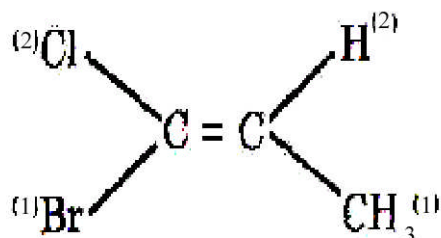The order of priority is Br > Cl and CH_3 > H.

E - 1 - bromo - 1 - chloro propene

Here the highest priority Br and CH_3 are on the opposite sides of the double bond. Hence it is E- configuration.

Z - Isomer :

In Z - Isomer the two atoms or groups of highest priority are on the same side of the double bond. In German, Z = Zusammen means 'together'.

Z - 1 - bromo - 1 - chloro Propane

4.3.13. Model Questions :

1. What are enantiomers ? What are the necessary conditions for a compound to exhibit enantiomerism ? illustrate with the help of a suitable example.

2. Write notes on diastereo isomers and mesoisomers giving example.

3. Explain optical isomerism with suitable examples.

4. Explain Walden inversion.

5. Write Fischer projection formula of D – glyceraldehyde, L- alanine and L- tartaric acid.

6. Write the configurations of

   a) E- But –2-ene

   b) Z- 2 – chloro but – 2 – ene

7. Explain resolution and recimisation with examples.

8. Write the optical isomers of Tartaric acid.

9. Assign R – and S – configuration to

   a) glyceraldehyde

   b) Amino Propionic acid

10. Explain Racemisation and Asymmetric synthesis.

11. What are the sequence rules for determining absolute configuration of optically active molecule.

12. What is Chiral Centre ? Explain molecules with similar chiral carbons and molecules with dissimilar Chiral Carbons.

13. Explain asymmetric and dissymmetric molecules with examples.

14. Define homomers and isomers. Explain conformational and configurational isomerism with example.

15. Write about classification of isomers.

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UNIT-IV

Lesson - 4

ASYMMETRIC (CHIRAL) SYNTHESIS

4.4.0 **Definitions - Asymmetric synthesis, enantiomeric excess, diastereomeric excess, Stereospecific reaction, definition, example dehalogenation of 1,2- dibromides by I. Stereoselective reaction, definition, example acid catalysed dehydration of I-Phenylproponol.**

4.4.1 ASYMMETRIC SYNTHESIS :

Asymmetric synthesis is defined as a method of preparing optically active compounds from non - optically active compounds by an intermediate use of optically active compounds.

First asymmetric synthesis was carried out by Marckwald in 1904. He prepared an active (–) valeric acid by heating with the brucine salt of ethyl methyl malonic acid at 170°c.
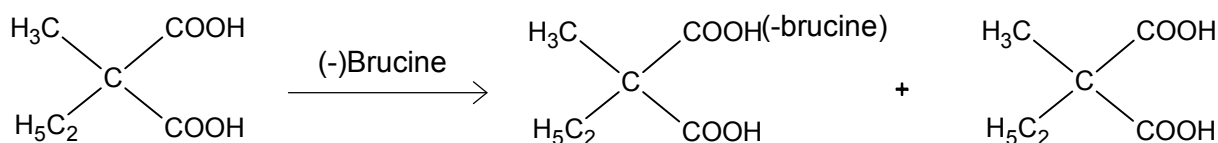
The asymmetric synthesis may be chemical in nature when a chemical reagent is used or It may be physical in nature when a physical reagent is used instead of optically active reagent. Then it is called absolute asymmetric synthesis. Circularly polarised light is called physical re-agent.
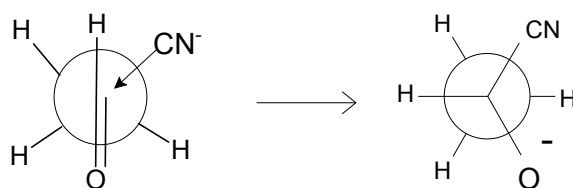
4.4.2 ENANTIOMERIC EXCESS :

Enantiomeric excess is defined as the difference in the yield of two enantiomers as a fraction of the total yield multiplied by 100%.

When both the components substrate and the reagent are symmetric recemic modification i.e equal amounts of the two enantiomers are formed.
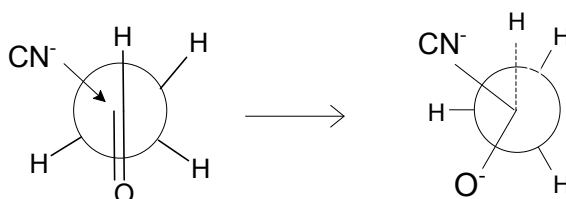
Symmetric substrate + Symmetric reagent equal amounts of the two enantiomers

Ex : Addition of HCN to CH_3CHO. If the approach of CN– ion to the aldehyde is in the conformation the product is R - lactonitrile.

R - Lactonitride

If the approach is in the mirror image conformation the product is S- lactonitrile.

S - Lactonitride

4.4.3 DIASTEREOMERIC EXCESS :

Diastereomeric excess is defined as the difference in the yields of the two diastereo isomers as a function of the total yield multiplied by 100%.
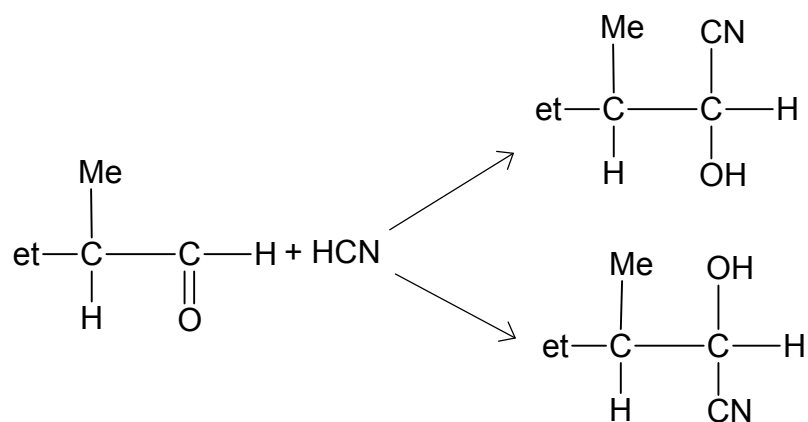
If one of the components either substrate or reagent is asymmetric two diastereo isomers are formed in different amounts.

Symmetric + Asymmetric

↓

two diastereo isomers in different amounts.

This is the basis for diastereo selective synthesis.

Here the incoming group preferentially attacks on the side of the plane containing the small group.
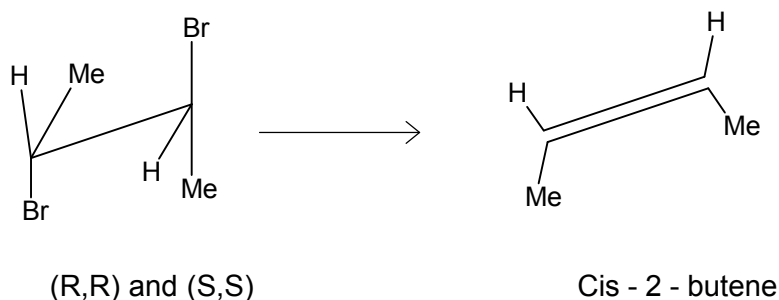
4.4.4 STEREO SPECIFIC REACTIONS :

A stereo specific reaction is one in which different stereo isomers are produced at different rates.
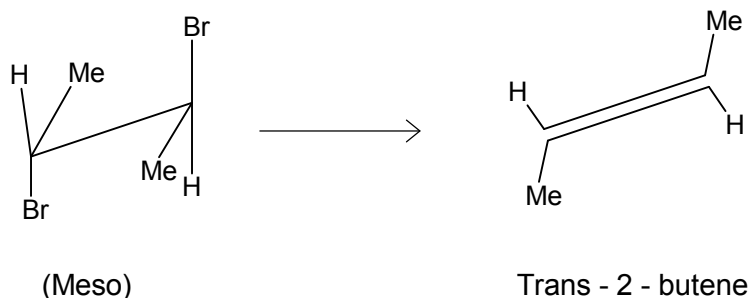
Ex : Dehalogenation of 1,2 - dibromides are E^2 type.

In these reactions the alkene formed by E^2 mechanism are stereospecific.

$(\pm)$ forms of 2,3 - dibromo butane on debromination gives is -2- butene.

(R,R) and (S,S)   Cis - 2 - butene

Meso form of 2,3 - dibromobutane gives trans -2- butene.

(Meso)   Trans - 2 - butene

The rate of formation of trans product in debtromination is greater than that of the Cis - product.

Thus E^2 reactions are stereospecific and proced easily when the departing groups are trans than when they are cis.
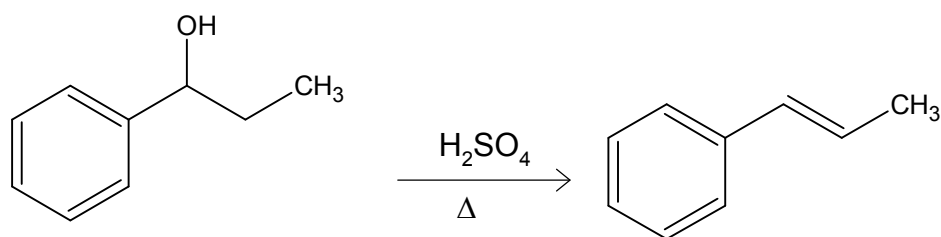
4.4.5 STEREO SELECTIVE REACTION :

A stereo selective reaction is a reaction that leads to the predominent or exclusive formation of one of the several possible stereomers.

In this reaction unequal amounts of stereisomers are formed.

Ex : Dehydration of alcohols are E^1 type. E^1 reactions are stereoselective.

Acid catalysed dehydration of 1 - phenyl propanol is a stereoselective reaction

1- Phenyl propanol   Trans 1- Phenyl propene

All stereospecific reactions are stereoselective but a stereoselective reaction need not be stereopecific.

4.4.6 Model Questions:

1. Define and explain the terms asymmetric synthesis, enantiomeric excess and diastereomeric excess.

2. What is meant by enantiomeric excess and diastereomeric excess. Give examples.

3. Explain the term stereospecific reaction with one example.

4. Define the term stereoselective reaction. Explain with one example.

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UNIT - IV

Lesson - 5

GENERAL PRINCIPLES OF INORGANIC QUALITATIVE ANALYSIS

4.5.1 :

Principles involved - solubility product, common ion effect, classification and reactions of anions. Elimination of interfering anions classification seperation and reactions of cations into groups - group reagents.

4.5.2. Semimicro qualitative analysis :

Semimicro qualitative analysis is the systematic identification of the constituents of materials using small amounts of 1ml or 0.1g of the material.

Advantages :

1. Reduced consumption of chemicals

2. Saving of time

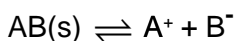3. Space required is also reduced.

4.5.3. Principles :

1. Solubility product.

2. Common ion effect.

1. Solubility product :

Solubility product is defined as the product of ionic concentrations of a sparingly soluble salt present in a solution at a given temperature.

Derivation :

Let us consider the saturated solution of a sparingly soluble salt AB.

$$AB(s) \rightleftharpoons A^+ + B^-$$

According to law of Mass Action,

$$K = \frac{\left[A^+ \right]\left[B^- \right]}{\left[AB \right]}$$

$K[AB] = [A^+][B^-].$

At a given temperature [AB] is a constant in a saturated solution.

$\therefore K[AB] = K_s = [A^+] [B^-]$

Where K_s is called solubility constant.

Results :

1. In a saturated solution solubility product and ionic product are equal.

2. When ionic product exceeds solubility product, the solution is supersaturated and precipitation occurs.

3. When ionic product is less than solubility product, the solution is unsaturated and no "precipitation occurs.

2. Common ion effect :

The solubility of a sparingly soluble salt decreases in the presence of another salt with common ion. This effect is called common ion effect.

Ex : 1. The solubility of soap decreases in the presence of NaCl due to the common ion Na^+. So, soap is precipitated due to common ion effect. It is called salting out of soap.

$RCOONa \rightleftharpoons RCOO^- + Na^+$
 Soap

$NaCl \rightleftharpoons Na^+ + Cl^-$
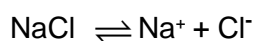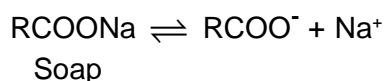
Here the common ion is Na^+

2. Ionisation of NH_4OH decreases in the presence of NH_4Cl due to the common ion NH_4^+

$NH_4OH \rightleftharpoons NH_4^+ + \overline{O}H$

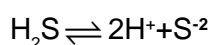$NH_4,Cl \rightleftharpoons NH_4^+ + Cl^-$
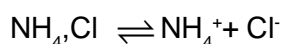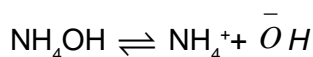
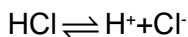Here the common ion is NH_4^+

Applications of solubility product :

Precipitation of II and IV group metals as sulphides :

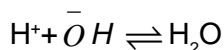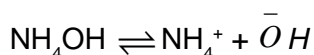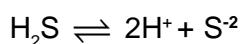Solubility product of II group metal sulphides is less than that of IV group metal sulphides.

a) In the presence of HCl, ionisation of H_2S decreases due to common ion effect. Here the common ion is H^+.

$H_2S \rightleftharpoons 2H^+ + S^{-2}$

$HCl \rightleftharpoons H^+ + Cl^-$

$\therefore$ The ionic product is greater than the solubility product of II group metal sulphides and less than that of the IV group metal sulphides. Hence only II group metal sulphides are precipitated in the presence of HCl.

b) In the presence of NH_4OH, $\overline{O}H$ ions remove H^+ ions.So, ionisation of H_2S increases. Now ionic product, exceeds the solubility product of IV group metal sulphides also.

$H_2S \rightleftharpoons 2H^+ + S^{-2}$

$NH_4OH \rightleftharpoons NH_4^+ + \overline{O}H$

$H^+ + \overline{O}H \rightleftharpoons H_2O$

So, IV group metal sulphides are also precipitated in the presence of Ammonium hydroxide.

Precipitation of III group metals as hydroxides :

Solubility product of III group metal hydroxides is less than that of IV, V and VI group metal hydroxides.

In the presence of Ammonium chloride, ionisation of NH_4OH decreases due to common ion effect. Here the common ion is NH_4^+.

$NH_4OH \rightleftharpoons NH_4^+ + \overline{O}H$

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$
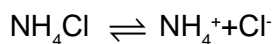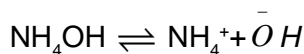
$\therefore$ Ionic product is greater than the solubility product of III group metal hydroxides and less than that of the IV, V and VI group metal hydroxides. Hence only 111 group metal hydroxides are precipitated.

4.5.4 Classification and reactions of anions :

Anions are generally classified in the following way.

1. Anions which evolve gases with dil. HC1.

2. Anions which evolve gases with cone. H_2SO_4.

3. Anions which can be identified by other reactions like precipitation.
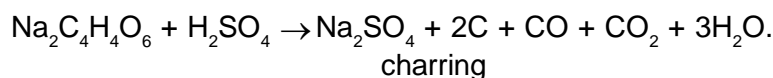
a) Anions which evolve gases with dilute HC1 :

This group is also known as carbonate group. This group includes carbonate. sulphide, sulphite, nitrite and Acetate. When these ions are treated with dilute HCl the following gases are evolved.

Anion	Gas evolved

Before heating :

1.Carbonate $(CO_3^{-2.})$

A colour less gas (CO_2) is evolved with quick effervescence

$$Na_2CO_{;3}+2HC1 \rightarrow 2NaCl + H_2O + CO_2 \uparrow$$

After heating :

2.Sulphide (S^{-2})

A colourless gas (H_2S) is evolved with rotten egg smell.

$$FeS+2HC1 \rightarrow FeCl_2+H_2S \uparrow$$

3.Sulphite (SO_3^{-2})

A colourless gas $\{SO_{2\}}$ is evolved with pungent smell.

$$Na_2SO_3+2HCl \rightarrow 2NaCl+H_2O+ SO_2 \uparrow$$

4. Nitrite (NO^-_2)

Reddish brown gas (NO_2) is evolved.

$$NaNO_2+HC1 \rightarrow NaCl+HNO_2$$
$$3HNO_2.+O_2 \rightarrow HNO_3+H_2O+2NO_2 \uparrow$$

5. Acetate (CH_3COO^-)

Acetic acid vapours with smell of vinegar are evolved.

$$Pb(CH_3COO)_2 + 2HCl \rightarrow PbCl_2 + 2CH_3COOH$$

b) Anions which evolve gases with concentrated H_2SO_4 :

This group includes Chloride, Bromide, Iodide, Nitrate, Borate and organic acids (Acetate, Oxalate. Tartrate). When these ions are treated with Cone. H_2SO_4 the following gases are evolved.

Anion	Gas evolved

Before heating :

1. Chloride (Cl^-)

A colourless gas (HC1) is evolved with pungent smell.

$$NaCl+H_2SO_4 \rightarrow NaHSO_4+HCl \uparrow$$

2.Bromide (Br^-)

Reddish brown vapours of Bromine (Br_2) are evolved.

$$2KBr + 3H_2SO_4 \rightarrow 2KHSO_4 + 2H_2O + SO_2 + Br_2 \uparrow$$

3.Iodide I⁻   Violet vapours of iodine (I_2)
                                              are evolved

$$8KI + 9H_2SO_4 \rightarrow 8KHSO_4 + 4H_2O + H_2S + 4I_2 \uparrow$$

After heating :

4. Nitrate (NO_3^-)   Reddish brown vapours of

                                              Nitrogen dioxide (NO_2) are evolved

$$4KNO_3 + 4H_2SO_4 \rightarrow 4KHSO_4, + 2H_2O + 4NO_2 \uparrow + O_2$$

5. Borate (BO_3^{-3})   White fumes of Boric acid

                                              (H_3BO_3) are evolved

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3 \uparrow + Na_2SO_4$$
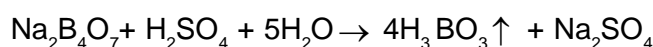
6. Oxalate ($C_2O_4^{-2}$)   Colourless gases of CO and CO_2 are evolved.
                                              CO burns with blue flame.

$$CaC_2O_4 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO + CO_2 \uparrow$$

7. Tartrate ($C_4H_4O_6^{-2}$)   The substance is charred with burning sugar
                                              smell CO and CO_2 gases are evolved.

$$Na_2C_4H_4O_6 + H_2SO_4 \rightarrow Na_2SO_4 + 2C + CO + CO_2 + 3H_2O.$$
                              charring

c). Anions which can be identified by precipitation reactions:

In regular course of analysis, precipitation tests are carried out by preparing sodium carbonate extract.

Preparation of Sodium Carbonate extract :

The substance is mixed three times with pure Sodium Carbonate. It is boiled for 5 minutes after adding distilled water and filtered. The filtrate is called Sodium Carbonate extract. It contains Anion as soluble Sodium salt.

Identification with Nitric Acid and Silver Nitrate solution :

The Sodium Carbonate extract is acidified with dil. $HNO_{(}$ and Silver nitrate solution is added in excess. It is filtered.

Residue	**Filtrate**
i) White precipitate insoluble in dil. HNO_3 and soluble in NH_3 is formed - chloride	i) Dilute ammonia is added drop by drop. Crimson red precipitate, is formed - Chromate
$NaCl + AgNO_3 \rightarrow AgCl \downarrow + NaNO_3$	$Na_2CrO_4 + 2AgNO_3 \rightarrow Ag_2CrO_4 + 2NaNO_3$
ii) Whitish yellow precipitate. insoluble in dil. HNO_3 and soluble in NH_3 is formed -Bromide	ii) Yellow precipitate is formed - phosphate $Na_3PO4 + 2AgNO_3 \rightarrow Ag_3PO_4 \downarrow + 2NaNO_3$
$NaBr + AgNO \rightarrow AgBr \downarrow + NaNO_3$	
iii) Yellow precipitate, insoluble in dil. HNO_3 and insoluble in $NH._5$ is formed - Iodide.	iii) Chacolate brown precipitate is formed - Arsenate $Na_3AsO_4 + 3AgNO_3$ $\rightarrow Ag_3AsO_4 \downarrow + 3NaNO_3$

Identification with HNO_3 and Ammonical $AgNO_3$ solution : (silver mirror test)

The extract is acidified with dilute Nitric acid and neutralized with dilute NH_3 In another test tube Ammonia is added drop by drop to silver nitrate solution till a precipitate formed is almost dissolved. This solution is added to the neutralized solution and warmed.

Silver mirror is formed - Tartrate.

Identification with dilute HC1 and $BaCl_2$ solution :

The extract is acidified with dilute HCl and $BaCl_2$ solution is added.   It is filtered.

| **Residue**	**Filtrate**
i) A white precipitate insoluble in excess HCl is formed - Sulphate $Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 \downarrow + 2NaCl.$	i) It is cooled and neutralized with NH_3 Yellow precipitate insoluble in acetic acid is formed - chromate $Na_2CrO_4 + BaCl_2 \rightarrow BaCrO_4 + 2NaCl$

d) Identification with Acetic acid and $CaCl_2$ solution:

The extract is acidified with acetic acid and $CaCl_2$ solution is added. A white precipitate is formed - Sulphate or oxalate.

Test for oxalate : The precipitate is heated with dil. H_2SO_4 and few drops of dil. $KMnO_4$ solution are added.
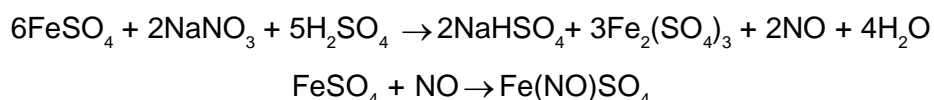
Permanganate colour is decolourised - oxalate.

$$CaC_2O_4 + H_2SO_4 + (O) \rightarrow CaSO_4 + H_2O + 2CO_2$$
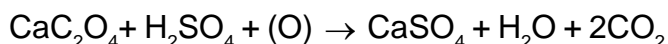
Identification with Acetic acid and $FeCl_3$ solution :

The extract is acidified with Acetic acid and $FeCl_3$ solution is added. A whitish yellow precipitate is formed - phosphate.

$$Na_3PO_4 + FeCl_3 \rightarrow FePO_4\downarrow + 3NaCl.$$
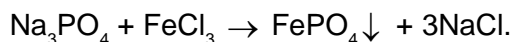
Identification with H_2SO_4 and $FeSO_4$ solution : (Brown ring test) :

The extract is acidified with dil. H_2SO_4 and freshly prepared Ferrous sulphate solution is added. Then Conc. H_2SO_4 is added slowly by the sides of the test tube. A brown ring (Ferrous Nitrnso sulphate $[Fe(NO)SO_4]$ is formed at the junction of the two layers - Nitrate.

$$6FeSO_4 + 2NaNO_3 + 5H_2SO_4 \rightarrow 2NaHSO_4 + 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$FeSO_4 + NO \rightarrow Fe(NO)SO_4$$

4.5.4.1 Interfering anions - their Elimination :

Elimination of oxalates and tartrates :

These are eliminated by ignition of the mixture in a china dish for about twenty to thirty minutes.The residue is cooled and digested with dil. HCl and centrifuged. The centrifugate is taken as original solution and tested for cations using group analysis.

Elimination of Chromates :

The given mixture is taken in a china dish and boiled with conc. HCl until the solution is perfectly green. The solution is diluted with water and taken as original solution for group analysis.

If chromate is present as anion, chromium cation is identified in the third group as blue precipitate of $Cr(OH)_3$ in addition to the normal two cations present in the mixture.

Elimination of Phosphates :

If phosphate is present in the mixture, cation iron is to be tested in the solution from the second group. The remaining part of the solution is treated with excess of NH_4Cl and NH_4OH is added drop wise till the smell of ammonia is observed. Then it is neutralised with 6N acetic acid and then neutral ferric chloride solution is added drop wise till reddish brown precipitate is formed. It is centrifused. The residue is tested for III group cations and the centrifugate is tested for further groups cations.
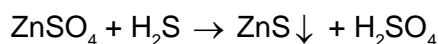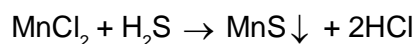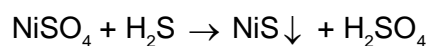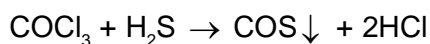
Alternative method :

The cetrifugate from group II is taken in a test tube and boiled to expel H2S gas. 1-2 drop of Conc. HNO_3 is added, boiled gently for 2 minutes. To this, few ml of distilled water, 2 drops of NH_4Cl solution and 2-3 drops of Zirconium. nitrate reagent are added, warmed on a water bath for 2 minutes and centrifuged. Tested for completeness of the precipitate by adding a drop of zirconium nitrate reagent to the centrifugate. (If precipitate forms, centrifuge again and repeat the process until the addition of one drop of the reagent to the centrifugate gives no precipitate). If is heated on a boiling water both and centrifuged.

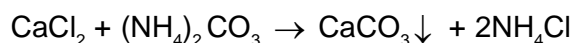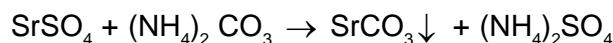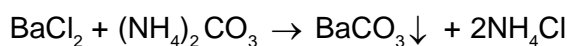## 4.5.5. Separation and reactions of cations in to groups :

Preparation of original solution : Original solution is prepared by dissolving the salt in water or dilute hydrochloric acid either in cold or in hot.

Group NO	Group reagent	Identification of group	Identification of cation
I.	Original solution + dil HCl	Precipitate is formed	White - Silver - Ag+, I group present Mercurous Hg+ or Lead Pb^{+2}

$$AgNO3 + HCl \rightarrow AgCl \downarrow + HNO_3$$

$$Pb (NO_3)_2 + 2 HCl \rightarrow PbCl_2 \downarrow + 2HNO_3$$

II.	Original Solution + dil. HCl + H$_2$S gas.	Precipitate is formed- II group present.	Black - Mercuric mercury, Hg^{+3} Lead Pb^{+2} or Copper Cu^{+2}.

$$CuSO_4 + H_2S \rightarrow CuS \downarrow + H_2SO_4$$
Yellow - Cadmium Cd $^{+2}$ or
$$CdCl_2 + H_2S \rightarrow CdS \downarrow + H_2SO_4$$
Arsenic.

$$2 BiCl_3 + 3H_2S \rightarrow Bi_2S_3 \downarrow + 6HCl$$
Brown - Bismuth Bi $^{+3}$

$$PbCl_2 + H_2S \rightarrow PbS \downarrow + 2HCl$$
Orange - Antimony Sb^{+3} red.

$$2SbCl_3 + 3H_2S \rightarrow Sb_2S_3 \downarrow + 6HCl$$

III.	Original Solution +NH$_4$Cl + NH$_4$OH in excess.	Precipitate is formed III group present.	White - Aluminium Al^{+3} Green - Chromium Cr^{+3} Light green - ferrous Fe^{+2} Brown - Feric Fe^{+3}

$$AlCl_3 + 3NH_4OH \rightarrow Al (OH)_3 \downarrow + 3 NH_4Cl$$

$$FeSO_4 + 2NH_4OH \rightarrow Fe (OH)_2 \downarrow + (NH_4)_2SO_4$$

$$FeCl_3 + 3NH_4OH \rightarrow Fe (OH)_3 \downarrow + 3 NH_4Cl$$

$$CrCl_3 + 3NH_4OH \rightarrow Cr(OH)_3 \downarrow + 3 NH_4Cl$$

IV. Orginal solution   Precipitate is formed   Black - Cobalt CO^{+2}

+ NH_4Cl + NH_4OH + H_2S IV group present   or Nickel Ni^{+2} gas

Flesh - Manganese Mn^{+2}

White   - Zinc Zn^{+2}

$$COCl_3 + H_2S \rightarrow COS\downarrow + 2HCl$$

$$NiSO_4 + H_2S \rightarrow NiS\downarrow + H_2SO_4$$

$$MnCl_2 + H_2S \rightarrow MnS\downarrow + 2HCl$$

$$ZnSO_4 + H_2S \rightarrow ZnS\downarrow + H_2SO_4$$

V. Original solution   Precipitate is formed   White - Barium, Ba^{+2},

+ NH_4Cl + NH_4OH V group present   Strontium, Sr^{+2} or Calcium
+ $(NH_4)_2CO_3$ Ca^{+2}

$$BaCl_2 + (NH_4)_2CO_3 \rightarrow BaCO_3\downarrow + 2NH_4Cl$$

$$SrSO_4 + (NH_4)_2CO_3 \rightarrow SrCO_3\downarrow + (NH_4)_2SO_4$$

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3\downarrow + 2NH_4Cl$$

VI. No Special reagent   VI group   Ammonium NH_4^+

Magnesium, Mg^{+2}

Potasssium, K^+

Sodium Na^+

4.5.5.1. Identification of Ammonium (NH_4^+) :

a)   The salt is heated with NaOH. A colourless gas Ammonia (NH_3) with smell of Ammonia is evolved - Ammonium NH_4^+.

$$NH_4C1 + NaOH \rightarrow NaCl + H_2O + NH_3\uparrow$$
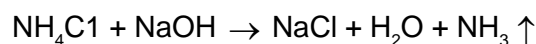
b)   The salt is warmed with NaOH and Nessler's reagent. A brown preciptate is formed Ammonium NH_4^+

$$NH_4C1 + 4NaOH + 2K_2HgI_4 \rightarrow O\begin{matrix} Hg \\ \diagup \quad \diagdown \\ \quad \quad NH_2I \\ \diagdown \quad \diagup \\ Hg \end{matrix}\downarrow + 3NaI + NaCl + 4KI + 3H_2O$$
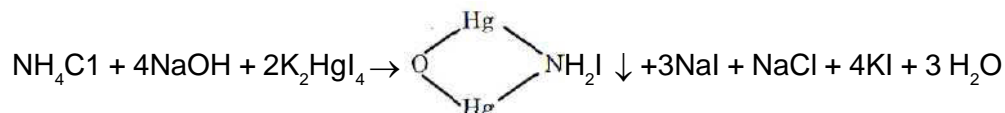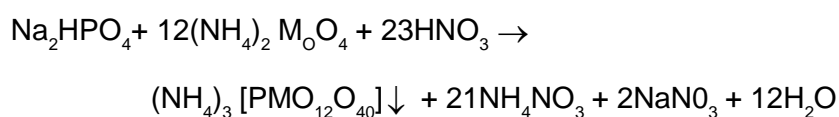
4.5.6. Some Special tests :

1. Chromyl chloride test :

The chloride salt is heated with potassium dichromate salt and Conc. sulphuric acid. Red vapours of chromyl chloride (CrO_2Cl_2) are evolved. An yellow precipitate of Lead chromate is formed when the vapours are passed into Lead acetate solution.
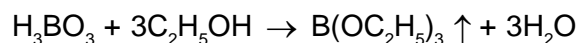
$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 4NaH\,SO_4 + 2KHSO_4 + 2CrO_2\,Cl_2 \uparrow + 3H_2O$$
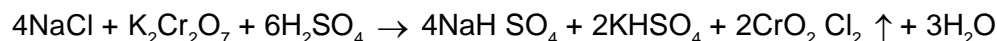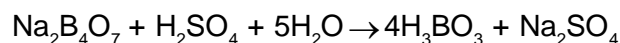
2. Ammonium Molybdate Test :

The phosphate salt is heated with cone. Nitric acid and excess of Ammonium Molybdate. A canary yellow precipitate of Ammonium phosphomolybdate is formed.

$$Na_2HPO_4 + 12(NH_4)_2\,M_OO_4 + 23HNO_3 \rightarrow$$

$$(NH_4)_3\,[PMO_{12}O_{40}] \downarrow + 21NH_4NO_3 + 2NaN0_3 + 12H_2O$$

3.Ethyl Borate test :

The Borate salt is heated with few drops of Ethyl alcohol and Conc. Sulphuric acid. Ethyl borate vapours are evolved. They burnt with green flame.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3 + Na_2SO_4$$

$$H_3BO_3 + 3C_2H_5OH \rightarrow B(OC_2H_5)_3 \uparrow + 3H_2O$$
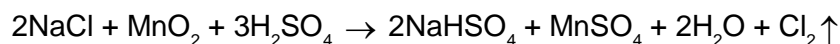
4. Copper turnings tests :

The Nitrate salt is heated with copper turnings and Conc. sulphuric acid. Reddish brown vapours of Nitrogen dioxide (NO_2) are evolved.

$$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_3$$

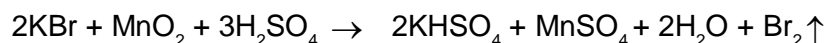$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 \uparrow + 2H_2O$$
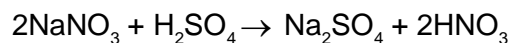
5. Manganese dioxide test :

The salt is treated with Manganese dioxide and Conc. sulphuric acid.

a) Greenish yellow chlorine (Cl_2) gas is evolved.

$$2NaCl + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2 \uparrow$$

b) Reddish brown vapours of Bromine (Br_2) are evolved.

$$2KBr + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2 \uparrow$$

c) Violet vapours of Iodine (I_2) are evolved.

$$2KI + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2\uparrow$$

6. Golden yellow spangles test :

Potassium iodide solution is added to the Lead salt solution. An yellow precipitate of Lead Iodide is formed.   It is dissolved in hot water and cooled. Golden yellow spangles are formed.

$$Pb(NO_3)_2 + 2KI \rightarrow PbI_2\downarrow + 2KNO_3$$

c) Violet vapours of iodine (I_2) are evolved.

$$2KI + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2\uparrow$$
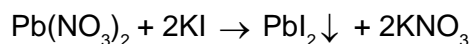
7, Distinction between Ferrous an Ferric salts :

| S.NO	Reagent	Ferrous salt (Fe^{+2})	Ferric Salt (Fe^{+3})
1.	Potassium Ferrocyanide solution	Light blue precipitate	Prussian blue precipitate
2.	Potassium Ferricyanide solution	Deep blue precipitate	No precipitate
3.	Ammonium Thiocyanate solution	No colour	Blood red colour
4.	Ammonia solution	Light green precipitate	Brown Precipitate

8. Ash test :

A filter paper is dipped in the salt solution and burnt to ash after adding a drop of cobalt nitrate solution.

a) Aluminum salts gave Thenald's blue ash

$$CoO + Al_2O_3 \rightarrow Co(Al_2O_2)_2$$
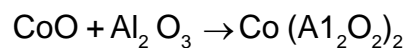
b) Zinc salts gave Rinmann's green ash.

$$CoO + ZnO \rightarrow CoZnO_2$$
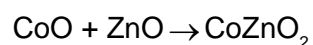
9. Flame test :

The salt is made into paste with cone. Hydrochloric acid on a watch glass. It is introduced into non-luminous flame by a platinum wire. The colour of the flame is observed.

Bluish green	Copper
Bright green	Boron
Apple green	Barium
Flashes of green	Zinc
Crimson red	Strontium
Brick red	Calcium
Lilacviolet	Potassium.

The paste is made with Conc. HCl because chlorides are volatile salts.

4.5.6. Model Questions :

1. What are the principles involved in semimicro qualitative Analysis ?

2. Discuss the precipitation of II nd group and IV group metal sulphides in qualitative analysis.

3. Explain the chemistry involved in the test of the following.

   a) Sulphate   b)   Nickel

   c) Phosphate   d)   Ammonium

4. What is solubility product ? What are its applications in the qualitative analysis ?

5. Explain

   a) Chromyl Chloride test   b) brown ring test

   c) golden spangles test   d) flame test

6. What is sodium carbonate extract ? How does it help in identifying the anions ? Why potassium carbonate cannot be used in place of sodium carbonate?

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CONTENTS

PREPARATIONS :