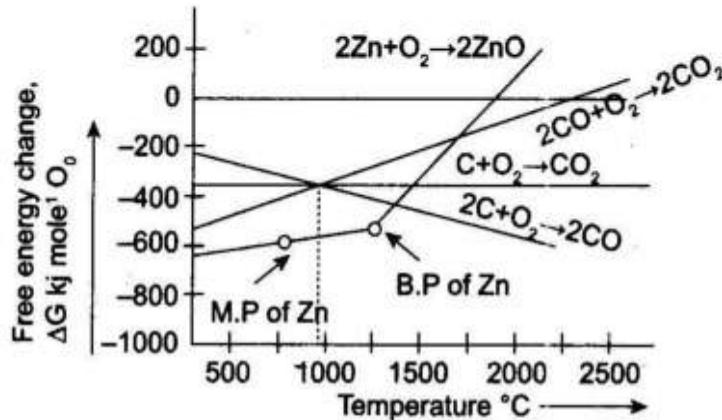


- (iv) A metal can reduce the oxide of metal placed above in the diagram, due to more negative free energy, e.g., Al can reduce Cr but not Mg or Ca.  
 (v) Reducing behaviour of carbon : There may be three types of reactions:



For reaction (i), the volume of  $\text{CO}_2$  formed is almost equal to volume of  $\text{O}_2$  consumed. So,  $\Delta S$  does not change significantly and Ellingham plot is almost horizontal.

For reaction (ii), plot is downward and unlike other reactions in this reaction  $\Delta G^\circ$  value becomes more negative as temperature is increased. It is due to positive value of  $\Delta S$  because here two volumes of CO are produced for one volume of  $\text{O}_2$  consumed, thus  $\Delta S$  is positive.

For reactions (iii), again  $\Delta S$  is negative because 3 moles of gases react to form two moles gas and so  $\Delta G^\circ$  becomes more positive with rise in temperature.

The plots for three reactions cross at  $710^\circ\text{C}$  and it shows that formation of  $\text{CO}_2$  from CO is more favoured below  $710^\circ\text{C}$  while at higher temperatures CO is formed preferably. Formation of  $\text{CO}_2$  from carbon is not much affected by temperature.

Due to downward slope theoretically C will reduce any metal oxide provided that temperature is sufficiently high. However, it is not attempted due to possibility of formation of carbide at high temperatures and maintenance of such high temperature is not economically profitable. Below  $710^\circ\text{C}$ , CO is a better reducing agent than carbon because of more negative value of  $\Delta G^\circ$  of the reaction,  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  upto this temperature.

## 18.5 REFINING OR PURIFICATION OF METAL

The metals extracted by any of the above operations are in their crude form. The crude form is usually contaminated with impurities of following nature.

- Impurities of other metals obtained by the simultaneous reduction of their respective oxides present in the ore as impurities.
- Impurities of non-metals like silicon or phosphorous formed by reduction in the furnace.
- Impurities of unreduced oxides and sulphides of the metals.
- Impurities of residual slag, flux, etc. introduced during treatment in the furnace.

To remove these impurities, the crude metal is subjected to the process of purification or refining. Refining of the crude metals may be done by the following methods depending upon the nature of the metal and impurities.

### **18.5.1 Electrolytic Refining**

In this method, the impure metal is converted into a block which forms the anode while cathode is a rod or plate of same pure metal. These electrodes are suspended in an electrolyte which is the solution of a soluble salt of the metal usually a double salt of the metal. When electric current is passed, metal ions from the electrolyte are deposited at the cathode in the form of pure metal while an equivalent amount of metal dissolves from the anode and goes into the electrolyte solution as metal ion. The soluble impurities present in the crude metal anode go into the solution while the insoluble impurities settle down below the anode as anode mud or anode sludge.

### **18.5.2 Liquation Process**

The refining process for crude metal based on the difference in fusibility of metal and impurities is named as liquation process. Zn-Pb mixture is separated by heating the crude Zn just above the melting point of Zn, whereas Pb remains as non fusible mass. The molten mass is allowed to flow on an inclined plane, whereas non-fusible mass is left behind.

### **18.5.3 Distillation Method**

Volatile metals (Hg, Zn and Cd) are easily purified by distillation. The impure metal is heated in a retort and vapours of volatile metals are collected and condensed in a receivers leaving behind non-volatile impurities in a retort.

### **18.5.4 Heating of Crude form with Ores**

Fe and Sb ores are heated with crude form which removes the contaminated reducing agents (S and C) with it and pure metal is obtained.

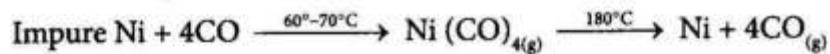
### **18.5.5 Oxidation Process**

Impurities in crude form having more affinity for  $O_2$  than the metal itself are oxidized in suitable furnaces. The oxides formed at the surface are skimmed off. The various oxidation processes used for different metals involve poling, puddling, bessemerization and cupellation.

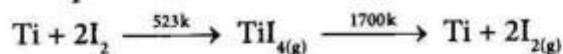
- (a) **Poling:** The molten impure metal (Cu) containing oxides as impurity is stirred with green poles of wood which releases hydrocarbon gases. These hydrocarbon gases reduce oxide to metal.
- (b) **Puddling:** It involves the preparation of nearly pure wrought iron from cast iron that contains a high percentage of carbon. The cast iron is heated with hematite ( $Fe_2O_3$ ), the oxygen of which oxidizes the carbon.
- (c) **Bessemerization:** A process for making steel from cast iron, named after its discoverer H. Bessemer. The impure molten metal is heated in a Bessemer converter (a large, egg-shaped vessel with holes below) and air is blown up to oxidize the impurities. Now the required amount of spiegel is added to introduce correct amount of carbon for the type of steel required.
- (d) **Cupellation:** The separation of silver, gold and other noble metals from impurities that are oxidized by hot air. The impure metal is placed in a cupel, a flat dish made of porous refractory material and a blast of hot air is directed upon it in a special furnace. The impurities are oxidized by air and are partly swept away by the blast and partly absorbed by cupel. This method is also based on different affinities of metal and impurity towards oxygen. Method is known as cupellation because impure

metal is fused in small boat shaped dishes of boneash or cement called cupels. This method is useful for removal of Pb impurity from Ag and Au.

- (e) **Mond's process:** Impure nickel is purified by this process. Ni forms  $\text{Ni}(\text{CO})_4$  on passing steam of CO over impure Ni at  $60^\circ\text{-}70^\circ\text{C}$  which on heating in another tower at  $180^\circ\text{C}$  decomposes.

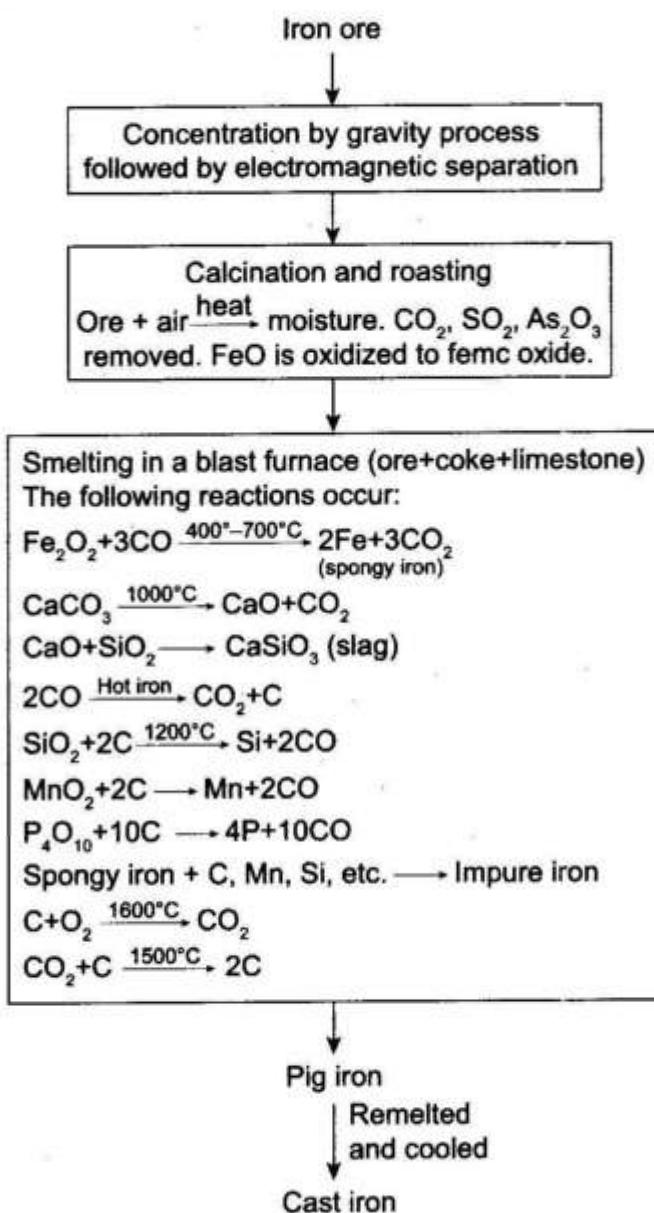


- (f) **Van-Arkel method:** This method is used to obtain ultrapure samples of Ti, Zr, HF, Si, etc. Such metals on heating with  $\text{I}_2$  gives vapours of iodides which decomposes on heating more to give ultrapure metals.



## 18.6 EXTRACTION OF IRON

Both iron and tin are extracted by the carbon reduction method.

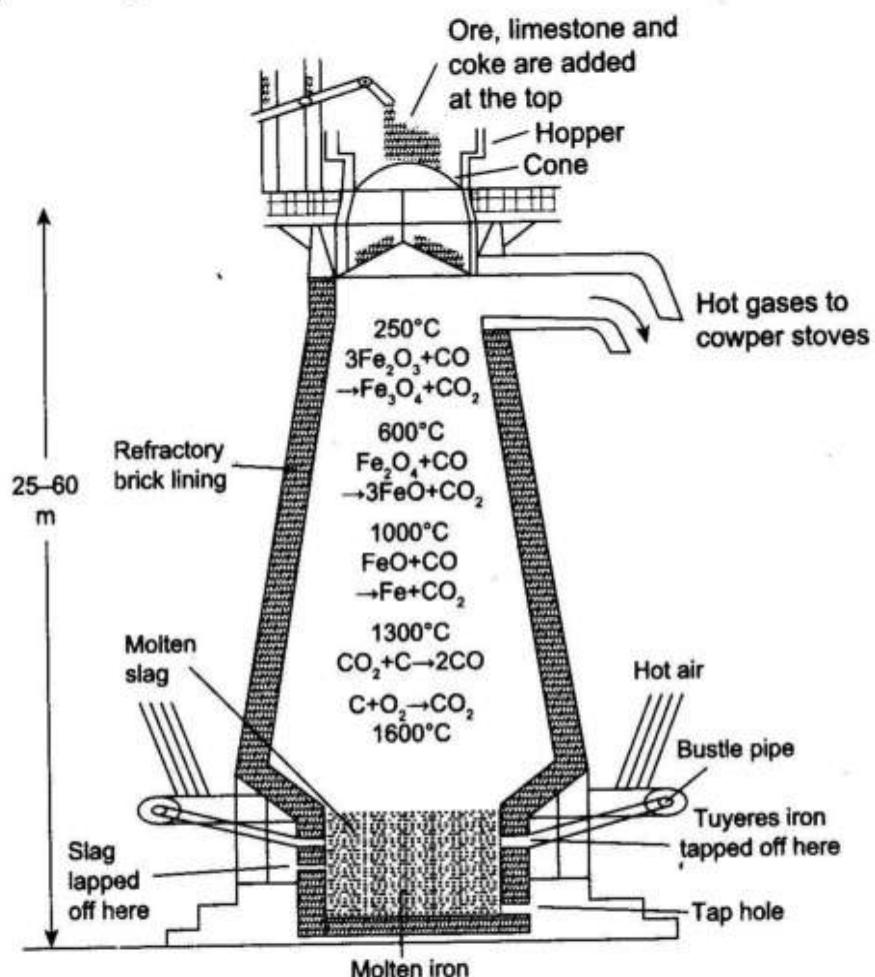


(Fe=93 per cent, C=5 per cent and impurities of Mn, P, Si, etc. = 2 per cent)

### 18.6.1 Extraction of Iron

Iron is extracted from its principal ore hematite.

After the preliminary washing, concentration and roasting, the ore is smelted in the presence of coke and limestone in a blast furnace. Roasted ore (8 parts) with desulphurized coke (4 parts) and limestone pieces (1 part) is fed into the blast furnace from the top. Preheated air is blown in through water-jacketed pipes called tuyers fixed in the lower part of the furnace. There is a temperature gradient as we move from the bottom (temperature about 2000 K) to the top (temperature around 500 K) of the blast furnace. The blast furnace may be broadly divided into three main parts as described hereunder.



- (i) **Zone of fusion:** The lower portion where coke burns and produces  $\text{CO}_2$  and a lot of heat is known as zone of fusion.  
 $\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \quad \Delta H = -406 \text{ kJ/mol}$   
 Here, the temperature is about 1775 K. A little above this, where temperature is about 1475 K–1575 K, iron is obtained in molten form.
- (ii) **Zone of heat absorption:** in the middle portion (temperature 1075K–275 K),  $\text{CO}_2$  rising up is reduced to CO with the absorption of heat:  $\text{CO}_2 + \text{C} \rightarrow 2\text{CO} \quad \Delta H = 163 \text{ kJ/mol}$ .  
 In this portion, limestone coming from above is decomposed and the resultant lime ( $\text{CaO}$ ), which acts as a flux, combines with silica (present as impurity, i.e., gangue) to form calcium silicate (fusible slag).  
 $\text{Ca CO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad \text{CaO} + \text{SiO}_2 \rightarrow \text{Ca SiO}_3 \text{ (slag)}$ .
- (iii) **Zone of reduction:** This is the upper portion (675 K–975 K) where iron oxide is reduced to spongy iron by carbon monoxide rising up the furnace:  $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ .

The reduction is believed to take place in stages:  $3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$ .



At the bottom of the furnace the molten iron sinks down while above this floats the fusible slag which protects the molten iron from oxidation. These two can be removed from different holes. Waste gases escaping at the top consists of about 30 per cent CO, 10 per cent  $\text{CO}_2$  and the rest nitrogen. Iron obtained from the blast furnace is known as pig iron.

### 18.6.2 Types of Iron

Following are the commercial varieties of iron depending on the percentage of carbon content.

- (i) **Cast iron:** It is the most impure form of iron containing the highest percentage of carbon (2.5 to 5 per cent) and about 2 per cent of other impurities like Si, P, Mn and S. Cast iron is of two types as listed hereunder.
  - 1. **White cast iron:** Carbon is present in the form of cementite,  $\text{Fe}_3\text{C}$ .
  - 2. **Grey cast iron:** Carbon is present in the form of graphite.
- Properties of cast iron:**
  - (a) Due to the presence of impurities, cast iron melts at  $1250^\circ\text{C}$ . whereas pure iron melts at  $1530^\circ\text{C}$ .
  - (b) The molten cast iron expands on solidification and thus produces good castings.
  - (c) It does not rust easily. It is neither tempered nor magnetized easily.
  - (d) It is hard and brittle due to high carbon content and cannot be welded.
  - (e) Due to very little ductility, it is not suitable for forging.
  - (f) It is used for casting, railing, hot water pipe, electric poles, etc. where strain is minimum.
- (ii) **Wrought iron:** It is the purest form of iron containing the lowest percentage of carbon from 0.1 to 0.25 per cent and 0.3 per cent as other impurities. It is manufactured from cast iron by puddling process in a special type of reverberatory furnace, the hearth of which is lined with hematite ( $\text{Fe}_2\text{O}_3$ ).
- (iii) **Properties of wrought iron:**
  1. Wrought iron is extremely tough, highly malleable and ductile and has high magnetic permeability.
  2. It softens at about  $1000^\circ\text{C}$  and then it can be forged and welded.
  3. Due to the presence of very small percentage of slag, it has fibrous structure and thus can withstand high stresses.
  4. Wrought iron is resistant towards rusting and corrosion.
- (iv) **Uses of wrought iron:** Wrought iron is used
  1. In the manufacture of articles capable to hold sudden stress, e.g., chains, nails, hooks, bolts, etc.
  2. In the manufacture of electromagnet and agricultural implements.
  3. In making wires and bars.

### 18.6.3 Steel

The most important commercial variety of iron having percentage of carbon in midway between that of cast iron and wrought iron, i.e., 0.25 to 2 per cent. The properties of steel depend upon its carbon contents, since with the increase in carbon content, the hardness of steel increases while its ductility decreases. The presence of Si gives steel a fibrous structure. Presence of Mn produces elasticity and increases tensile strength. Cr imparts resistance to chemical action.

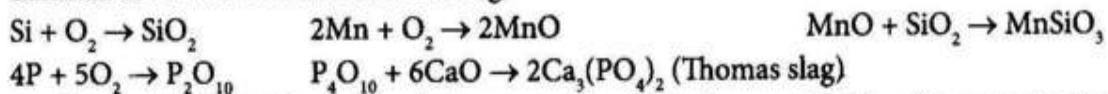
- 1. Alloy steel:** Steel mixed with small amounts of nickel, cobalt, chromium, tungsten, molybdenum, manganese, etc., acquires special properties. Such products are called special steels or alloy steels. Some important alloy steels are given in the table hereunder.

S. No.	Name of Alloy Steel	Metal Added	Properties	Uses
1.	Invar	36 per cent Ni	Coefficient of expansion is very small	Measuring tapes and pendulums
2.	Chrome vanadium steel	1 per cent Cr, 0.15 per cent V	High tensile strength	Springs, shafts, axles, etc.
3.	Manganese steel	12-15 per cent Mn	Hard and tough	Rock crushing machinery safes, helmets, etc.
4.	Stainless steel	11.5 per cent Cr, 2 per cent Ni	Resists corrosion	Common articles
5.	Tungsten steel	14-20 per cent W, 3-8 per cent Cr	Very hard	High speed tools

## 18.7 MANUFACTURE OF STEEL

Manufacture of steel is made by either of the following methods.

- (a) **The Bessemer process:** The process is carried out in Bessemer converter made up of steel plates lined with silica bricks (if impurities in cast iron are of basic nature, i.e., MnO) or lined with CaO or MgO (if impurities in cast iron are of acidic nature, i.e., P<sub>2</sub>O<sub>10</sub> or SO<sub>2</sub> or SiO<sub>2</sub>). The molten cast iron is introduced in the converter and a blast of hot air is blown through it from the bottom, keeping the mouth of the converter vertically upwards. Impurities of MnO or P or S present in cast iron are first oxidized and then combine to form slag.



Finally carbon is oxidized to carbon monoxide which burns with blue flame at the mouth of the converter. Some iron is also oxidized which converts the carbon into carbon monoxide.



When whole of the carbon is oxidised (i.e., the blue flame suddenly dies out), the air supply is stopped for a while and the requisite amount of spiegeleisen (an alloy of Fe, Mn and C) is added. The blast is continued just for a moment to ensure complete mixing. Mn and C serve as deoxidizer and reduce FeO (if any) and the rest amount of Mn and C is mixed with molten steel to give manganese steel. Mn makes steel harder and increases its tensile strength.

- (b) **Open Hearth process or Siemens-Martin process :**

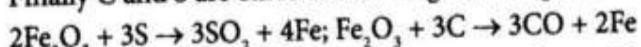
This is the modern process and the furnace used consists of an open hearth lined with silica or calcined dolomite (CaO·MgO) depending upon the nature of impurities present in pig or cast iron. Silica lining is used if the impurities are of manganese, silicon, etc. and calcined dolomite lining is used if phosphorus is present in appreciable amount.

The charge consisting of pig or cast, iron scrap, iron ore (hematite) and lime heated on the hearth of the furnace at about 1500°C by producer gas. The following reactions occur.

**Acidic process:**  $3\text{Si} + 2\text{Fe}_2\text{O}_3 \rightarrow 4\text{Fe} + 3\text{SiO}_2$ ;  $3\text{Mn} + \text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe} + 3\text{MnO}$ ;  $\text{MnO} + \text{SiO}_2 \rightarrow \text{MnSiO}_3$  (slag)

**Basic process:**  $12\text{P} + 10\text{Fe}_2\text{O}_3 \rightarrow 3\text{P}_2\text{O}_{10} + 20\text{Fe}$ ;  $6\text{CaO} + \text{P}_2\text{O}_{10} \rightarrow 2\text{Ca}_3(\text{PO}_4)_2$  (slag)

Finally C and S are oxidized forming volatile gases:  $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$  (slag)



Samples of steel drawn from time to time and tested for carbon content, finally spiegeleisen (an alloy of iron, manganese and carbon) is added to the molten mass to obtain desired steel. The process takes about 8 to 10 hours for completion, i.e., longer time than Bessemer process (20–30 minutes) but it has the following advantages over the Bessemer's process.

- (i) The temperature can be controlled as the heating is done externally.
  - (ii) The composition and quality can be well controlled as it is a slow process.
  - (iii) In this process, scrap iron is reused.
  - (iv) The loss of iron in this process is only 4 per cent while the loss is about 15 per cent in Bessemer's process.
  - (v) This yields better quality of steel.
- (c) **Duplex process:** This is actually a combination of acid Bessemer process and open hearth process. Si, Mn, S and C (partially) are oxidized and removed as slag or volatile oxides.

## 18.8 HEAT TREATMENT OF STEEL

- (a) **Annealing:** It is a process of heating steel to bright redness and then cooling it very slowly to make the steel soft and ductile.
- (b) **Quenching:** It is a process of heating steel to bright redness and then cooling it suddenly by plunging in water or oil to have extremely hard and brittle steel. It has very low elasticity.
- (c) **Tempering:** It is a process of heating the quenched steel to a temperature much below redness and then cooling it slowly. Such a steel is neither hard nor so brittle. During the process of tempering, a thin film of the oxide is formed on the surface of steel. The colour of the oxide film depends on the temperature at which the quenched steel is heated.

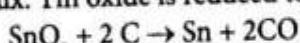
Temperature range (°C)	Colour of the oxide film
200°–230 °C	Yellow
225°–270 °C	Brown
300 °C	Blue

## 18.9 EXTRACTION OF TIN

Metallic tin is extracted from tin stone or cassiterite ( $\text{SnO}_2$ ) which contains about 10 per cent of the metal as  $\text{SnO}_2$ . The rest being siliceous matter and tungstates of Fe, Cu and As.

After crushing, the ore is concentrated by washing in a current of water (gravity process to remove lighter gangue particles) and by magnetic separator to remove tungstates of Fe and Mn.

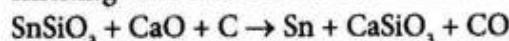
Finally, the ore is smelted in a reverberatory furnace or in a blast furnace at 1475–1575 K. The ore is mixed with one-fifth of its mass of powdered anthracite (coal) and little of lime or fluorspar which is used as flux. Tin oxide is reduced to tin.



### 18.9.1 Refining of Tin

- (i) **Liquation or sweating:** When the block of impure tin is heated on the sloping hearth of reverberatory furnace, tin along with Pb and Bi (all having much lower melting points than other metals) run off leaving a dross of an alloy of Mn, Fe, Cu, W and As.

- (ii) **Poling:** The sweated tin is stirred with logs of green wood where impurities get oxidized and scum formed is skimmed off, from where 99 per cent pure tin is obtained. Scum and dross are repurified. Slag contains 10–25 per cent Sn as  $\text{SnSiO}_3$ , because of amphoteric nature of tin. This is recovered by smelting with carbon and  $\text{CaO}$  flux at a much higher temperature.



- (iii) **Electrolytic refining:**

**Cathode:** Pure tin

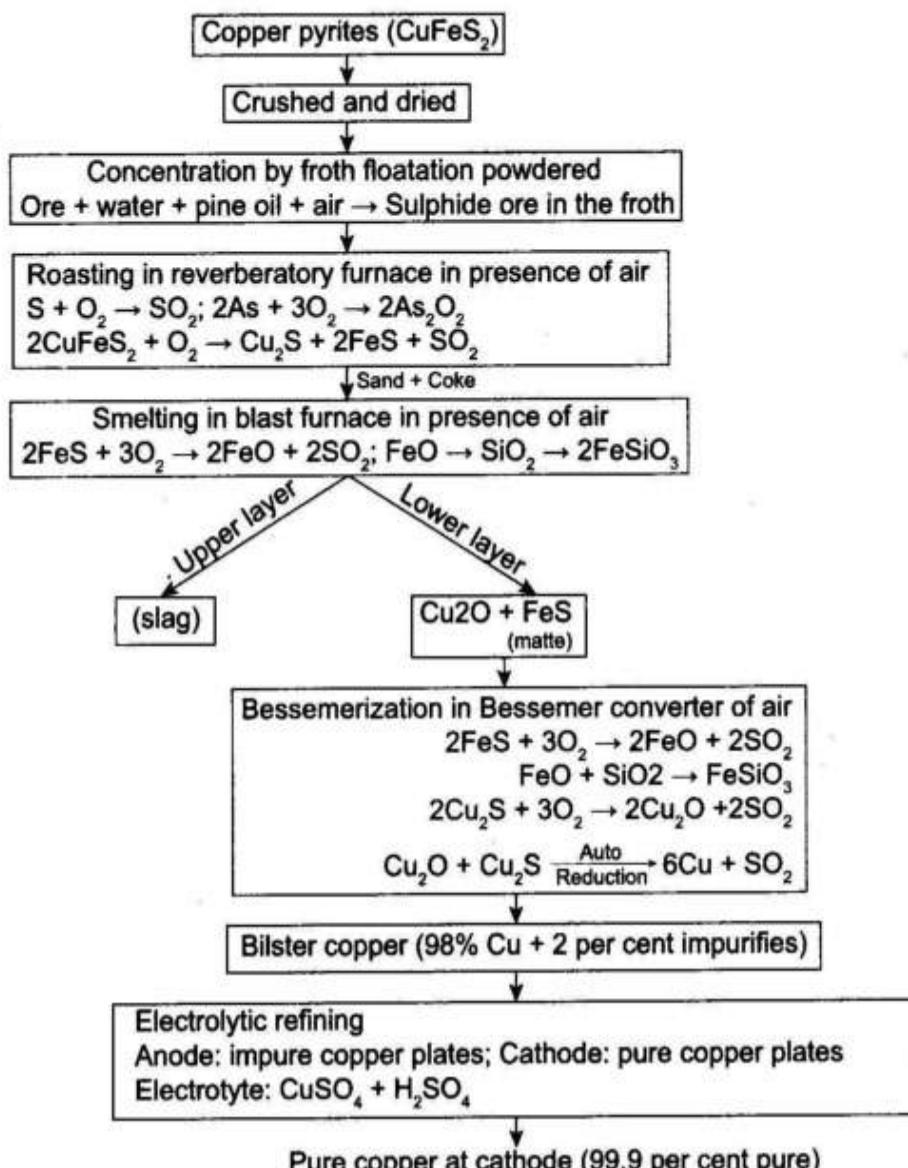
**Anode:** Impure tin

**Electrolyte:**  $\text{SnSO}_{4(\text{aq})}$  with sulphuric acid and hydro fluorosilicic acid.

## 18.10 EXTRACTION OF COPPER

Both Cu and lead may be extracted by self-reduction method. Cu is mainly extracted from copper pyrites.

After the concentration of its ore by froth floatation process, the ore is roasted by current of air to remove arsenic, Sb and much of sulphur. The ore is then mixed with a little of coke and sand and smelted in a water jacketed blast furnace. The minor reactions that occurred during roasting continue here too. Ferrous oxide combines with sand to form a slag. Cuprous oxide formed combines with ferrous sulphide to give, ferrous oxide and cuprous sulphide. This is because iron has more affinity for oxygen than Cu.



Molten mass collected from the bottom of furnace contain large cuprous sulphide and a little ferrous sulphide. This molten mass is known as matte. The molten matte is finally transferred to Bessemer converter. A blast of sand and air is blown in the converter through tuyeres which are situated a little above the bottom and this causes removal of sulphur and arsenic oxides and ferrous oxide as slag. At the same time,  $\text{Cu}_2\text{S}$  is oxidised mostly into  $\text{Cu}_2\text{O}$  and partly into  $\text{CuO}$  and  $\text{CuSO}_4$ . All of these react with  $\text{Cu}_2\text{S}$  giving Cu. Finally, copper may be refined electrolytically, using an electrolyte (copper sulphate).

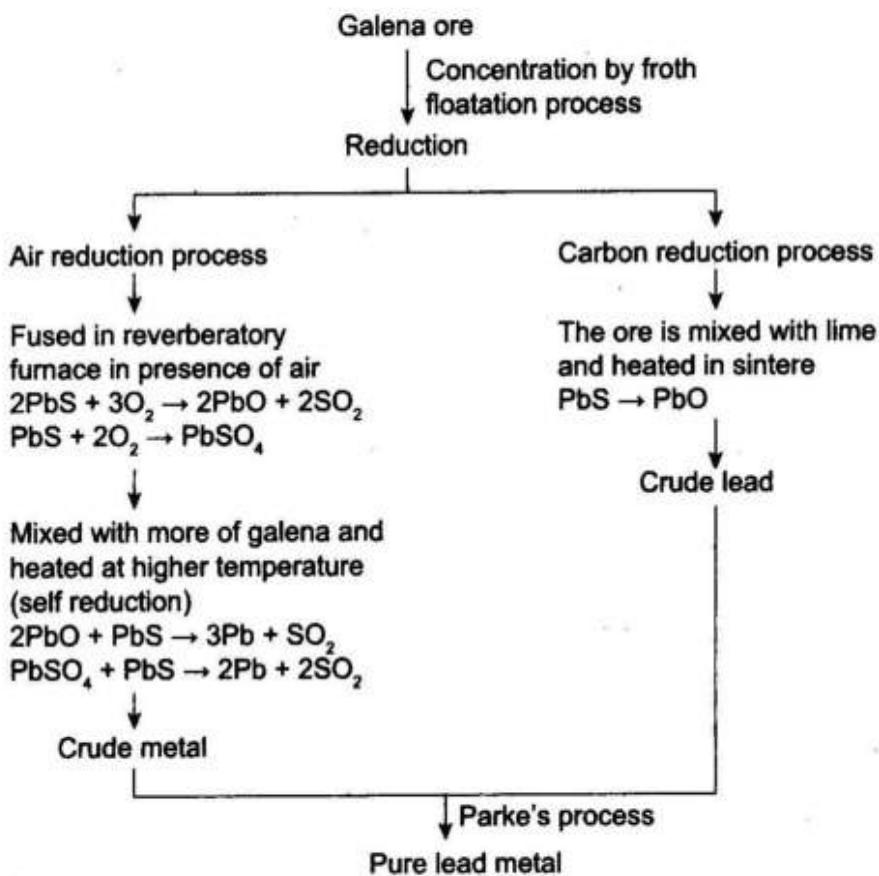
**At anode**  $\rightarrow$  Impure Cu

**At Cathode**  $\rightarrow$  Pure Cu

## 18.11 EXTRACTION OF LEAD

Pb is mainly extracted from galena. After the concentration of the ore by the froth floatation process, the ore is roasted in a reverberatory furnace.

**Flow sheet for the extraction of lead**



Hof conc.  $\text{H}_2\text{SO}_4$  dissolves lead with evolution of  $\text{SO}_2$  but the reaction becomes lower due to formation of insoluble  $\text{PbSO}_4$ .

The obtained lead contains impurities such as Cu, Ag, Bi, Sb and Sn. Ag is removed by **Parke's process**, where molten Zn is added to molten impure lead. The former is immiscible with the later. Ag is more soluble in molten Zn than in molten lead. Zn-Ag alloy solidifies earlier than molten lead and thus can be separated. After this, crude lead is refined electrolytically.

**Electrolyte** → Lead silica fluoride ( $PbSiF_6$ ) and hydro fluoro silicic acid ( $H_2SiF_6$ ) with a little gelatin

**At anode** → Crude lead

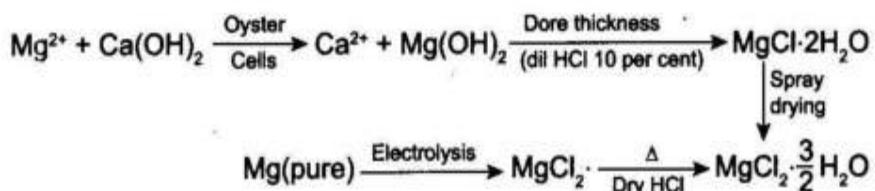
**At cathode** → Pure lead

## 18.12 EXTRACTION OF MAGNESIUM

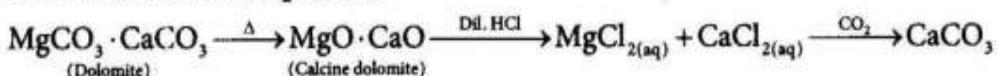
It is commonly obtained by the electrolysis of fused magnesium chloride containing a little (25 per cent) NaCl and NaF at  $700^{\circ}C$  in an air-tight from pot which itself serves as the cathode. The anode being a graphite rod which dips into the electrolyte. The anode is surrounded by a perforated porcelain tube for the exit of chlorine. The electrolysis is carried in the atmosphere of a cool gas so as to prevent the attack of atmospheric oxygen and nitrogen on Mg. Molten Mg, being lighter than the electrolyte, floats over the fused electrolyte and is withdrawn.

In Dow's process, Mg is recovered from sea water as magnesium chloride which is then electrolyzed using a cell as described hereunder:

- (i) **DOW's sea-water process:** Sea water contains about 0.13 per cent  $Mg^{2+}$  ions and the extraction of Mg depends on the fact that  $Mg(OH)_2$  is very much less soluble than  $Ca(OH)_2$  [slaked lime].  $Ca(OH)_2$  is added to sea water and calcium ions dissolve and  $Mg(OH)_2$  is precipitated. This is filtered off, treated with HCl to produce  $MgCl_2$  and electrolyzed.



- (ii) **DOW's natural brine process:**



- (iii) **Electrolysis:** Anhydrous carnallite ( $KCl \cdot MgCl_2 \cdot 6H_2O$ ) may also be employed as the starting material of  $MgCl_2$ . The cathode may be a layer of molten lead on the floor of the cell and anode may be the graphite rod which are suspended above the molten lead. Mg liberated at the cathode dissolves in the molten lead. The alloy of Pb-Mg is subjected to electrolysis to obtain pure Mg.

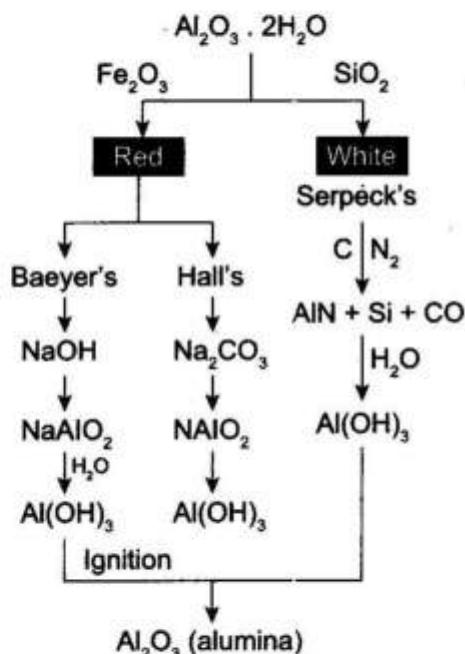
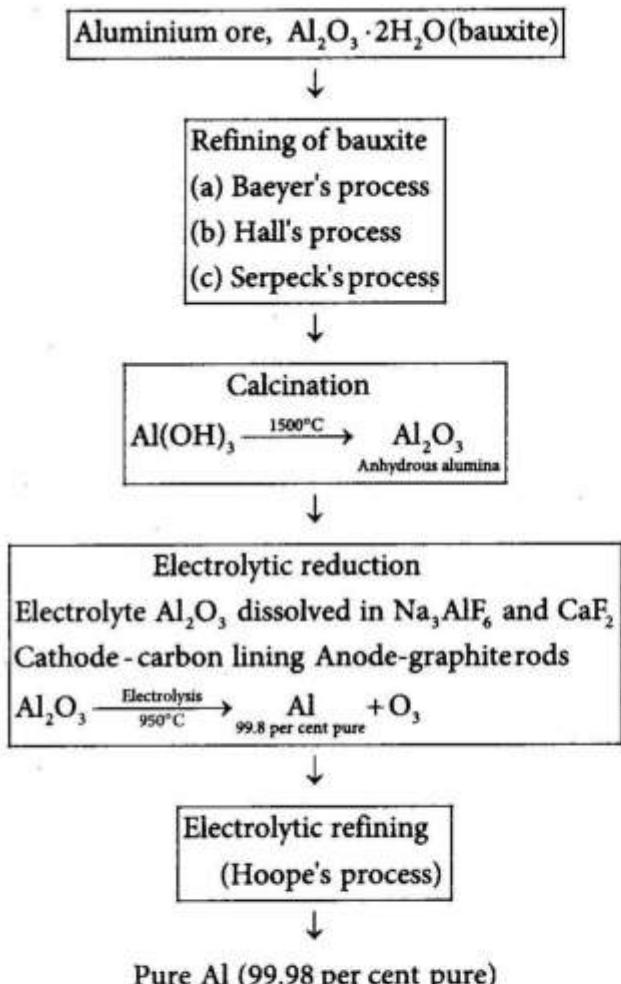
**Electrolyte used** → Fused carnallite

**Anode** → Pb-Mg alloy

**Cathode** → Steel rods

## 18.13 EXTRACTION OF ALUMINIUM

Al is isolated from the electrolysis of bauxite ( $Al_2O_3 \cdot 2H_2O$ ). Since it is difficult to purify Al, bauxite ore is purified either by Baeyer's process or Hall's process or Serpeck's process. Depending upon the impurity present in the ore, if the bauxite contains iron oxide as the impurity one can use Baeyer's or Hall's process as described hereunder:



**Electrolytic reduction of  $\text{Al}_2\text{O}_3$ :** After obtaining pure  $\text{Al}_2\text{O}_3$ , it is dissolved in fused cryolite ( $\text{Na}_3\text{AlF}_6$ ) with a little fluorspar ( $\text{CaF}_2$ ) and is electrolyzed in an iron tank lined with blocks of carbon which serve as the cathode. The anode consist of a number of graphite rods suspended vertically inside the tank. Aluminium gets settled at the bottom of the tank and can be removed.

## **18.14 EXTRACTION OF SILVER AND GOLD**

Silver and gold are extracted by the cyanide process (MacArthur forest process).

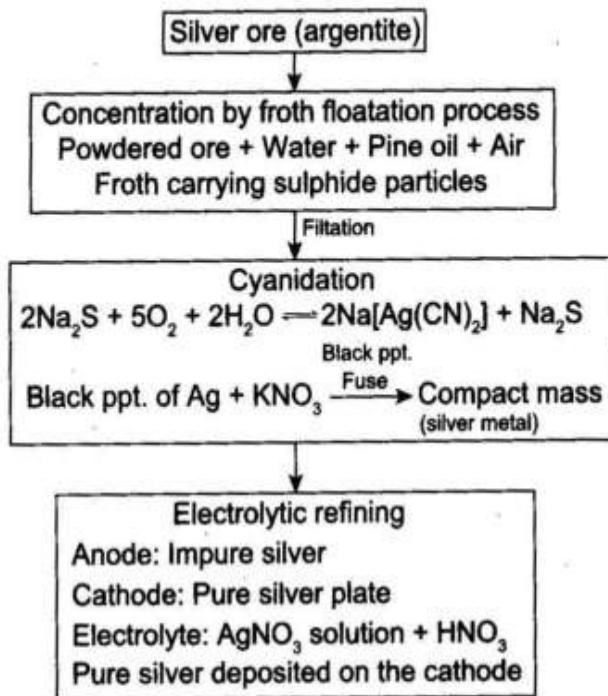
### 18.14.1 Mac Arthur Forest Process

After the preliminary crushing and concentration by froth floatation process the ore (crushed auriferous rocks in the case of gold) is leached with dilute (0.4 – 7 per cent) solution of NaCN (made alkaline by adding lime and kept agitated by a current of air). Ag (or Au) pass into the solution as argento-cyanide (or aurocyanide).

Air is blown into remove  $\text{Na}_2\text{S}$  as  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_4$  causes the above reaction to proceed to completion. The solution obtained is filtered and treated with scrap iron or zinc where Ag (or Au) gets precipitated. The obtained Ag is purified electrolytically (electrolyte is silver nitrate solution containing 1 per cent  $\text{HNO}_3$ ).

**At anode:** Impure Ag      **At cathode:** Pure Ag

## Flow sheet for the extraction of silver



## Methods of extraction of metals: A brief review

Electrode process	Standard Electrode Potential/V	Main Occurrence	Main Method of Extraction	Equation for Extraction
Na, $\text{Na}^+$	-2.7	Rock salt NaCl, Chile saltpeter, $\text{NaNO}_3$	Electrolysis of fused NaCl with $\text{CaCl}_2$ added	↑
Mg, $\text{Mg}^{2+}$	-2.37	Carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , Magnesite, $\text{MgCO}_3$	Electrolysis of fused $\text{MgCl}_2$ with KCl added	Most of these involve electrolytic reduction $\text{M}^{n+} + n\text{e}^- \rightarrow \text{M}$
Al, $\text{Al}^{3+}$	-1.66	Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ Silicate rocks	Electrolysis of $\text{Al}_2\text{O}_3$ in molten $\text{Na}_3\text{AlF}_6$	↓
Mn, $\text{Mn}^{2+}$	-1.18	Pyrolusite $\text{MnO}_2$ , Hausmannite $\text{Mn}_3\text{O}_4$	Reduction of oxide with Al or C	$3\text{Mn}_3\text{O}_4 + 8\text{Al} \rightarrow 9\text{Mn} + 4\text{Al}_2\text{O}_3$
Zn, $\text{Zn}^{2+}$	-0.76	Zinc blende $\text{ZnS}$ , Calamine $\text{ZnCO}_3$	Reduction of $\text{ZnO}$ with C or electrolysis of $\text{ZnSO}_4$	$\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}$
Fe, $\text{Fe}^{2+}$	-0.44	Magnetite, $\text{Fe}_3\text{O}_4$ , Haematite, $\text{Fe}_2\text{O}_3$	Reduction of oxide with CO	$\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$
Sn, $\text{Sn}^{2+}$	-0.14	Cassiterite, $\text{SnO}_2$	Reduction of $\text{SnO}_3$ with C	$\text{SnO}_2 + 2\text{C} \rightarrow \text{Sn} + 2\text{CO}$
Cu, $\text{Cu}^{2+}$	-0.13	Galena $\text{PbS}$ , C	Reduction of $\text{PbO}$ with C	$\text{PbO} + \text{C} \rightarrow \text{Pb} + \text{CO}$

Electrode process	Standard Electrode Potential/V	Main Occurrence	Main Method of Extraction	Equation for Extraction
Cu, Cu <sup>2+</sup>	+0.34	Copperpyrite, CuFeS <sub>2</sub> Cuprite, Cu <sub>2</sub> O	Partial oxidation of sulphide ore	$2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$
Ag, Ag <sup>2+</sup>	+0.80	Argentite, Ag <sub>2</sub> S, occurs as metal	Special method involving use of sodium cyanide	$\text{Ag}_2\text{S} + 4\text{NaCN} \rightarrow 2\text{NaAg(CN)}_2 + \text{Na}_2\text{S}$ $2\text{NaAg(CN)}_2 + \text{Zn} \rightarrow 2\text{Ag} + \text{Na}_2\text{Zn(CN)}_4$
Hg, Hg <sup>2+</sup>	+0.85	Cinnabar, HgS	Directional reduction of HgS by heat alone	$\text{HgS} + \text{O}_2 \rightarrow \text{Hg} + \text{SO}_2$
Au, Au <sup>3+</sup>	+1.50	Occurs as metal	Special methods involving use of sodium cyanide	Similar to that for silver $2\text{NaAu(CN)}_2 + \text{Zn} \rightarrow 2\text{Au} + \text{Na}_2\text{Zn(CN)}_4$

Metals found in traces in living organisms			
From Living Organisms	Metals Obtained	From Living Organisms	Metals Obtained
(i) Haemoglobin	Iron	(v) Eyes of cats and cows	Zn
(ii) Blood	Sodium	(vi) Prawns	Cr
(iii) Chlorophyll	Magnesium	(vii) Bones	Ca
(iv) Chloroplast	Mn, Fe and Cu	(viii) Cucumbers	Vanadium

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## COORDINATION COMPOUNDS

### 19.1 COORDINATION COMPOUNDS

#### 19.1.1 Addition Compound

Addition compounds are formed when stoichiometric amount of two or more stable compounds join together.

**Examples:**

1.  $\text{KCl} + \text{MgCl}_2 + 6\text{H}_2\text{O} \longrightarrow \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$   
(Carnallite)
2.  $\text{K}_2\text{SO}_4 + \text{Al}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O} \longrightarrow \text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
(Potassium alum)
3.  $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O} \longrightarrow \text{CuSO}_4 \cdot 4\text{NH}_3\text{H}_2\text{O}$   
(Tetraammine copper (II) sulphate monohydrate)
4.  $\text{Fe}(\text{CN})_2 + 4\text{KCN} \longrightarrow \text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$   
(Potassium ferrocyanide)

#### 19.1.2 Classification of Addition Compounds

(a) Addition compounds are of two types as listed hereunder:

- (i) **Double salts:** Double salts are those which lose their identity in solution, e.g., carnallite, potash alum, etc., when crystals of carnallite are dissolved in water, the solution shows the properties of  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  ions.
- (ii) **Complexes or coordination compound:** Complexes are compounds which retain their identity in solutions.

E.g.,  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4$ ,  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , etc. When these two are dissolved in water they do not form simple ions  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{CN}^-$ , etc. but instead their complex ions remain intact. Thus the cupraammonium ion  $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$  and the ferrocyanide ion  $[\text{Fe}(\text{CN})_6]^{4-}$  exist as distinct entities both in the solid and in the solution.

A complex or coordination compound is a compound consisting either of complex ions with other ions of opposite charge.

**Examples:**

1.  $K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$   
(other ion) (complex anion)
2.  $[Pt(en)_3]Cl_4 \longrightarrow 4Cl^- + [Pt(en)_3]^{4+}$   
(other ion) (complex cation)
3.  $[Pt(en)_2Cl_2] \rightarrow$  no ionization (neutral complex)

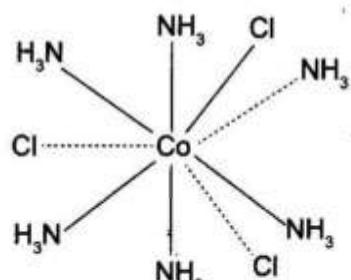
**19.2 WERNER'S COORDINATION THEORY**

In 1823, Werner put forward his famous theory of coordination to explain the formation and structures of complex compounds.

The important postulates of Werner's coordination theory are as follows:

1. In coordination compounds, the metal atoms exhibit two types of valency, viz., the primary valency and the secondary valency. The primary valency is ionizable and is non-directional whereas the secondary valency is non-ionizable and is directional. In modern terminology, the primary valency corresponds to oxidation state and the secondary valency corresponds to the coordination number.
2. Every metal atom has a fixed number of secondary valencies, i.e., it has a fixed coordination number.
3. The metal atom tends to satisfy both its primary as well as secondary valencies. Primary valencies are satisfied by negative ions, whereas secondary valencies are satisfied either by negative ions or by neutral molecules.
4. The secondary valencies are always directed towards fixed positions in space and this leads to definite geometry of the coordination compound. For example, if a metal ion has six secondary valencies these are arranged octahedrally around the central metal ion. If the metal ions has four secondary valencies, these are arranged in either tetrahedral or square planar arrangement around the central metal ion. The secondary valencies, thus, determine the stereochemistry of the complex. The secondary valencies are represented by thick lines and the primary valencies by dotted lines.

Structure of  $CoCl_3 \cdot 6NH_3$  Complex



Number of  $Cl^-$  ions precipitated = 3  
Total number = 4

**19.2.1 Ligands**

A ligand is a species that is capable of donating an electron pair to a central ion. It is a Lewis base. In accepting electron pairs, the central ion acts as a lewis acid.

### 19.2.1.1 Classification of ligands

- (i) Neutral molecules such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , etc.
- (ii) Anions such as  $\text{CN}^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{Cl}^-$ , etc. The name organic ligand ends with -o.
- (iii) Cations (but in rare cases since an electron pair of an cation is held firmly by the positive charges and would not be involved in coordinate bonding) such as  $\text{NO}^+$ , etc. The name of cationic ligand ends with -ium.

On the basis of denticity, ligands can be classified into two types as listed hereunder.

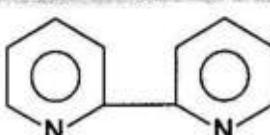
- (a) **Unidentate ligands:** A ligand is said to be unidentate if it has only one pair of electrons that it can donate.

Some common unidentate ligands are listed hereunder

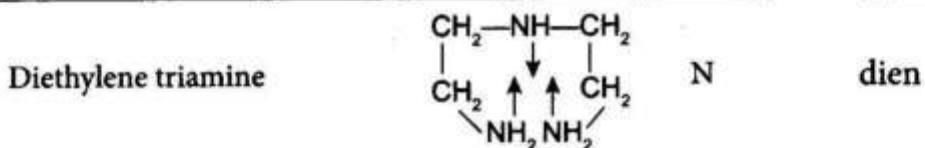
Name of Ligand	Formula	Donor	Name of Ligand	Formula	Donor
(aqua)	$\text{H}_2\text{O}$	O	Hydroxido	$\text{OH}^-$	O
ammine	$\text{NH}_3$	N	Cyano	$\text{CN}^-$	C
Pyridine	$\text{C}_5\text{H}_5\text{N}$	N	Nitro	$\text{NO}_2$	N
Carbonyl	CO	O	Nitrito	$\text{ONO}^-$	O
Nitrosyl	NO	N	Oxo	$\text{O}^-$	O
Triphenyl phosphine	$(\text{C}_6\text{H}_5)_3\text{P}$	P	Thiocyanato	$\text{CSN}^-$	S or N
Halido	$\text{X}^-$	X	isothiocynato	$\text{NCS}^-$	S or N

- (b) **Multidentate ligands:** If a ligand is capable of donating more than one electron pairs, then it is called multidentate ligand.

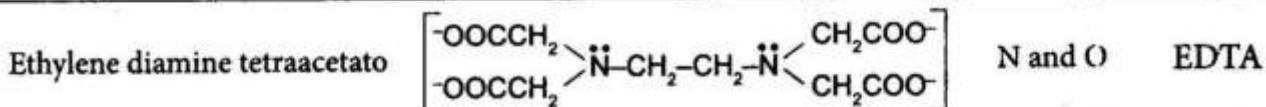
Some common multidentate ligands

Name of Ligand	Structure/Formula	Donor Atom	Abbreviation
Ethylene diamine	$\begin{array}{c} \text{CH}_2\ddot{\text{N}}\text{H}_2 \\   \\ \text{CH}_2\ddot{\text{N}}\text{H}_2 \end{array}$	N	en
Oxalato	$\begin{array}{c} \text{COO}^- \\   \\ \text{COO}^- \end{array}$	O	Ox
Glycinato	$\begin{array}{c} \text{H}_2\text{C} \backslash \text{NH}_2 \\ \quad \quad / \\ \quad \quad \text{COO}^- \end{array}$	N and O	gly
Dimethyl glyoximato	$\begin{array}{c} \text{CH}_3-\text{C}=\text{NO}^- \\   \\ \text{CH}_3-\text{C}=\text{NOH} \end{array}$	N and O	DMG
2, 2-Dipyridyl		N	dipy.

### **Tridentate ligands**

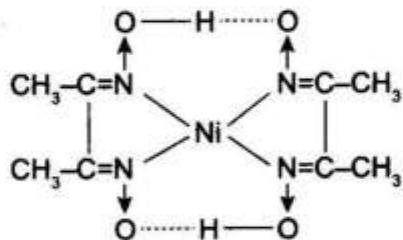


## Hexadentate ligands



**Ambidentate ligands:** Some ligands can be coordinated to the metal through either of the sides. They are called 'ambident' ligands. E.g.,  $\text{CN}^-$  and  $\text{NC-NO}_2$ , and  $\text{ONO}$ , etc.

**Chelates:** Some ligands are capable of donating more than a single electron pair, from different atoms in the ligands and to different sites in the geometrical structure of a complex. These are called multidentate ligands. When the bonding of a multidentate ligand to a metal ion produces a ring (usually five or six-membered), we refer to the complex as a chelate. The multidentate ligand is called a chelating agent and the process of chelate formation is called chelation.



## Nickel (II) dimethyl glyoximate (chelate) [bis-(dimethyl glyoximato nickel (II) ]

## 19.3 COORDINATION NUMBER OF METAL IONS

The coordination number of a metal atom in a complex is the total number of bonds the metal atom forms with ligands.

Metal ion	Coordination number	Metal ion	Coordination number
$\text{Ag}^+$	2	$\text{Co}^{3+}$	6
$\text{Cu}^+$	2, 4	$\text{Ni}^{2+}$	4, 6
$\text{Cu}^{2+}$	4, 6	$\text{Zn}^{2+}$	4
$\text{Fe}^{2+}, \text{Fe}^{3+}$	6	$\text{Cr}^{3+}$	6
$\text{Co}^{2+}$	4, 6	$\text{Pt}^{2+}/\text{Pt}^{4+}$	4

### 19.3.1 Complexes of various coordination number

Complex	Coordination Number	Complex	Coordination Number
$[\text{Ag}(\text{NH}_3)_2]^+$	2	$[\text{CO}(\text{NH}_3)_6]^{3+}$ , $[\text{W}(\text{CO})_6]$	6
$[\text{PtCl}_4]^{2-}$ , $[\text{Ni}(\text{CO})_4]$	4	$\text{Fe}(\text{CO})_5$ , $[\text{Co}(\text{CN})_5]^{3-}$	5

### 19.4 ISOMERISM IN COORDINATION COMPOUNDS

The compounds having same molecular formula but different physical and chemical properties on account of different structure are called isomers and the phenomenon is known as isomerism. Isomerism in coordination compounds may be divided into two main types:

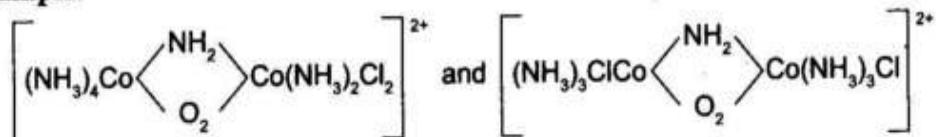
1. Structural isomerism
2. Stereo isomerism

#### 19.4.1 Structural Isomerism

It is displayed by compounds that have different ligands within their coordination spheres. The different types of structural isomerism shown by coordination compounds are discussed hereunder.

- (i) **Ionization isomerism:** This type of isomerism arises when the coordination compounds give different ions in solution. For example, there are two isomers of formula  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ .  
 $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4 = [\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} + \text{SO}_4^{2-}$   
 This isomer gives a white precipitate of  $\text{BaSO}_4$  with  $\text{BaCl}_2$  solution.  
 $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br} = [\text{Co}(\text{NH}_3)_5\text{SO}_4]^{+} + \text{Br}^{-}$   
 The above isomer a gives light yellow precipitate with  $\text{AgNO}_3$  solution.
- (ii) **Hydrate isomerism:** This type of isomerism arises when different number of water molecules are present inside and outside the coordination sphere. This isomerism is best illustrated by the three isomers that have the formula  $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ .
  - (a)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ : Violet. All the six water molecules are coordinated to Cr. It has three ionizable chloride ions.
  - (b)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2\cdot \text{H}_2\text{O}$ : Green. Five water molecules are coordinated to Cr. It has two ionizable  $\text{Cl}^{-}$  ions.
- (iii) **Coordination isomerism:** This type of isomerism is observed in the coordination compound having both cationic and anionic complex ions. The ligands are interchanged in both the cationic and anionic ions to form isomers. Here, complete exchange of liquid is done, e.g.,  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$  and  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$
- (iv) **Linkage isomerism:** This type of isomerism occurs in complex compounds which contain ambidentate ligands like  $\text{NO}_2^-$ ,  $\text{SCN}^-$ ,  $\text{CN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{NCO}^-$ . These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex. These types of isomerism are distinguished by infra-red (IR) spectroscopy. E.g.,  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ .
- (vi) **Coordination position isomerism:** This type of isomerism is exhibited by polynuclear complexes by changing the position of ligands with respect to different metal atoms present in the complex.

For example:



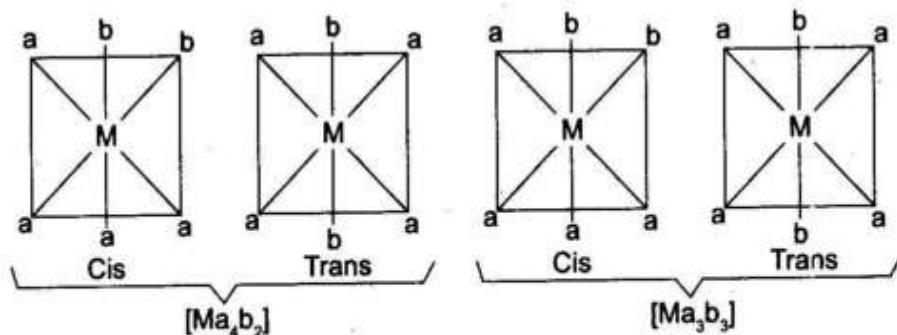
## 19.5 STEREO ISOMERISM

Compounds are stereo isomers when they contain the same ligands in their coordination spheres but differ in the way that these ligands are arranged in space. Stereoisomerism is of two types, viz., geometrical isomerism and optical isomerism.

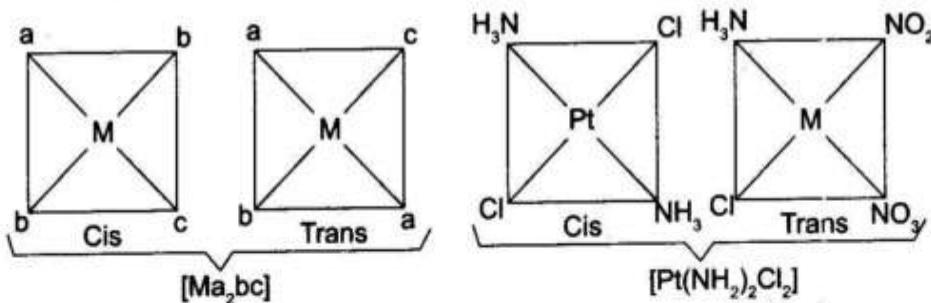
### 19.5.1 Geometrical Isomerism

This isomerism is due to ligands occupying different positions around the central metal atom or ion. The ligands occupy positions either adjacent or opposite to one another. This type of isomerism is also known as cis- and trans isomerism. Geometrical isomerism is very much common in coordination number 4 and 6 complexes.

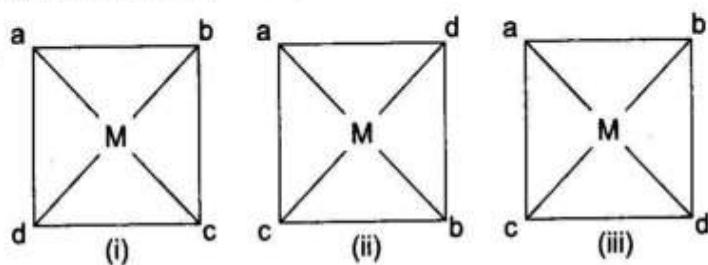
Square planar complexes (coordination number four) exhibit geometrical isomerism



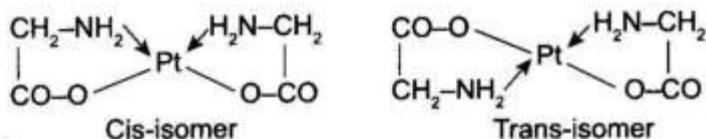
- (i) Complexes with general formula  $\text{Ma}_2\text{b}_2$  (where both a and b are monodentate) can have cis and trans-isomers.
- (ii) Complexes with general formula,  $\text{Ma}_2\text{bc}$  can have cis and trans-isomers.



- (iii) Complexes with general formula,  $\text{Mabcd}$  can have three isomers.



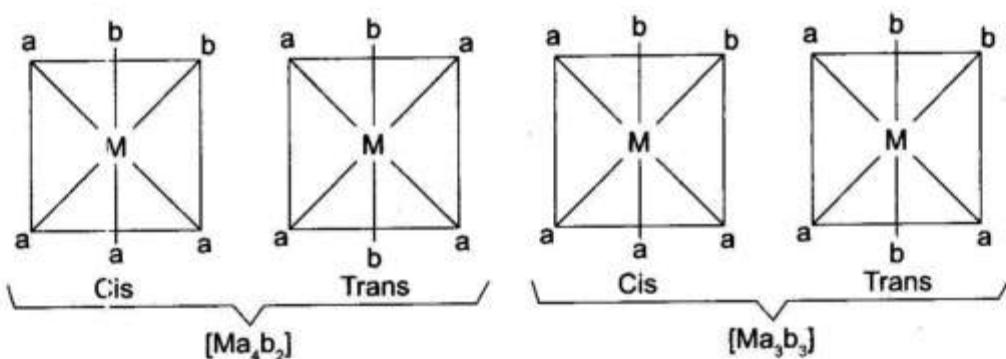
- (iv) Square planar complexes having unsymmetrical bidentate ligands can also show geometrical isomerism. For example, platinum glycinate complex,  $[\text{Pt}(\text{Gly})_2]$ , exhibits geometrical isomerism.



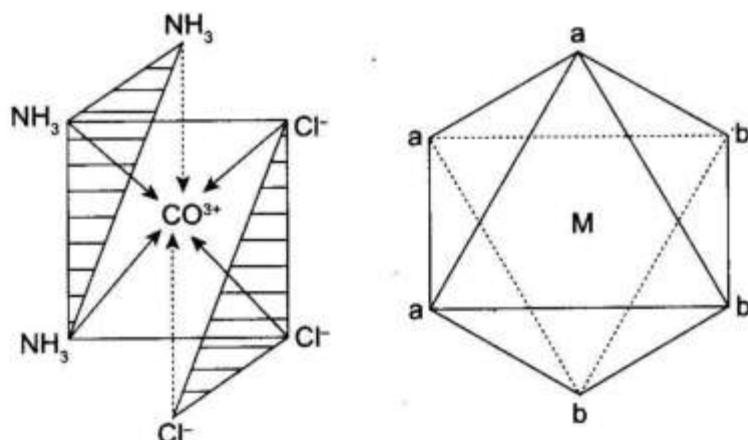
$[\text{Ma}_4]^{n+}$  and  $[\text{Ma}_3\text{b}]^{n+}$  type square planar complexes do not show geometrical isomerism.

**Tetrahedral and linear complexes:** do not show geometrical isomerism.

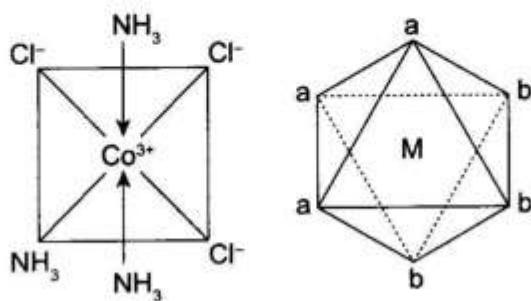
**Octahedral complexes:** of the type  $\text{Ma}_4\text{b}_2$  and  $\text{Ma}_3\text{b}_3$  exhibit geometrical isomerism



**Facial and meridional isomers:** A set of three ligands (similar) may be arranged on an octahedron in all cis-fashion, giving facial or 'fac' isomer. In other words, three similar ligands on the same face of an octahedron give rise to a facial isomer.



A set of three similar ligands may be arranged on an octahedron with one pair trans (meridian of octahedron), giving rise to meridional or 'mer' isomer.



### 19.5.2 Optical Isomerism

A coordination compound which can rotate the plane of polarized light is said to be optically active. The essential requirement for a substance to be optically active is that the substance should not have a plane of symmetry in its structure. The isomer which rotates the plane of polarized light to right direction is termed dextro (D-form) while the isomer which rotates the plane of polarized light to left direction is termed leavo (L-form).

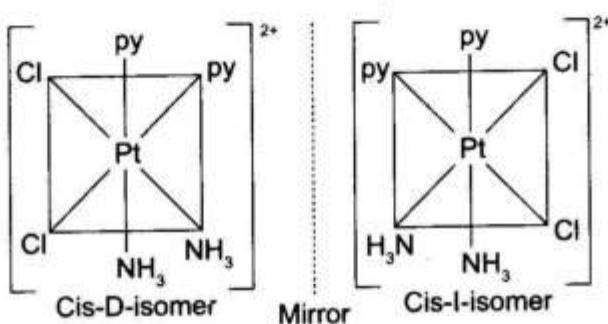
Optical isomerism is expected in tetrahedral complexes of the type  $Mabcd$  but no optical isomer has been isolated until now.

However, compounds containing two unsymmetrical bidentate ligands have been resolved into optical isomers.

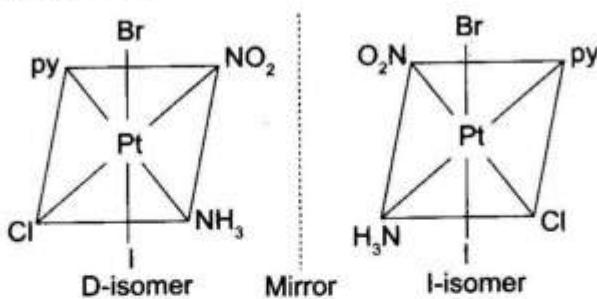
Optical isomerism rarely occur in square planar complexes on account of the presence of axis of symmetry. Optical isomerism is very common in octahedral complexes. Octahedral complexes of general formulae

$[Ma_2b_2c_2]^{n\pm}$ ,  $[Mabcdef]^{n\pm}$ ,  $[M(AA)_3]^{n\pm}$  and  $[M(AA)_2a_2]^{n\pm}$  (where AA = symmetrical bidentate ligands)  $[M(AA)_2ab]^{n\pm}$  and  $[M(AB)_3]^{n\pm}$  (where A and B are unsymmetrical ligands), show optical isomerism.

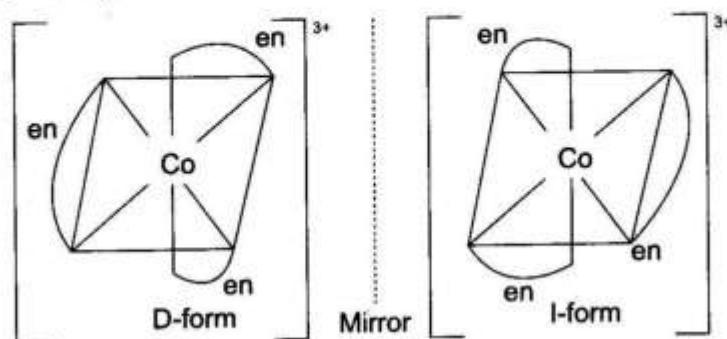
**Examples:**



(b)  $[Mabcdef]$ ;  $[Pt(py)NH_3NO_2ClBrI]$



(c)  $[MAA)_3]$ ;  $[Co(en)_3]^{3+}$



## 19.6 NOMENCLATURE OF COORDINATION COMPOUNDS

- While writing the IUPAC name of a complex, the name of cation is written first followed by the name of anion.
- While writing the IUPAC name of the complex, the ligands are written in alphabetical order, regardless of their charge followed by the name of metal.
- When there are several ligands of the same kind we normally use the prefixes di, tri, tetra, penta and hexa to show the number of ligands of that type.  
Exception occurs when the name of ligand includes a number, e.g., dipyridyl or ethylenediamine. To avoid confusion in such cases bis, tris and tetrakis are used instead of di, tri, tetra and the name of the ligand is placed in brackets.
- The oxidation state of central metal is shown by a roman numeral in brackets immediately following its name, e.g., titanium (III).
- Complex positive ions and neutral molecules have no special ending but complex negative ions ends with -ate.

e.g.,  $[\text{Pt}(\text{py})_4]$   $[\text{Pt Cl}_4]$  can be named as Tetra pyridine platinum (II) tetra chloro platinato (II).

- If the complex contains two or more metal atoms, it is termed as polynuclear. The bridging ligands which link the two metal atoms together are indicated by the prefix  $\mu$ - . If there are two or more bridging groups of the same kind, this is indicated by di- $\mu$ -, tri- $\mu$ -, etc. Bridging groups are listed alphabetically with the other groups unless the symmetry of the molecules allows a simpler name. If a bridging group bridges more than two metal atoms it is shown as  $\mu_3$ ,  $\mu_4$ ,  $\mu_5$  or  $\mu_6$  to indicate how many atoms it is bonded to.

e.g.,  $[(\text{NH}_3)_5\text{Co}\cdot\text{NH}_2\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$

$\mu$ -amido bis [pentaammine cobalt (III)] nitrate  $[(\text{CO})_3\text{Fe}(\text{CO})_3\text{Fe}(\text{CO})_3]$

Tri -  $\mu$  - carbonyl - bis [tricarbonyl iron (O)]

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	Hexa ammine cobalt (III) chloride
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	Penta ammine chloro cobalt (III) ion
$[\text{CoCl CN. NO}_2 (\text{NH}_3)_3]$	Tri ammine chloro cyano nitro cobalt (III).
$\text{Li}[\text{Al H}_4]$	Lithium tetrahydrido aluminate (III)
$\text{K}_4[\text{Fe}(\text{CN})_6]$	Potassium hexa cyano ferrate (II)
$\text{K}_2[\text{Os Cl}_5\text{N}]$	Potassium penta chloro nitrido osmate (VI)
$[\text{Cr}(\text{PPH}_3)_3(\text{CO})_5]$	Penta carbonyl triphenyl phosphine chromium (O)
$[\text{Co}(\text{en})_2\text{F}_2]\text{ClO}_4$	Bis (ethylenediamine) difluoro cobalt (III) perchlorate
$[\text{Ni}(\text{dmg})_2]$	Bis (dimethylglyoximato) nickel (II)
$\text{Co}(\text{NH}_3)_4\text{Cl}_2]_3 [\text{Cr}(\text{CN})_6]$	Tetra ammine dichloro cobalt(III)hexa cyano chromate (III)

### 19.6.1 Effective Atomic Number

Effective atomic number (EAN) of the metal in a complex is given by

EAN = z - (ON) + 2(CN) where ON is oxidation number, CN is coordination number and z is the atomic number.

Complex Ion	Central Metal Atom	Atomic No.	Oxidation State of Metal in Emplexion	Number of Electron Donated by Ligands	EAN
$[\text{Fe}(\text{CN})_6]^{4-}$	Fe	26	+2	$6 \times 2 = 12$	$26 - 2 + 12 = 36$
$[\text{Cu}(\text{CN})_4]^{3-}$	Cu	29	+1	$4 \times 2 = 8$	$29 - 1 + 8 = 36$
$[\text{Pt}(\text{NH}_3)_6]^{4-}$	Pt	78	+4	$6 \times 2 = 12$	$78 - 4 + 12 = 86$
$[\text{Co}(\text{en})_3]^{3+}$	Co	27	+3	$3 \times 4 = 12$	$27 - 3 + 12 = 36$

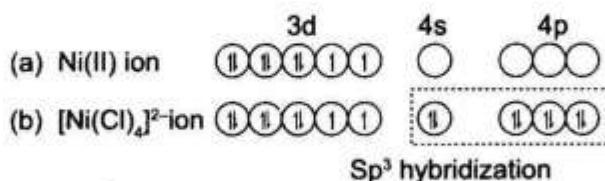
## 19.7 BONDING IN COMPLEXES

There are three theories of metal to ligand bonding in complexes.

### 19.7.1 Valence Bond Theory

This theory was proposed by Pauling. The main points of this theory are given as follows:

1. The central metal ion in the complex makes available an adequate number of empty orbitals for the formation of coordinate bonds with suitable ligands. The number of empty orbitals made available for the purpose is equal to the coordination number of the central metal ion.



2. The appropriate atomic orbitals of the metal hybridize to give an equal number of new orbitals of equivalent energy called hybrid orbitals. The hybrid orbitals are directed towards the ligand positions according to the geometry of the complex.
3. The d-orbitals involved in the hybridization may be inner, viz.,  $(n - 1)d$  orbitals or the outer, viz., nd orbitals. The complexes thus formed are referred to as low spin and high spin complexes, respectively.
4. Each ligand has at least one orbital containing a lone pair of electrons.
5. The empty hybrid orbitals of metal ion overlap with the fully filled orbitals of the ligand, forming the ligand–metal coordinate bond. The number of such bonds varies with the number of empty orbitals made available by the central metal ion.

### 19.7.2 Limitations of Valence Bond Theory

The valence bond theory was fairly successful in explaining qualitatively the geometry and magnetic properties of complexes. However, it has a number of limitations.

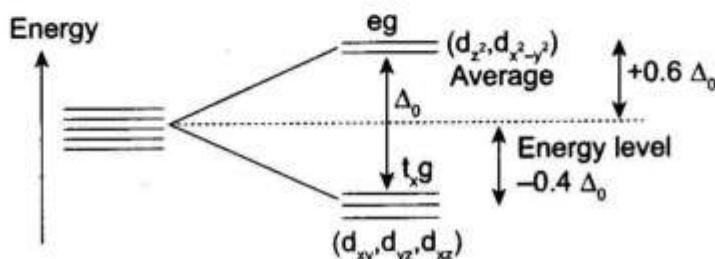
- (i) The theory does not offer any explanation about the spectra of complex.
- (ii) Sometimes, the same metal ion assumes different geometry when formation of complex ion takes place. The theory is unable to explain why at one time the electrons are arranged against the Hund's rule while at other times the electronic configuration is not disturbed.

- (iii) The theory does not offer an explanation for the existence of inner-orbital and outer-orbital complexes.
- (iv) The theory does not explain why certain complexes are labile while other are inert.

### 19.7.3 Crystal Field Theory

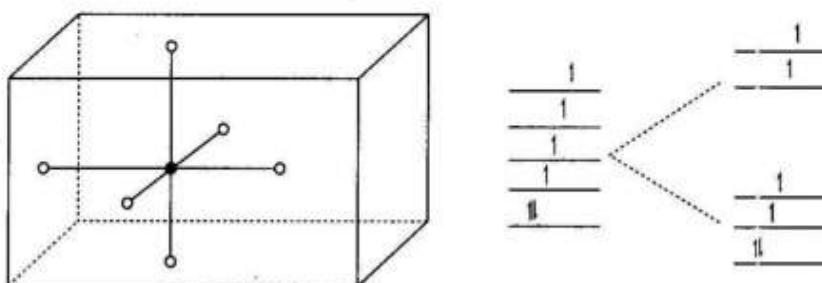
Crystal field theory was proposed by H. Bethe and Van Vleck and was originally applied to ionic crystals to explain their optical properties and is, therefore, called crystal field theory. The main points of the theory are:

- (a) According to crystal field theory, the bonding in complex ions is purely electrostatic. This theory regards the ligand atoms of ionic ligands such as  $F^-$ ,  $Cl^-$  or  $CN^-$  as negative point charges and if the ligand molecules are neutral, these are regarded as point dipoles or simply dipoles, the negative end pointing towards central metal ion.
- (b) The complex is regarded as a combination of a central metal ion surrounded by ligands which act as point charges or point dipoles. The arrangement of ligands around the central metal ion or atom is such that the repulsion between these negative points or dipoles is minimum.
- (c) Interactions between positively charged nucleus of the central metal ion or atom and the negatively charged ligands are of two types:
  - (i) The attractive forces arise due to the positive metal ion and the negatively charged ligands or the negative end of polar neutral molecules.
  - (ii) The repulsive forces arise between the lone pairs on the ligands and electrons in the d-orbitals of the metal.
- (d) In a free transition metal or ion, there are five d-orbitals which are designated as  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ . The five d-orbitals are divided into two sets depending on the nature of their orientation in space.
  - (i) The three d-orbitals which orient in the regions between coordinate axes are designated as  $t_{2g}$  orbitals.  $t_{2g}$ -orbitals are three-fold degenerate. These are non-axial orbitals.
  - (ii) The other two orbitals  $d_{x^2-y^2}$ ,  $d_{z^2}$  which orient along the axis are called  $e_g$  orbitals.  $e_g$  orbitals are twofold degenerate. These are also called axial orbitals. All the five d-orbitals have same energy, i.e., they are degenerate. However, when the ligands approach the central metal ion or atom, the electrons of the d-orbitals of the central metal ion or atom are repelled by lone pairs of the ligands. The d-orbitals thus split into two sets of orbitals having different energies. This is called crystal field splitting. The extent of splitting depends on the number of ligands and their position around the metal atom or ion. The splitting is different in different structures with different coordination numbers.



### 19.7.4 Formation of an Octahedral Complex

We may consider an octahedral complex as a cube, having the metal ion at the centre of the body and the 6 ligands at the face centres and if we take the metal ion as the origin of a Cartesian coordinate, the ligands will be along the axes.



The orbitals lying along the axes ( $d_{z^2}$ ,  $d_{x^2-y^2}$ ) will be more strongly repelled than the orbitals with lobes directed between the axes ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ). The d-orbitals are thus split into two sets with the  $d_{z^2}$  and  $d_{x^2-y^2}$  at a higher energy than the other three.

### 19.7.5 Formation of a Square Planar Complex

If the central metal ion has eight d-electrons, these will be arranged as 

1	1	1	1	1
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.

Under the influence of a strong field ligand, the electrons in the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals may pair up, leaving one vacant d-orbital, which can accept a lone pair from a ligand. E.g.,  $[\text{Ni}(\text{CN})_4]^{2-}$ .

The electronic configuration of  $\text{Ni}^{2+}$  ion is 

1	1	1	1	1
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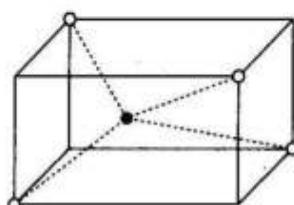
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.   
4s                  4p

Consider a  $\text{Ni}^{2+}$  ion with one electron in the  $d_{x^2-y^2}$  and one in  $d_{z^2}$  orbital. The approach of ligands along x, y and z axes will result in the energy of these orbitals increasing. Because the  $d_{x^2-y^2}$  orbital is attacked by four ligands and the  $d_{z^2}$  by only two, the energy of  $d_{x^2-y^2}$  orbital will increase most. If the ligands have enough strong field, the electrons will be forced out of the  $d_{x^2-y^2}$  orbital into the  $d_{z^2}$ . Thus, four ligands can approach along x, -x, y and -y. A ligand approaching in the z or -z direction attempting to denote a lone pair meets the very strong repulsive forces from a completely filled  $d_{z^2}$  orbital. Thus, only four ligands succeed in bonding to the metal.

### 19.7.6 Formation of tetrahedral complexes

A regular tetrahedron is related to a cube with an atom at the centre and four of the eight corners occupied by the ligands.



The directional x, y and z points to the centre of the faces. The  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals point along x, y and z axes and  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals point in between x, y and z.

The directions of approach of the ligands do not coincide exactly with either the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals or  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  orbitals. The approach of ligands raises the energy of both sets of orbitals, but since the  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  orbitals correspond more closely to the position of the ligands, their energy increases most and the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals are filled first. This is opposite to what happens in octahedral complexes. E.g.  $[\text{FeCl}_4]^-$ .

3d                  4s                  4p

The electronic configuration of  $\text{Fe}^{3+}$  ion is 

1	1	1	1	1			
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.

Since  $\text{Cl}^-$  ion is a weak field ligand it is unable to pair the unpaired electron and hence, the  $\text{Cl}^-$  ion uses 4s and 4p orbitals to form a tetrahedral complex of  $\text{sp}^3$  hybridization.

#### (a) Factors affecting the magnitude of $\Delta_0$ :

**The nature of the ligands:** Based on experimental observation for a wide variety of complexes, it is possible to list ligands in order of increasing field strength in a spectrochemical series.

#### Spectrochemical series: weak field ligands

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{C}_2\text{H}_5\text{OH} < \text{oxalate}, \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{EDTA} < \text{py}, \text{NH}_3 < \text{en} < \text{dipyridyl} < \text{o-phenanthroline} < \text{NO}_2^- < \text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}$

**Strong field ligands:** The spectrochemical series is an experimentally determined series.

However, the order of strength of ligand field is theoretically summarized as follows:

Halide donors < O donors < N donors < C donors

The amount of crystal field splitting is determined by the strength of the ligand field.

**Oxidation state of the metal ion:** The magnitude of  $\Delta_0$  increases with increasing atomic charge on the central metal ion. As the ionic charge on the metal ion increases greater is the attraction for the ligands, greater the repulsion between ligand orbitals and metal orbitals and hence greater the magnitude of  $\Delta_0$ .

#### Hybridization and geometry of some complexes:

(i)  $[\text{Fe}(\text{CN})_6]^{4-}$  oxidation state of Fe = +2

Coordination number of Fe = 6

Six empty hybrid orbitals are required by six  $\text{CN}^-$  ligands (a strong field ligand)

Fe [Ar]	$3d^6$ <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td></td><td></td><td></td></tr></table>	1	1	1	1	1				$4s^2$ <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td></td><td></td><td></td></tr></table>	1				$4p$ <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td></td><td></td><td></td><td></td></tr></table>				
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Fe <sup>2+</sup> [Ar]	$3d^6$ <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td></td><td></td></tr></table>	1	1	1	1	1			$4s$ <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td></td><td></td><td></td><td></td></tr></table>					$4p$ <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td></td><td></td><td></td><td></td></tr></table>					
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Since  $\text{CN}^-$  is a strong field ligand making unpaired electrons paired.

$[\text{Fe}(\text{CN})_6]^{4-}$ [Ar]	<table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td></td><td></td></tr></table>	1	1	1	1	1	1			$d^2\text{sp}^3$
1	1	1	1	1	1					

→ Complex ion has  $\text{d}^2\text{sp}^3$  hybridized  $\text{Fe}^{2+}$ .

→ Inner d-orbital complex

→ Diamagnetic

→ Magnetic moment = 0

→ Octahedral geometry, bond angle 90°

- (ii)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  Oxidation number of Fe = + 3 coordination number of Fe = 6

Fe	[Ar]	3d <sup>6</sup>	4s <sup>2</sup>	4p															
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Fe <sup>3+</sup>	[Ar]	3d <sup>5</sup>	4s	4p															
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$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	[Ar]	3d <sup>6</sup>	4s	4p															
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		4d	sp <sup>3</sup> d <sup>2</sup>																
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Since  $\text{H}_2\text{O}$  is a weak ligand hence no change in electron spin; so, outer d-orbitals will be used for taking electron pairs from  $\text{H}_2\text{O}$ .

→ sp<sup>3</sup>d<sup>2</sup> hybridization

→ outer d-complex

→ A high spin complex with five unpaired e<sup>-</sup>, paramagnetic, magnetic moment is  $\sqrt{35}$  BM

→ Octahedral geometry, bond angle 90°

- (iii)  $[\text{Ni}(\text{CN})_4]^{2-}$

CN<sup>-</sup> is a strong ligand, hence unpaired electrons in Ni<sup>2+</sup> are paired, making one inner orbital vacant for the ligand.

$[\text{Ni}(\text{CN})_4]^{2-}$	[Ar]	3d <sup>8</sup>	4s	4p									
		<table style="margin-left: auto; margin-right: auto; border-collapse: collapse;"> <tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr> </table>	1	1	1	1	1	<table style="margin-left: auto; margin-right: auto; border-collapse: collapse;"> <tr><td></td><td></td><td></td><td></td><td></td></tr> </table>					
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dsp<sup>2</sup>

→ dsp<sup>2</sup> hybridization Ni, inner d-orbital complex

→ Diamagnetic

→ Square planar geometry, bond angle 90°

### 19.7.7 Calculation of CFSE

Each electron occupying t<sub>2g</sub> orbital results in lowering of energy by  $-0.40 \Delta_0$  (or  $-4 \text{ Dq}$ ). Similarly, each electron occupying e<sub>g</sub> orbital results in increase of energy by  $+0.60 \Delta_0$  (or  $+6 \text{ Dq}$ ). Thus

CFSE =  $(-0.4x + 0.6y) \Delta_0$ ; where, x = number of electrons occupying t<sub>2g</sub> orbitals and y = number of electrons occupying e<sub>g</sub> orbitals.

Negative value of CFSE indicates net lowering in energy, i.e., gain in stability.

For tetrahedral complex:  $[0.4x + (-0.6)y]\Delta_t$ ; where x is number of e<sup>-</sup> present in t<sub>2</sub> orbitals and y is number of e<sup>-</sup> in eg orbitals.

#### 19.7.7.1 Magnetic Nature

The transition metal complexes containing one or more unpaired electrons possess a definite value of magnetic moment. An unpaired electron because of its spin is equivalent to an electric current flowing in a circular conductor. Hence, it behaves as a magnet.

[The magnetic moment is expressed as:  $\mu = \frac{e\hbar}{4\pi mc} = 9.274 \times 10^{-21}$  erg gauss<sup>-1</sup> = one Bohr magneton (BM)]

where e = charge on electron; m = mass of electron; h = Planck's constant and c = velocity of light.]

The substances having magnetic moments are attracted in an external magnetic field. Such substances are termed paramagnetic substances. Most of the coordination compounds are paramagnetic. The substances having no unpaired electron or having only paired electrons show zero magnetic moment and are called diamagnetic substances.

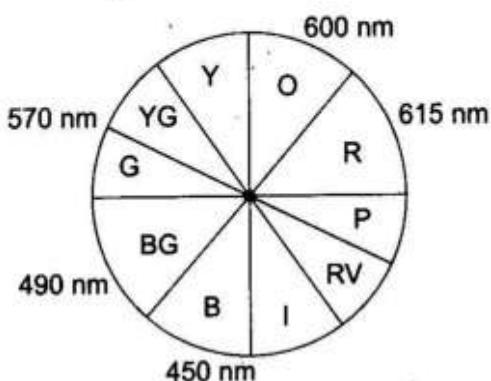
The magnetic nature or magnetic moment of a coordination compound, thus depends on the number of unpaired electrons. The magnetic moment is approximately given by the relation.

Magnetic moment,  $\mu = \sqrt{n(n+2)}$  BM, where n is the number of unpaired electrons.

### 19.7.8 Colour

A substance appears coloured because it absorbs light of specific wavelengths in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmits or reflects the rest of the wavelength. Each wavelength of visible light represents a different colour, where light, such as sunlight, is a combination of all colours; however, an object that absorbs all visible light appears black.

It is general observation that colour of complex observed is complimentary to the colour of light absorbed as given in following colour diagram.



When the energy of the photon ( $h\nu$ ) is equal to the difference between the lower and higher d-orbital energy levels, an electron is promoted from a lower to higher level. If the wavelength of the photon absorbed by an ion lies outside the visible region, then the transmitted light looks the same as the incident light and the ion appears colourless.

Complex Ion	Wavelength of Light Absorbed (nm)	Colour of Light Absorbed	Colour of Complex Observed
$[\text{Co}(\text{F})_6]^{3-}$	700	Red	Green
$[\text{Co}(\text{C}_2\text{O}_4)_6]^{3-}$	600	Yellow	Dark green
$[\text{Co}(\text{NH}_3)_6]^{3+}$	600	Yellow	Blue green
$[\text{Co}(\text{en})_6]^{2+}$	475	Blue	Yellow orange
$[\text{Co}(\text{en})_3]^{4+}$	470	Blue	Yellow orange
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet	Pale yellow

## 19.8 STABILITY OF COORDINATION COMPOUNDS IN SOLUTIONS

The overall stability constant from  $M + nL \rightleftharpoons ML_n$

The higher the overall stability constant value of the complex, the more stable it is.

- Factors affecting stability of the compounds: In general, higher the charge density on the central ion, the greater is the stability of its complexes,
- The more basic a ligand, the greater is the ease with which it can donate its lone pairs of electrons and therefore, the greater is the stability of the complexes formed by it.
- The higher the oxidation state of the metal, the more stable is the complex. The charge density of  $\text{Co}^{3+}$  ion is more than  $\text{Co}^{2+}$  ion and thus  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is more stable than  $[\text{Co}(\text{NH}_3)_6]^{2+}$ . Similarly,  $[\text{Fe}(\text{CN})_6]^{3-}$  is more stable than  $[\text{Fe}(\text{CN})_6]^{4-}$ .
- Chelating ligands form more stable complexes as compared to monodentate ligands. Greater is the chelation, more is the stability of complex.  
 $[\text{Cr}(\text{NH}_3)_6]^{3+} < [\text{Cr}(\text{en})(\text{NH}_3)_4]^{3+} < [\text{Cr}(\text{en})_2(\text{NH}_3)_2]^{2+} < [\text{Cr}(\text{en})_3]^{3+}$ .
- 4d and 5d series metals form more stable complex in 3d series metals.

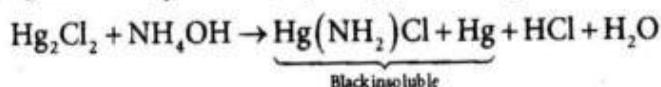
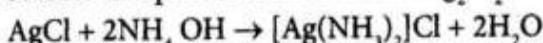
## 19.9 IMPORTANCE OF COORDINATION COMPOUNDS

The complexes are of immense importance on account of their applications in various fields. During complex formation there are drastic changes in the properties of metal atom or ion and these changes in properties are made use of in the applications of metal complexes.

### 19.9.1 Analytical Chemistry

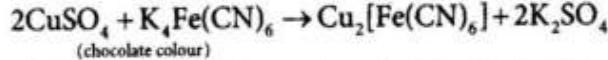
Coordination compounds find their application in both qualitative and quantitative methods of analysis.

- The separation of  $\text{Ag}^+$  from the first group of analysis is based on the fact that silver chloride is soluble in aqueous ammonia and  $\text{Hg}_2\text{Cl}_2$  forms a black insoluble material.

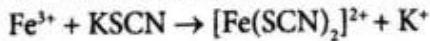


- The detection of  $\text{Cu}^{2+}$  is based on the formation of a blue tetraammine copper sulphate complex which gives a deep blue coloured solution.  $\text{CuSO}_4 + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

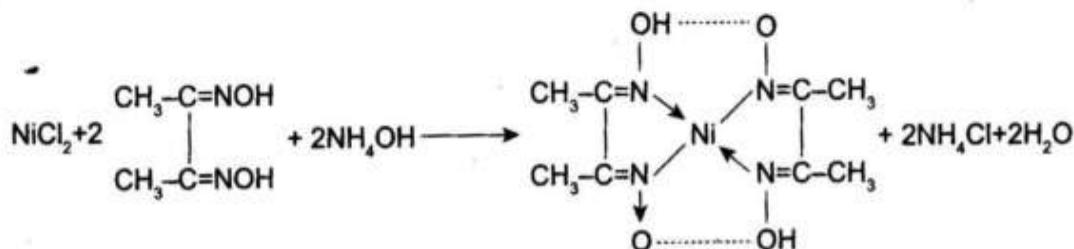
It also forms a chocolate-coloured precipitate with potassium ferrocyanide.



- $\text{Fe}^{3+}$  is detected by formation of a blood red coloured complex with KSCN.



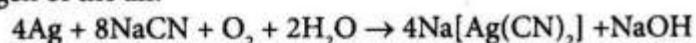
- The detection and estimation of  $\text{Ni}^{2+}$  is based on the formation of a scarlet red complex with dimethyl glyoxime.



- (g) EDTA is used as a complexing agent in volumetric analysis of metal ions like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$ .

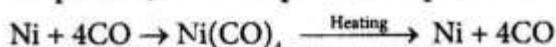
## 19.10 METALLURGICAL OPERATIONS

Silver and gold are extracted by the use of complex formation. Silver ore is treated with sodium cyanide solution with continuous passing of air through solution. Silver dissolves as a cyanide complex and pure silver is precipitated by the addition of scrap zinc.  $\text{Ag}_2\text{S} + 4\text{NaCN} = 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$  active Ag and Au also dissolve in NaCN solution in presence of oxygen of the air.



Ag and Au are precipitated by addition of scrap zinc.

Nickel is extracted by converting it into a volatile complex, nickel carbonyl by use of carbon monoxide (Mond's process). The complex decomposes on heating again into nickel and carbon monoxide.



### 19.10.1 Photography

In photography, the image on the negative is fixed by dissolving all the remaining silver halides with hypo solution in the form of a soluble complex.  $\text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + \text{NaBr}$

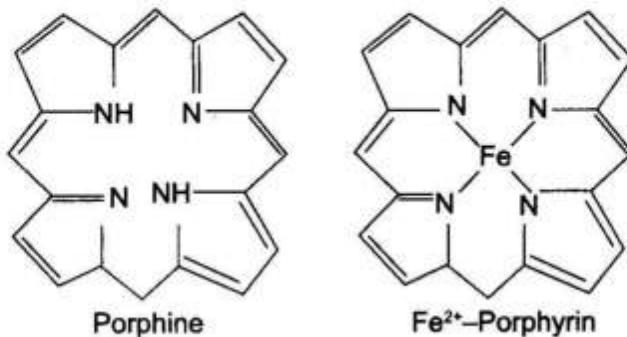
### 19.10.2 Electroplating

Metal complexes release metal slowly and thus give a uniform coating in electroplating of the metal on the desired object. Cyano complexes of silver, gold, copper, etc. are used for the electrodeposition of these metals.

## 19.11 BIOLOGICAL PROCESSES

Coordination compounds play many important roles in animals and plants. They are essential in storage and transport of oxygen, as electron transfer agents, as catalysts and in photosynthesis. Three important examples are given below :

- (i) **Haemoglobin:** Haemoglobin is a protein which is present in blood. The main function of haemoglobin is to carry oxygen in the blood from the lungs to the tissues where it delivers the oxygen molecules to myoglobin, the quadridentate macrocyclic ligand.



The porphine molecule is an important part of haemoglobin structure. The two  $H^+$  ions bonded to nitrogen atoms are displaced and the metal ion coordinates simultaneously with all the four nitrogen atoms. The complex formed from porphine is called porphyrin.

- (ii) **Chlorophyll:** The chlorophyll molecule, which plays an essential role in photosynthesis also contains the porphyrin ring but the metal ion there is  $Mg^{2+}$  rather than  $Fe^{2+}$ . It is a green plant pigment and acts as a photosensitizer in the synthesis of carbohydrates in plants.
- (iii) **Vitamin B<sub>12</sub>:** It is a complex of cobalt with a quadridentate ligand which is similar to porphyrin ligand of haemoglobin.

## 19.12 IN MEDICINAL FIELD

- (i) The complex of calcium with EDTA is used for the treatment of lead poisoning. Lead readily replaces calcium in the complex and lead-EDTA complex is finally eliminated from the body in urine.
- (ii) The platinum complex cis  $[Pt(NH_3)_2Cl_2]$  known as cis platin is used as an antitumour agent in the treatment of cancer.

## 19.13 ORGANOMETALLIC COMPOUNDS

Compounds that contain at least one carbon–metal bond are called organometallic compounds.

Zeise, in 1830, prepared the first organometallic compound by the action of ethylene on a solution of potassium chloroplatinate (II). In the last four decades, enormous work has been done in this field and many fascinating compounds have been synthesized and investigated. Grignard reagent,  $RMgX$  is a familiar example of organometallic compounds where R is an alkyl group. Diethyl zinc  $[Zn(C_2H_5)_2]$ , lead tetraethyl  $[Pb(C_2H_5)_4]$ , ferrocene  $[Fe(C_5H_5)_2]$ , bisbenzene chromium  $[Cr(C_6H_6)_2]$  and metal carbonyls are other examples of organometallic compounds. The compounds of metalloids such as germanium and antimony and non-metallic elements such as boron and silicon are also included under this classification.

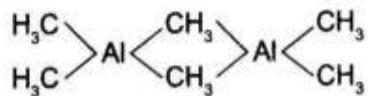
### 19.13.1 Classification of Organometallic Compounds

1. Sigma ( $\sigma$ )-bonded complexes
2. Pi ( $\pi$ )-bonded complexes
3. Complexes containing both  $\sigma$  and  $\pi$  bonding

#### 19.13.1.1 Sigma bonded organometallic compounds

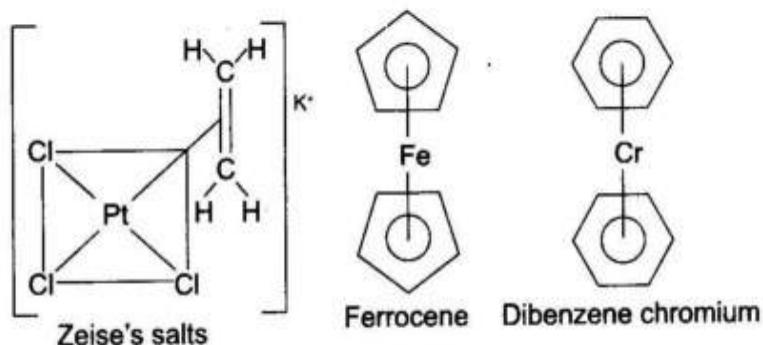
In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond, i.e., the ligand contributes one electron and is, therefore, called one electron donor. Examples are:

- (i) Grignard reagent,  $R - Mg - X$   
Zinc compounds of the formula  $R_2Zn$  ( $CH_3$ )<sub>4</sub>Sn, ( $C_2H_5$ )<sub>4</sub>Pb,  $Al_2(CH_3)_6$ ,  $Al_2(C_2H_5)_6$   
 $Al_2(CH_3)_6$  is a dimeric compound and has a structure similar to diborane,  $B_2H_6$ . It is an electron-deficient compound and two methyl groups act as bridges between two aluminium atoms.



### 19.13.1.2 $\pi$ -bonded organometallic compounds

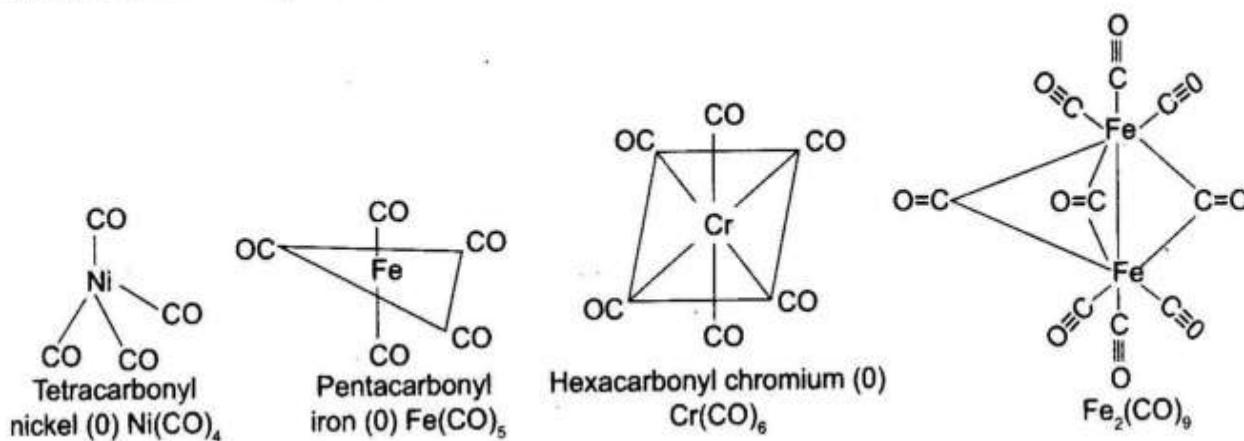
These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond that involves the  $\pi$ -electrons of the ligand. Three common examples are Zeise's salt, ferrocene and dibenzene chromium. These are shown here:



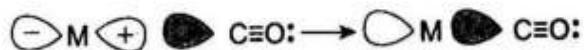
### 19.13.1.3 $\sigma$ -and $\pi$ -bonded organometallic compounds

Metal carbonyls, compounds formed between metal and carbon monoxide belong to this class. These compounds possess both  $\sigma$ - and  $\pi$ -bonding. The oxidation state of metal atoms in these compounds is zero. Carbonyls may be monomeric, bridged or polynuclear. Carbonyls are mainly formed by the transition metals of VI<sup>th</sup>, VII<sup>th</sup> and VIII<sup>th</sup> groups.

Some well-known examples are:



In a metal carbonyl, the metal carbon bond possess both  $\sigma$ - and  $\pi$ -character. A  $\sigma$ -bond between metal and carbon atom is formed when a vacant hybrid orbital of the metal atom overlaps with an orbital on C atom of carbon monoxide containing a lone pair of electrons.

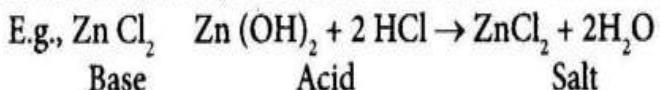


Formation of  $\pi$ -bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding  $\pi^*$  orbital of C atom of carbon monoxide. This overlap is also called back donation of electrons by metal to carbon.

## SALT ANALYSIS

### 20.1 INTRODUCTION

Qualitative analysis of inorganic compounds involves the identification of radicals (cations and anions) in an inorganic salt or in a mixture of salt. A salt consists of two parts known as radicals. The positively charged part of a salt (cation), derived from a base is termed as a basic radical and the negatively charged part of the salt (anion) derived from an acid is termed as an acidic radical.



So, the salt  $\text{ZnCl}_2$  contains  $\text{Zn}^{2+}$  as the basic radical and  $\text{Cl}^-$  as the acidic radical.

#### 20.1.1 Physical Appearance of Inorganic Salt

S. No.	Inorganic Salt	Colour	S. No.	Inorganic Salt	Colour
1.	$\text{Cu}^{+2}$	Blue	2.	$\text{Cr}^{+3}, \text{Cr}^{+6}$	Dark green
3.	$\text{Fe}^{+2}$	Green	4.	$\text{Fe}^{+3}$	Yellow or brown
5.	$\text{Mn}^{+2}$	Light pink	6.	$\text{Co}^{+2}$	Pink
7.	$\text{Ni}^{+2}$	Green or blue	8.	$\text{HgO}, \text{HgI}_2, \text{Pb}_3\text{O}_4$	Red
9.	Salt of Pb, Hg, Bi and Ba	Relatively heavier.			

- Heavier salts are salts of Pb, Hg, Bi and Ba.
- Lighter salts are carbonates of Be, Mg, Al, Zn, Ca and Sr.
- Deliquescent substances are  $\text{CdCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{MnCl}_2$ , nitrates and nitrites.

#### 20.1.2 Characteristic Colour Changes in Hot and Cold

Cold	Hot	Inference	Cold	Hot	Inference
Red	Chocolate	$\text{Pb}_3\text{O}_4$	Red	Black	$\text{HgO}$
Scarlet	Black	$\text{HgS}$	Crimson	Yellow	$\text{HgI}_2$
Yellow	Brown	$\text{Bi}_2\text{O}_3$	White	Yellowish brown	$\text{SnO}_2$

Cold	Hot	Inference	Cold	Hot	Inference
White	Orange is yellow	ZnO	Violet	Green	Chromic salts
Yellow	Brownish black	FeCl <sub>3</sub> ·6H <sub>2</sub> O	Red	Violet	CoI <sub>2</sub> ·6H <sub>2</sub> O
Red	Green	CoBr <sub>2</sub> ·6H <sub>2</sub> O	Blue	White	CuSO <sub>4</sub> ·5H <sub>2</sub> O

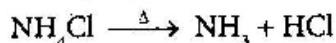
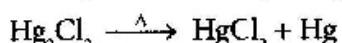
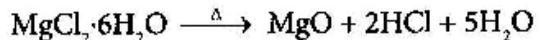
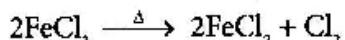
### 20.1.3 Action of Heat

1. All carbonates except (Na, K, Rb and Cs) decompose on heating, giving CO<sub>2</sub>.

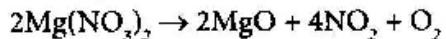
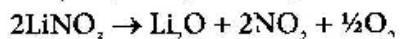
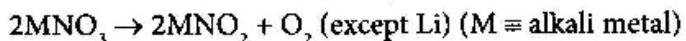
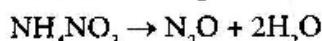


2. All bicarbonates decompose to give carbonates and CO<sub>2</sub>. 2 NaHCO<sub>3</sub>  $\xrightarrow{\Delta}$  Na<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O + CO<sub>2</sub>

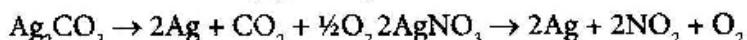
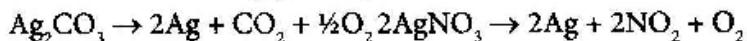
3. Halides are normally stable to heat; however, some halides decompose as



4. Nitrates decompose on heating



5. Silver salt on heating gives Ag.



### 20.1.4 Solubility of Salts

- (i) Nitrates, acetates and nitrites of all the metals are water soluble.
- (ii) All sulphates except (Pb, Ba and Sr) are water soluble. CaSO<sub>4</sub> is slightly soluble in water.
- (iii) Halides of Ag, Pb, mercurous and cuprous forms are insoluble. The order of their solubility is fluoride > chloride > bromide > iodide.
- (iv) CaF<sub>2</sub> is insoluble in water, other halides of Ca are soluble.

### 20.1.5 Colour of the Sublimate

If the substance sublimes and the colour of the sublimate is

S. No.	Colour	Name of Sublimate
1.	White	HgCl <sub>2</sub> , Hg <sub>2</sub> Cl <sub>2</sub> , As <sub>2</sub> O <sub>3</sub> , Sb <sub>2</sub> O <sub>3</sub>
2.	Yellow	AlCl <sub>3</sub> and NH <sub>4</sub> X (where X is F, Cl, Br or I)
		As <sub>2</sub> S <sub>3</sub> and HgI <sub>2</sub> (turns red when rubbed with glass rod)
3.	Grey	HgO, Hg(NO <sub>3</sub> ) <sub>2</sub>
4.	Blue-black or violet	Iodides
5.	Black	As, Sb, Hg sulphides and iodides

## 20.2 DRY TESTS

### 20.2.1 Classification of Ores

Ores may be divided into four groups. Following tests are performed in dry state.

- (i) Flame test
- (ii) Borax bead test
- (iii) Charcoal cavity test
- (iv) Micro cosmic salt bead test
- (v) Cobalt nitrate charcoal test

### 20.2.2 Flame test

Some volatile salts impart characteristic colour to the non-luminous flame. The platinum wire fused in a glass rod is heated in the flame till it imparts colourless flame. The tip of the wire is now dipped in conc. HCl and then into the substance. The tip of the wire is strongly heated in the non-luminous flame and the colour of the flame is observed by the naked eye.

S. No.	Observation	Inference
1.	Substance melts	Salts of alkali metals and salts having water of crystallization.
2.	Substance decomposes (crackling noise)	NaCl, KI, Pb(NO <sub>3</sub> ) <sub>2</sub> and Ba(NO <sub>3</sub> ) <sub>2</sub>
3.	Substance swells (due to loss of water following crystallization)	Alums, borates and phosphates
4.	Gas is evolved	
	(a) Colourless and odourless	
	(i) O <sub>2</sub> - rekindles a glowing splinter	Alkali nitrates $2\text{KNO}_3 \rightarrow 2\text{KNO}_2 + \text{O}_2$
	(ii) CO <sub>2</sub> - turns lime water milky	Carbonates and oxalates $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
	(iii) N <sub>2</sub>	Ammonium nitrite $\text{NH}_4\text{NO}_2 + 2\text{H}_2\text{O}$
	(b) Colourless gas with odour	
	(i) NH <sub>3</sub> - turns red litmus blue and mercurous nitrate paper black	Ammonium salts $(\text{NH}_4)_2\text{SO}_4 \rightarrow \text{NH}_4\text{HSO}_4 + \text{NH}_3$
	(ii) SO <sub>2</sub> - Smell of burning sulphur, turns acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> paper green	Sulphites and thiosulphates $\text{CaSO}_3 \rightarrow \text{CaO} + \text{SO}_2$
	(iii) HCl - Pungent smell, white fumes with NH <sub>3</sub>	Hydrated chlorides $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 4\text{H}_2\text{O} + 2\text{HCl}$
	(iv) H <sub>2</sub> S - Smell of rotten eggs, turns lead acetate paper black	Sulphides $\text{Na}_2\text{S} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2\text{S}$
	(c) Coloured gas	
	(i) NO <sub>2</sub> - Brown, turns starch iodide paper blue	Nitrites and nitrates of heavy metals $2\text{Cu}(\text{NO}_3)_2 \rightarrow 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$

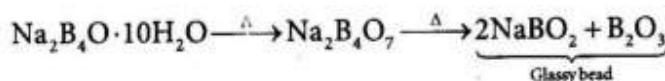
S. No.	Observation	Inference
	(ii) $\text{Br}_2$ - Reddish brown (A) Turns starch paper yellow (B) Turns starch iodide paper blue	Bromides $2\text{CdBr}_2 + \text{O}_2 \rightarrow 2\text{CdO} + 2\text{Br}_2$
	(iii) $\text{I}_2$ - Violet, turns starch paper blue	Iodides $2\text{CdI}_2 + \text{O}_2 \rightarrow 2\text{CdO} + 2\text{I}_2$
	(iv) $\text{Cl}_2$ -greenish yellow (A) Bleaches moist litmus paper (B) Bleaches indigo solution (C) Turns starch iodide paper blue	Chlorides $\text{CuCl}_2 + \text{H}_2\text{O} \rightarrow \text{CuO} + 2\text{HCl}$ $\text{CuO} + 2\text{HCl} \rightarrow \text{Cu} + \text{H}_2\text{O} + \text{Cl}_2$

S. No.	Colour of salt	Inference
1.	Pale greenish	Lead
2.	Green with a blue centre	$\text{Cu}$ salt, $\text{BO}_3^{3-}$
3.	Brick red	Ca
4.	Red	Li
5.	Golden yellow	Na
6.	Violet (lilac)	K
7.	Violet (reddish)	Rb
8.	Violet (bluish)	Cs
9.	Crimson red	Sr
10.	Apple green	Ba

- Be and Mg do not give flame test.
- Flame test should not be performed in the presence of As, Sb, Bi, Sn and Pb as these radicals form an alloy with platinum and hence, the wire is spoiled.
- The white salt with colourless solution cannot have Cu, Ni, Co, Fe, Mn, Cr, etc.

### 20.2.3 Borax Bead Test

On heating borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) on a loop of platinum wire, a transparent colourless glassy bead of sodium metaborate and boric anhydride is formed.



On heating coloured salt on the glassy bead, a coloured metaborate is formed in the oxidizing flame.  
 $\text{CuSO}_4 \rightarrow \text{CuO} + \text{SO}_3$ ;  $\text{CuO} + \text{B}_2\text{O}_3 \rightarrow \text{Cu}(\text{BO}_2)_2$

#### Copper metaborate (blue)

Similarly,  $\text{CoO} + \text{B}_2\text{O}_3 \rightarrow \text{Co}(\text{BO}_2)_2$ .

#### Cobalt metaborate (blue)

The metaborates posses different characteristic colours in oxidizing flame and reducing flame.

The different colours, in the reducing flame may be due to different reactions. E.g., copper metaborate may be reduced to colourless cuprous metaborate or to metallic copper which appears red and opaque.



Metal	Colour of bead in			
	Oxidizing Flame		Reducing Flame	
	Hot	Cold	Hot	Cold
Copper ( $\text{Cu}^{+2}$ )	Green	Blue	Colourless	Brown red
Iron ( $\text{Fe}^{+2}$ )	Yellowish brown	Pale yellow	Bottle green	Bottle green
Chromium ( $\text{Cr}^{+3}$ )	Green	Green	Green	Green
Cobalt ( $\text{Co}^{+2}$ )	Blue	Blue	Blue	Blue
Manganese ( $\text{Mn}^{+2}$ )	Violet	Amethyst red	Grey	Grey
Nickel ( $\text{Ni}^{+2}$ )	Violet	Grey	Grey	Grey

#### 20.2.4 Charcoal Cavity Test

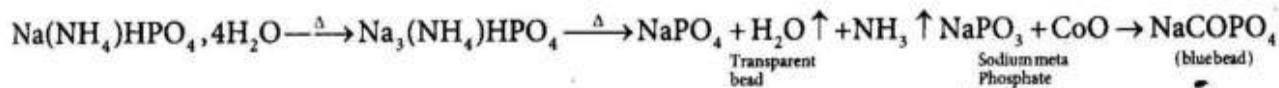
This test is carried out on a charcoal block having a small cavity in it. Little substance is mixed with anhydrous  $\text{Na}_2\text{CO}_3$  or fusion mixture is placed in the cavity. The mass is moistened with a drop of water and heated in a reducing flame with the blow pipe. Metallic salt on heating with  $\text{Na}_2\text{CO}_3$  gives metal carbonate which decomposes into metal.



S. No.	Observation	Inference
1.	<b>Formation of metallic bead</b>	
	(a) Lustrous white, malleable	Ag
	(b) Greyish white, marks paper	Pb
	(c) White, does not mark paper	Sn
	(d) Red	Cu
2.	<b>Incrustation with metal</b>	
	(a) White incrustation, brittle metal	Sb
	(b) Yellow incrustation, brittle metal	B
	(c) Yellow incrustation, malleable metal	Pb
3.	<b>Incrustation without metal</b>	
	(a) White and yellow when hot	$\text{ZnO}, \text{SnO}$
	(b) Yellow and orange when hot	$\text{BiO}$
	(c) Brown	$\text{CdO}$
	(d) White (volatile, garlic odour)	$\text{As}_2\text{O}_3$

#### 20.2.5 Microcosmic Salt Bead Test

When microcosmic salt is heated on a loop of Pt wire, a colourless transparent bead of sodium metaphosphate is formed.



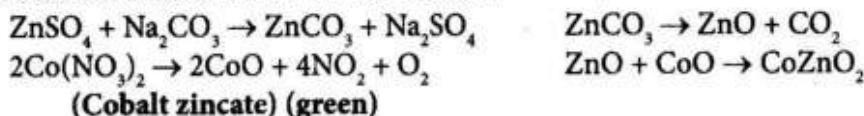
Sodium metaphosphate combines with metallic oxides to form orthophosphates which are usually coloured.

Metal	Colour of bead in			
	Oxidizing Flame		Reducing Flame	
	Hot	Cold	Hot	Cold
Copper ( $\text{Cu}^{+2}$ )	Green	Blue	Colourless	Red
Iron ( $\text{Fe}^{+2}$ )	Yellow or reddish Brown	Yellow	Yellow	Colourless
Chromium ( $\text{Cr}^{+3}$ )	Green	Green	Green	Green
Manganese ( $\text{Mn}^{+2}$ )	Violet	Violet	Colourless	Colourless
Cobalt ( $\text{Co}^{+2}$ )	Blue	Blue	Blue	Blue
Nickel ( $\text{Ni}^{+2}$ )	Brown	Brown	—	Grey

### 20.2.6 Cobalt Nitrate Charcoal Test

A small amount of the substance with twice its bulk of sodium carbonate is placed in the charcoal cavity. A drop of water is added and the mass is heated in an oxidizing flame with the help of a blow pipe. After cooling, one or two drops of cobalt nitrate solution are added and the mass is again heated in the oxidizing flame.

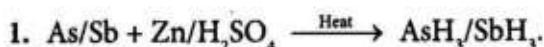
By heating the salt with sodium carbonate, the oxide is formed which on heating with cobalt nitrate form a mixed oxide of a characteristic colour.



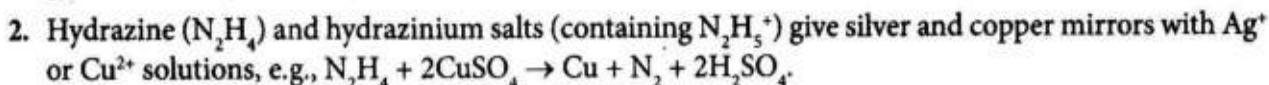
The colour produced in cavity is noticed.

	Observation	Inference
(a)	Blue mass	Aluminium
(b)	Green residue	Zinc
(c)	Pink residue	Magnesium
(d)	Bluish green	Tin

### 20.2.7 Mirror Test



When passed through a heated glass tube,  $\text{AsH}_3$  and  $\text{SbH}_3$  give a silver mirror due to decomposition of unstable hydrides.  $\text{SbH}_3$ , being more unstable, gives a mirror (of Sb) before the flame only and  $\text{AsH}_3$ , gives a mirror (of arsenic) after the flame.



### 20.3 TEST FOR ACID RADICALS

1. Add dil.  $HCl/H_2SO_4$  to a small amount of substance and warm gently. Observe.

Radical <sup>-2</sup>	Test/Observation/Analysis	Reaction
1. $CO_3^{2-}$ (carbonate)	(i) Brisk effervescence of colourless gas ( $CO_2$ ) (ii) The gas turns lime water milky (iii) Excess of passage of gas through lime water removes milkiness	$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$ $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$ milky
2. $SO_3^{2-}$ (sulphite)	(i) Colourless gas with suffocating odour of burning sulphur ( $SO_2$ ) (ii) The gas turns moistened paper with acidified $K_2Cr_2O_7$ , green (iii) The sulphites also give a white ppt. with $BaCl_2$ , soluble in dil. $HCl$	$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$ (soluble) $CaSO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + SO_2$ $K_2Cr_2O_7 + H_2SO_4 + 2SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$ (green) $Na_2SO_3 + BaCl_2 \rightarrow 2NaCl + BaSO_3 \downarrow$
3. $S^{2-}$ (sulphide)	Colourless gas with smell of rotten eggs ( $H_2S$ ) The gas turns lead acetate paper black The sulphide also turns sodium nitroprusside solution violet	$CaS + H_2SO_4 \rightarrow CaSO_4 + H_2S$ $(CH_3COO)_2Pb + H_2S \rightarrow PbS \downarrow + 2CH_3COOH$ (black) $Na_2S + Na_2[FeNO(CN)_5] \rightarrow Na_4[Fe(NOS)(CN)_5]$ (violet)
4. $CH_3COO^-$ (acetate)	Smell of vinegar comes out, may be acetate The acetate gives blood red colour with neutral $FeCl_3$ solution (after removing $CO_3^{2-}$ , $SO_3^{2-}$ , $PO_4^{3-}$ and $F^-$ , ions by adding $AgNO_3$ , since these also combine with $Fe^{3+}$ )	$(CH_3COO)_2Ca + H_2SO_4 \rightarrow 2CH_3COOH + CaSO_3$ , (vinegar smell) $3(CH_3COO)_2Ca + 2FeCl_3 \rightarrow 2Fe(CH_3COO)_3 + 3CaCl_2$ blood red coloration
5. $NO_2^-$ (nitrite)	(i) Reddish brown vapours of $NO_2$ come out, may be nitrite (ii) The gas turns acidified $KI +$ Starch paper blue	$2KNO_2 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_2$ $3HNO_2 \rightarrow HNO_3 + 2NO + H_2$ $2NO + O_2 \rightarrow 2NO_2$ $2KI + 2NO_2 \rightarrow 2KNO_2 + I_2$ Starch + $I_2 \rightarrow$ Blue colour

□ Remember! If cation (e.g.,  $Pb^{2+}$ ,  $Ba^{2+}$ , etc.) forms an insoluble precipitate with  $HCl$  and/or  $H_2SO_4$ , the reaction may stop after sometime, e.g., if dil.  $H_2SO_4$  is added to  $PbCO_3$  or  $BaCO_3$ , effervescence will be observed initially but reaction will stop quickly because of formation of a layer of  $PbSO_4$  or  $BaSO_4$  on carbonate.  $CaCO_3$  will dissolve in dil.  $HCl$  (since  $CaCl_2$  is water soluble) but not in dil.  $H_2SO_4$  (since  $CaSO_4$  will cover the surface and prevent further reaction). In such cases, dil.  $HNO_3$  should be used.

□  $SO_2$  also turns lime water milky due to formation of  $CaSO_3$ . Milkiness disappears on prolonged passage due to formation of soluble calcium bisulphite  $Ca(HSO_3)_2$ .

2. Add Conc.  $H_2SO_4$  to a small amount of the substance and warm gently. Observe.

Radical <sup>v</sup>	Test/Observation/Analysis	Reaction
6. $Cl^-$ (Chloride)	<ul style="list-style-type: none"> <li>(i) Colourless fuming gas (HCl) with pungent smell</li> <li>(ii) The chlorides give white precipitate with <math>AgNO_3</math>, soluble in <math>NH_4OH</math>.</li> </ul> <p>White precipitate of <math>AgCl</math> reappears on adding <math>HNO_3</math></p> <ul style="list-style-type: none"> <li>(iii) Chromyl chloride test (not given by covalent chlorides, e.g., <math>Hg_2Cl_2</math>)</li> </ul> <p>On heating chloride salt with <math>K_2Cr_2O_7</math> and Conc. <math>H_2SO_4</math> orange red vapours of chromyl chloride (<math>CrO_2Cl_2</math>) come out</p> <ul style="list-style-type: none"> <li>(a) on heating chloride salt with <math>K_2Cr_2O_7</math> and Conc. <math>H_2SO_4</math> (a) <math>4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O</math></li> <li>(b) <math>CrO_2Cl_2 + 4NaOH \rightarrow Na_2CrO_4 + 2NaCl + 2H_2O</math></li> <li>(c) <math>Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow 2CH_3COONa + (CH_3COO)_2Pb + PbCrO_4 \downarrow</math> (yellow ppt.)</li> </ul> <p>(c) Acidified solution of <math>Na_2CrO_4</math> given yellow ppt. with (c) Acidified solution of <math>Na_2CrO_4</math> given yellow ppt. with (c) Acidified solution of <math>Na_2CrO_4</math> given yellow ppt. with</p> <ul style="list-style-type: none"> <li>(a) Brown vapours (<math>Br_2</math>) come out (<math>Br^-</math> or <math>NO_3^-</math>, possible)</li> <li>(b) The bromide gives light yellow precipitate with <math>AgNO_3</math>, that is partially soluble in <math>NH_4OH</math></li> <li>(c) Brown vapours of <math>Br_2</math>, on passing in <math>H_2O</math> give brown colour whereas of <math>NO_2</math>, does not impart any colour to <math>H_2O</math></li> <li>(d) Sodium carbonate extract of bromine on addition of <math>CHCl_3</math>, and chlorine water gives brown layer to <math>CHCl_3</math> (excess chlorine water decolorizes it due to formation of <math>HBrO</math>)</li> </ul>	$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$ $NaCl + AgNO_3 \rightarrow AgCl \downarrow + NaNO_3$ $(light\ yellow)$ $2KBr + Cl_2(\text{water}) \rightarrow 2KCl + Br_2$ $Br_2 + \text{Chloroform} \rightarrow \text{Brown-coloured chloroform}$ $2NaI + H_2SO_4 \rightarrow Na_2SO_4 + 2HI$ $2HI + H_2SO_4 \rightarrow I_2 + 2H_2O + SO_2$ (violet) $I_2 + \text{Starch} \rightarrow \text{Blue-coloured complex}$ $NaI + AgNO_3 \rightarrow AgI \downarrow + NaNO_3$ (yellow) $2KI + Cl_2(H_2O) \rightarrow 2KCl + I_2 + \text{chloroform}$ $\text{violet coloured}$
7. $Br^-$	<ul style="list-style-type: none"> <li>(a) Dark violet fumes (<math>I_2</math>) come out</li> <li>(b) Iodine turns starch blue</li> <li>(c) Iodides give yellow ppt. with <math>AgNO_3</math>, insoluble in <math>NH_4OH</math></li> <li>(d) Similar to <math>Br^-</math></li> </ul>	$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$ $4HNO_3 \rightarrow 2H_2O + O_2 + 4NO_2$ $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$ $6FeSO_4 + 2HNO_3 + 3H_2O \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$ $FeSO_4 + NO \rightarrow [Fe(NO)]SO_4$ (brown ring), Nitrosiferous sulphate $NO_3^- + 8H \rightarrow OH^- + 2H_2O + NH_3$
8. $I^-$ Iodide		
9. $NO_3^-$	<ul style="list-style-type: none"> <li>(a) Brown fumes come out (intensified on adding copper turnings)</li> <li>(b) <b>Brown ring test</b></li> </ul> <p>An aqueous solution of salt is mixed with freshly prepared <math>FeSO_4</math> and conc. <math>H_2SO_4</math> is poured in a test tube from sides, brown ring is developed.</p> <ul style="list-style-type: none"> <li>(c) Boiling nitrate with Al or Zn in Conc. <math>NaOH</math> ammonia is evolved.</li> <li>(not a CT) (<math>NO_3^-</math>, <math>Br^-</math> or <math>I^-</math> may interfere with this test)</li> </ul>	(Continued)

Radical <sup>V</sup>	Test/Observation/Analysis	Reaction
10. $\text{C}_2\text{O}_4^{2-}$ Oxalate	(a) Colourless gas ( $\text{CO} + \text{CO}_2$ ) comes out (b) These gas burn with blue flame at the mouth of test tube (c) A solution of oxalates gives (i) White ppt. with $\text{CaCl}_2$ solution (ii) This ppt. gets dissolved in dil. $\text{H}_2\text{SO}_4$	$\text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{CO} + \text{CO}_2 + \text{Na}_2\text{SO}_4$ $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ (i) $\text{Na}_2\text{C}_2\text{O}_4 + \text{CaCl}_2 \rightarrow \text{CaC}_2\text{O}_4 \downarrow + 2\text{NaCl}$ (white) (ii) $\text{CaC}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{C}_2\text{O}_4 + 2\text{KMnO}_4^+$ $3\text{H}_2\text{SO}_4 + 5\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 8\text{H}_2\text{O} + 10\text{CO}_2$
11. $\text{SO}_4^{2-}$ Sulphate	A small amount of substance + Conc. $\text{HNO}_3$ ; heat this mixture and add $\text{Na}_2\text{SO}_4 + 2\text{HNO}_3 \rightarrow 2\text{NaNO}_3 + \text{H}_2\text{SO}_4$ $\text{BaCl}_2$ . White ppt. insoluble in any acid or alkali, sulphate is confirmed. $\text{H}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 \downarrow + 2\text{HCl}$ (white) ( $\text{Ag}^+$ or $\text{Pb}^{2+}$ , if present, will also give ppt. with $(\text{Cl}^-)$ )	
12. $\text{PO}_4^{3-}$ Phosphate	(a) Add Conc. $\text{HNO}_3$ to small amount of substance, heat and then add ammonium excess molybdate yellow ppt. confirms the presence of phosphate. (• ppt. dissolves in excess phosphate) (• as also gives yellow ppt. of $(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3$ )	(a) $\text{Na}_3\text{PO}_4 + 3\text{HNO}_3 \rightarrow 3\text{NaNO}_3 + \text{H}_3\text{PO}_4$ (b) $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3$ Amm. molybdate $\rightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \downarrow + 12\text{H}_2\text{O} + 21\text{NH}_4\text{NO}_3$ Amm. phosphomolybdate (yellow ppt.)

Grp. No.	Radical <sup>V</sup>	Test/Observation/Analysis	Reaction
I Group	$\text{Hg}^{2+}$ , $\text{Ag}^+$ , $\text{Pb}^{2+}$	Add dil. $\text{HCl}$ to clear solution of substance white ppt. indicates the presence of $\text{Hg}^+$ , $\text{Ag}^+$ or $\text{Pb}^{2+}$	$2\text{HgNO}_3 + 2\text{HCl} \rightarrow \text{Hg}_2\text{Cl}_2 \downarrow + 2\text{HNO}_3$ $\text{AgNO}_3 + \text{HCl} \rightarrow \text{AgCl} \downarrow + \text{HNO}_3$ $\text{Pb}(\text{NO}_3)_2 + 2\text{HCl} \rightarrow \text{PbCl}_2 \downarrow + 2\text{HNO}_3$
	(a) $\text{Pb}^{2+}$	$\text{Pb}^{2+}$ ions gives yellow ppt. with $\text{K}_2\text{CrO}_4$ and $\text{KI}$ separately	$\text{PbCl}_2 + \text{K}_2\text{CrO}_4 \rightarrow \text{PbCrO}_4 \downarrow + 2\text{KCl}$ (yellow) $\text{PbCl}_2 + 2\text{KI} \rightarrow \text{PbI}_2 \downarrow + 2\text{KCl}$ (yellow)
	(b) $\text{Hg}_2^{2+}$	$\text{Hg}_2^{2+}$ ions gives black ppt. with $\text{NH}_3$ , $\text{Hg}_2\text{Cl}_2 + 2\text{NH}_3\text{OH} \rightarrow \text{Hg}(\text{NH}_3)_2\text{Cl} + \text{Hg} \downarrow$ (black) +	$\text{Hg}_2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Hg}(\text{NH}_3)_2\text{Cl} + 2\text{H}_2\text{O}$
(c) $\text{Ag}^+$	1. $\text{AgCl}$ is soluble in $\text{NH}_3\text{OH}$ 2. $\text{Ag}^+$ ions give (a) yellow ppt. with $\text{KI}$ 3. Red ppt. with $\text{K}_2\text{CrO}_4$	1. $\text{AgCl} + 2\text{NH}_3\text{OH} \rightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl} + 2\text{H}_2\text{O}$ 2. $\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI} \downarrow$ (yellow) 3. $\text{K}_2\text{CrO}_4 + 2\text{Ag}^+ \rightarrow \text{Ag}_2\text{CrO}_4 + 2\text{K}^+$ (red)	(Continued)

Grp. No.	Radical <sup>v</sup>	Test/Observation/Analysis	Reaction
II Group	Hg <sup>+2</sup> , Pb <sup>+2</sup> , Cu <sup>+2</sup> , Cd <sup>+2</sup> , Bi <sup>+3</sup> (IIA), As <sup>+3</sup> , Sb <sup>+3</sup> , Sn <sup>+2</sup> , Sn <sup>+4</sup> (IIB), Cd <sup>+2</sup> , As <sup>+3</sup> , Sn <sup>+4</sup> , Sb <sup>+3</sup> , Sn <sup>+2</sup> , Hg <sup>+2</sup> , Pb <sup>+2</sup> , Bi <sup>+3</sup> , Cu <sup>+2</sup>	The ppt. obtained can be distinguished by treating with yellow ammonium sulphide ( $\text{NH}_4$ ) <sub>2</sub> S, to give insoluble IIA and soluble IIB parts.	
II A	(d) Hg <sup>+2</sup>	Hg <sup>+2</sup> ion in solution, on addition of SnCl <sub>2</sub> , give white ppt. turning black copper turnings in HgCl <sub>2</sub> , give grey deposit	$\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \rightarrow \text{SnCl}_4 + 2\text{Hg}\downarrow$ Black
	(e) Pb <sup>+2</sup>	1. Pb <sup>+2</sup> ions in solution give white ppt. with H <sub>2</sub> SO <sub>4</sub> 2. Pb <sup>+2</sup> ions in solution give yellow ppt. with K <sub>2</sub> CrO <sub>4</sub> and KI (separately)	Pb <sup>+2</sup> + H <sub>2</sub> SO <sub>4</sub> → PbSO <sub>4</sub> ↓ + 2H <sup>+</sup> Pb <sup>+2</sup> + CrO <sub>4</sub> <sup>-2</sup> → PbCrO <sub>4</sub> ↓ (yellow) Pb <sup>+2</sup> + 2I <sup>-</sup> → PbI <sub>2</sub> (yellow)
	(f) Cu <sup>+2</sup>	1. These ions in solution give deep blue colour with excess of NH <sub>4</sub> OH 2. Cu <sup>+2</sup> ions give chocolate ppt. with K <sub>4</sub> Fe(CN) <sub>6</sub>	Cu <sup>+2</sup> + 4NH <sub>4</sub> OH → Cu(NH <sub>3</sub> ) <sub>4</sub> <sup>+2</sup> + 4H <sub>2</sub> O (deep blue in colour) 2Cu <sup>+2</sup> + K <sub>4</sub> Fe(CN) <sub>6</sub> → Cu <sub>4</sub> [Fe(CN) <sub>6</sub> ] <sub>3</sub> <sup>4-</sup> + 4K <sup>+</sup> chocolate or red brown ppt.
	(g) Bi <sup>+3</sup>	1. Bi gives white ppt. with NH <sub>4</sub> OH soluble in dilute HCl 2. Bi <sup>+3</sup> ions in solution of HCl on addition of water give white cloudy ppt.	BiCl <sub>3</sub> + 3NH <sub>4</sub> OH → Bi(OH) <sub>3</sub> + 3NH <sub>4</sub> C BiCl <sub>3</sub> + H <sub>2</sub> O → BiOCl↓ + 2HCl White bismuth oxychloride 2BiCl <sub>3</sub> + 3Na <sub>2</sub> SnO <sub>3</sub> + 6NaOH → 2Bi↓ + 3Na <sub>2</sub> SnO <sub>3</sub> + 6NaCl + 3H <sub>2</sub> O (Sod. stannite)
	(h) Cd <sup>+2</sup>	Cadmium gives soluble complex with NH <sub>4</sub> OH Cd <sup>+2</sup> ions give yellow ppt. on passing H <sub>2</sub> S	(black) sod. stannate CdSO <sub>4</sub> + 4NH <sub>4</sub> OH → [Cd(NH <sub>3</sub> ) <sub>4</sub> ]SO <sub>4</sub> + 4H <sub>2</sub> O Tetramine Cad. sulphate colourless [Cd(NH <sub>3</sub> ) <sub>4</sub> ]SO <sub>4</sub> + H <sub>2</sub> S → CdS↓ + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 2NH <sub>3</sub> (yellow)

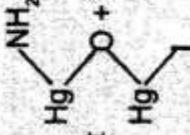
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Grp. No.	Radical <sup>v</sup>	Test/Observation/Analysis	Reaction
II B	(i) $\text{As}^{+3}$	As <sup>+3</sup> ions in solution give yellow ppt. with ammonium molybdate and $\text{HNO}_3$	$\text{As}^{+3} \xrightarrow{\text{HNO}_3} \text{As}^{+5}$ (as $\text{H}_3\text{AsO}_4$ ) $\text{H}_3\text{AsO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 \rightarrow (\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3 \downarrow + 21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$ (yellow)
	(j) $\text{Sn}^{+2}$	$\text{Sn}^{+2}$ ions in solution as $\text{SnCl}_2$ give white ppt. with $\text{HgCl}_2$ , turning black on standing	$\text{SnCl}_2 + 2\text{HgCl}_2 \rightarrow \text{SnCl}_4 + \text{Hg}_2\text{Cl}_2 \downarrow$ (White) $\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \rightarrow \text{SnCl}_4 + 2\text{Hg} \downarrow$ (Black)
	(k) $\text{Sn}^{+4}$	aluminium reduces $\text{Sn}^{+4}$ to $\text{Sn}^{+2}$ ion then tested	$\text{SnCl}_4 + \text{Al} \rightarrow 2\text{AlCl}_3 + 3\text{SnCl}_2$ $\text{SnCl}_2 + \text{HgCl}_2 \rightarrow \text{SnCl}_4 + \text{Hg}$ (Black)
	(l) $\text{Sb}^{+3}$	$\text{Sb}^{+3}$ ions in solution as $\text{SbCl}_3$ on addition of water gives white ppt.	$\text{SbCl}_3 + \text{H}_2\text{O} \rightarrow \text{SbOCl} \downarrow + 2\text{HCl}$ white
III Group	Fe <sup>+3</sup> , Cr <sup>+3</sup> & Al <sup>+3</sup>	These ions are precipitated as hydroxides on addition of $\text{NH}_4\text{Cl}$ and $\text{NH}_4\text{OH}$	$\text{Fe}^{+3} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3$ (red ppt.) $\text{Cr}^{+3} + 3\text{OH}^- \rightarrow \text{Cr}(\text{OH})_3$ (green ppt.) $\text{Al}^{+3} + 3\text{OH}^- \rightarrow \text{Al}(\text{OH})_3$ (white ppt.)
	(m) $\text{Al}^{+3}$	Few drops of conc. $\text{HNO}_3$ is also added before test of III gr to oxidise $\text{Fe}^{+2}$ to $\text{Fe}^{+3}$ . White ppt. of $\text{Al}(\text{OH})_3$ is soluble in $\text{NaOH}$ precipitate reappears on boiling with $\text{NH}_4\text{Cl}$ .	$\text{Al}(\text{OH})_3 + \text{NaOH} \rightarrow 2\text{H}_2\text{O} + \text{NaAlO}_2$ <b>Sod. metal aluminate</b>
	(n) $\text{Cr}^{+3}$	Green ppt. of $\text{Cr}(\text{OH})_3$ is soluble in $\text{NaOH} + \text{Br}_2$ water and addition of $\text{BaCl}_2$ to this solution gives yellow ppt.	$\text{NaAlO}_2 + \text{NH}_4\text{Cl} + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{NaCl} + \text{NH}_3$ $\text{Br}_2 + \text{H}_2\text{O} \rightarrow 2\text{HBr} + \text{O}$ $2\text{Cr}(\text{OH})_3 + 4\text{NaOH} + 3\text{O} \rightarrow 2\text{Na}_2\text{CrO}_4 + 5\text{H}_2\text{O}$ $\text{Na}_2\text{CrO}_4 + \text{BaCl}_2 \rightarrow \text{BaCrO}_4 \downarrow + 2\text{NaCl}$ <b>Yellow ppt.</b>
	(o) $\text{Fe}^{+3}$	(i) (a) Brown ppt. of $\text{Fe}(\text{OH})_3$ is dissolved in $\text{HCl}$ and (b) addition of $\text{KCNS}$ to this soln. gives blood red colour (ii) Also on addition of $\text{K}_4[\text{Fe}(\text{CN})_6]$ to this solution a prussian blue colour is obtained	$\text{Fe}(\text{OH})_3 + 3\text{HCl} \rightarrow \text{FeCl}_3 + 3\text{H}_2\text{O}$ $\text{FeCl}_3 + 3\text{KCNS} \rightarrow \text{Fe}(\text{CNS})_3 + 3\text{KCl}$ Ferric thiocyanate <b>Blood red colour</b>
IV Group	$\text{Zn}^{+2}$ , $\text{Mn}^{+2}$ , $\text{Co}^{+2}$ , $\text{Ni}^{+2}$ , $\text{Co}^{+2}$ , $\text{Ni}^{+2}$ , $\text{Zn}^{+2}$ , $\text{Mn}^{+2}$	These ions are precipitated as sulphides on passing $\text{H}_2\text{S}$ in presence of $\text{NH}_4\text{OH}$ Black ( $\text{CoS}$ , $\text{NiS}$ ) ppt. (soluble in aqua regia) White ( $\text{ZnS}$ ) (soluble in $\text{HCl}$ ) Pink ( $\text{MnS}$ ) soluble in $\text{HCl}$ or buff coloured	$2\text{FeCl}_3 + 3\text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl}$ <b>Ferric ferricyanide (Prussian blue)</b> $\text{MCl}_2 + \text{H}_2\text{S} \rightarrow \text{MS} \downarrow + 2\text{HCl}$

(Continued)

Grp. No.	Radical <sup>v</sup>	Test/Observation/Analysis	Reaction
		Solution with $\text{Ni}^{2+}$ or $\text{Co}^{2+}$ + $\text{NaHCO}_3$ + bromine water Apple green colour confirms $\text{Co}^{2+}$ . If no ppt. heat.	$\text{CoCl}_2 + 6\text{NaHCO}_3 \rightarrow \text{Na}_4\text{Co}(\text{CO}_3)_3 + 3\text{H}_2\text{O} + 2\text{NaCl} + 3\text{CO}_2$ $2\text{Na}_4\text{Co}(\text{CO}_3)_3 + \text{H}_2\text{O} \xrightarrow[\text{from Br}_2, \text{water}]{\text{O}} 2\text{Na}_2\text{Co}(\text{CO}_3)_3$ (green coloration)
		$\text{NiCl}_2 + 2\text{NaHCO}_3 \rightarrow \text{NiCO}_3 + 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$ $2\text{NiCO}_3 + \text{O} \rightarrow \text{Ni}_2\text{O}_3 + 2\text{CO}_2$ (black)	
(p) $\text{Ni}^{2+}$		Nickel salt reacts with dimethyl glyoxime (DMG) in presence of $\text{NH}_4\text{OH}$ to give red ppt. of nickel dimethyl glyoxime	$\text{NiCl}_2 + \text{NH}_4\text{OH} \rightarrow \text{CH}_3-\overset{\text{C}=\text{NOH}}{\underset{\text{CH}_3-\overset{\text{(DMG)}}{\text{C}=\text{NOH}}}{\text{N}}}+\text{NiCl}_2 + \text{NH}_4\text{OH}$
			$\text{CH}_3-\overset{\text{OH}}{\text{C}=\text{N}}-\overset{\text{O}}{\underset{\text{CH}_3-\overset{\text{C}=\text{N}}{\text{C}=\text{N}}-\overset{\text{O}}{\underset{\text{OH}}{\text{C}=\text{N}}}}{\text{N}}}+\text{2NH}_4\text{Cl} + 2\text{H}_2\text{O}$
			Nickel dimethylglyoxime (red ppt.)
(q) $\text{Co}^{2+}$		(i) Cobaltous salts gives blue colour with $\text{NH}_4\text{CNS}$ (ii) $\text{CH}_3\text{COOH} + \text{KNO}_2 + \text{Co}^{2+} \rightarrow$ yellow ppt. which dissolves in excess of $\text{NaOH}$	$\text{CoCl}_2 + 4\text{NH}_4\text{CNS} \rightarrow (\text{NH}_4)[\text{CO}(\text{CNS})_4] + 2\text{NH}_4\text{Cl}$ Amm. cabaltothiocyanate (blue colour) $7\text{KNO}_2 + 2\text{CH}_3\text{COOH} + \text{COCl}_2 \rightarrow \text{K}_3\text{CO}(\text{NO}_2)_4$ Yellow $+ 2\text{KCl} + 2\text{CH}_3\text{COOK} + \text{NO} + \text{H}_2\text{O}$
(r) $\text{Zn}^{2+}$		$\text{Zn}^{2+}$ ions in soln. give white ppt. with $\text{NaOH}$ , which dissolves in excess of $\text{NaOH}$	$\text{Zn}^{2+} + 2\text{NaOH} \rightarrow \text{Zn}(\text{OH})_2 \downarrow + 2\text{Na}^+$ White $\text{Zn}(\text{OH})_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O}$ Soluble sod. zincate
(s) $\text{Mn}^{2+}$		(a) $\text{Mn}^{2+}$ ions in soln. give pink ppt. with $\text{NaOH}$ (b) Turning black or brown on heating $\alpha, \beta, \gamma$	$\text{Mn}^{2+} + 2\text{NaOH} \rightarrow \text{Mn}(\text{OH})_2 \downarrow + 2\text{Na}^+$ $\text{Mn}(\text{OH})_2 + \text{O} \xrightarrow{\Delta} \text{MnO}_2 + \text{H}_2\text{O}$ Brown or black

(Continued)

Grp. No.	Radical <sup>V</sup>	Test/Observation/Analysis	Reaction
V Group	Ba <sup>+2</sup> , Sr <sup>+2</sup> Ca <sup>+2</sup>	These ions are precipitated as carbonates on addition of (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> solution  (t) Ba <sup>+2</sup> Ba <sup>+2</sup> ions in solution give (i) Yellow ppt. with K <sub>2</sub> CrO <sub>4</sub> (ii) White ppt. with (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (iii) White ppt. with (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>  (u) Sr <sup>+2</sup> Sr <sup>+2</sup> ions give white ppt. with (i) (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> → (ii) (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> → Ca <sup>+2</sup> ions give white ppt. with only (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (v) Ca <sup>+2</sup> These are tested in the order Ba <sup>+2</sup> then Sr <sup>+2</sup> then Ca <sup>+2</sup> Mg <sup>+2</sup> ions give white ppt. with NH <sub>4</sub> OH and (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> (white)	M <sup>+2</sup> + (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> → MCO <sub>3</sub> + 2NH <sub>4</sub> <sup>+</sup> BaCO <sub>3</sub> , CaCO <sub>3</sub> , SrCO <sub>3</sub> (white) soluble in CH <sub>3</sub> COOH Ba <sup>+2</sup> + K <sub>2</sub> CrO <sub>4</sub> → BaCrO <sub>4</sub> ↓ + 2K <sup>+</sup> yellow Ba <sup>+2</sup> + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> → BaSO <sub>4</sub> ↓ + 2NH <sub>4</sub> <sup>+</sup> (white) Ba <sup>+2</sup> + (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> → BaC <sub>2</sub> O <sub>4</sub> + 2NH <sub>4</sub> <sup>+</sup> (white) Sr <sup>+2</sup> + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> → SrSO <sub>4</sub> ↓ + 2NH <sub>4</sub> <sup>+</sup> (white ppt.) Sr <sup>+2</sup> + (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> → SrC <sub>2</sub> O <sub>4</sub> + 2NH <sub>4</sub> <sup>+</sup> (white ppt.) Ca <sup>+2</sup> + (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> → CaC <sub>2</sub> O <sub>4</sub> + 2NH <sub>4</sub> <sup>+</sup> (white)
VI Group	(w) Mg <sup>+2</sup> Zero group	V. Imp.:  (x) NH <sub>4</sub> <sup>+</sup>	Mg <sup>+2</sup> + (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> + NH <sub>4</sub> OH → MgNH <sub>4</sub> PO <sub>4</sub> + 2NH <sub>4</sub> <sup>+</sup> + H <sub>2</sub> O  (i) (a) All ammonium salts on treating with any alkali (e.g., NaOH) give smell of NH <sub>3</sub> (b) The gas coming out (NH <sub>3</sub> ) shows white fumes with HCl (c) On passing this gas to Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> , a black colour is formed (d) with Nessler's reagent, a brown ppt. is noticed. 2K <sub>2</sub> HgI <sub>4</sub> + 4KOH + NH <sub>4</sub> Cl
			 Nessler's reagent + 7KI + KCl + 3H <sub>2</sub> O <sub>2</sub>   Iodide of Millon's base (brown ppt.)

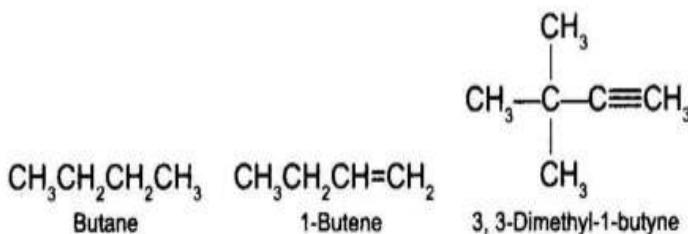
## NOMENCLATURE OF ORGANIC COMPOUNDS

### 21.1 CLASSIFICATION OF ORGANIC COMPOUNDS

All the known organic compounds have been broadly divided into the following classes. These are discussed below

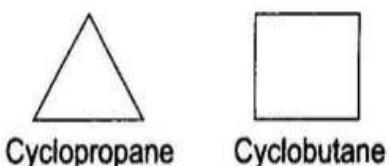
#### 21.1.1 Acyclic Compounds

Example:

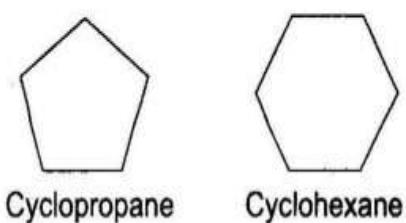


#### 21.1.2 Cyclic Compounds

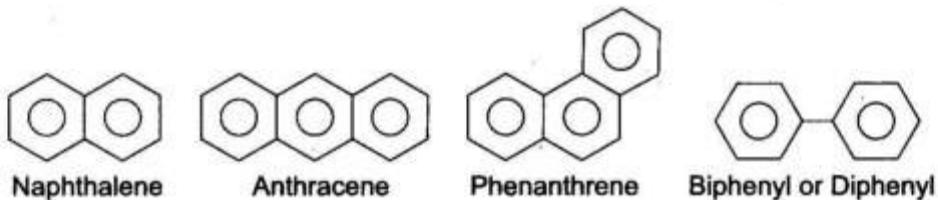
- (a) **Homocyclic compounds:** Contain rings which are made up of only one kind of atoms. These are of two types:



- (i) **Alicyclic compounds:** are carbocyclic compounds which resemble aliphatic compounds in their properties. For example

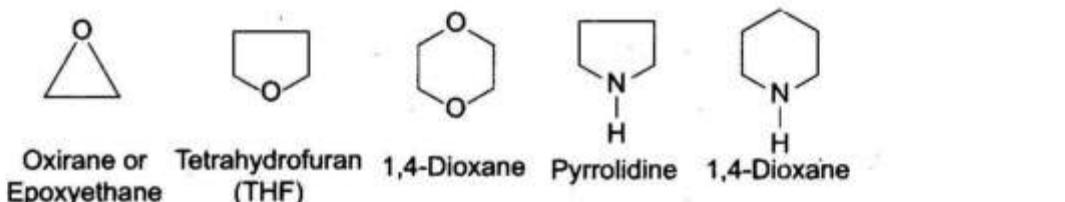


(ii) **Aromatic compounds:** These are also called benzenoid compounds or arenes. For example

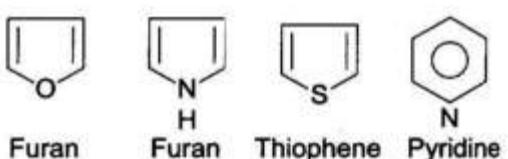


(b) **Heterocyclic compounds:** Cyclic compounds containing one or more heteroatoms (e.g., O,N,S, etc.) in the ring are called heterocyclic compounds. These are of two types:

(i) **Alicyclic heterocyclic compounds:** Heterocyclic compounds which resemble aliphatic compounds in their properties are called alicyclic heterocyclic compounds. For example



(ii) **Aromatic heterocyclic compounds.** Heterocyclic compounds which resemble benzene and other aromatic compounds in most of their properties are called aromatic heterocyclic compounds. For example



## 21.2 SYSTEM OF NOMENCLATURE FOR ORGANIC COMPOUNDS

Nomenclature of organic compounds consists of the following two systems.

### 21.2.1 Trivial System or Derived System

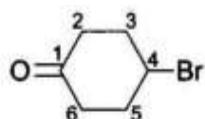
In the trivial system, the name of the compound could indicate a compound source from which it is derived.

Compound	Source	Root Word
Maleic acid	Apples	Malus
Tartaric acid	Grapes	Tartar
Acetic acid	Vinegar	Acetum
Formic acid	Ants	Formical
Citric acid	Lemon	Citrus

### 21.2.2 IUPAC Name or Standard System

According to the IUPAC rule, 'Any given organic structure has only one IUPAC name and any IUPAC name represents only one molecular structure of compound'. The complete IUPAC name of an organic compound consists of the following parts:

Secondary prefix + Primary prefix + Word root + Primary suffix + Secondary suffix



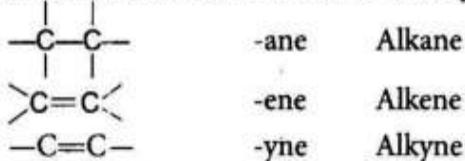
4-Bromo + Cyclo + Hex + an (e)\* +1-one  
 (Sp) (Pp) (Wr) (Ps) (Ss)

- (a) **Root word:** Select the word root to denote the longest possible continuous chain of carbon atoms containing the functional group.

Chain Length	Root Word	Chain Length	Root Word	Chain Length	Root Word
C <sub>1</sub>	Meth-	C <sub>2</sub>	Eth-	C <sub>3</sub>	Prop-
C <sub>4</sub>	But-	C <sub>5</sub>	Pent-	C <sub>6</sub>	Hex-
C <sub>7</sub>	Hept-	C <sub>8</sub>	Oct-	C <sub>9</sub>	Non
C <sub>10</sub>	Dec	C <sub>11</sub>	Undec	C <sub>12</sub>	Dodec
C <sub>13</sub>	Tridec	C <sub>14</sub>	Tetradec	C <sub>15</sub>	Pentadec
C <sub>20</sub>	Eicos				

- (b) **Suffix:** They are of two types:

**Primary suffix.** A primary suffix is added to the word root to indicate whether the carbon chain is saturated or unsaturated. The three basic primary suffixes are:



If the carbon chain contains more than one double or triple bonds, then the name of root word is modified by adding 'a' suffix.

### 21.2.2.1 Secondary Suffix

	Functional group	Suffix	Prefix
1. Carboxylic acids	—COOH	-oic acid	Carboxy
2. Anhydride		-oic anhydride	-----
3. Ester		-oate	Carboalkoxy
4. Acid halide		-oyl halide	Haloformyl or halomethanoyl
5. Amide		-amide	Carbamoyl or carboxamido

<b>6. Cyanides</b>	$\text{—C}\equiv\text{N}$	nitrile	Cyano
<b>7. Isocyanide</b>	$\text{—N}\equiv\text{C}$	isonitrile	Isocyano
<b>8. Aldehydes</b>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—H} \end{array}$	-al	Formyl or methanoyl or aldo
<b>9. Ketones</b>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \end{array}$	-one	Oxo, keto
<b>10. Alcohol</b>	$—\text{OH}$	-ol	Hydroxyl
<b>11. Ethers</b>	$—\text{O—}$	-----	Alkoxy
<b>12. Amines</b>	$—\text{NH}_2$	amine	Amino

(c) **Secondary suffix:** A secondary suffix indicates the functional group present in the organic compound. Some important secondary suffixes are:

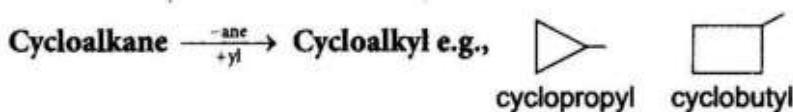
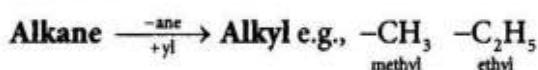
Chain terminating functional group when attached with alicyclic ring have different secondary suffix.

$—\text{C}\equiv\text{N}$	Carbonitrile	$\begin{array}{c} \text{H} \\   \\ \text{—C=O} \end{array}$	Carboldehyde
$\begin{array}{c} \text{OH} \\   \\ \text{—C=O} \end{array}$	Carboxylic acid	$\begin{array}{c} \text{H} \\   \\ \text{—C=O} \end{array}$	Carboxamide
$\begin{array}{c} \text{X} \\   \\ \text{—C=O} \end{array}$	Carbonyl halide	$\begin{array}{c} \text{OR} \\   \\ \text{—C=O} \end{array}$	Carboxylate

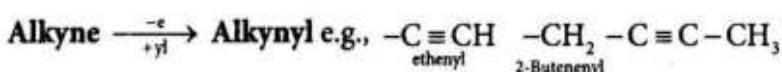
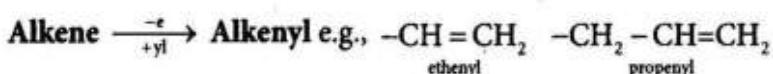
**Prefix:** Prefixes are of two types:

- (a) **Primary prefix:** A primary prefix is used simply to distinguish cyclic compound from acyclic compounds. For example, in case of carbocyclic compounds, a primary prefix cyclo is used immediately before the word root.
- (b) **Secondary prefix:** In the IUPAC system of nomenclature, certain groups are not considered as functional groups but instead are treated as substituents. They are arranged in alphabetical order to denote the substituent or the side chains.

#### Side chain

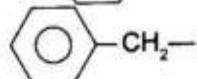


#### Unsaturated side chain



**Aromatic side chain**

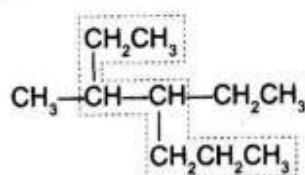
**Phenyl-**φ; Ph-; C<sub>6</sub>H<sub>5</sub>-; 

**Benzyl** C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>- 

## 21.3 RULES FOR WRITING NOMENCLATURE OF ORGANIC COMPOUNDS HAVING NO FUNCTIONAL GROUP

### 21.3.1 Selection of Principal Chain

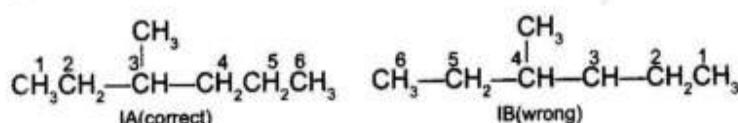
Select the longest continuous chain of carbon atoms containing maximum number of side chains or substituents in the molecule. For example



### 21.3.2 Numbering of Principal Chain

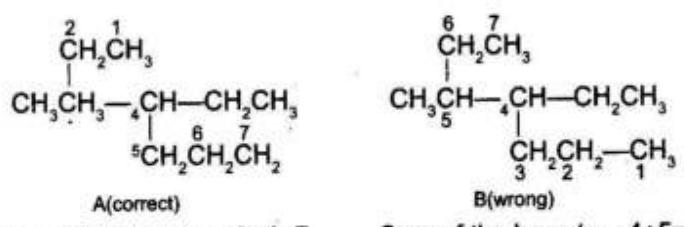
Numbering of principal chain is done on the basis of the following three rules in their given order of priority.

- (a) **Lowest locant rule:** Number the carbon atoms of the parent chain starting from that end which gives the lowest possible number to the carbon atom carrying the substituent.



The number that indicates the position of the substituent on the parent chain is called the positional number or the locant.

- (b) **Lowest sum rule:** When two or more substituents are present, then numbering of the carbon atoms of the parent chain is done in such a way that the sum of locants is the lowest. This is called the lowest sum rule.

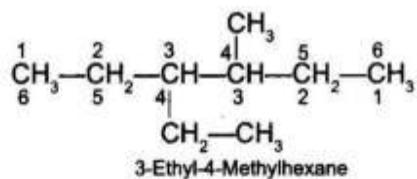


$$\text{Sum of the locants} = 3+4=7$$

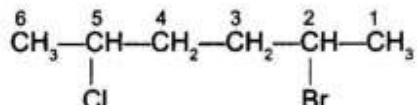
$$\text{Sum of the locants} = 4+5=9$$

- (d) Rule of equivalent position:

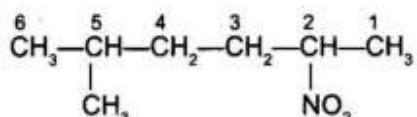
- (i) When two different side chains are present at equivalent positions, the numbering of the parent chain is done in such a way that the side chain which comes first in the alphabetical order (written first in the name) gets the lower number. For example



- (ii) When two different substituents are present at equivalent positions, the numbering of the parent chain is done in such a way that the substituent which comes first in the alphabetical order (written first in the name) gets the lower number. For example



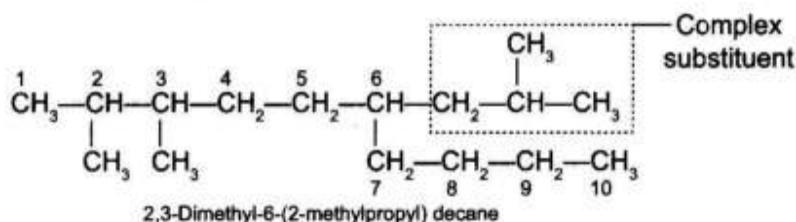
- (iii) When a side chain and a substituent are present at equivalent position, then substituent gets less locant.



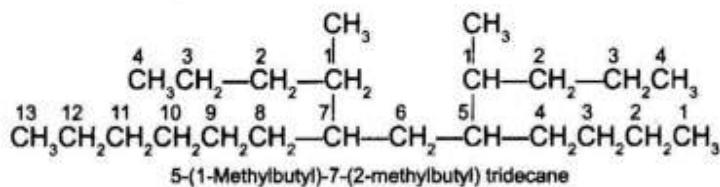
**(e) Naming of the complex substituent:**

If a side chain contains a side chain or a substituent inside is called complex side chain.

The name of such a substituent is always enclosed in brackets to avoid confusion with the numbers of the parent chain. For example

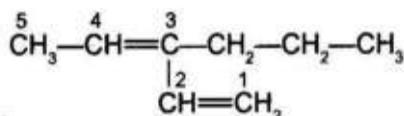


- (b) While deciding the alphabetical order of the various substituents, the name of the complex substituent is considered to begin with the first letter of its complete name.
  - (c) When the names of two or more substituents are composed of identical words, priority of citation is given to that substituent which has the lowest locant at the first cited point of difference within the complex substituent. For example

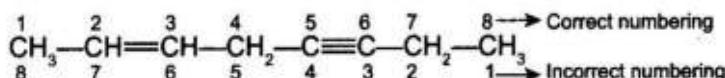


## **21.4 RULES FOR IUPAC NOMENCLATURE OF UNSATURATED HYDROCARBONS**

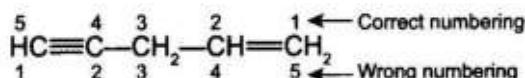
1. The parent chain must contain the multiple bond regardless of the fact whether it also denotes the longest continuous chain of carbon atoms or not. For example



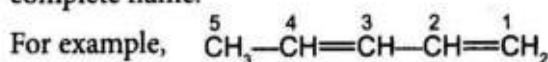
2. If both double and triple bonds are present, the numbering of the parent chain should always be done from that end which is nearer to the double or the triple bond, i.e., the lowest locant rule for the multiple bonds must be followed. For example



3. If, however, there is a choice in numbering the double bond is always given preference over the triple bond. For example



4. If both double and triple bonds are present in the compound, their locants are written immediately before their respective suffixes and the terminal 'e' from the suffix 'ene' is dropped while writing its complete name.



Pent + 3-en(e) + 1-yne

= Pent-3-en-1-yne

## 21.5 IUPAC NOMENCLATURE OF COMPOUNDS CONTAINING FUNCTIONAL GROUP

**Classification of functional group:** Functional groups are of two types as discussed hereunder.

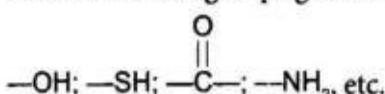
### 21.5.1 Chain Terminating Functional Group

Functional group in which the carbon of functional group is appeared to be trivalent belongs to this category. Carbon of these functional groups always gets number one locant and number is usually not written with these functional group. E.g.,

—CN; —CHO; —COOH; —CONH<sub>2</sub>; —COX; —COOH, etc.

### 21.5.2 Nonchain Terminating Functional Group

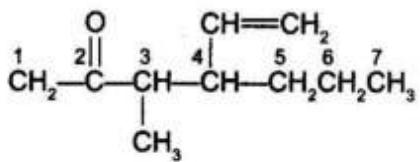
Carbon of these groups gets lowest locant but it may or may not get number one locant. E.g.,



While naming organic compounds containing one functional group, double and triple bonds and substituents, the following additional rules are observed.

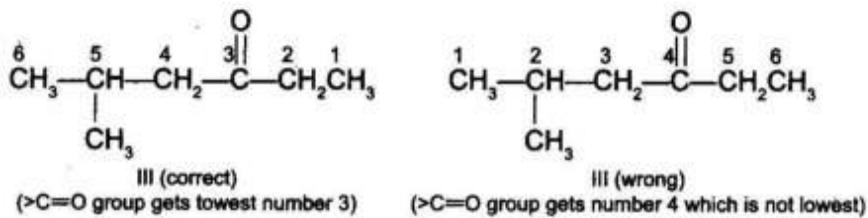
- (a) **Selection of parent chain:** Select the longest possible chain of carbon atoms containing the functional group and the maximum number of multiple bonds as the parent chain without caring

whether it also denotes the longest possible carbon chain or not. Parent chain contains four rather than five carbon atoms

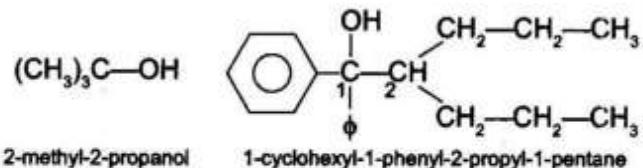


Parent chain contains six rather than seven carbon atoms.

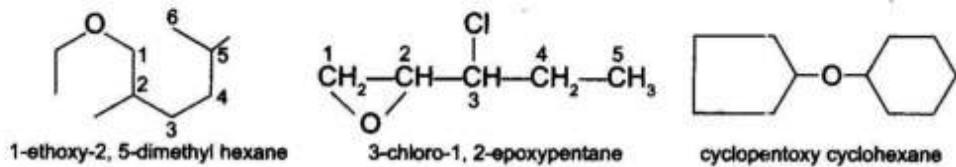
- (b) **Numbering of principal chain:** Number the parent chain in such a way that the functional group gets the lowest possible number followed by double and triple bonds even if it violates the lowest sum rule.



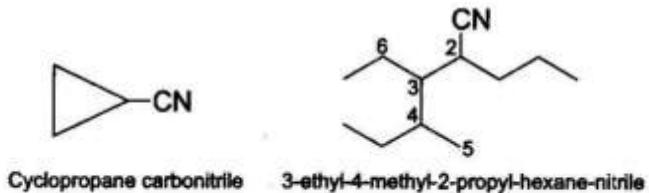
- (c) **IUPAC name of alcohols:** General name: Alkanol. E.g.,



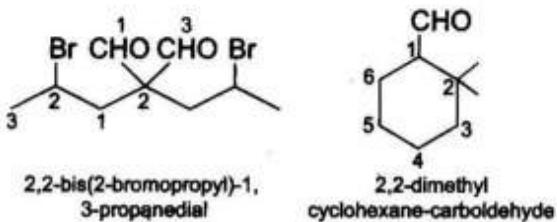
- (d) **IUPAC name of ethers:** General name: Alkoxy alkane or alkoxy cycloalkane



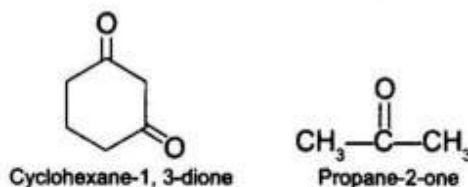
- (e) **IUPAC name of cyanides:** General name: Alkane nitrile or cycloalkane carbonitrile



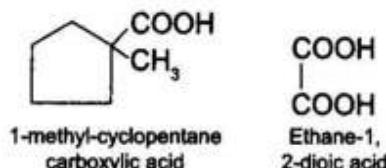
- (f) **IUPAC name of aldehyde:** General name: Alkanal or cycloalkane carboldehyde



(g) IUPAC name of ketones: General name: Alkanone or cycloalkanone

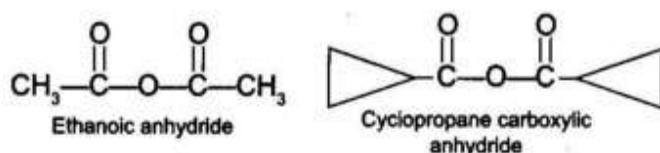


(h) IUPAC name of carboxylic acid: General name: Alkanoic acid or cycloalkane carboxylic acid

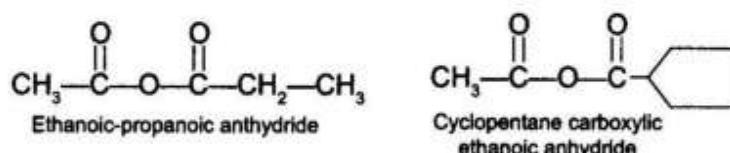


(i) IUPAC name of acid anhydride:

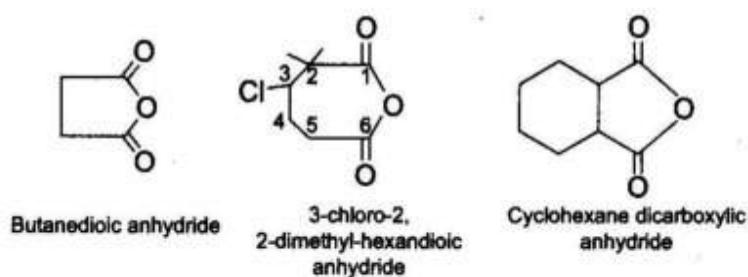
- 1. Simple anhydride:** General name: Alkanoic anhydride or cycloalkane carboxylic anhydride



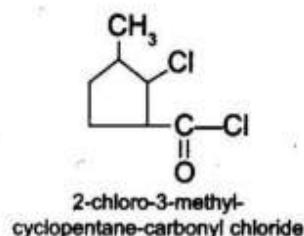
- 2. Mixed anhydride:** General name: Alkanoic alkanoic anhydride or cycloalkane carboxylic cycloalkane carboxylic anhydride or cycloalkane carboxylic alkanoic anhydride.



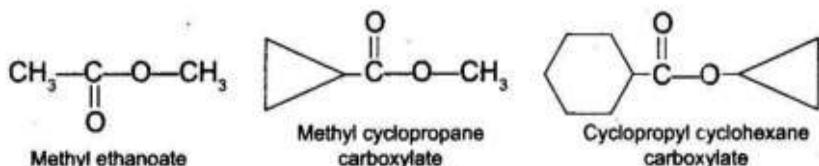
- 3. Cyclic anhydride:** General name: Alkanedioic anhydride or cycloalkane dicarboxylic anhydride.



(j) **IUPAC name of Acid halide:** General name: Alkanoyl halide or cycloalkane carbonyl halide.

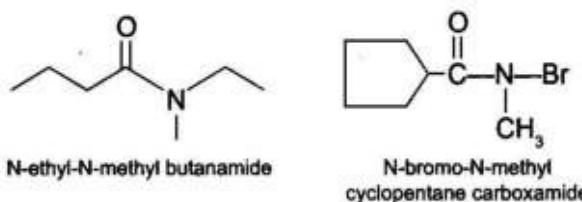


(k) IUPAC name of esters: General name: Alkyl alkanoate or alkyl cycloalkane carboxylate.

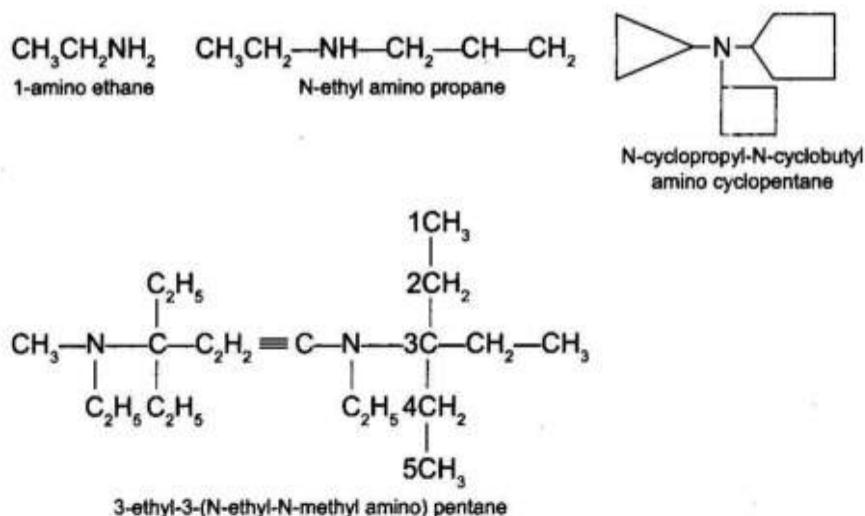


Alkyl group attaches with oxygen atom and in case of ester is always written first though it follows whatsoever order alphabetically.

(l) IUPAC name of amide: General name: Alkanamide or cycloalkane carboxamide.



(m) IUPAC name of amines: General name: Alkanamine (old name) and Amino alkane (new name).



## 21.6 RULES FOR IUPAC NOMENCLATURE OF POLYFUNCTIONAL COMPOUNDS

Organic compounds which contain two or more functional groups are called polyfunctional compounds. Their IUPAC names are obtained as follows:

### 21.6.1 Principal Functional Groups

If the organic compound contains two or more functional groups, one of the functional groups is selected as the principal functional group while all the remaining functional groups (also called the secondary functional groups) are treated as substituents.

### 21.6.2 Selection of the Principal Chain

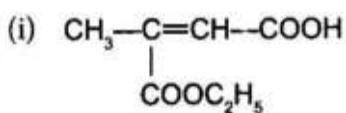
Select the longest continuous chain of carbon atoms containing the principal functional group and maximum number of secondary functional groups and multiple bonds, if any.

### 21.6.3 Numbering of Principal Chain

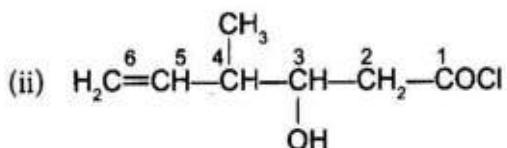
Number the principal chain in such a way that the principal functional group gets the lowest locant followed by double bond, triple bond and the substituents.

### 21.6.4 Alphabetical Order

Identify the prefixes and the locants for the secondary functional groups and other substituents and place them in alphabetical order before the word root as explained hereunder:



IUPAC name: 2-carboethoxybut-2-en-1-oic acid



IUPAC name: 3-hydroxy-4-methylhex-5-yn-1-oyl chloride

## 21.7 NOMENCLATURE OF BICYCLO AND SPIRO COMPOUNDS

### 21.7.1 Bicyclic Compounds

Compounds having two cyclic rings and two shared carbon atoms at the apex are called bicyclic compounds. Numbering in a bicyclic compound starts from one of the bridgehead carbon atom and longest bridge is numbered first followed by longer bridge followed by smallest bridge. This numbering rule is followed even in presence of principal functional group and multiple bond. General rule for writing IUPAC name is Prefixes+Bicyclo [x, y, z] + Root word + Primary suffix + Secondary suffix, where  $x > y > z$ .

### 21.7.2 Spiro Compounds

Compounds having two cyclic rings and one shared quaternary carbon atom are called spiro compounds. Numbering starts from adjacent to bridgehead carbon atom and smaller bridge is numbered first followed by longer bridge. This rule is followed even in presence of principal functional group and multiple bond. General rule for writing IUPAC name is Prefixes + Spiro [x, y] + Root word + Primary suffix + Secondary suffix, where  $x < y$ .

## 21.8 COMMON NAME OF ORGANIC COMPOUNDS

S. No.	Compound	Common Name	Specific Properties, if any
<b>Group A: ALKANES</b>			
1.	$\begin{array}{ccccccc} & \text{CH}_3 & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ &   & & & \\ & \text{CH}_3 & & & \end{array}$	Isopentane	-----
2.	$  \begin{array}{ccccc}  & \text{CH}_3 & & & \\  &   & & & \\  \text{CH}_3 & -\text{C} & -\text{CH}_2 & -\text{CH} & -\text{CH}_3 \\  &   & &   & \\  & \text{CH}_3 & & \text{CH}_3 &   \end{array}  $	Isooctane	Having octane number = 100
3.	$  \begin{array}{ccccc}  & \text{CH}_3 & & & \\  &   & & & \\  \text{CH}_3 & -\text{C} & -\text{CH}_3 & & \\  &   & & & \\  & \text{CH}_3 & & &   \end{array}  $	Neopentane	-----
4.	$  \begin{array}{ccccc}  & \text{CH}_3 & & & \\  &   & & & \\  \text{CH}_3 & -\text{C} & -\text{CH} & -\text{CH}_3 & \\  &   &   & & \\  & \text{CH}_3 & \text{CH}_3 & &   \end{array}  $	Triptane	-----
5.	$  \begin{array}{ccccc}  & \text{CH}_3 & & & \\  &   & & & \\  \text{CH}_3 & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & \\  &   & & & \\  & \text{CH}_3 & & &   \end{array}  $	Iso-pentyl i.e., active amyl	-----
6.	$  \begin{array}{ccccc}  & \text{CH}_3 & & & \\  &   & & & \\  \text{CH}_3 & -\text{CH}_2 & -\text{CH}_2 & -\text{CH}_2 & -\text{CH}_2  \end{array}  $	n-pentyl	Amyl group
<b>Group B: ALKENES</b>			
7.	$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	$\alpha$ -Butylene	-----
8.	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	$\beta$ -Butylene	-----
9.	$  \begin{array}{ccccc}  & \text{CH}_3 & & & \\  &   & & & \\  \text{CH}_3 & -\text{C} & = & \text{CH}_2 & \\  &   & & & \\  & \text{CH}_3 & & &   \end{array}  $	Isobutylene	-----
10.	$\text{CH}_2=\text{CH}-\text{CH}_2-$	Allyl group	-----
11.	$\text{CH}_2=\text{C}=\text{CH}_2$	Allene	-----
12.	$  \begin{array}{ccccc}  & \text{CH}_3 & & & \\  &   & & & \\  \text{CH}_2 & =\text{C} & -\text{CH}=\text{CH}_2 & &   \end{array}  $	Isoprene	-----
13.	$\text{CH}_2=\text{CH}-$	Vinyl group	-----
<b>Group C: ALKYNES</b>			
14.	$\text{CH}\equiv\text{CH}$	Purified acetylene or Norcelyne	-----
15.	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	Vinyl acetylene	-----

16.	$\text{CH}_3-\text{C}\equiv\text{CH}$	Allylene	-----
17.	$\text{HC}\equiv\text{C}-\text{CH}_3$	Propargyl group	-----
<b>Group D: ALKYLHALIDE</b>			
18.	$\text{CH}_3\text{CHCl}_3$	Ethyldene chloride	A gem dihalide
19.	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\   \quad   \\ \text{Cl} \quad \text{Cl} \end{array}$	Ethylene dichloride	A vic dihalide
20.	$\begin{array}{c} \text{CH}_2\text{Cl} \quad \text{CH}_2\text{Cl} \\   \quad   \\ \text{CH}_2-\text{S}-\text{CH}_2 \end{array}$	Mustard gas or sulphur musted	Poisonous; used in war
21.	$\begin{array}{c} \text{CHCl}_2 \\   \\ \text{CHCl}_2 \end{array}$	Westron	Solvent
22.	$\text{ClCH}=\text{CCl}_2$	Westrosol or triclene	Solvent
23.	$\text{Cl}_2\text{C}=\text{CCl}_2$	Tetraclene or perclene	Solvent
24.	$\begin{array}{c} \text{Cl} \\   \\ \text{Cl}-\text{C}-\text{NO}_2 \\   \\ \text{Cl} \end{array}$	Chloropicrin	Tear gas or nitrochloroform
25.	$\begin{array}{c} \text{CCl}_3 \\   \\ \text{CH}_3-\text{C}-\text{CH}_3 \\   \\ \text{OH} \end{array}$	Chloretone	Hypnotic agent used in sleeping pill
26.	$\begin{array}{c} \text{Cl} \\   \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	Chloroprene	A monomer
27.	$\begin{array}{c} \text{H}-\text{C}-\text{Cl} \\    \\ \text{H}-\text{C}-\text{AsCl}_2 \end{array}$	Lewisite	Highly poisonous also called as war gas
<b>Group E: ALCOHOL</b>			
28.	$\begin{array}{c} \text{CH}_2-\text{OH} \\   \\ \text{CH}_2-\text{OH} \end{array}$	Ethylene glycol	Anti-freezing agent
29.	$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2 \\   \quad   \quad   \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	Glycerol	Trihydric alcohol
30.	$\text{CH}\equiv\text{C}-\text{CH}_2-\text{OH}$	Propargyl alcohol	-----
31.	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{OH}$	Allyl alcohol	Vinyl carbinol
32.	$\text{CH}_2=\text{CH}-\text{OH}$	Vinyl alcohol	-----
33.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{OH} \\   \\ \text{CH}_3-\text{C}-\text{OH} \\   \\ \text{CH}_3 \end{array}$	Pinacol	-----

**Group F: ETHER**

34.	$\text{C}_6\text{H}_5-\text{O}-\text{CH}_3$	Anisole	Methyl phenyl ether
35.	$\text{C}_6\text{H}_5-\text{O}-\text{C}_2\text{H}_5$	Phenetole	Ethyl phenyl ether
36.	$\begin{array}{c} \text{H} & \text{OCH}_3 \\   & / \\ \text{H} & \text{C} \\   & \backslash \\ \text{OCH}_3 & \end{array}$	Methyial	Acetal of formaldehyde

**Group G: ALDEHYDE**

37.	$\begin{array}{c} \text{CHO} \\   \\ \text{COOH} \end{array}$	Glyoxalic acid	-----
38.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{CHO} \text{ or } (\text{CH}_3)_3\text{C}-\text{CHO} \\   \\ \text{CH}_3 \end{array}$	Pivaldehyde	-----
39.	$\text{CH}_3\text{CH}=\text{CH}-\text{CHO}$	Crotonaldehyde	-----
40.	$\text{CH}_2=\text{CH}-\text{CHO}$	Acrylaldehyde or acrolein	Having pungent odour
41.	$(\text{CH}_3)_2\text{CHCHO}$	Isobutyraldehyde	-----
42.	$\begin{array}{c} \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \\    \quad    \\ \text{O} \quad \text{O} \end{array}$	Dimethyl glyoxal	-----
43.	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}-\text{CHO} \\   \quad   \\ \text{HO} \quad \text{OH} \end{array}$	Glyceraldehyde	-----
44.	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{H} \\   \\ \text{C}-\text{H} \\ \parallel \\ \text{O} \end{array}$	Glyoxal	-----
45.	$\text{CH}_3-\text{C}-\text{C}-\text{H}$	Methyl glyoxal or pyruvaldehyde	-----

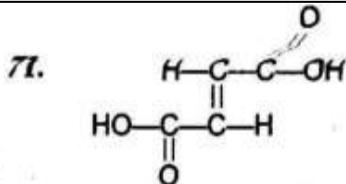
**Group H: KETONE**

46.	$\text{CH}_3\text{COCH}_3$	Acetone	-----
47.	$\begin{array}{c} \text{CH}_3 & & \text{CH}_3 \\ >& \text{C}=\text{CH}-\text{C}-\text{CH}=\text{C} & \\ \text{CH}_3 & & \text{CH}_3 \end{array}$	Phorone	-----
48.	$\begin{array}{c} \text{CH}_3 & & \text{CH}_3 \\ >& \text{C}=\text{CH}-\text{C}-\text{CH}_3 \\ \text{CH}_3 & & \text{O} \end{array}$	Mesityl oxide	-----
49.	$\begin{array}{c} \text{H} & \\   & \\ \text{H} & \text{C}=\text{C}=\text{O} \end{array}$	Ketene	-----

**Group I: CARBOXYLIC ACID**

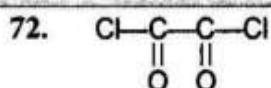
50.	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$	Valeric acid	n-Pentanoic acid
51.	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	Caproic acid	n-Hexanoic acid

52.	$\begin{array}{c} \text{CH}_2-\text{COOH} \\   \\ \text{CH(OH)}-\text{COOH} \end{array}$	Malic acid	Present in apple
53.	$\begin{array}{c} \text{OH} \\   \\ \text{CH}_2-\text{C}-\text{CH}_2 \\   \quad   \\ \text{COOH} \quad \text{COOH} \quad \text{COOH} \end{array}$	Citric acid	Present in lemon
54.	$\text{CH}_2=\text{CH}-\text{COOH}$	Acrylic acid	-----
55.	$\begin{array}{c} \text{H} \\   \\ \text{CH}_3-\text{C}-\text{COOH} \\   \\ \text{OH} \end{array}$	Lactic acid	Present in curd
56.	$\text{HO}-\underset{\text{O}}{\text{C}}-\text{OH} (\text{H}_2\text{CO}_3)$	Carbonic acid	-----
57.	$\text{CH}_3-\text{CO}-\text{COOH}$	Pyruvic acid	-----
58.	$\text{CH}_3-\text{CH}=\text{CH}-\text{COOH}$	Crotonic acid	-----
59.	$\begin{array}{c} \text{C}_6\text{H}_5-\text{CH}-\text{COOH} \\   \\ \text{OH} \end{array}$	Mendelic acid	-----
60.	$\text{NH}_2-\text{CH}_2-\text{COOH}$	Glycine	Amino acetic acid
61.	$\text{NH}_2\text{COOH}$	Carbamic acid	Amino formic acid
62.	$\text{COOH}-(\text{CH}_2)_4-\text{COOH}$	Adipic acid	-----
63.	$\text{C}_6\text{H}_5\text{CH}=\text{CHCOOH}$	Cinnamic acid	-----
64.	$\begin{array}{c} \text{CH}_3 \\   \\ \text{NH}_2-\text{C}-\text{H} \\   \\ \text{COOH} \end{array}$	Alanine	-----
65.	$\begin{array}{c} \text{CH}_2\text{COOH} \\   \\ \text{OH} \end{array}$	Glycolic acid	-----
66.	$\begin{array}{c} \text{COOH} \\   \\ \text{COOH} \end{array}$	Oxalic acid	-----
67.	$\begin{array}{c} \text{CH}_2-\text{COOH} \\   \\ \text{COOH} \end{array}$	Malonic acid	-----
68.	$\begin{array}{c} \text{CH}_2-\text{COOH} \\   \\ \text{CH}_2-\text{COOH} \end{array}$	Succinic acid	-----
69.	$\begin{array}{c} \text{HO}-\text{CH}-\text{COOH} \\   \\ \text{HO}-\text{CH}-\text{COOH} \end{array}$	Tartaric acid	-----
70.	$\begin{array}{c} \text{O} \\    \\ \text{H}-\text{C}-\text{C}-\text{OH} \\    \\ \text{H}-\text{C}-\text{C}-\text{OH} \\    \\ \text{O} \end{array}$	Maleic acid	Cis form/z-form



Fumaric acid

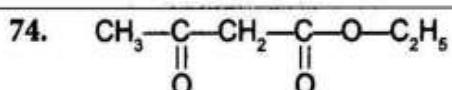
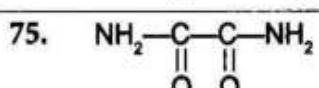
Trans form/E-form

**Group J: ACID DERIVATIVES**

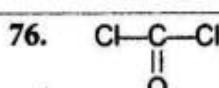
Oxalyl chloride



Ammonium Carbamate

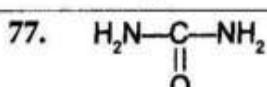
Aceto acetic ester or  
Ethyl aceto acetate

Oxamide



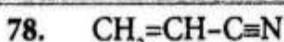
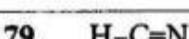
Phosgene

Poisonous gas



Urea

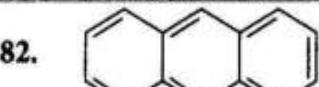
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**Group K: N-DERIVATIVES**Vinyl cyanide or  
*Acrylo nitrile*

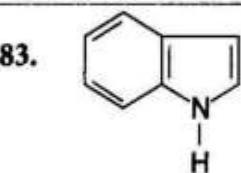
Formo nitrile



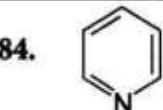
Aceto nitrile

Methyl isocyanate  
(MIC)Responsible for  
bhopal tragedy**Group L: AROMATIC COMPOUNDS**

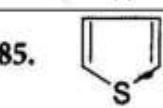
Anthracene



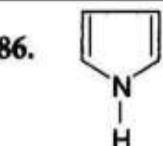
Indole



Pyridine

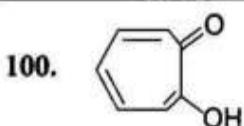


Thiophene



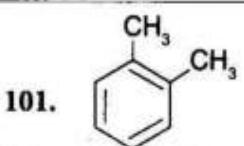
Pyrrole

87.		Sulphanilic acid	-
88.		Azulene	having zwitter ionic character
89.		Naphthalene	-
90.		Methyl orange II	Coloured substance used as indicator
91.		Butter yellow	Coloured dye
92.		Phenanthrene	-
93.		Cresol	O-hydroxy toluene
94.		Furfural	-
95.		Furan	-
96.		Coumarin	-
97.		Michler's ketone	-----
98.		Phenolphthalein	Acid-base indicator
99.		Tropone	Cycloheptatrienone



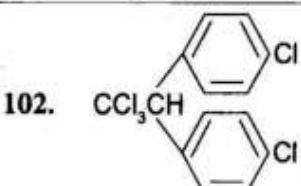
Tropolone

Cycloheptatrienolone



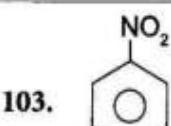
O-xylene

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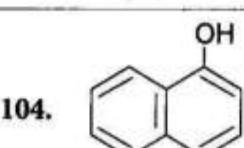
DDT

Dichlorodiphenyltrichloroethane (powerful insecticide)



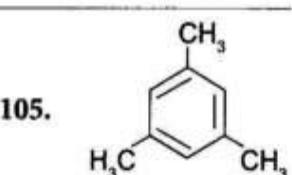
Nitrobenzene

Oil of mirbane



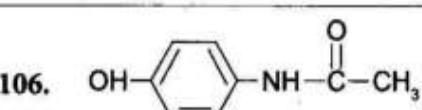
α-naphthol

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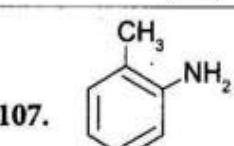
Mesitylene

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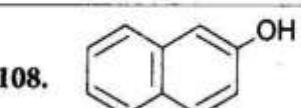
p-hydroxy acetanilide

Paracetamol



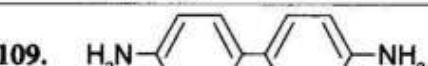
O-toluidine

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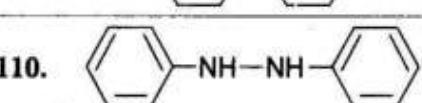
β-naphthol

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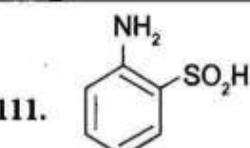
Benzidine

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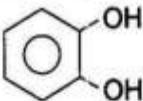
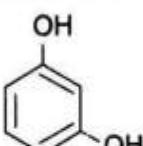
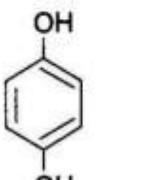
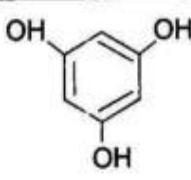
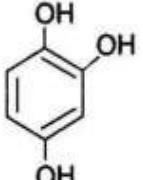
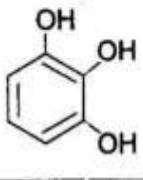
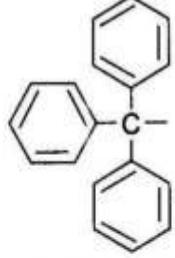
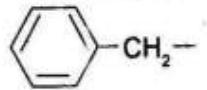
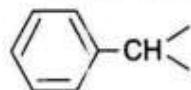
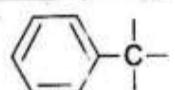
Hydrazobenzene

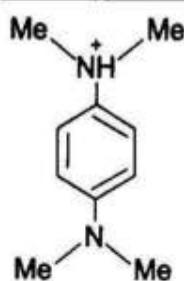
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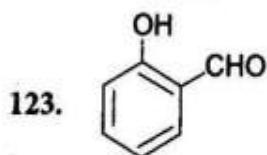
Orthanilic acid

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112.		Catechol	-----
113.		Resorcinol	-----
114.		Quinol or hydroquinone	-----
115.		Phloroglucinol	-----
116.		$\alpha$ -hydroxy quinol	-----
117.		Pyrogallol	Used as an absorbent for oxygen
118.		Trityl group	Triphenyl methyl group
119.		Benzyl group	Phenyl methyl group
120.		Benzal group	Benzylidene
121.		Benzo group	Benzylidyne

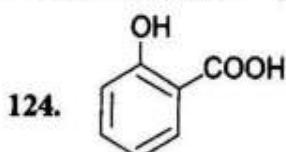


Wurster salts -----



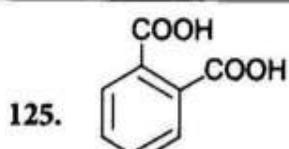
Salicylaldehyde

O-hydroxybenzaldehyde

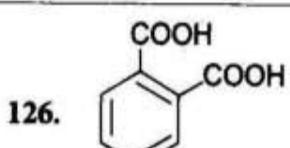


Salicylic acid

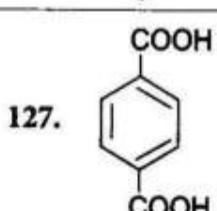
O-hydroxy benzoic acid



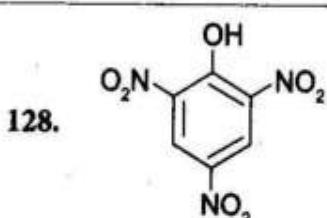
Phthalic acid -----



Isophthalic acid -----

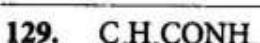


Terephthalic acid -----

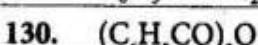


Picric acid

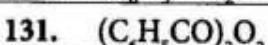
Behaves as a strong acid



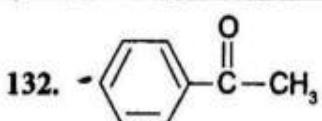
Benzamide -----



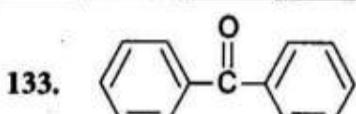
Benzoic anhydride -----



Benzoyl peroxide -----



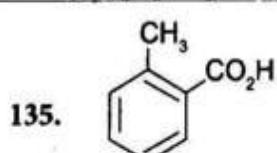
Acetophenone -----



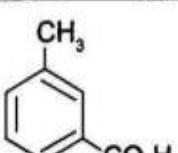
Benzophenone -----

134.  $C_6H_5CO_3H$ 

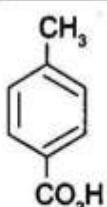
Perbenzoic acid



135.



o-toluic acid,  
m.p. 105°C

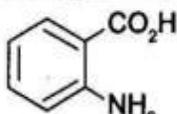


m-toluic acid,  
m.p. 111°C

Toluic acids

p-toluic acid,  
m.p. 180°C

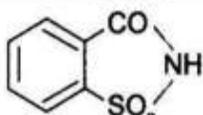
136.



Anthranilic acid

O-aminobenzoic acid

137.



Saccharin

O-sulphobenzoic imide  
(artificial sweetener)

138.



Styrene

Monomer of polystyrene  
oil of bitter almond

139.



Benzaldehyde

140.



Benzil

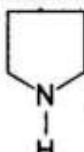
141.



Benzilic acid

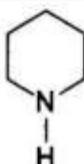
## Group M: HETROCYCLIC COMPOUNDS

142.



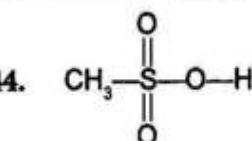
Pyrrolidine

143.

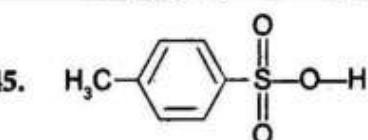


Piperidine

144.

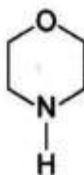
Mesylic acid or methyl  
sulphinic acid Ms-OH

145.

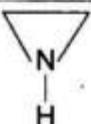
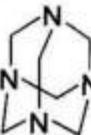
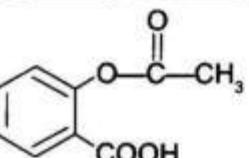
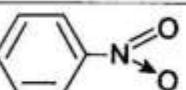
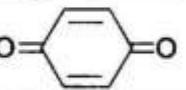
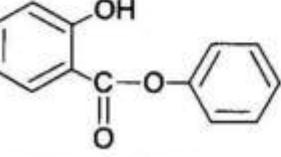
Tosylic acid or p-  
toluene sulphinic acid

Ts-OH

146.



Morpholine

147.		Aziridine	-----
148.		Tetrahydrofuran (THF)	Important solvent
149.		Hexa-methylenetetramine or urotropine	Urinary antiseptic
150.		Oxirane or ethylene oxide Oxa cyclo propane	-----
151.		Oxetane	-----
152.		Aspirin	Pain reliver
153.		Nitro benzene	Oil of mirabane
154.		p-benzo-quinone	-----
155.		Salol or phenyl salicylate	Oil of wintergreen

**An Institute  
which challenged  
ALL  
the IIT-JEE Coaching Institutes  
of India,  
Including those of  
Kota, Delhi, Mumbai,  
Kolkata, Hyderabad,  
Patna, Chennai etc., etc.....  
(National or Local Level)  
In a question  
of JEE-Advanced 2014  
and finally  
winning through  
decision of IIT  
on 1<sup>st</sup> June, 2014.**

## ISOMERISM

### 22.1 INTRODUCTION

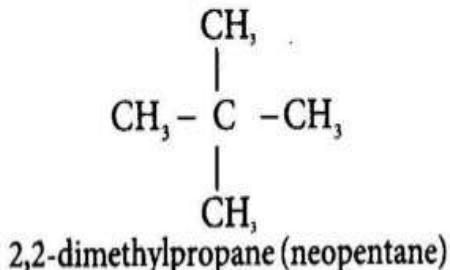
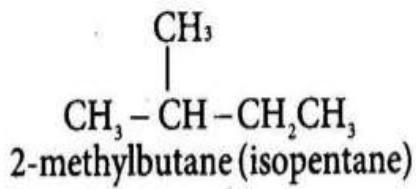
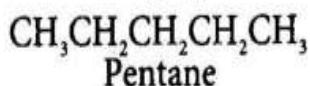
Isomeric compounds having the same molecular formula but different physical and chemical properties are called isomers and the phenomenon is called isomerism.

### 22.2 STRUCTURAL ISOMERISM I

Compounds which have the same molecular formula but different structures (i.e., different arrangement of atoms within the molecule) are called structural isomers and the phenomenon is called structural isomerism. It is of the following types:

- (a) **Chain or nuclear isomerism:** Compounds which have the same molecular formula but different structures (straight or branched) of the carbon chain. Chain isomers always belongs to the same homologous series (i.e., functional group) and class of the compound (i.e., whether it is cyclic or acyclic).

Pentane ( $C_5H_{12}$ ) has three isomers:

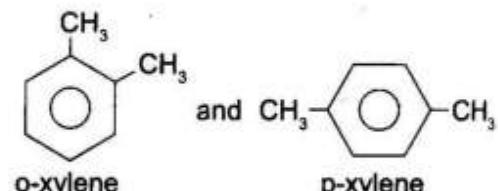
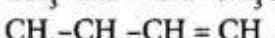
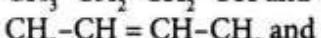
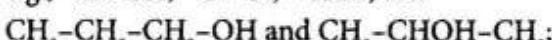


No. of C-atoms	Molecular Formula	No. of Isomers	No. of C-atoms	Molecular Formula	No. of Isomers
1	$C_1H_4$	1	7	$C_7H_{16}$	9
2	$C_2H_6$	1	8	$C_8H_{18}$	15
3	$C_3H_8$	1	9	$C_9H_{10}$	35
4	$C_4H_{10}$	2	10	$C_{10}H_{22}$	75
5	$C_5H_{12}$	3	11	$C_{15}H_{32}$	4347
6	$C_6H_{16}$	5	12	$C_{20}H_{42}$	36719

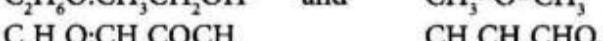
(b) **Position isomerism:** Compounds which have the same structure of a carbon chain but differ only in the term of position of the multiple bond or the functional group.

- Position isomers belong to the same homologous series and class of the compound.
- Chain isomerism and position isomerism can never be possible together.
- Position isomerism is never observed in presence of chain terminating functional group.

e.g.,  $\text{-COOH}$ ,  $\text{-C} \equiv \text{N}$ ,  $\text{-CHO}$ , etc.



(c) **Functional isomerism:** Compounds having the same molecular formula but different functional groups are called functional isomers.



Further examples of functional isomerism:

(i) Nitroalkanes and alkyl nitrites, e.g.,  $\text{CH}_3\text{CH}_2\text{-NO}_2$  and  $\text{CH}_3\text{CH}_2\text{-O-N=O}$

(ii)  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  amines

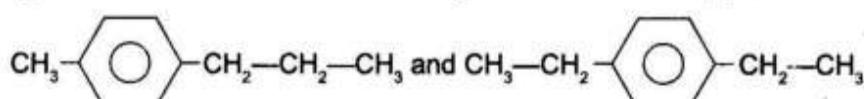
(iii) Aromatic alcohols, phenols and ethers

(iv) Cyanides and isocyanides

- Functional and chain isomerism and functional and position isomerism can never be possible together.
- Functional isomers belongs to different homologous series and different class.

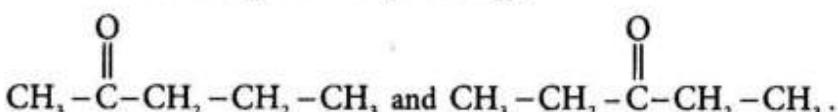
(d) **Ring-chain isomerism:** It is the special case of functional isomerism. Here, one isomer is cyclic and other is acyclic, e.g.,  $\text{CH}_2=\text{CH-CH}_2\text{-CH}_3$ , and  $\boxed{\text{ }}$ .

(e) **Metamerism:** Compounds having the same molecular formula but different number of carbon atoms or different alkyl groups on either side of the functional group (i.e.,  $-\text{O-}$ ,  $-\text{S-}$  and  $-\text{NH-}$ ) are called metamers and the phenomenon is called metamerism. It may be noted here that metamerism occurs among the members of the same homologous series. For example, metamic pairs



$\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3$  and  $\text{CH}_3\text{-O-CH}_2\text{CH}_2\text{CH}_3$ ;  $\text{CH}_3\text{CH}_2\text{-S-CH}_2\text{CH}_3$  and  $\text{CH}_3\text{-S-CH}_2\text{CH}_2\text{CH}_3$ ,  
 $\text{CH}_3\text{CH}_2\text{-NH-CH}_2\text{CH}_3$  and  $\text{CH}_3\text{-NH-CH}_2\text{CH}_2\text{CH}_3$ .

- If principal chain is continuous in presence of functional group, then position isomerism and metamerism can be possible together. E.g.,



- If principal chain is discontinuous due to presence of functional group or cyclic ring, then chain isomerism and metamerism can be possible together.  
E.g.,  $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3$  and  $\text{CH}_3\text{-O-CH}_2\text{CH}_2\text{CH}_3$ .

## 22.3 STRUCTURAL ISOMERISM II

(a) **Tautomerism:** It arises due to 1, 3-migration of a proton from one polyvalent atom to the other within the same molecule. The two isomers thus obtained which exist in dynamic equilibrium with each other are called tautomers. Tautomerism is also known as **desmotropism** or **allelotropism** or **kryptomerism** or **keto-enol isomerism**.

**Condition required for tautomerism:**

(i) **Properties of tautomerism:**

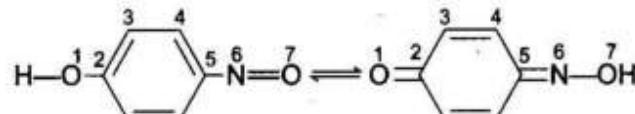
1. Tautomers exist in dynamic equilibrium.
2. Tautomers are always functional isomers.
3. Tautomerism is a chemical phenomenon which occurs only in liquid state.
4. Tautomerism have same number of lone pair, bond pair and multiple covalent bond.
5. Tautomerism is catalysed by acids as well as bases both.

(ii) **Classification of tautomerism:**

1. **1, 3-tautomerism or triad system:** If migration of H atom occurs between alternate atoms then tautomerism belongs to this category.
2. **1, 2-tautomerism or diad system:** If migration of hydrogen occurs between adjacent atoms, then tautomerism belongs to this category. It is observed only in case of nitriles and nitro compounds.
  - Nitriles always participate in 1,2-tautomerism.
3. **1, n-tautomerism, i.e., polyad system:** If migration of hydrogen occurs between first to nth atom where  $n \geq 4$ , then phenomenon is termed as 1, n-tautomerism or polyad system.

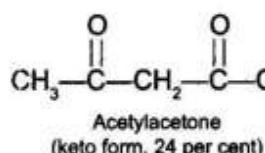
**Condition for 1,n-tautomerism**

- (i) Keto form must be conjugated.
- (ii) One of the odd positions with respect to keto functional group must be saturated.
- (iii) This saturated odd position must have atleast one acidic hydrogen.

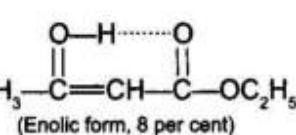
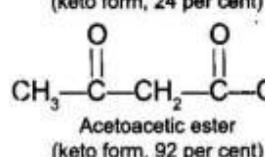
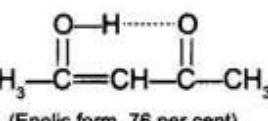


- (iii) **Stability of tautomerism:** In general, enolic form is less stable than keto form; however, when keto form has an active methylene group or enol form is aromatic then enol form becomes more stable when compared to keto form. In an active methylene compound, enol form is more stable when compared to keto form due to

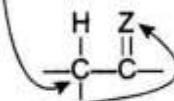
1. Intramolecular H-bonding



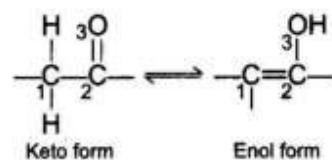
2. Resonance stabilization



1. A carbon atom have atleast one acidic hydrogen atom and should not be present in unsaturation



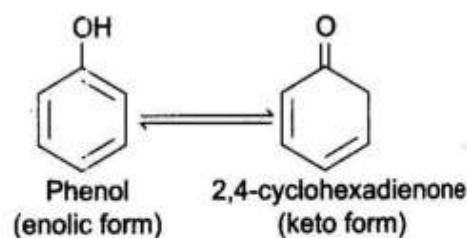
2. Highly electronegative atom attach with multiple covalent bond, e.g., O, N, S



Likewise, phenol can exhibit keto-enol tautomerism but here the amount of the keto-form is negligibly small because enol form is aromatic in nature.

### **Effects of solvent on stability.**

- In a polar protic solvent, keto form is more stable when compared to enol form.
  - In a polar aprotic solvent and in a non-polar solvent, enol form is more stable than keto form.



## 22.4 STEREOISOMERISM

Compounds having the same structural formula but different spatial arrangement of atoms or groups are called stereoisomers and the phenomenon is known as stereoisomerism.

**Classification of stereoisomerism:** It is of the following two types:

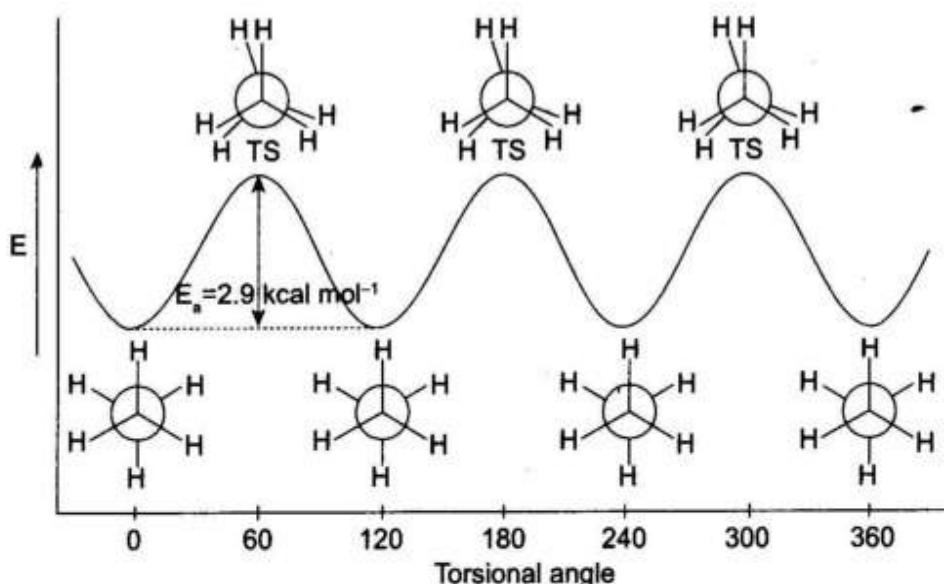
1. Conformational isomerism
  2. Configurational isomerism
  - The operational distinction between conformational and configurational isomers is that whether they interconvert at room temperature or not. Conformational isomers can interconvert at room temperature so they cannot be separated from the reaction mixture, whereas configurational isomers cannot interconvert at room temperature so they can be separated from the reaction mixture.

### 22.4.1 Conformational Isomerism

The infinite number of momentary arrangements of atoms or groups in space which result through rotation about a single bond are called conformations or rotational isomers or simply rotamers.

### **Factors affecting stability of conformational isomers:**

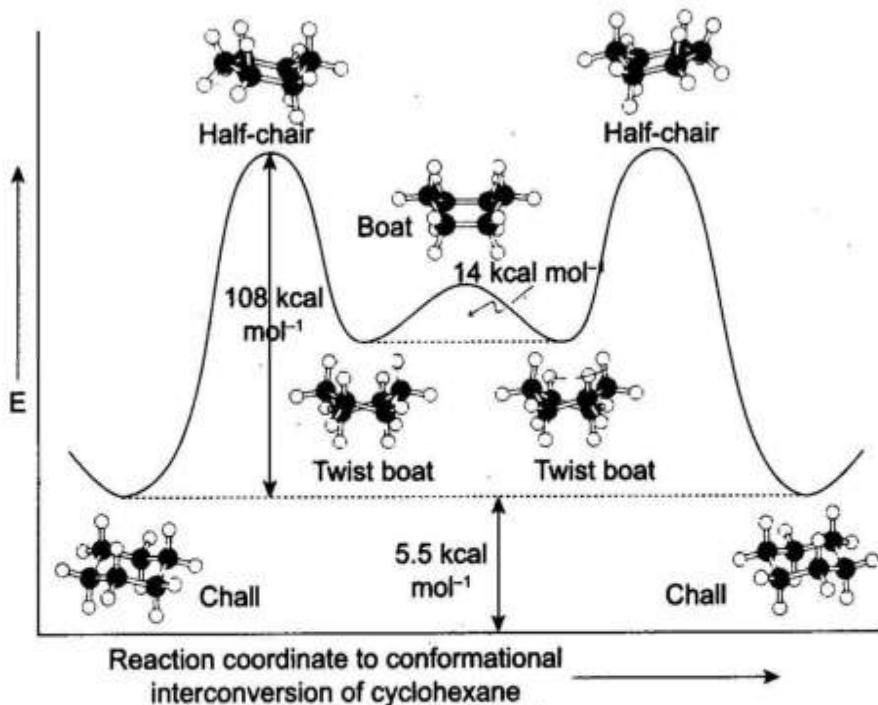
- (a) **Angular strain:** Deviation from normal bond angle creates angular strain. Greater the angular strain lesser will be the stability of conformation. Angular strain is observed only in cyclic compounds.
  - (b) **Torsional strain:** Repulsive interaction between bond pairs of both carbon which affect stability of conformation is called torsional strain. Greater the torsional strain lower will be the stability of conformation.
  - (c) **Steric strain:** When distance between two non bonded atoms is less than the sum of their Van der Waal's radius steric strain is developed. It is also known as Van der Waal's strain.
  - (d) **Dipole-dipole interaction:** Greater the distance between like poles, i.e., like charges greater will be the stability of the conformations.
  - (e) **Intramolecular hydrogen bonding:** Intramolecular hydrogen bonding stabilizes gauche form much more; therefore, it becomes more stable when compared to the antiform.
    - (i) **Conformations of ethane :** Ethane, in principle, can have an infinite number of conformations but only two extreme conformations, i.e., staggered and eclipsed are important.
      - In general, order of stability of various conformations is anti > gauche > partially eclipsed > fully eclipsed.
      - If intramolecular hydrogen bonding is present, then order of stability is gauche > anti > partially eclipsed > fully eclipsed.



(f) **Conformations of cyclohexane:** In principle, cyclohexane can have a large number of conformations. Out of these four conformations, i.e., chair form, boat form, twist boat form and half-chair forms. The chair conformation is more stable than the boat conformation because of the following reasons:

- In chair conformation, all the H-atoms on  $C_1-C_2$ ,  $C_2-C_3$ ,  $C_3-C_4$ ,  $C_4-C_5$ ,  $C_5-C_6$  and  $C_6-C_1$  are in more stable staggered orientations and hence the force of attraction between these non-bonded H-atoms is the minimum. On the other hand, in boat conformation, the adjacent hydrogens on  $C_2-C_3$  and  $C_5-C_6$  are in the less stable eclipsed orientation.
- The boat conformation is further destabilized by the close proximity of the flagpole hydrogens (i.e., trans nuclear hydrogens). These hydrogens are 1.8 Å apart but Van der Waal radius is 2.4 Å, due to which steric strain is developed.

#### Conformations of ethane



## 22.5 GEOMETRICAL ISOMERISM

**Conditions for geometrical isomerism:**

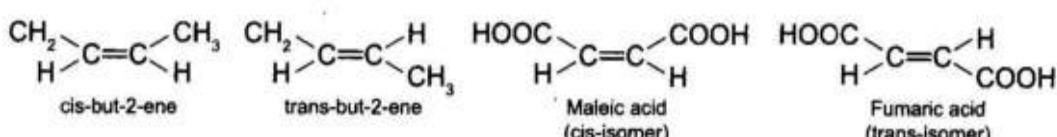
- There must be hindered rotation between two adjacent atoms of the molecule.  
e.g.,  $\text{>C=C<} , \text{>C=C—} , \text{—N=N—}$ , etc.
- If atom about which hindered rotation is observed possess two atoms or groups, then they must be different; however, if only one atom or group is attached then there is no condition.  
e.g.,  $\begin{array}{c} \text{H}_2\text{C} \\ | \\ \text{H} \end{array} \text{>C=C} \begin{array}{c} \text{Br} \\ | \\ \text{Cl} \end{array}$

Geometrical isomerism also called cis-trans isomerism which arises due to the difference in the relative spatial arrangement of atoms or groups around the double bond. It is of the following three types.

- Cis-trans
- E-Z
- Syn-anti

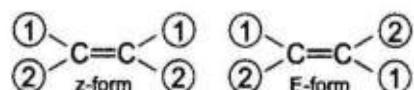
### 22.5.1 Cis-Trans Isomerism

The isomer in which the two similar atoms or groups lie on the same side of the double bond is called the cis-isomer and if these similar atoms or groups lie on the opposite sides of the double bond, it is called the trans-isomer, for example,



### 22.5.2 E-Z Isomerism

Compounds of the formulae  $\text{baC = Cde}$  will show E - Z isomerism. If two higher priority groups are present on same side of the double bond, then isomer is called Z-form, e.g.,



However, if they are of opposite sides, then isomer is called E-form. Priority of atom or group is decided on the basis of sequence rule.

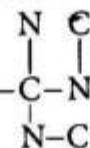
#### 22.5.2.1 Sequence rule

To assign priorities to the atoms or groups, Cahn, Ingold and Prelog developed following sequence rules.

- The atom with lowest atomic number is given the lowest priority.
- If isotopes of same element are attached, then the isotope with higher mass number is given higher order of priority, e.g.,  ${}^2\text{D} > {}^1\text{H}$  and  ${}^{37}\text{Cl} > {}^{35}\text{Cl}$ .
- In the groups the order of precedence is also decided on the basis of atomic number of first atom of the group. E.g., Cl >  $-\text{SO}_3\text{H}$  >  $-\text{OH}$  >  $-\text{COOH}$ .
- When the order of precedence of the groups is not decided by the first atom as it is same in all the groups, the second or subsequent atoms in the groups are considered.

E.g.,  $\text{--COOH} > \text{--CH}_2\text{--CH}_3$ .

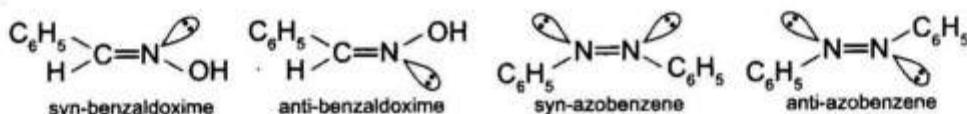
- (e) A doubly or triply bonded atom is considered equivalent to two or three such atoms.



E.g., the group  $\text{>C=O}$  is equal  $\text{>C--O}$  and the group  $\text{--C}\equiv\text{N}$  is equal to  $\text{--C}=\text{N}$ .

### 22.5.3 Syn-Anti Isomerism

Geometrical isomerism in compounds containing  $\text{C}=\text{N}$  and  $\text{N}=\text{N}$  bonds. Besides alkenes compounds containing  $\text{C}=\text{N}$  (aldoximes and ketoximes) and  $\text{N}=\text{N}$  (azo compounds) bonds also show geometrical isomerism. However, in these cases, the prefixes syn- and anti- instead of cis- and trans- are more frequently used. For example

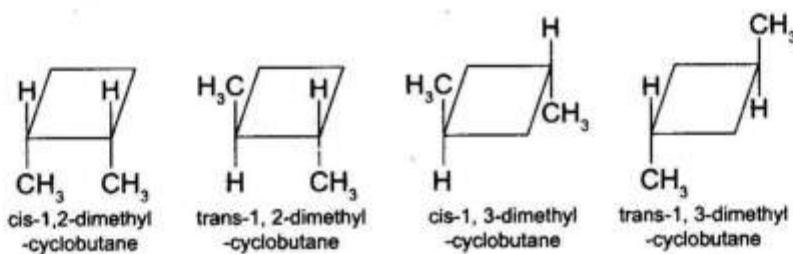


In ketoximes (i.e., oximes derived from ketones) the prefixes syn and anti indicate the relationship of first group named w.r.t. OH group.

(a) **Geometrical isomerism in cyclic compounds:**

Geometrical isomerism is also exhibited by compounds which may have hindered rotation due to reasons other than the presence of a double bond. Thus, cyclic compounds because of their rigid ring structures also show hindered rotation about carbon–carbon single bonds and hence exhibit geometrical isomerism.

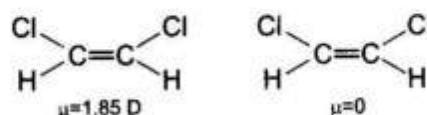
Disubstituted cyclobutanes and cyclopentanes show two position isomers (i.e., 1, 2 and 1, 3) each one of which can exhibit geometrical isomerism.



(b) **Determination of configuration of geometrical isomers:** Distinction between cis- and trans-isomers can be made as follows:

1. **On the basis of their physical properties:**

- (i) **Melting points:** In general, the melting point of a trans-isomer is higher than that of the corresponding cis-isomer.
- (ii) **Solubility:** In general, the solubility of a cis-isomer is higher than that of the corresponding trans-isomer in a polar solvent.
- (iii) **Dipole moments:** In general, cis-isomers have higher dipole moments than the corresponding trans-isomers which may have even zero dipole moment when the atoms or groups on each carbon atom of the double bond are the same.



- (iv) **Boiling points:** In general, the boiling points of the cis-isomer are higher than those of the corresponding trans-isomers. Since the cis-isomers have higher dipole moments (more polar) than the corresponding trans-isomers (less polar), therefore, the boiling points of cis-isomers are higher than those of their corresponding trans-isomers.
2. **By cyclization method:** In cis-isomers, the reacting groups being on the same side of the double bond, interact with each other resulting in the formation of cyclic compounds. On the other hand, in trans-isomers, the reacting groups being on the opposite sides of the double bond, do not interact with each other to form cyclic compounds.
- (c) **Determination of total number of isomerism in polyene.**
- Case I:** If compound has  $n$  double bond and two ends of polyene are not same, then total number of geometrical isomers is equal to  $2^n$ .
- Case II:** If two ends of polyene are same, then
- If  $n$  is even then total number of geometrical isomer =  $2^{(n-1)} + 2^{(n/2)-1}$ .
  - If  $n$  is odd number of geometrical isomer =  $2^{(n-1)} + 2^{\left(\frac{n-1}{2}-1\right)}$ .

## 22.6 OPTICAL ISOMERISM

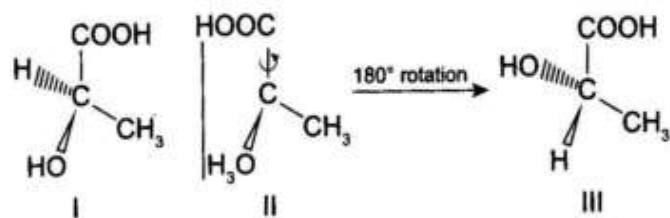
Stereoisomers which resemble one another in their chemical properties and most of their physical properties but differ in their behaviour towards plane polarized light are called **optical isomers** and the phenomenon is called **optical isomerism**.

- (a) **Optical activity:** Compounds which can rotate the plane of polarized light are called optically active and the property of a substance to rotate the plane of polarized light is called **optical activity**. d-isomer rotates the plane of polarized light clockwise and are called **dextrorotatory** and l-isomer rotates the plane polarized light anticlockwise and are called **laevorotatory**.
- **Plane polarized light:** Plane polarized light has vibrations only in one plane. It is obtained by passing ordinary light through a nicol prism. It is made up of calcite or Iceland spar, a crystalline form of  $\text{CaCO}_3$ .
- (b) **Angle of rotation ( $\alpha$ ):** It is the angle through which the plane of polarized light gets rotated when passed through the solution of an optically active substance.
- Factors affecting angle of rotation:**
- Nature of the optically active substance
  - Concentration of the solution in  $\text{g/cm}^3$
  - Length of the solution in dm through which light passes
  - Nature of the solvent
  - Wavelength of the monochromatic light used
  - Temperature of the sample
- (c) **Specific rotation:** It is the angle of rotation produced when the plane polarized light passes through one decimetre ( $1 \text{ dm} = 10 \text{ cm}$ ) of a solution of an optically active compound having a unit concentration (i.e.,  $1 \text{ g/cm}^3$ ) at a given wavelength of light ( $\lambda$ ) and at a given temperature ( $T$ ). It is given by the relation

$$\text{Specific rotation, } [\alpha]_T = \frac{\text{Observed angle of rotation}}{\text{Length in dm} \times \text{Conc. in g/cm}^3 \text{ solution}}$$

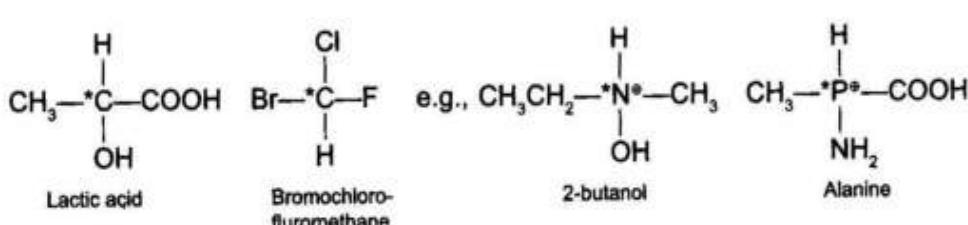
- The instrument used for measuring the optical rotation is called a polarimeter and the light source is yellow light from a sodium lamp (i.e., d-line of sodium lamp with a wavelength of  $5893 \text{ \AA}$ ) is often used.

- (d) **Chiral objects/molecules:** A molecule (or an object) is said to be chiral or dissymmetric if it is not superimposable on its mirror image and the property of non-superimposability is called **chirality**. Such molecules/objects do not possess any element of symmetry such as a centre of symmetry, a plane of symmetry or an alternating axis of symmetry. E.g.,



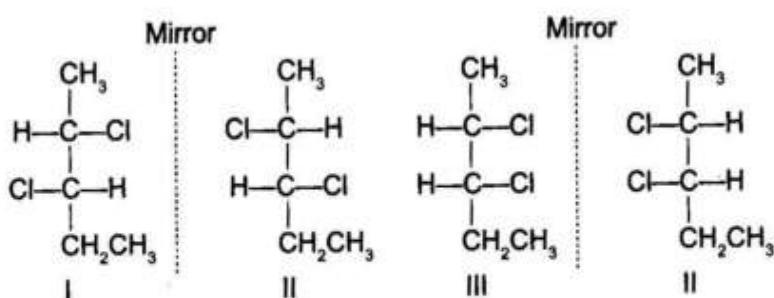
If I and III are non-superimposable, then the object is chiral otherwise it is achiral.

- (e) **Achiral objects/molecules:** A molecule (or an object) is said to be achiral if it is superimposable on its mirror image. Such molecules/objects possess some elements of symmetry (centre of symmetry, plane of symmetry or an alternating axis of symmetry).
- (f) **Chiral or asymmetric carbon atom:** A sp<sup>3</sup> hybridized atom which is attached to four different atoms or groups is called a chiral or an asymmetric atom. Such a carbon atom is often marked by an asterisk (\*).

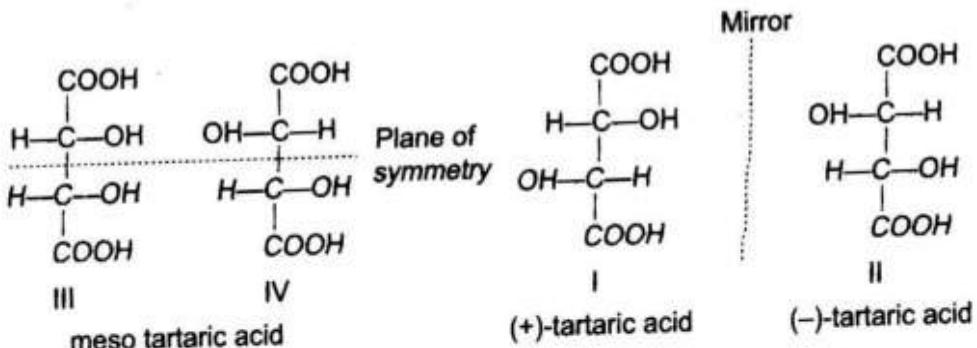


## 22.7 TERMS USED IN OPTICAL ISOMERISM

**Enantiomers:** Stereoisomers which are non-superimposable mirror images of each other are called **enantiomers** and the phenomenon is called **enantiomerism**. Enantiomers have identical physical and chemical properties (except towards chiral reagents) but rotate the plane of polarized light in the opposite direction but to the same extent.

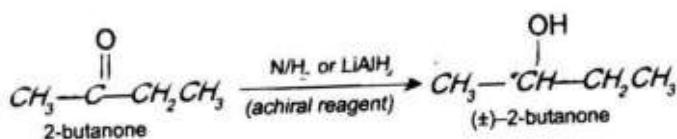


**Diastereomers:** Stereoisomers which are not mirror images of each other are called **diastereomers** and the phenomenon is called **diastereomerism**. Tartaric acid exists in three stereoisomeric forms, i.e., I and II and III.



Here again, I and II are enantiomers while I and III or II and III are diasteromers.

- Geometrical isomers are also called diastereomers, e.g., -cis-trans; E-Z and syn-anti isomers are diastereomers.
- (a) **Properties:** Diastereomers have different melting points, boiling points and solubilities and hence can be separated by fractional crystallization and fractional distillation.
- (b) **Meso-compounds:** Compounds which do not show optical activity inspite of the presence of chiral carbon atoms are called **meso-compounds**. The absence of optical activity in these compounds is due to the presence of a plane of symmetry in their molecules. They are optically inactive due to **internal compensation**.
- Walden inversion:** When a group directly attached with chiral carbon is substituted by another group by  $SN^2$  mechanism then configuration of product obtained is opposite to the configuration of reactant taken this phenomenon is termed as Walden inversion or optical inversion as umbrella inversion.
- (c) **Racemic mixture:** An equimolar mixture of (+) and (-) enantiomers is called racemic mixture or modification. It is denoted by the prefix dl or  $(\pm)$  before the name of the compound. A racemic mixture is optically inactive due to **external compensation** since the rotation due to one enantiomer is cancelled by equal and opposite rotations caused by the other enantiomer.
- (d) **Racemization:** Formation of racemic mixture from optically active or inactive substance is called **racemization**. When an optically active compound is synthesized in the laboratory from reagents, having planar geometry, the product is always a racemic mixture. For example



When 2-butanone is reduced with usual (achiral reagents) such as  $\text{Ni}/\text{H}_2$  or  $\text{LiAlH}_4$ , an approximately 50:50 mixture of (+) and (-)- enantiomers will be formed, i.e., a **racemic mixture is obtained**. This is due to the reason that carbonyl group being planar is attacked by the reagent from the top and the bottom faces with almost equal ease giving an almost equimolar mixture of (+)- and (-)-forms.

- (e) **Resolution:** It is the process of separating a racemic mixture into (+)- and (-)- enantiomers. Since enantiomers have identical physical and chemical properties, they cannot be separated by ordinary physical and chemical methods. Therefore, special techniques are used for their separation. One of the most widely used is the chemical method. In this method, the racemic mixture is treated with a suitable optically active reagent to give a mixture of two diastereomers which are separated by

fractional crystallization. After the separation, each diastereomer is treated separately with a suitable reagent to give back the original enantiomer.

- (f) **Enantiomeric excess:** Measurement of optical purity is known as enantiomeric excess. percentage of enantiomeric excess is determined as follows.

$$\text{per cent enantiomeric excess} = \frac{\text{Enantiomeric excess} \times 100}{\text{Total number of moles of both enantiomer}}$$

$$= \frac{\text{Observed specific rotation} \times 100}{\text{Specific rotation of pure enantiomer}} = \frac{[d] - [l]}{[d] + [l]} \times 100.$$

- If enantiomeric excess of (+) isomer is 50 per cent it means that 50 per cent of the mixture consists of (+) enantiomer (the excess) and the other 50 per cent consist of the racemic form, so actual stereoisomeric composition is 75 per cent (+) form and 25 per cent (-) form.

- (g) **Determination of total number of optically active isomers.**

**Case I:** If molecule is not divisible into two identical halves and molecule has  $n$  chiral carbon atoms, then total number of configurational isomers ( $a + m$ ) =  $2^n$ .

Number of optically active forms ( $a$ ) =  $2^n$ ; number of enantiomeric pair ( $e$ ) =  $(a/2)$

Number of racemic mixture ( $r$ ) =  $(a/2)$ ; number of meso-form ( $m$ ) = 0

**Case II:** If molecule is divisible into two identical halves and molecule has  $n$  chiral carbon atoms; where  $n$  is even then total number of configurational isomers ( $a + m$ ) =  $2^{n-1} + 2^{n/2-1}$ .

Number of optically active forms ( $a$ ) =  $2^{n-1}$ .

Number of enantiomeric pair ( $e$ ) =  $(a/2)$

Number of racemic mixture ( $r$ ) =  $(a/2)$

Number of meso form ( $m$ ) =  $2^{n/2-1}$ .

**Case III:** If molecule is divisible into two identical halves and molecule has  $n$  chiral carbon atoms; where  $n$  is odd then total number of configurational isomers ( $a + m$ ) =  $2^{n-1}$ .

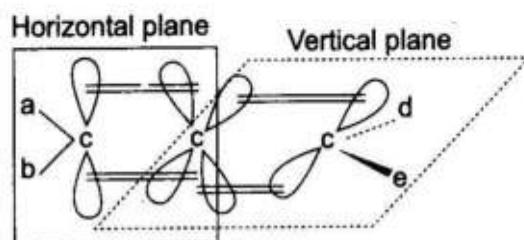
number of optically active forms ( $a$ ) =  $2^{n-1} - 2^{(n-1)/2}$ .

number of enantiomeric pair ( $e$ ) =  $(a/2)$

number of racemic mixture ( $r$ ) =  $(a/2)$

number of meso form ( $m$ ) =  $2^{(n-1)/2}$

- (h) **Optical activity in molecules containing no chiral carbon atoms:** Substituted allenes of the general formula,  $abC = C = Cab$  or  $abC = C = Cde$  are chiral molecules. The central carbon atom in allenes is  $sp$  hybridized and the two  $p$ -bonds are in planes perpendicular to each other as shown below.



## GENERAL ORGANIC CHEMISTRY

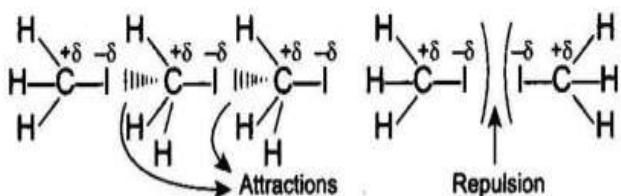
### 23.1 INTRODUCTION

In covalent compounds, the structural units (molecules) are covalent molecules. These molecules are held together by very weak forces. These forces are termed as **intermolecular forces, intermolecular non-bonding attractions or secondary forces**. Secondary forces are of the following types:

1. Dipole-Dipole interactions
2. Van der Waal's forces
3. Hydrogen bond

#### 23.1.1 Dipole-Dipole Interactions

Except in a highly dispersed gas, molecules attract and repel each other. These attractions and repulsions arise primarily from molecular dipole-dipole interactions. E.g., in the liquid state, molecules of methyl iodide can either attract or repel each other, depending on the orientation of the molecules. When iodine ends of two molecules approach closely, the two molecules repel each other.



Dipole-dipole interaction can only be possible if molecule has a permanent dipole. An ordinary covalent bond has energy in the range of 30 to 100 kcal/mole. Dipole-dipole interactions are much weaker, approximately 1 to 3 kcal/mole. Magnitude of dipole-dipole interactions depends on the dipole moment of the bond of the compound and intermolecular distance  $DDE \propto \frac{1}{d^2}$ .

#### 23.1.2 Van der Waal's Forces

These forces of attractions exist between non-polar molecules. This force of attraction is intermolecular attraction due to the electrostatic attractions between nuclei of one molecule and electrons of the other molecule.

Van der Waal's forces are very weak and are significant only when the molecules are very close together, i.e., between the surface molecules. Van der Waal's force of interaction  $VF \propto \frac{1}{d^6}$ . They are effective only over short intermolecular distances.

Magnitude of Van der Waal interaction depends on number of electrons and protons in the molecule as well as on the intermolecular distance.

### Note:

$VF \propto$  number of electrons and protons  $\propto$  molecular weight

$\propto$  Surface area of the molecule

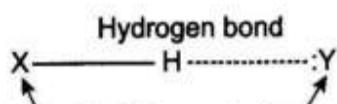
$\propto$  Symmetry of the molecule

If structure of a molecule is symmetrical then molecules are packed well in the crystal lattice (solid and liquid phases) which decreases distance, hence increases van der Waal's attraction.

## 23.1.3 Hydrogen Bonding

The strongest secondary force is of interaction of the hydrogen bond, which consists of bond between an H attached to a highly electronegative atom, X and an electronegative atom bearing an unshared pair of electrons, either in another molecule or in a different part of the same molecule.

### 23.1.3.1 Condition for H-bonding



- |  |   |
|--|---|
| 1. It must be highly EN.<br>2. It must have small size<br>3. It must have atleast one hydrogen | 1. It must be highly EN.<br>2. It must have small size<br>3. It must have atleast one large pair of $e^-$ |
|--|---|

**Classification of hydrogen bonding:** Hydrogen bonding is of two types.

- (i) Intermolecular hydrogen bonding
- (ii) Intramolecular hydrogen bonding

## 23.1.4 Substrate and Reagent

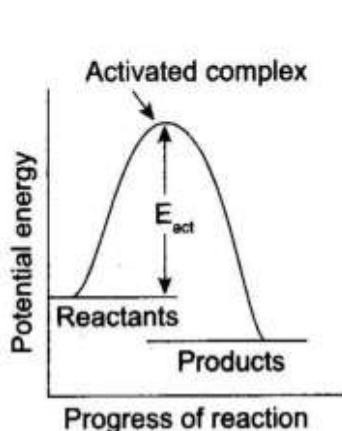
Whenever a chemical reaction occurs between two or more substance, new compounds are formed. The substances with which we start a reaction are called **reactants** or starting materials and the new compounds formed as a result of a chemical reaction are called **products**. The reactants are further classified as substrates and reagents.

Substrate + Reagent  $\rightarrow$  Products

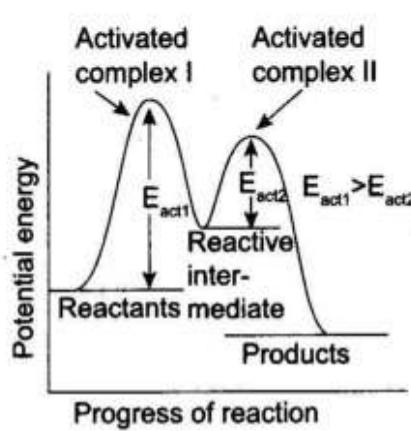
- (i) **Reagent:** A more reactive reactant which is usually present in small amounts is called a reagent.
- (ii) **Substrate:** A less reactive reactant which is usually present in large amounts is called a substrate.

### 23.1.5 Reaction Mechanism

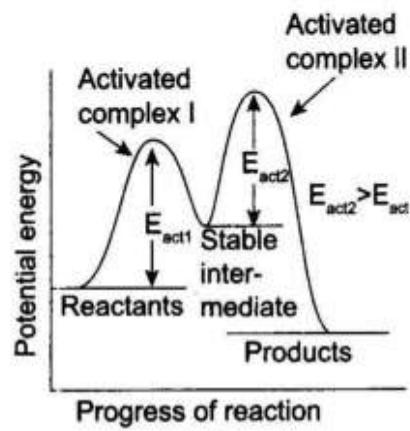
A chemical reaction is believed to occur through collision between substrate and reagent molecules. As a result of these collisions, a highly energetic species called the **activated complex** or the **transition state** is first formed which subsequently decomposes to give the products.



(a)  
A one-step or  
concerted reaction



(b)  
A two-step reaction with  
a reactive intermediate



(c)  
A two-step reaction with  
a stable intermediate

Alternatively, in some cases a relatively less energetic but more stable chemical species than the activated complex may be first formed. This chemical species which is relatively less energetic but more stable than the activated complex is called the **reaction intermediate**. This reaction intermediate then gets converted into the product through another activated complex.

Thus, a two-step reaction occurs through two activated complexes. If the energy of activation of the first activated complex is more than that of the second, then the intermediate rapidly gets converted into the products, i.e., the intermediate cannot be isolated. In such cases, the first step is the rate-determining step of the reactions.

If, however, the energy of activation of the second activated complex is higher than that of the first then the intermediate is quite stable and hence can be isolated. In such cases, the second step is the rate-determining step of the reaction. In the light of the above discussion, a reaction may follow either of the following two paths:

**Path I:** Substrate + Reagent  $\rightarrow$  Activated complex  $\rightarrow$  Products

**Path II:** Substrate + Reagent  $\rightarrow$  Activated complex  $\rightarrow$  Reaction intermediate  $\rightarrow$  Activated complex  $\rightarrow$  product

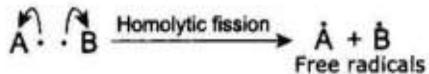
A detailed step-by-step description of a chemical reaction showing as to how reactants are converted into products is called mechanism of the reaction. If a reaction involves simultaneous making and breaking of bonds without the formation of any intermediate, it is said to be a **concerted reaction**. Such a reaction occurs through a single **activated complex** or **transition state**. On the other hand, if a reaction occurs in two or more steps with the formation of a reactive or isolable intermediate it is said to be a **step wise** or **non-concerted reaction**.

- Concerted reaction is also called elementary or simple reaction while non-concerted reactions are termed as non-elementary or complex reaction.

### 23.1.6 Type of Bond Cleavage

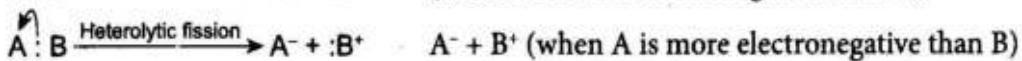
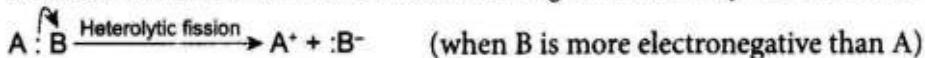
(a) **Symmetrical cleavage or homolysis:** If a covalent bond breaks in such a way that each atom takes away one electron of the shared pair, it is called symmetrical cleavage or **homolysis**.

The neutral chemical species (such as A and B) which contain an unpaired electron and which are produced by homolytic fission of covalent bonds are called free radicals.



- **Condition for homolysis:** Homolytic fission usually occurs in non-polar bonds and is favoured by high temperature, ultra-violet (UV) radiations and by the presence of radical initiators such as peroxides, diazo compounds, etc. in gaseous phase and in non-polar solvents.

(b) **Unsymmetrical cleavage or heterolysis:** When a covalent bond joining two atoms A and B breaks in such a way that both the electrons of the covalent bond (i.e., shared pair) are taken away by one of the bonded atoms, then the mode of bond cleavage is called **unsymmetrical cleavage or heterolysis**.



- **Condition of heterolysis:** It usually occurs in polar covalent bonds and is favoured by polar solvents in presence of polar reagents like acids or bases at low temperature.

## 23.2 TYPES OF REAGENTS

### 23.2.1 Electrophiles

They are electron-deficient species. They attack at the centre of high electron density acts as Lewis acid and have oxidizing tendency.

(a) **Classification of electrophiles:**

- (i) **Positive electrophiles:**  $H^+$ ,  $H_3O^+$ ,  $Cl^+$ ,  $Br^+$ ,  $I^+$ ,  $NO_2^+$ ,  $NO^+$ ,  $R^+$  (carbocation), etc.
- (ii) **Neutral electrophiles:**  $R$ ,  $:CR_2$ ,  $:NR$ ,  $BF_3$ ,  $AlCl_3$ ,  $ZnCl_2$ ,  $FeCl_2$ ,  $SnCl_4$ ,  $PCl_5$ ,  $IF_7$ ,  $SnCl_2$ ,  $CO_2$ ,  $SO_3$ ,  $BeCl_2$ , etc.
- Alkali and alkaline earth metal cations as well as  $NH_4^+$  cannot act as electrophiles.

### 23.2.2 Nucleophiles

They are electron-rich species, they attack at the centre of low electron density, i.e., +ve charge centre. They acts as Lewis bases and have reducing tendency.

(a) **Classification of nucleophiles:**

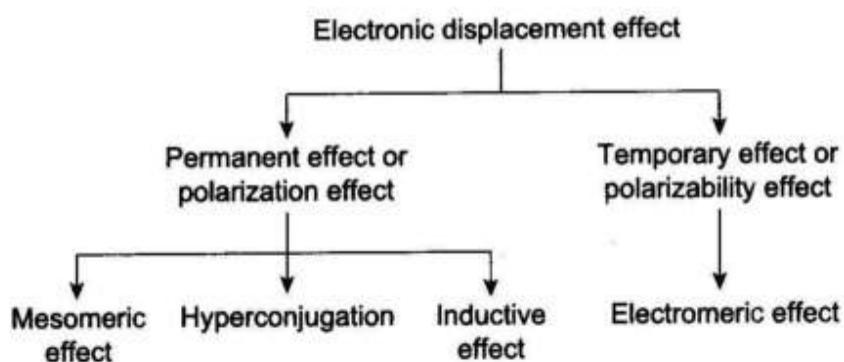
- (i) **Charged nucleophiles:**  $H^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $R^-$ ,  $RC\equiv C^-$ ,  $OH^-$ ,  $OR^-$ ,  $SR^-$ ,  $C_6H_5O^-$ ,  $NH_2^-$ ,  $NO_2^-$ ,  $CN^-$ ,  $RCOO^-$ , etc.
- (ii) **Neutral nucleophiles:**  $H_2O^{\cdot\cdot}$ ,  $NH_3^{\cdot\cdot}$ ,  $RNH_2$ ,  $R\ddot{O}H$ ,  $R\ddot{S}H$ ,  $R\ddot{O}R$ ,  $R\ddot{S}R$ ,  $R-MgX$ ,  $R-Li$ ,  $NaBH_4$ ,  $LiAlH_4$ .
  - Organic compound having carbon–carbon multiple bond also act as neutral nucleophile.

(b) **Factors affecting nucleophilic character:**

- (i) Negatively charged species are better nucleophiles in comparison to neutral species.  
E.g.,  $H_2O < OH^- < CH_3-O^-$ .

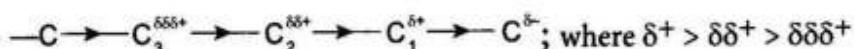
- (ii) Among base and its conjugate acids, nucleophilic character of base is greater.  
E.g.,  $\text{OH}^- > \text{H}_2\text{O}$      $\text{NH}_2^- > \text{NH}_3$
- (iii) In a polar protic solvent, nucleophilic character and basic character are antiparallel to each other while moving from top to bottom, i.e., nucleophilic character increases while basic character decreases.
- $\text{F}^- \text{ Cl}^- \text{ Br}^- \text{ I}^-$   
Basic character ← Nucleophilic character →
- (iv) While moving from left to right in a period, nucleophilicity and basicity are parallel to each other, i.e., both decreases from left to right
- $\text{CH}_3^- \text{ NH}_2^- \text{ OH}^- \text{ F}^-$   
Basic character ← Nucleophilic character →
- (v) In a group of nucleophile in which the nucleophilic atom is same, nucleophilicity parallels basicities.
- $\text{RO}^- \text{ OH}^- \text{ RCOO}^- \text{ ROH} \text{ H}_2\text{O}$   
Basic character ← Nucleophilic character →
- (vi) When adjacent atom to nucleophilic site has lone pair of electrons, nucleophilic character increases.
- $\text{H}\ddot{\text{O}}\text{O}^- > \text{OH}^-$      $\text{N}\ddot{\text{H}}_2 \text{N}\ddot{\text{H}}_2 > \text{N}\ddot{\text{H}}$

### 23.3 ELECTRONIC DISPLACEMENT EFFECT

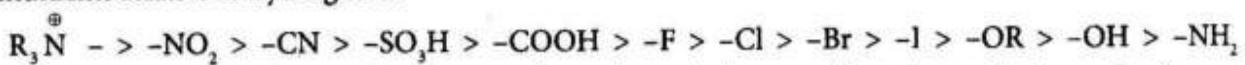


#### 23.3.1 Inductive Effect

The permanent displacement of  $\sigma$ -electrons along a saturated carbon chain towards the more electronegative substituent (atom or group) resulting in development of polarity is termed as inductive effect. The effect weakens steadily with increasing distance from the substituent and actually becomes negligible after two carbon atoms.



Groups or atoms which withdraw electrons of the  $\sigma$ -bond towards themselves as compared to hydrogen are said to have electron-withdrawing or electron-attracting or -I effect. The order of -I effect of some substituents relative to hydrogen is:



Groups or atoms which donate electrons to the carbon chain are said to have electron-releasing or electron-donating or +I effect.

E.g.,  $-\bar{O} > -COO < (CH_3)_3C -> (CH_3)_2CH -> CH_3CH_2 - CH_3 - D -> H -$ . Now little space between different substituents.

- Inductive effect is a permanent effect and is responsible for change in physical and chemical properties of the compounds.

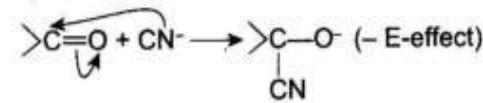
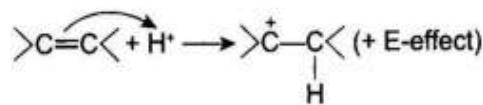
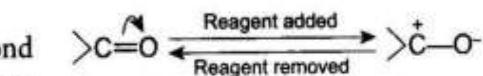
### 23.3.2 Electromeric Effect

It involves the complete transfer of electrons of a multiple bond (double or triple bond) to one of the bonded atoms (usually more electronegative) in presence of an attacking reagent. It is called E-effect.

- This effect is temporary and takes place only in the presence of a reagent. As soon as the reagent is removed, the molecule reverts back to its original position.

#### (a) Classification of electromeric effect:

- +E effect:** If the electrons of the  $\pi$ -bond are transferred to that atom of the double bond to which the reagent gets finally attached, the effect is called +E-effect. Reaction which proceeds through the attack of an electrophile belongs to this category.
- E effect:** If the attack of an attacking reagent and transfer of  $\pi$ -electron occurs to two different atoms, then reaction is known as -E effect. Reaction which occurs through the attack of nucleophile belongs to this category.



### 23.3.3 Resonance

The phenomenon in which more than one electronic structure of a compound is written but none of them is able to represent all the observed properties of the compound completely is termed as resonance. The actual structure of the compound is termed as resonance hybrid while various alternative structures are termed as resonating structures or canonical structures. Resonance phenomenon is further classified into two categories.

- Mesomeric effect
- Hyperconjugation

#### 23.3.3.1 Condition for resonance

- The various resonating structures should differ only in the position of electrons and not in the position of atoms or nuclei.
- All the resonating structures should have the same number of unpaired electrons.
- In case of atoms of the second period in the periodic table, such resonating structures which violate octet rule should not be considered.
- Resonance occurs only in planar molecule or planar part of the molecule, any structural feature which affects the planarity of the molecules also affect the resonance.
- Resonance occurs only in conjugated system, i.e., a system having any one of the following structural feature.
  - $\pi \sigma \pi$
  - $\pi \sigma \oplus$
  - $\pi \sigma \ominus$
  - $\pi \sigma$  odd electron
  - lone pair  $\sigma \oplus$ .



## (a) Stability of resonating structures:

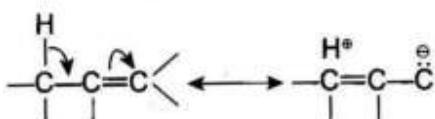
- (i) Non-polar structure, i.e., uncharged structures are more stable in comparison to polar structure.
- (ii) Resonating structures having greater number of covalent bond are more stable in comparison to resonating structures having lesser number of covalent bond.
- (iii) Resonating structures in which octet of all atoms is complete are more stable in comparison to the resonating structure where octet of some atom is incomplete.
- (iv) Among polar structures greater the charge separation between like charges greater will be their stability.
- (v) Among polar structures greater the charge separation between unlike charges lesser will be their stability.
- (vi) Among polar structure in which -ve charge is present on more electronegative atom and +ve charge is present on less electronegative atom will be more stable.

**23.3.4 Hyperconjugation Effect**

The phenomenon of displacement of electrons by conjugative mechanism involving  $\sigma$ ,  $\pi$  and p-electrons is called hyperconjugation. Nathan and Baker pointed out that alkyl groups having atleast one hydrogen atom on the carbon atom, attached to an unsaturated carbon atom either having a double bond odd electron free radical, positively charged carbonium ions are able to release electrons due to delocalization of  $\sigma$  and  $\pi$ -bonds (or p-orbitals).

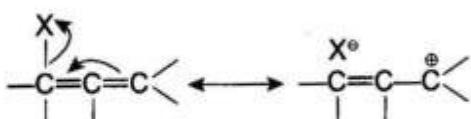
- Hyperconjugation is also called Boher Nathan-effect or no bond resonance or sacrificial conjugation.

(a) **Classification of conjugation:** Because number of covalent bonds is not equal in all hyperconjugating structures.

(i)  $\sigma$ - $\pi$  conjugation or heterovalent hyperconjugation:(ii)  $\sigma$ -p conjugation or isovalent hyperconjugation:

Because number of covalent bonds is equal in all hyperconjugating structures.

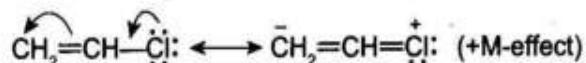
## Reverse hyperconjugation:



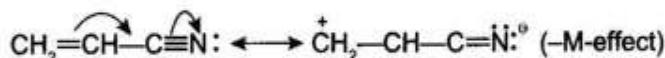
(iii) **Mesomeric effect:** In case of conjugated systems (having alternate  $\sigma$ -and  $\pi$ -bonds)  $\pi$ -electrons can flow from one part of the molecule to the other due to resonance. As a result, centres of low and high electron density are created in such molecules. This flow of electron (or generation of centres of low and high electron density) in conjugated systems as a result of the phenomenon of resonance is called mesomeric effect (M-effect).

## (b) Classification of mesomeric effect:

(i) **+M effect:** Groups which donate electrons to the double bond of a conjugated system are said to have + M effect. For example, -OH, -OR, -SH, -SR, -NH<sub>2</sub>, -NHR, -NR<sub>2</sub>X (halogens), etc. Thus,



(ii) **-M effect:** Groups which withdraw electrons from the double bond or from a conjugated system towards themselves due to resonance are said to have -M effect. For example, > C=O, —CHO, —COOR, —CN, —NO<sub>2</sub>, —SO<sub>3</sub>H, —COR, —CONH<sub>2</sub>.



## 23.4 REACTION INTERMEDIATES

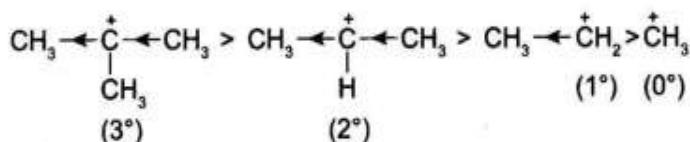
The highly reactive short-lived ( $10^{-6}$  s to a few seconds) chemical species through which majority of the organic reactions occur are called the reaction intermediates. They are formed by the action of a suitable reagent on the substrate molecule. E.g., carbocations, carbanions, free-radicals, carbenes, nitrenes and benzyne.

### 23.4.1 Carbocations

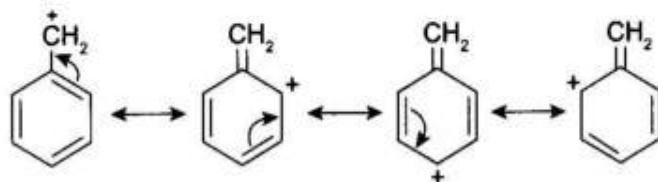
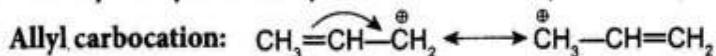
Chemical species bearing a positive charge on carbon atom and carrying six electrons in its valence shell are called carbocations. They are formed by heterolytic cleavage of covalent bonds. The carbocations are planar species. The carbon atom carrying the positive charge is  $sp^2$ -hybridized. The unhybridized p-orbital which is perpendicular to the plane of the three  $\sigma$ -bonds is, however, empty.

- Stability of carbocation  $\propto \frac{1}{\text{Intensity of positive charge}}$  on carbon atom

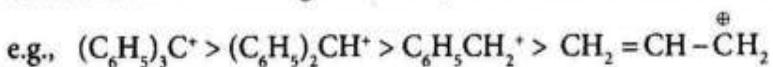
(a) **Stability of alkyl carbocations:** Order of stability of alkyl carbocation depends upon (i) + I-effect and (ii) hyperconjugation. The relative stability of simple alkyl carbocations follows the sequence:  $3^\circ > 2^\circ > 1^\circ$ , i.e.



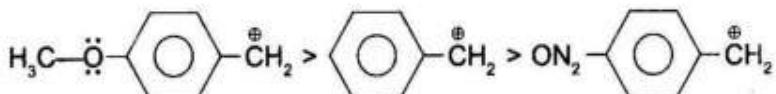
(b) **Stability of allyl and benzyl carbocation:** Allyl and benzyl carbocations are stabilized by resonance.



Greater the number of phenyl groups attached to the carbon atom bearing the positive charge, larger the number of resonating structures, more stable is the carbocation.

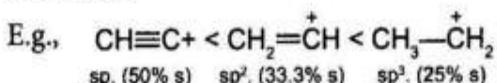


- Electron-donating substituents in the benzene ring tend to stabilize the substituted carbocation relative to benzyl carbocation by dispersal of the positive charge. Conversely, electron withdrawing groups in the benzene ring tend to destabilize the substituted carbocations relative to benzyl carbocation by intensification of the positive charge. E.g.,

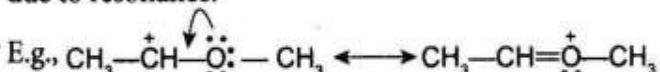


- (c) **Stability of vinyl carbocation:** Carbocations in which the positive charge is located on a doubly bonded carbon such as vinyl ( $\text{CH}_2 = \overset{+}{\text{CH}}$ ) and phenyl  $\text{C}_6\text{H}_5^+$  cannot be stabilized by resonance and hence are quite unstable.

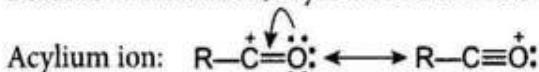
  - As the s-character of the carbon bearing the positive charge increases, the stability of the carbocation decreases.



- (d) **Stabilization due to heteroatom:** If a heteroatom (O, N, Cl, etc.) having a lone pair of electrons is present next to the carbon atom bearing the positive charge, the stability of the carbocation increases due to resonance.



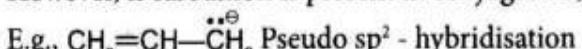
- Because of resonance, acylium ion is almost as stable as tert-butyl carbocation.



### 23.4.2 Carbanions

Chemical species in which the carbon atom bears a negative charge and is surrounded by an octet of electrons are called carbanions. They are produced by heterolytic cleavage of covalent bonds. The structure of simple carbanions is usually pyramidal. The carbon atom carrying the negative charge is  $sp^3$ -hybridized.

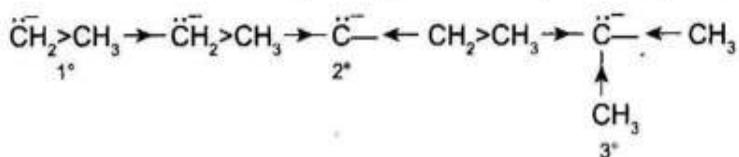
However, if carbanion is present in conjugation, then its hybridization is assumed to be  $sp^2$ .



- (a) Stability of carbanions.**

- Stability of carbanion  $\propto \frac{1}{\text{Intensity of } -\text{ve charges}}$  of carbon atom

- (i) **Stability of alkyl carbanions:** It follows a sequence which is exactly reverse of that of alkyl free radicals and carbocations, i.e., primary > secondary > tertiary, i.e.,

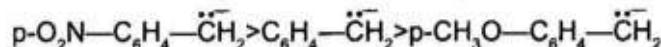


As the number of alkyl groups increases the intensity of the negative charge on the central carbon atom increases and hence the stability decreases accordingly.

- (ii) **Allyl and benzyl carbanions:** Though they are primary, still are more stable than simple primary alkyl carbanions due to resonance.

As the number of phenyl groups attached to the carbon atom bearing the negative charge increases the stability increases accordingly.

- (iii) Electron-donating substituents in the benzene ring tend to decrease while electron-withdrawing substituents tend to increase the stability of substituted carbanions relative to benzyl carbanion.

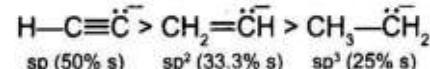
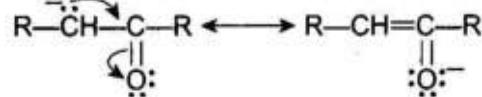


- (iv) If the  $\alpha$ -position of a carbanion has a functional group which contains a multiple bond ( $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ ,  $\text{C}\equiv\text{N}$ ,  $\text{NO}_2$ , etc.) or carries an electronegative atom, such carbanions are stabilized by resonance and hence are more stable than simple aryl carbanions.

E.g., the stabilizing effect of the various  $\alpha$ -substituents follows the order:  $\text{NO}_2 > \text{RCO} > \text{COOR} > \text{CN} > \text{X}$  (halogen).

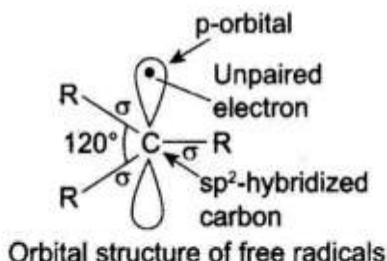
- (v) If the  $\alpha$ -position of a carbanion has a functional group which contains a multiple bond ( $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ ,  $\text{C}\equiv\text{N}$ ,  $\text{NO}_2$ , etc.) or carries an electronegative atom, such carbanions are stabilized by resonance and hence are more stable than simple aryl carbanions. E.g., the stabilizing effect of the various  $\alpha$ -substituents follows the order:  $\text{NO}_2 > \text{RCO} > \text{COOR} > \text{CN} > \text{X}$  (halogen).

- The stability of the carbanion increases as the per cent s-character of carbon holding the negative charge increases.



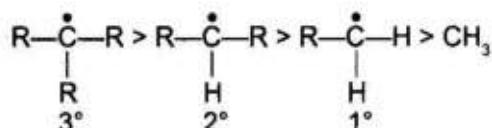
### 23.4.3 Free Radicals

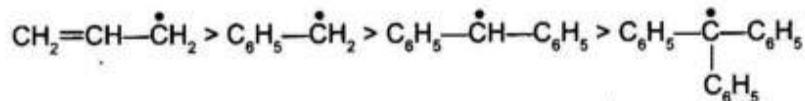
An atom or a group of atoms carrying an odd or unpaired electron is called a free radical. They are paramagnetic due to the presence of an unpaired electron and are formed by homolysis of covalent bonds either by heat or by light. Free radicals like carbocations are planar chemical species. The carbon atom carrying the unpaired electron is  $\text{sp}^2$ -hybridized. The unhybridized 2p-orbital which is perpendicular to the plane of three  $\sigma$ -bonds contains the unpaired electron.



#### Stability of free radicals:

- The order of stability of free radicals is the same as that of carbocations i.e., this order of stability can be easily explained on the basis of hyperconjugation effect of the alkyl groups.
- Allyl and benzyl free radicals are stabilized by resonance and hence are more stable than alkyl free radicals. Further, as the number of phenyl groups attached to the carbon atoms holding the odd electron increases, the stability of the free radicals increases accordingly.



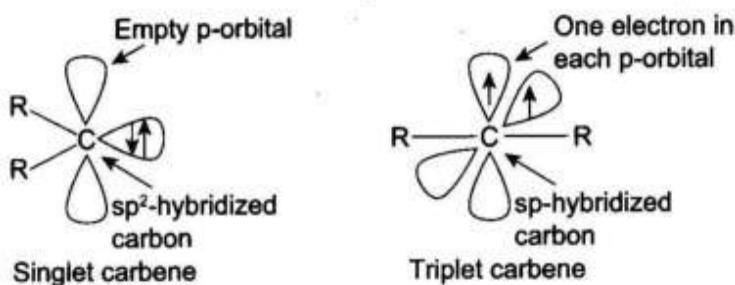


### 23.4.4 Carbenes

Neutral divalent carbon species in which the carbon is bonded to two monovalent atoms or groups and is surrounded by a sextet of electrons are called carbenes.

E.g.,  $\text{CH}_2$  (methylene),  $\text{CCl}_2$  (dichlorocarbene), etc.

Like in carbocations, the central carbon atom in carbenes has only a sextet of electrons in its valence shell and thus has a strong tendency to complete its octet by gaining two more electrons. Carbenes, thus, behave as Lewis acids and electrophiles.



**Classification of carbenes:**

#### 1. Singlet carbene

#### 2. Triplet carbene

In **singlet carbenes**, the central carbon atom is  $\text{sp}^2$ -hybridized and two of the  $\text{sp}^2$ -hybridized orbitals form two  $\sigma$ -bonds with two monovalent atoms or groups while the third  $\text{sp}^2$ -hybridized orbital contains two non-bonding electrons. The unhybridized p-orbital is, however, empty. Thus, a singlet carbene has a bent structure. They are also called excited-state carbene because they exist in higher energy state.

In **triplet carbenes**, the central carbon is  $\text{sp}$ -hybridized and the two  $\text{sp}$ -hybridized orbitals form two  $\sigma$ -bonds with two monovalent atoms or groups while the two unhybridized p-orbitals have one electron each. Thus, a triplet carbene has a linear structure and behaves as a diradical. They are also called ground state carbene.

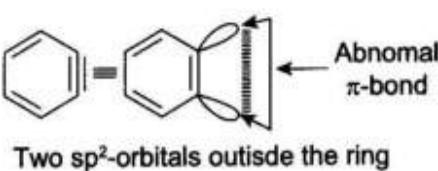
- It may be noted that a triplet carbene is always more stable than a singlet carbene.

**Stability:** Due to interelectronic repulsions between the two electrons present in the same orbital in a singlet carbene, a triplet carbene is generally more stable than a singlet carbene by about  $38\text{--}46\text{ kJ mol}^{-1}$ .

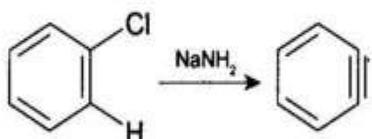
- The decreasing order of stability of different types of singlet carbenes is as follows:  
 $\ddot{\text{C}}\text{H}_2 > \ddot{\text{C}}\text{F}_2 > \ddot{\text{C}}\text{Cl}_2 > \ddot{\text{C}}\text{Br}_2$

### 23.4.5 Benzyne

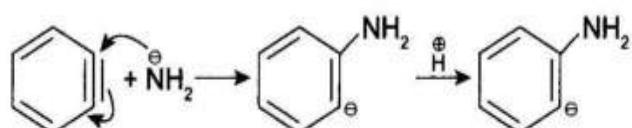
1. 1, 2-didehydrobenzene,  $\text{C}_6\text{H}_4$ , and its derivatives are called benzyne or arynes and the simplest member is benzyne.



2. It is a neutral reaction intermediate derived from benzene ring by removing two substituents, of ortho positions, one in the form of electrophile and other in the form of nucleophile leaving behind two electrons to be distributed between two orbitals.



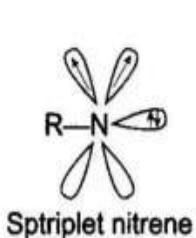
3. Benzyne intermediate is aromatic in character.  
 4. When halobenzene is heated with sodamide, formation of benzyne takes place.  
 5. (i) It behaves as a dienophile and gives Diels-Alder reaction with diene.  
 (ii) It reacts with strong nucleophile like NH<sub>2</sub>.



### 23.4.6 Nitrenes (R - N<sup>+</sup>)

1. The nitrogen analogue of carbenes are called nitrenes.  
 2. There is a possibility of two spin states for nitrenes depending on whether the two non-bonding electrons (the normal nitrogen lone pair remains paired) have their spins paired or parallel.

R - N<sup>+</sup> These two are lone pair of electrons.



These two may be paired or unpaired.

3. In general, nitrenes obey Hund's rule and are ground state triplets with two degenerate sp-orbitals containing a single electron each.

## ORGANIC REACTIONS

### 24.1 INTRODUCTION

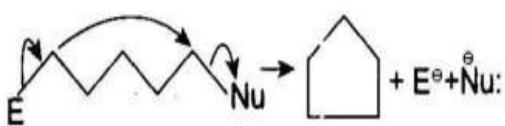
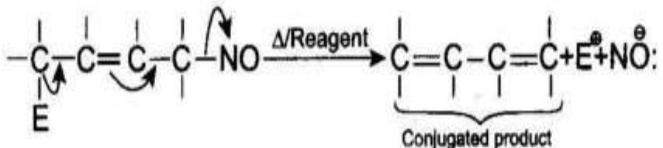
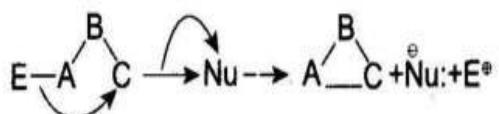
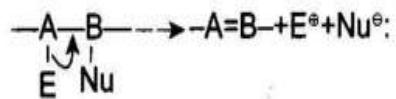
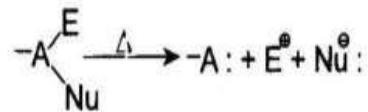
Organic reaction belongs to following categories:

- |                           |                          |                                |
|---------------------------|--------------------------|--------------------------------|
| 1. Elimination reaction   | 2. Addition reaction     | 3. Substitution reaction       |
| 4. Rearrangement reaction | 5. Condensation reaction | 6. Disproportionation reaction |

### 24.2 ELIMINATION REACTION

If two groups are removed from a substrate molecule, then the reaction is termed as elimination reaction. Depending upon the relative position of leaving groups, they are classified into four categories.

- (i)  **$\alpha$ -elimination reaction:** If both leaving group are present on same atom of substrate molecule, then the reaction is termed as  $\alpha$ -elimination. This reaction always results in the formation of carbenes and nitrenes which are unstable and therefore this reaction is always endothermic.
- (ii)  **$\beta$ -elimination reaction:** If leaving groups are present on the adjacent atom of a substrate molecule, then the reaction is termed as  $\beta$ -elimination. Mostly elimination reaction belongs to this category. In such a reaction, there occurs loss of two sigma bond and gain of one  $\pi$ -bond and therefore product system is less stable than that of reactant system and therefore this reaction is always endothermic.
- (iii)  **$\gamma$ -elimination reaction:** If leaving groups are present on alternate atom of a substrate molecule, then the reaction is termed as  $\gamma$ -elimination.  $\gamma$ -elimination always results in the formation of cyclo-propyl ring which is a strained structure. This reaction is also endothermic.
- (iv)  **$\delta$  or higher order elimination:** If leaving groups are present on (1, n) position of a substrate molecule where  $n \geq 4$ , then the reaction is termed as  $\delta$  or higher-order elimination. This elimination always results in the formation of either a conjugated product or a cyclic ring. If a conjugated product is obtained as a product, then it is termed as conjugate elimination (here,  $n \geq 4$  and always even) for cyclic ring ( $n \geq 4$ ; and can be odd or even)



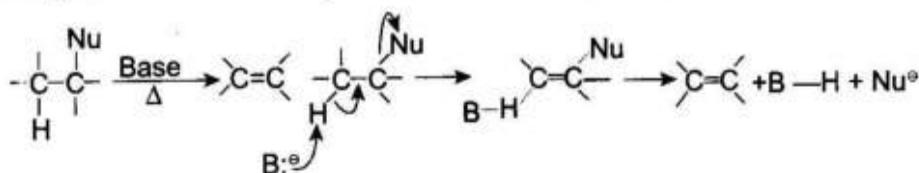
$\beta$ -Elimination reaction: It is further classified into three categories.

1. Bimolecular elimination reaction ( $E_2$ )
2. Unimolecular elimination reaction
  - (a)  $E_1$  reaction (carbocationic elimination)
  - (b)  $E_1\text{cb}$  reaction (carbanionic elimination)
3. Pyrolytic elimination reaction

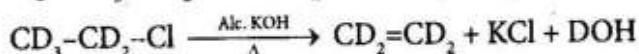
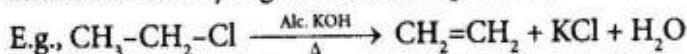
**Bimolecular elimination reaction ( $E_2$ ):** When a substrate molecule having a good nucleofuge and having atleast one  $\beta$ -hydrogen w.r.t. nucleofuge, is heated with strong base then elimination product alkene or alkyne is obtained.

Reaction proceeds in a single step and therefore involved in the formation of a transition state.

Transition state produced during the reaction must acquire anti-periplanar arrangement in which five atoms including base atom lie in one plane and both leaving groups must be exactly anti to each other.

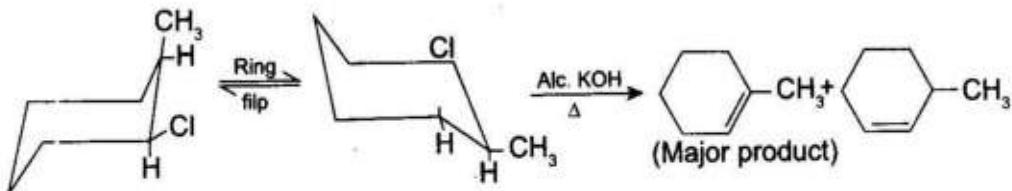


1. **Characteristics of  $E_2$  reaction:** Rate of reaction depends upon substrate concentration as well as base concentration or both. Therefore, reaction follows second-order kinetics.
2. Since reaction proceeds in single step, whose molecularity is 2, therefore reaction is termed as bimolecular elimination reaction.
3. Presence of good leaving group on substrate increases its reactivity towards  $E_2$  reaction.  
 $R-\text{F} < R-\text{Cl} < R-\text{Br} < R-\text{I}$
4. Since reaction rate depends upon base concentration therefore by considering high concentration of strong base,  $E_2$  reaction is favourable.
5. Reaction best proceeds in polar aprotic or less polar solvents.
6. Rearrangement is impossible during the reaction.
7. Reaction has very high kinetic isotope effect.



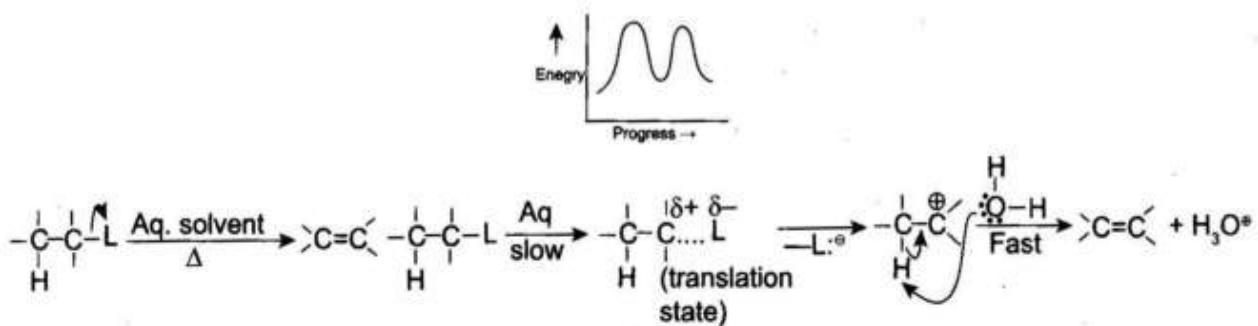
first reaction system is seven times more reactive than the second reaction system under similar conditions.

8. Both leaving groups must be exactly anti to each other, e.g., in case of cyclo-hexyl substrate in order to participate in  $E_2$  mechanism, both leaving groups must be present at the axial position in chair conformation rather than equatorial position.



**II Uni molecular elimination reaction:** It is further classified into two categories.

1.  $E_1$  reaction (carbocationic elimination): When a substrate molecule having a good nucleofuge leaving group is heated in a polar protic solvent, then elimination product is obtained.  
 Reaction proceeding through the formation of carbocation reaction inter mediate is the slowest step.



### 24.2.1 Characteristics

1. In slowest step of  $E_1$  reaction, only substrate molecule is present therefore reaction follows first order kinetics.
2. Since slowest step of reaction is independent from base concentration therefore,  $E_1$  reaction is favourable in presence of low base concentration or when weak base is involved.
3. Presence of good nucleofuge increases the reactivity of substrate towards  $E_1$  reaction.
4. Reaction best proceeds in a polar protic solvent because it favours the formation of transition state as well as stabilizes the carbocation intermediate.
5. Rearrangement is always possible in  $E_1$  reaction.

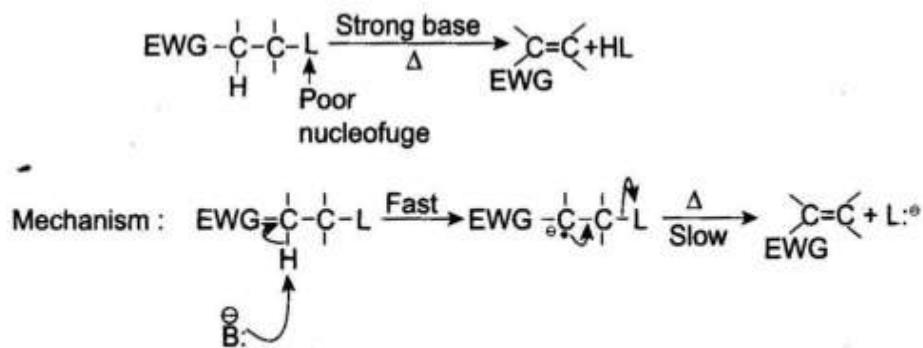
## 24.3 $E_1 \text{ CB}$ REACTION (CARBANIONIC ELIMINATION)

In this reaction removal of electrofuge mostly hydrogen occurs first from substrate nucleophile which results in the formation of carbanion intermediate followed by the removal of nucleophile in a slowest step to give elimination product.

### 24.3.1 Conditions for $E_1 \text{ cb}$

1. Substrate molecule must have a poor nucleophile.
2.  $\beta$ -carbon with respect to nucleophile must have atleast one H.
3. Reaction must proceed in presence of a strong base.

In  $E_1 \text{ cb}$  electrofuge is removed first resulting in the formation of carbanion followed by removal of nucleophile in a slowest step to give elimination product.



**General elimination rules:** The following four rules are taken into consideration for this purpose.

1. **Saytzeff's rule (Zaitsev's rule):** According to this rule, during elimination reaction, hydrogen is always removed from that  $\beta$ -carbon which possess minimum number of hydrogen atoms. Under such conditions, formation of more stable substrate alkene occurs, which is more stable because of hyper conjugation.

**Note:**

Saytzeff's rule is followed in all E<sub>1</sub> reactions and in majority of E<sub>2</sub> reactions.

2. **Hofmann's rule, i.e., Anti-Saytzeff's rule**

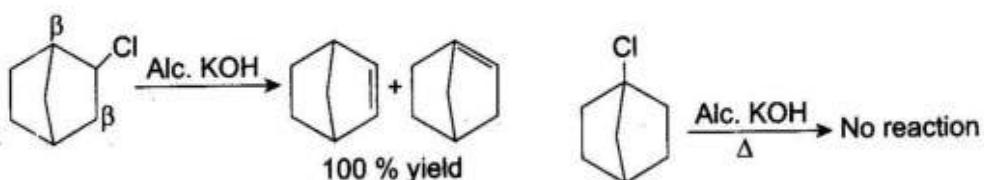
According to this rule, if reaction condition is favourable, then H is removed from that  $\beta$ -carbon with respect to nucleophile which posses more number of hydrogen atoms.

**Note:**

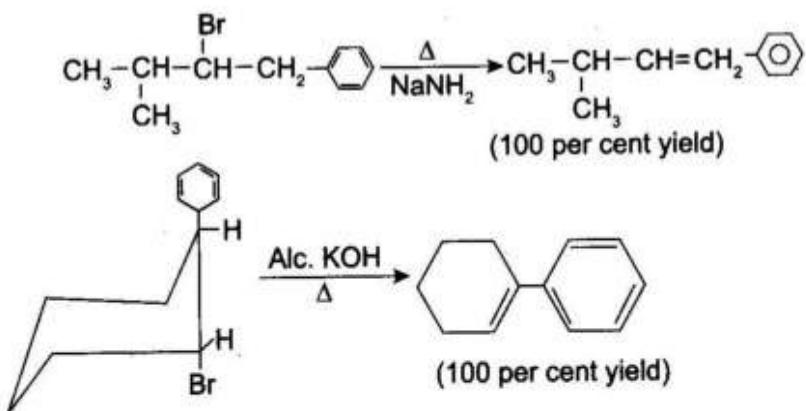
Hofmann's rule is followed in some E<sub>2</sub> reaction and in all E<sub>1,ab</sub> reactions as well as in pyrolytic elimination reaction.

3. **Bredt's rule**

According to this rule, no matter reaction follows whatsoever mechanism a multiple bond never go to the bridge head carbon of a bridged bicyclic compound unless excellent nucleophile is present or ring size is large enough.

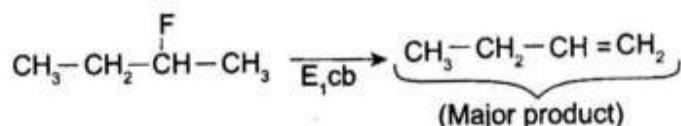


4. **Conjugation rule:** According to this rule, no matter a reaction follows whatsoever the mechanism is if a substrate molecule already possess a multiple bond then newly formed multiple bond is produced in such a manner that it is present in conjugation with old multiple bond. This rule is followed even in those cases where stereochemistry is unfavourable.

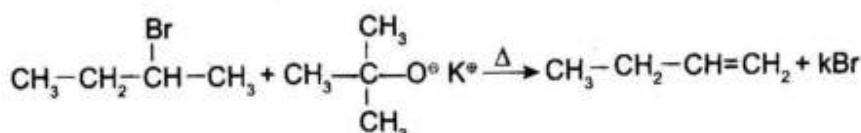


**E<sub>2</sub> reaction where Hofmann's rule is followed:**

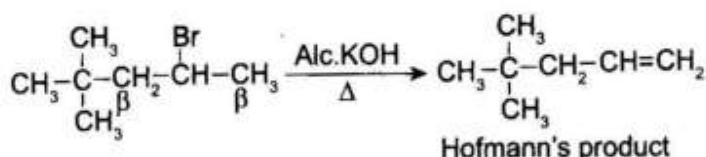
1. **De-hydrohalogenation of alkyl halide having poor nucleophile produces Hofmann's product as the major product**



2. If a bulky base is involved in a E<sub>2</sub> reaction, then Hofmann's product is the major product.

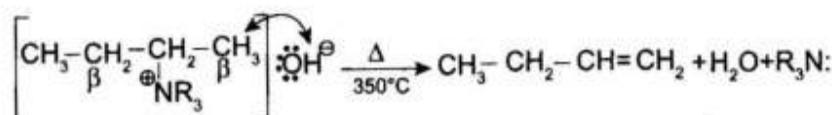


3. If  $\gamma$ -carbon w.r.t. nucleophile is quaternary, then Hofmann's product is the major product.



4. If a substrate molecule contains bulky leaving group, then Hofmann's product is the major product.

**Hofmann's degradation:** When quaternary ammonium hydroxide having atleast one hydrogen at  $\beta$ -carbon is heated at 350°C, alkene is obtained according to Hofmann's elimination rule.



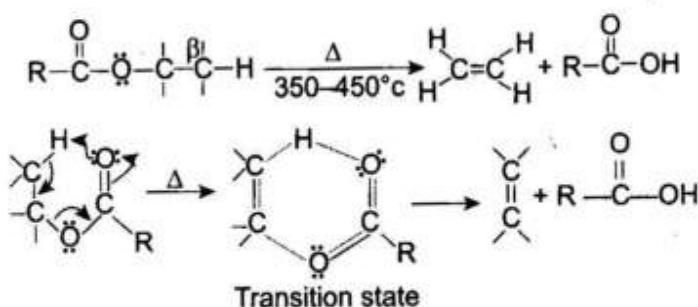
**Pyrolytic elimination:** This elimination is given by a very small family of organic compounds like ester, xanthate and amine oxides. This reaction proceeds in a gaseous phase at high temperature, (usually above the boiling point of the substrate) and does not involve any catalyst. Reaction is example of syn elimination because it proceeds through the formation of a cyclic transition state.

Reaction always follows Hofmann's elimination rule.

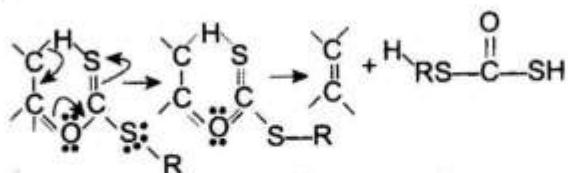
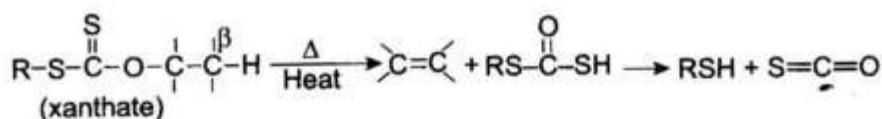
### 24.3.2 Pyrolysis of ester

1. When ester containing atleast one  $\beta$ -hydrogen on the alkyl group attached with oxygen atom is heated at 350– 450°C, alkene is obtained.

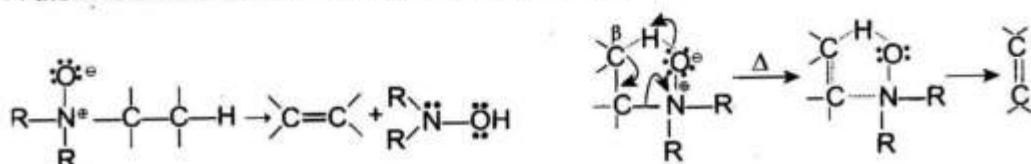
**Mechanism**



2. **Pyrolysis of xanthates:** When xanthate having atleast one  $\beta$ -hydrogen on alkyl group attached with oxygen atom is heated at 200–300°C, alkene is obtained.



**3. Pyrolysis of amine oxide:** When amine oxide having atleast one  $\beta$ -hydrogen on alkyl group attached with N atom is heated at 150–250°C, alkene is obtained.



**Addition reaction:** A substrate molecule having a multiple bond can participate in addition reaction except cyclopropane. Cyclopropane is the only substrate which possess no multiple bond; still, it can participate in addition reaction because of presence of angular strain.

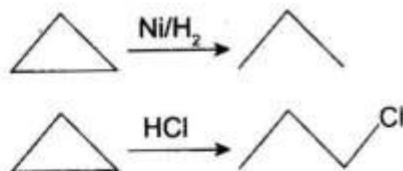
In addition reaction, there occurs loss of one  $\pi$  bond and gain of two  $\sigma$ -bonds, therefore, product system is more stable than that of reactant system due to which reaction is always exothermic.

Depending upon the type of reagents involved in slowest step, addition reaction reactions are classified into three categories:

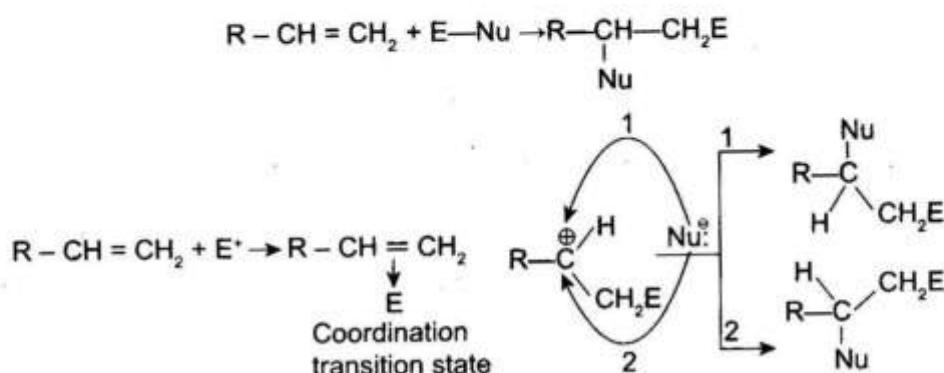
(i) **Electrophilic addition:** This reaction is mainly given by alkene and alkyne.

- In general, reaction proceeds in two steps through the formation of carbocation intermediate.
- Due to formation of carbocation intermediate, rearrangement is possible during the reaction.
- If the reagent involved is a weak electrolyte like water, alcohol, HCN, etc. then reaction is catalysed by some Lewis acid or some protonic acids.
- If substrate and reagent both are unsymmetrical, then reaction follows Markownikoff's addition rule and is an example of Regio; Selective reaction.

All addition reaction which follow either markownikoff's rule and elimination reaction which follow saytzeff and anti Saytzeff's rule are example of Regio -Selective reaction.

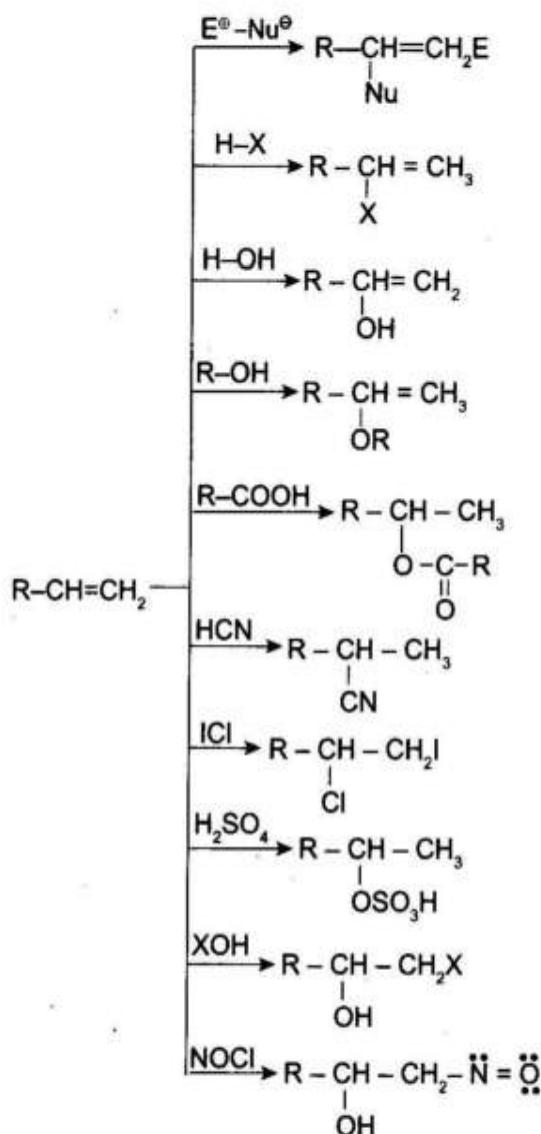


## 24.4 GENERAL REACTION MECHANISM

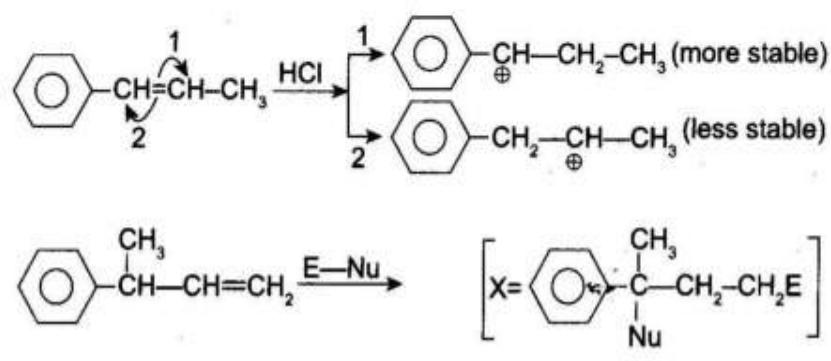


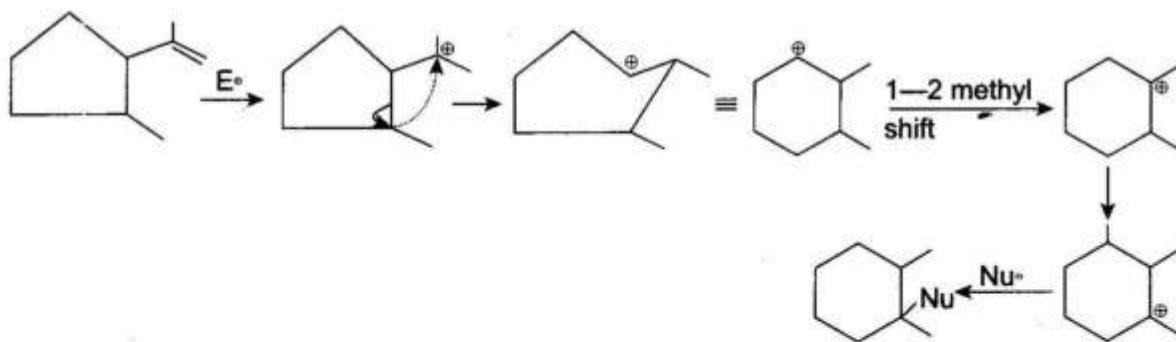
### 24.4.1 Markownikoff's Rule

**Old statement:** If both substrate and reagent are unsymmetrical, then positive part of the reagent is attached with that part of multiple bond which possess more number of hydrogen atom.



**Modern statement:** If both reagent and substrate are unsymmetrical, then attack of electrophile occurs in such a manner that the formation of more stable carbocation occur.





**Nucleophilic substitution reaction:** When part of a substrate is replaced by nucleophilic part of reagent, then reaction is termed as nucleophilic substitution substrate. In nucleophilic substitution, involved is either neutral or positively charged whereas substrate reagent involved is either neutral or negatively charged.

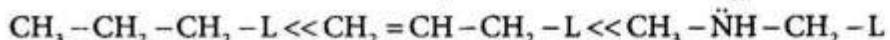
#### Factors affecting Nucleophilic substitution reaction

**Structural feature of substrate:** Branching present at  $\alpha$  or  $\beta$ -carbon of the substrate w.r.t. nucleophile decreases its reactivity towards  $S_N2$  reaction because of increase in steric hindrance  $R - L + Nu^- \rightarrow R - Nu + L^+$

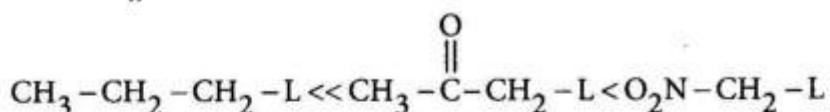
Alkyl part of Substrate	Relative reaction rate
1. $C_2H_5-$	1
2. $CH_3-$	30
3. $CH_3 - CH_2 - CH_2 -$	0.4
4. $\begin{array}{c} CH_3 \\   \\ CH - \\ H_3C \end{array}$	0.025
5. $\begin{array}{c} CH_3 \\   \\ CH_3 - CH - CH_2 - \end{array}$	0.03
6. $CH_3 - CH_2 - CH_2 - CH_2 -$	$\sim 0.4$
7. $\begin{array}{c} CH_3 \\   \\ H_3C - C - CH_2 - \\   \\ CH_3 \end{array}$	$10^{-5}$
8. $\begin{array}{c} CH_3 \\   \\ H_3C - C - \\   \\ CH_3 \end{array}$	0
9. $CH_2 = CH - CH_2 -$	40
10. $\begin{array}{c} \text{C}_6\text{H}_5 \\    \\ CH_2 \end{array}$	120

Branching present at  $\gamma$  or  $\delta$  carbon creates steric effect but not hindrance.

- Branching present at  $\alpha$  or  $\beta$ -carbon increases the reactivity of substrate towards  $S_N1$  reaction.
- Unsaturation present at  $\beta$ -carbon or heteroatom containing lone pair of electron present on  $\alpha$ -carbon increases the reactivity of substrate towards  $S_N1$  reaction.

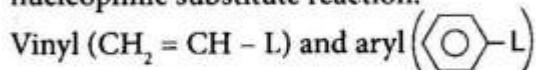


3. Presence of strong electron with - drawing group on  $\alpha$ -carbon of substrate increases its reactivity towards  $S_N2$  mechanism.



Strong electron withdrawing group increases the charge intensity on  $\alpha$ -carbon due to which attraction for nucleophile increases.

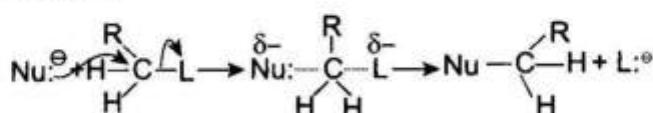
4. Unsaturation present at  $\alpha$ -carbon may increase or decrease the reactivity of substrate towards nucleophilic substitution reaction.



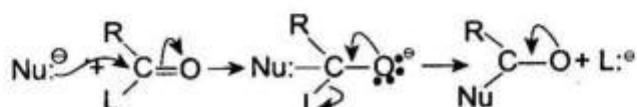
Substrates are almost inert toward nucleophilic substitution reaction.

Comparative study between nucleophilic acyl substitution and aliphatic nucleophilic substitution:

Nucleophilic acyl substitution

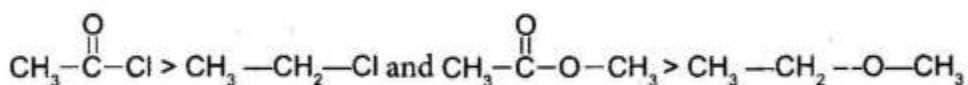


Aliphatic nucleophilic substitution

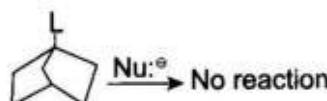


Acyl substrates ( $\text{R}-\text{C}(=\text{O})-\text{L}$ ) are more reactive than that of alkyl substrate ( $\text{R}-\text{CH}_2-\text{L}$ ) because of the following facts.

S. No.	Nucleophilic acyl substitution	Aliphatic nucleophilic substitution
1.	During the attack of nucleophile cleavage of a weak $\pi$ -bond occur	During the attack of nucleophile cleavage of a strong $\sigma$ bond occurs
2.	Carbon of aryl substrate is more electron deficient; therefore, offers more attraction for nucleophile.	Carbon of alkyl substrate is less electron deficient; therefore, offers less attraction for nucleophile
3.	Substrate molecule is planar and therefore offers less steric hindrance	Substrate molecule is tetrahedral, i.e., nonplanar and therefore offers more steric hindrance
4.	Reaction involves the formation of a tetrahedral intermediate which is more stable	Reaction involves the formation of transition state which is less stable



5. Leaving groups present on bridged carbon of bridged bicyclic compound are always inert towards any kind of nucleophilic substitution.



**Nature and concentration of nucleophilic:** In slowest step of  $S_N1$  reaction, nucleophile is not involved and therefore rate of  $S_N1$  reaction is independent from the nature and concentration of nucleophile. If nucleophile is weak and its concentration is low, then  $S_N1$  mechanism is favourable. In most of the  $S_N1$  reactions solvent molecule acts as a nucleophile itself.

Since  $S_N2$  reaction proceeds through a single step, therefore the rate of reaction depends upon the nature as well as identity of nucleophile, i.e., if nucleophile is strong and its concentration is high, then  $S_N2$  mechanism is favourable. Nucleophilicity depends upon

$$1. \text{ In polar protic solvents like water, alcohol, etc. nucleophilicity} \propto \frac{1}{\text{Extent of hydration}}$$

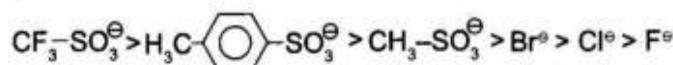
$$\text{Extent of hydration} \propto \frac{1}{\text{Size of nucleophilic atom}}$$

2. **Polarizability of nucleophilic atom:** Nucleophilicity  $\propto$  polarizability of nucleophilic atom

**Nature of leaving group:** Presence of good nucleofuse increases the reactivity of substrate towards  $S_N1$  and  $S_N2$  reactions.

$$\text{Leaving tendency of nucleofuse, i.e., nucleofusity} \propto \frac{1}{\text{Basicity}}$$

Therefore, we can say that weakest bases are best nucleofuses. Order of nucleofusity



**Nature of solvent used:** This is a very important factor. Some reactions may not proceed due to improper selection of solvent only.

Selection of solvent towards  $S_N1$  reaction

Substrate	Transition State Product	Stabilization of Transition State w.r.t Substrate in Polar Protic Solvent	Effect on Reaction State
1. $(R - L)$	$R^{\delta+} \dots L^{\delta-}$	More	Increases
2. $R - L^{\delta+}$	$R^{\delta+} \dots L^{\delta+}$	Less	Decreases

Selection of solvent towards  $S_N2$  reaction

Reactant System	Transition State Produced	Stabilization of Transition State w.r.t Reactant in Polar Protic Solvent.	Effect on Reaction State
1. $R - L + Nu$	$\overset{\delta+}{Nu} \dots \overset{\delta-}{R} \dots L$	More	Increases
2. $R - L + Nu^{\delta-}$	$\overset{\delta-}{Nu} \dots \overset{\delta-}{R} \dots L$	Less	Decreases