Chapter 1

Solid State

Solids have definite shape and volume. They are incompressible and rigid. They posses strongest inter molecular forces.

Classification of solids

Solids are broadly classified in to crystalline solids and amorphous solids. In crystalline solids, the constituent particles are arranged in an ordered manner.

Eg: NaCl, KCl, KNO_3, Ice Diamond, graphite etc.

In amorphous solids, the constituent particles are arranged in an irregular manner.

Eg: glass, plastics, rubber, polymers etc.

Crystalline solids	Amorphous solids
• Regular arrangement of particles	• Irregular arrangement of particles
• Posses Long range order	• Posses only short range order
• Posses sharp melting point	• Do not posses sharp Melting point
• Anisotropic	• Isotropic

Anisotropy and Isotropy

In Crystalline solids, the properties like refractive index, electrical resistance, co-efficient of thermal expansion etc show different values in different directions. This is called anisotropy. But is Amorphous solids the properties like refractive index, electrical resistance, thermal expansion etc show same values is all directions. This is called isotropy.

Glass sheets of old buildings are slightly thicker at the bottom than at the top. This is due to slow flowing tendency of glass. ∴Glass is a super cooled liquid (Pseudo solid).

Crystalline solids are again classified in to 4 types based on the nature of constituent particles.

1) ***Molecular solids*** – Constituent particles are molecules. They are held by van-der-waals forces. Eg: Ice, dry ice, I_2 etc.

2) ***Ionic solids*** – constituent particles of ions and they are held by ionic bond.

   Eg: NaCl, CaF_2, $MgCl_2$ etc.

3) ***Metallic solids*** – Constituent particles are +ve ions (Kernels) surrounded by pool of electrons. The Kernels are held by Metallic bond.

   Eg: All metals, Alloys etc.

Covalent solids (Network Solids)

In covalent solids, the constituent particles are atoms. They are held together by covalent – bonds.

Eg: Diamond, Graphite, Silica (SiO_2), Carborandum (SiC) etc.

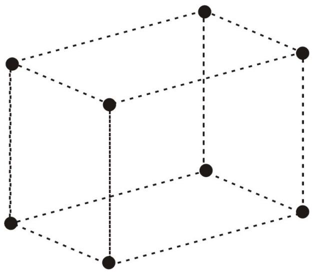
In Diamond, 'C' atoms are sp^3 hybridised. It has three dimensional network structure of c- atoms. Since the network structure is very strong, diamond is very hard and hence used in cutting and drilling tools.

But is graphite 'C' atoms are sp^2 hybrdised. It has two dimensional layer structure of C atoms with free electron between the hexagonal layers. Due to free electrons one layer steps over other layer. $\therefore$Graphite is soft since there are free electrons, it is a good conductor of electricity.

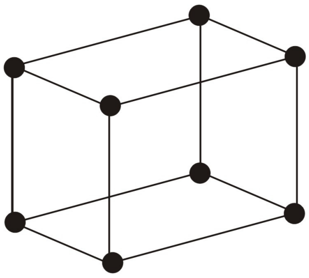
Crystal lattice & Unit cell

A regular three dimensional arrangements of points is space showing how particles are arranged in crystal is called crystal lattice (space lattice)

The smallest repeating unit of a crystal is called unit cell.



Crystal lattice



Unit cell

Crystal systems

Depending on the edge lengths a, b, c and arial angles α, β, γ crystal systems are of 7 types. They are cubic, tetragonal orthorhombic, Hexagonal, Rhombohedral, Monoclinic and triclinic. Each crystal system is again classified in to primitive, bodycentered, face centered and end centered. Cubic system is the simplest crystal system. For cubic system $a = b = c$ & $\alpha = \beta = \gamma = 90°$ for tetragonal system $a = b \neq c$, $\alpha = \beta = \gamma = 90°$ for orthorhombic, $a \neq b \neq c$ & $\alpha = \beta = \gamma = 90°$ (match box type) etc..

Types of cubic system

Cubic crystal system is of three types.

1. ***Simple cubic (primitive cubic)***

   In simple cubic, all the corners are occupy by particles. Each corner particle is shared by 8 cubes... only $\frac{1}{8}$ th of a particle is inside a cube. $\therefore$number of particles per unit cell = $8\times\frac{1}{8}$ =1.

2. ***Body centred cubic (BCC)***

   In BCC, all the corners and centre of the unit cell are occupied by particles. $\therefore$Number of particles per unit cell in BCC = $(\frac{1}{8} \times 8) + 1 = 1 + 1 = 2$

3. ***Face centred cubic (FCC)***

   In FCC all the corners and all the face centers are occupied by particles. ½ of each face particle is inside a unit cell.

   $\therefore$ No of particles per unit cell in FCC = $(\frac{1}{8}\times 8) + (\frac{1}{2}\times 6) = 1 + 3 = 4$

Close packing of particles

In solids, the constituent particles are closely packed together to occupy maximum space. There are three ways of close –packing in 3 dimension.

a) ***Primitive close packing (PCP)***

It starts from SCP in 2D. In PCP, the particles are arranged in A A A A..... pattern.

b) ***Hexagonal close packing (HCP)***

It begins from 2D HCP. In HCP, the particles are arranged in AB AB AB.... pattern. It is formed when particles of third layer are placed are tetrahedral voids of 2nd layer.

c) ***Cubic close packing (CCP)***

It also begins from 2D HCP. In CCP, the particles are arranged in AB CA BC.... pattern. It is formed when particles of 3rd layer are placed over octahedral voids of the 2nd layer.

- **Coordination Number**

The no of nearest touching particles in a close – packing arrangement is called coordination number.

- Co-ordination number in PCP = 6
- Co-ordination number in HCP and CCP = 12.

- **Voids (Holes)**

The space left between particles in a close-packed arrangement is called void. Voids are of two types.

a) ***Tetrahedral voids :*** Tetrahedral void is formed when one particle is placed over 3 other particles. i.e, it is surrounded by 4 particles.

b) ***Octahedral voids*** : An octahedral void is formed when three particles are placed on three other particles. i.e, it is surrounded by 6 particles.

- If 'N' is the number of particles in a close-packed structure.

Number of tetrahedral voids = 2N

Number of octahedral voids = N

Total numbers of voids present in the close packed arrangement = 3N

- **Packing Efficiency**

The percentage of total space in a unit cell filled by particles is called packing efficiency.

$$\text{i.e, packing efficiency} = \frac{\text{Total volume of particles}}{\text{Total volume of unit cell}} \times 100$$

- Packing efficiency in HCP and CCP (FCC) = 74%

  (Remaining 26% is vacant)
- Packing efficiency in BCC = 68% (Remaining 32% is vacant)
- Packing efficiency in simple cubic lattice = 52.4% (Remaining 47.6% is vacant)

- **Density of the unit cell**

$$\text{Density of the unit cell, } \rho = \frac{Z \times M}{a^3 \times N_A} \text{ gm cm}^{-3}$$

where, z = No. of particles per unit cell

M = Atomic / molecular mass

N_A = Avogadro no (6.022×10^{23})

- Density of the substance is same as the density of the unit cell.

- **Imperfections (Defects) in solids**

Any deviation from perfectly ordered arrangement of particles is called an imperfection or defect. When the deviation exists at a point, it is called *point defect*. When the deviation exists along a row, it is called *line defect*.

- **Types of point defects**

Points defects are of 3 types. They are; *stoichiometric defect*, *impurity defect* and *non-stoichiometric defect*.

A) Stoichiometric Defect

The compounds in which number of positive and negative ions are exactly in the ratio, as indicated by their formula Stoichiometric compounds.

The defects which do not affect the stoichiometry of the compound are called *stoichiometric defects*.

They are of four types;

a) ***Vacancy defect :*** In this effect, some of the lattice points are vacant. Vacancy defect decreases the density of the crystal.

b) ***Interstitial defect :*** In this defect, some of the constituent particles occupy interstitial sites (voids) of the crystal. The defect increases the density of the crystal.

c) ***Frenkel defect (Dislocation defect) :*** In Frenkel defect, particles are missing from the lattice points and missing particles occupy nearby voids. It is shown by ionic compounds with large difference in size. Eg : Silver halides, like AgCl, AgBr, AgI and ZnS.

d) ***Schottky defects :*** In Schottky defect, particles are missing as pairs from lattice points and missing particles are far away from the missing point. It is shown by ionic compounds having similar ionic size. Eg : Alkali halides like NaCl, KCl and CsCl & AgBr. AgBr shows both *Frenkel* and *Schottky* defects.

B) Impurity Defect

The defects due to replacement of one type of cation or anion by another type of cation or anion of similar size is called *impurity defect*.

Eg : i) $SrCl_2$ in NaCl ii) $CdCl_2$ in AgCl

C) Non –Stoichiometric Effect

The defects which affect the stoichiometry of the compound are called non-stoichiometric defect. It is of different types.

a) ***Metal excess defect due to anion vacancy (F-centre) :*** The electrons trapped in anion vacancies are called F-centres. F-centre electrons in NaCl absorb heat energy and emit yellow light. $\therefore$NaCl becomes yellow, when heated in sodium vapour. Similarly, KCl becomes violet, when heated in K-vapour. LiCl shows pink colour in Li-vapour.

b) ***Metal excess defect due to extra cation :*** It is the defect due to the extra metal ions in the voids. Eg : ZnO.

c) ***Metal Deficiency defect :*** It is the defect due to cation vacancies. Eg : FeO

- **Properties of Solids**

Electrical properties : Based on electrical conductivity, materials (solids) are classified into conductors, semiconductors and insulators.

- **Band Theory of conductivity**

According to band theory, atomic orbitals of the metal atom mix together to form molecular orbitals. Molecular orbitals of adjacent atoms are so close in energy that they appear as bands. The highest occupied band is called ***valence band***. The lowest unoccupied band is called ***conduction band***. The energy gap between valence band and conduction band determines the conductivity of materials.

- In conductors, the energy gap is very small.
- In semiconductors, the energy gap is average.
- In insulators, the energy gap is very large.

Semiconductors

Semiconductors show moderate conductivity. Their conductivity can be increased either by heating (intrinsic conductivity due to thermal motion of electrons) or by dopping (extrinsic conductivity due to extra electrons or holes).

- The process of adding impurities to 'Si' or 'Ge' to increase their conductivity is called Doping. Based on dopping, semiconductors are of two types.

  i) n-type semiconductors ($\bar{e}$ rich impurities)

  n-type semiconductors are prepared by mixing Si/Ge with group 15 elements like As and Sb

  ii) p-type semiconductors ($\bar{e}$ deficit impurities)

  p-type semiconductors are prepared by mixing Si/Ge with group 13 elements like Ga and In

- Uses of semiconductors:

  i) used as amplifiers ii) used as rectifiers. iii) used in solar cells.

II **Magnetic properties :** Based on magnetic behaviour, solids are classified into following types.

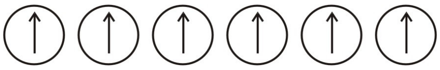
a) ***Diamagnetic substances :*** The substances that are weakly repelled in magnetic field are called diamagnetic materials. It is due to the presence of paired electrons.

Eg : NaCl, C_6H_6, H_2O, N_2.... etc..

b) ***Paramagnetic substances :*** The substances that are weakly attracted in magnetic field are called paramagnetic materials. It is due to the presence of unpaired electrons.

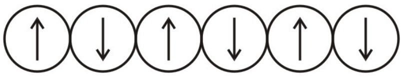
Eg: CuO, VO_2, O_2(g)... etc.

c) ***Ferromagnetic substances :*** The substances which are strongly attracted in magnetic field are called ferromagnetic materials. They can retain the magnetism even when the magnetic field is removed. It is due to the arrangement of magnetic moments in same direction. Eg : Fe, Co, Ni, Gd.

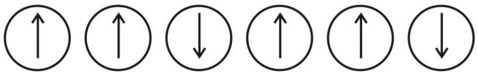


d) ***Antiferromagnetic substances :*** The substances which show zero net magnetic moment are called antiferromagnetic substances, Actually, they are expected to show higher magnetic moment. But they are non-magnetic due to the arrangement of magnetic moments in opposite directions in equal numbers.

Eg : MnO, MnO_2, M_2O_3



e. ***Ferrimagnetic substances :*** The substances which show partial magnetic moments are called ferrimagnetic. It is due to arrangement of magnetic moment in opposite directions in unequal numbers. Eg : Magnetite (Fe_3O_4), Zineferrate ($ZnFe_2O_4$) Magnesium ferrate ($MgFe_2O_4$) etc.



***

Chapter 2
Solutions

Solution is a homogeneous mixture of two or more chemically non reaching substances. A binary solution is made up of two component the solute (in smallest amount) and the solvent (in largest amount).

Binary solution may be classified into:

1. ***Gaseous solutions*** - where the solvent is a gas and solute may be gas, liquid, or solid.
2. ***Liquid solutions*** - where the solvent is a liquid and solute may be gas, liquid, or solid.
3. ***Solid solution*** - where the solvent is a solid and solute may be gas, liquid, or solid.

Different modes of expressing concentration of solution

1. Mass percentages w/w of solute $= \frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$
2. Volume percentages v/v of component $= \frac{\text{Volume of compound}}{\text{Volume of solution}} \times 100$
3. Mass by volume percentage w/v is the mass of solute dissolved in 100 parts by volume of solution.
4. Parts per million (used when the amount of salute is very less) $= \frac{\text{Mass (volume) of solute}}{\text{Mass (volume) of solution}} \times 10^6$
5. ***Molarity (M)*** - Number of moles of solute present in one litre (1000 cm^3) of the solution.
6. ***Molality(m)*** - Number of moles of solute presents in one kilogram (1000g) of the solvent.
7. ***Mole fraction (X)*** - of a component in solution is the ratio of number of moles of that component to the total number of moles of all the component in solution.

Solubility of solids in liquids: - solubility is the maximum amount of solute that can be dissolved in given amount of solvent.

Saturated solution is one in which no more solute can be dissolved at the same temperature and pressure.

Solubility of substance increases with increase in temperature (Le Chatelier principle) where dissolution is endothermic and vice- versa.

Solubility of gases in liquid – is governed by Henry's Law which can be stated in two ways.

1. ***Solubility of a gas*** – in a liquid at a particular temperature is directly proportional to the pressure of the gas above the liquid or
2. ***The partial pressure of the gas*** – in vapors phase is directly proportional to the mole fraction of gas in solution. ie. $P = K_HX$ (Where K_H is the Henry's Law constant and P & X an pressure & mole fractions of gas in solution).Higher the K_H value lowers the solubility.

Solubility of most of the gases like O_2, in water is exothermic and there for decreases with increase in temperature. For this reason aquatic life is more comfortable in cold water than in warm water.

- **Application of Henry's law.**
  - To increase solubility CO_2 in soft drinks, the bottle is sealed under pressure.
  - Air diluted with Helium gas (less soluble in blood) is used as breathing gas for deep sea (Scuba) divers in order to reduce the pain full effect of 'bends'.
  - Climbers and people living at high attitude become physically weak and unable to think clearly (a condition called 'anoxia') due to less concentration of O_2 in air.
- **Vapor pressure of solution**

Vapour pressure of a liquid is the pressure exerted by the vapours of the liquid in equilibrium with the liquid at a given temperature.

The vapour pressure of a solution that contains two volatile components is contributed by the vapours of both the components whereas the vapour pressure of the solutions that contain a non volatile component in a volatile solvent is contributed only by the vapours of solvent.

The vapour pressure of a solution that contain a non volatile component is less than that of the vapour pressure of the pure solvent because the surface of solution from where evaporation takes place is occupied partly by particles of solute which can not be evaporated.

Raoult's law – States that the partial vapour pressure of volatile component in a solution at a given temperature is directly proportional to the mole fraction of the component gas in solution. For a solution that contains two volatile components A and B according to Raoult's Law, $P_A \propto \chi_A$, $P_B \propto \chi_B$ or $P^0_A = P^0_A \chi_A$ and $P_B = P^0_B\chi_B$ (When P_A & P_B are partial vapour pressure of A & B and χ_A & χ_B an their mole fractions in solution.

According to Dalton law, $P_A + P_B = P_{total}$

According to Raoult's law for solution that contains a non- volatile solute in volatile solvent.

$P_{total} = P_A$ and $P^0_A = P_A \chi_A$ where A = solvent

- **Ideal and Non ideal solution**

Ideal solution – a solution that obeys Raoult's law at all concentrations and temperature

- **Conditions for an ideal solution**

i) $P_A = P°_A \chi_A$ ii) $\Delta H_{mixing} = 0$ iii) $\Delta V_{mixing} = 0$

In case of these solution, the attractive interaction between A –A (Solvent – solvent) and B –B (Solute – solute) are nearly the same between A –B (Solvent – Solute). Eg: Benzene + toluene, Ethylbromide + Ethyl iodide. n – hexane + n – heptane etc.

Non ideal solution are those which do not obey Raoult's law. For non ideal solution

$P_A \neq P°_A \chi_A$; $\Delta H_{mixing} \neq 0$ and $\Delta \chi_{mixing} \neq 0$

Non ideal solutions : showing positive deviation

In this type of solution, the partial V.P of each volatile component and therefore the total V.P are higher than that expected by Raoults law because solvent – solute, interactions are weaker than solute – solute and solvent – solute, interaction. For these solutions;

$P_A > P°A\ \chi_A$; $\Delta H_{mixing} > 0$ and $\Delta \chi_{mixing} > 0$

eg : Acetone + carbon disulphide, Ethanol + water etc

Non ideal solutions - showing negative deviation :

The partial vapour pressure of each volatile component and the total V.P of there solution are lower than that exported by Raoults law become solvent – solute interaction are stronger than solvent- solvent and solute- solute interaction. For these solutions;

$P_A < P°n\ X_A$; $\Delta H_{mixing} < 0$ and $\Delta X_{mixing} < 0$

Eg : HCl + H_2O, $CHCl_3$ + ether, Phenol + aniline , chloroform + nitric acid etc

- **Azeotropes**

The liquid mixtures which distil out completely without change in composition. For solution showing positive deviation, the azeotropic mixture is that intermediate composition for which the vapour pressure of solution is maximum ($\therefore$the boiling point, the minimum) and in called *minimum boiling azeotrope.*

For solution showing negative deviation the azeotropic mixture is that composition where the V.P of solution is the minimum (boiling point, the maximum) and is called *maximum boiling azeotrope.*

- **Colligative properties**

The properties of solution which depend only on the number of particles of solute and not on its nature. Following are the colligative properties

1. Relative lowering of vapour pressure

The vapour pressure of solution that contains a non volatile solute will be less than the V.P of pure solvent.

The ratio of lowering of vapour pressure of a solution to VP of pure solvent is called relative lowering of VP.

i.e $$\frac{P_A^\circ - P_A}{P_A^\circ} = \text{relative lower of V.P}$$

(P_A – V.P of solution, $P°_A$ V.P of pure solvent). It is also found that $P°_A - P_A = \chi_B$. (χ_B - mole fraction of solute)

Molar mass of solute $M_B = \dfrac{W_B \times M_A \times P_A^\circ}{W_B \times (P_A^\circ - P_A)}$

(W_B and M_B = mass and molar mass of solute W_A & M_A mass and molar mass of solvent respectively)

2. Elevation in boiling point ΔT_b

Boiling point – The temperature at which the V P of a liquid is equal to atmospheric pressure.

Since the VP of a solution that contains a non volatile solute is less than that of the pure solvent, the boiling point of the solution will be higher. The difference in boiling point of solution and pure solvent is called elevation in boiling point. The elevation in boiling point depends upon the extent of lowering of vapor pressure which in turn depends upon concentration of solute. ie. elevation of boiling point is a colligative property.

$\Delta T_b \propto m$ and $\Delta T_b = Kb \times m$

(Where Kb – molar elevation constant or ebullioscopic constant and 'm' is the molality.)

Molar mass of solute $M_B = \dfrac{1000 \times K_b \times W_B}{\Delta T_b \times W_B}$

3. *Depression in freezing point ΔT_f*

Freezing point of liquid in that temperature at which V.P of liquid in equal to V.P of solid. Since the V.P of a solution that contains a non volatile solute is less than pure solvent, at the freezing point of pure solvent, the VP of solution and solvent are not equal. Only at a lower temperature the V.P of solution will be equal to that of the solvent. i.e freezing point of a solution is less than that of pure solvent. The difference in freezing point of solvent and solution is called *Depression in freezing point* (***ΔT_f***.). Since this depends on lowering of vapor pressure, which in turn depends on concentration of solution, it is a colligative property.

$\Delta T_f \propto m$ and $\Delta T_f = Kfm$ K_f – molal depression constant cryoscopic constant)

Molar mass of solute M_B = $\dfrac{1000 \times K_f \times W_B}{\Delta T_f \times W_A}$

4. *Osmotic pressure (π)*

Osmosis - the spontaneous flow of solvent from pure solvent to solution or from solution of lower concentration to higher when the two are separated by a semi permeable membrane.

Osmotic pressure is the minimum pressure which must be applied on solution side to just prevent osmosis.

It is found that osmotic pressure is directly proportional to concentration which in turn depends on no : of particles and hence it is collegative property.

$\pi \propto CT$ or $\pi = CRT$ or $\pi = \dfrac{n}{V} RT$

and $\pi v = nRT$ (where C = molar concentration, R- gas constant, V – volume & n – no of moles of solute).

Molar mass of solute $M_B = \dfrac{W_B RT}{\pi v}$

For finding molecular mass of solute, osmotic pressure method is preferred since it can be done in room temperature and the magnitude of π is high enough to be measured.

Isotonic solution – solution having equal osmotic pressure

Hypertonic solution – a solution having higher osmotic pressure than another.

Hypotonic solution – solution having lower osmotic pressure than another.

Blood is isotonic with 0.9 % NaCl.

Reverse osmosis is the movement of solvent from solution to pure solvent, through a semi permeable membrane when a pressure greater than osmotic pressure is applied on solution. It is used in purification of water.

- **Abnormal molar mass**

Molar masses calculated by colligative properties are some times higher or lower than the actual value. It is either due to association or dissociation of solute particles. When solute molecules is dissociated, number of properties increases, collligative property increases and molar mass decreases.

In association number of particles decreases, colligative property decreases and molar mass calculated increases.

To calculate extent of association or dissociation factor called Vant Hoff's, factor introduced and is given by $i = \frac{\text{Observed value of colligative property}}{\text{Normal colligative property}}$ Or $\frac{\text{Normal molar mass of solute}}{\text{Observed molar mass}}$

Or $\frac{\text{No. of particles of a molecule after dissociation or association}}{\text{No. of particles of molecules before association or dissociation}}$

Modified colligative property equations are

$$\frac{\Delta P}{P^0_A} = i\,\chi_B$$

$$\Delta T_b = i \times K_b \times m$$

$$\Delta T_f = i \times K_f \times m$$

$$\pi v = i \times n \times R \times T$$

***

Chapter 3

Electrochemistry

- **Electrode potential and cell potential**

When a metal strip is in contact with the solution of its ions, it constitutes a half cell or an electrode and it can either undergo oxidation or reduction. The potential difference set up between a metal and it ions in solution s known as ***Half Cell Potential*** or ***Electrode Potential*** and it can be oxidation or reduction electrode potential. The reduction potential of an electrode, when the concentration of the electrolyte is unity is called ***Standard Electrode Potential*** (E°).

The different electrodes will have different electrode potential. Due to the potential difference between electrodes electrons flow from the electrode with lower electrode potential (lower reduction potential) to the electrode with higher electrode potential (higher reduction potential). Thus electricity is created when two electrodes are connected.

The difference between the electrode potential of two electrodes or two half cells is known as ***Cell Potential*** (E_{cell}) or ***Electromotive Force*** (EMF).

Electrochemical cells

A device that produces electricity as a result of redox reaction is called an ***electrochemical cell*** or ***galvanic cell***.

A galvanic cell contains two half cells or electrodes. The half cell in which the standard electrode potential is low undergoes oxidation and is called oxidation half cell or the anode and it is the negative electrode. The half cell or electrode with high electrode potential under goes reduction and it is the cathode and is the positive electrode.

In order to complete the electrical circuit and maintain electrical neutrality of the solution in the half cells a salt bridge is connected.

Eg : Daniel cell Anode : Zn rod in $ZnSO_4$ solution; the electrode reaction is oxidation.

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\,e^{-}$

Cathode : Cu rod in $CuSO_4$ soln : $Cu^{2+}_{(aq)} + 2\,e^{-} \rightarrow Cu_{(s)}$

Over all reaction $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(g)} + Cu_{(s)}$

E_{cell} of Daniel cell = 1.10V

Representation of an electrochemical cell

Anode$_{(left)}$ || cathode $_{(Right)}$

Anode | anode electrolyte ion with conc || Cathode electrolyte ion with conc | cathode

Daniel cell is represented as $Zn_{(s)} \mid Zn^{2+}_{(1M)\,(aq)} \parallel Cu^{2+}_{(1M)\,(aq)} \mid Cu_{(s)}$

Cell potential of an electrochemical cell is calculated as

$E_{cell} = E_{cathode} - E_{anode}$ or $E_{cell} = E_{right} - E_{left}$

Standard Hydrogen electrode (SHE)

The common reference electrode used for measuring electrode potential is Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode (NHE). In SHE H_2 gas is bubbled into an acid solution of 1M H^+ ion concentration in a glass tube having an inert electrode, platinum.

If SHE acts as anode; $\frac{1}{2} H_2 \rightarrow H^{+}_{(g)}\ 1e^{-}$

and if SHE acts as cathode; $H^{+} + 1e^{-} \rightarrow \frac{1}{2} H_{2(g)}$

Informer case SHE is represented as $Pt \mid H_{2\,(g)\,(1\,bar)} \mid H^{+}_{(g)\,(1M)}$ and in the later case $H^{+}_{(g)\,1M} / H_{2\,(1\,bar)}$ / pt. The electrode potential of SHE is taken as zero.

Measurement of electrode potential

To determine the potential of an electrode it is coupled with SHE to form an electrochemical cell and the cell potential is measured. Since the electrode potential of SHE is zero, electrode potential of the given electrode can be calculated using the equation $E_{cell} = E_{cathode} - E_{anode}$.

Electrochemical series

The arrangement of electrodes (elements) in the order of standard electrode potentials is called electrochemical cell.

Applications of electrochemical series

1. To compare relative reactivities of metals : Metals having low electrode potential values are more reactive. Metals having negative electrode potentials can displace hydrogen from acid solution.
2. To compare relative oxidising and reducing properties. Larger the value of electrode potential more easily is the substance reduced and vice – versa.
3. To construct electro chemical cells and calculate their standard EMF. The substance with higher electrode potential is reduced and acts as the cathode and vice versa.

- **Nernst equation -** equation that provides relationship between concentration of electrolyte and the electrode potential

  For the electrode reaction $M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$

  The nearest equation is given by

$$E_{electrode} = E^\circ_{electrode} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}_{(aq)}]} \text{ or } E_{M^{n+}/M(s)} = E^\circ_{M^{n+}/M(s)} - \frac{2.303\ RT}{nF} \log \frac{1}{[M^{n+}]}$$

(F = Faradays constant)

- **Nernst Equation for cell potential**

  For a general cell reaction

  aA + bB → cD + dD. The Nernst equation

$$\text{is } E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ or } E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{nF} \log \frac{[\text{product ion}]}{[\text{Reactant ion}]}$$

  Eg : for Daniel cell the cell reaction

  is $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

  and the Nearest equation is $E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{nF} \log \frac{[Zn^{2+}_{(aq)}]}{[Cu^{2+}_{(aq)}]}$

- **Std cell potential and equilibrium constant**

$$E^\circ_{cell} = \frac{2.303 \times RT}{nF} \log Kc$$

  Gibb's energy and cell potential

  $\Delta G^\circ = -nF E^\circ_{cell}$ or $\Delta G^\circ = -2.303RT \log Kc$

- **Conductance of Electrolyte solution**

$$\text{Conductance } G = \frac{1}{R} = \frac{1}{\rho} \times \frac{A}{l} = \kappa \frac{A}{l} = \frac{1}{R} \times \frac{A}{l}$$

  (Where R – resistance, ρ – resistivity, A – area of the conductor, *l* - the length of conductor and κ – Kappa, the conductivity)

  The quantity $\frac{l}{A}$ is called cell constant.

  Electrolytic conducton depends on number of ions and mobility of ions.

- **Factors affecting conductivity of electrolyte solution**

  The factors which can increase the number ions and mobility of ions can increase the conductivity electrolyte solution.

1. ***Nature of electrolyte :*** Strong electrolyte completely ionise in solution and conduct electricity to larger extent
2. ***Size of ion produced and their solvation :*** Smaller the ion and lesser the solvation, greater the conductivity
3. ***Concentration of electrolyte :*** Higher the concentration lesser the conductivity.
4. ***Nature of solvent and its viscosity :*** Higher the viscosity lower the conductivity
5. ***Temperature :*** Electrolytic conduction increases with increase in temperature.

Molar conductivity - Λ_m is the conductance of an electrolyte solution containing one mole of electrolyte such that the entire solution is placed between two electrodes at a distance of unit length.

$$\Lambda_m = \frac{1000\ K}{M}$$; where M is the molarity of solution

Conductivity of an electrolyte solution can be measured by measuring the resistance of a solution using wheatstone bridge method.

- **Variation of conductivity with concentration**

Conductivity of an electrolyte solution decreases with decrease in concentration (or increase in dilution) due to decrease in the number of ions per unit volume.

- **Variation of molar conductivity with concentration**

i) Strong electrolyte

Due to decrease in interionic attraction molar conductivity increase with decrease in concentration (or increase in dilution) and reaches a certain limiting value as the concentration approaches zero (i.e at infinite dilution). This limiting value of Λ_m is called the liming molar conductivity Λ_m or molar conductivity at infinite dilution $\Lambda_m^{\propto}$ or

Variations of λ_m with concentration of strong electrolyte is given by Debye Huckel Onsagar equation , $\Lambda_m = \Lambda_m^0 - A\sqrt{C}$ (When A is a constant and C the molar concentration)

Molar conductivity at infinite dilution of strong electrolyte can be obtained by extrapolation of the graph obtained between Λ_m and $\sqrt{C}$

ii) Weak electrolyte

For weak electrolyte Λ_m increases rapidly with dilution. The reason is that upon dilution the degree of dissociation of weak electrolyte increases leading to an increase in number of ions. Determination of Λ_m^0 for weak electrolyte is not possible by extrapolation of the graph between Λ_m and $\sqrt{C}$, since it is a curve.

- **Kohlrausch's law**

States that the limiting molar conductivity of an electrolyte is the sum of the limiting molar ionic conductivities of cation and anions of the electrolyte.

- **Applications of Kohlrausch's law**

1. The limiting molar conductivity of a weak electrolyte can be calculated using limiting molar conductivities of strong electrolytes

$$\Lambda_m^0{}_{CH_3COOH} = \Lambda_m^0{}_{CH_3COONa} + \Lambda_m^0{}_{HCl} - \Lambda_m^0{}_{NaCl}$$

2. Degree of dissociation of a weak electrolyte can be calculated using Λ_m and Λ_m^0

Degree of dissociation (α) = $\frac{\Lambda_m}{\Lambda^0_m}$ and dissociation constant of weak electrolyte Ka = $\frac{c\alpha^2}{(1-\alpha)}$

- **Electrolysis**

The process of chemical decomposition of an electrolyte by the passage of electricity through its molten or dissolved state is called electrolysis. The process is carried out in an electrolytic cell.

To deposit a metal like Na from its ion, Na^+ the charge of one mole of electron, $1.602 \times 10^{-19} \times 6.022 \times 10^{23}$ = 96490 coulomb or one Faraday (1F) of electricity is required.

- **Faradays laws of electrolysis**

First Law **–** mass of substance liberated (or deposited) at the electrode is directly proportional to the quantity electricity passed through the electrolyte solution.

Second law – When the same quantity of electricity is passed through different electrolyte connected in series, the masses of substances formed at the electrodes are proportional to their respective chemical equivalent masses.

Products of electrolysis **–** depends on the nature, types and electrode potential of electrode.

Eg : The electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode, where the electrolysis of molten NaCl gives Na metal at cathode Cl_2 gas at anode.

- **Commercial cells**

Battery **–** the arrangement of two or more galvanic cells in series

Primary cell **–** the galvanic cell in which redox reaction occurs only once and cannot be recharged or used again.

Eg : Dry cell, Mercury cells etc.

Secondary cell **–** the one which can be recharged by passing electricity and can be used again and again

Eg : Lead storage battery, nickel – cadmium cell etc.

Fuel cell **–** the devices which can convert the energy produced by the combustion of a fuel directly into electrical energy

H_2 –O_2, fuel cell consist of porous carbon electrodes and 3-compartments of which two are fed with O_2 and H_2 gases and central compartment with an electrolyte (NaOH/KOH)

Reactions; Anode : $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4\ H_2O + 4\ e^-$

Cathode : $O_{2\ (g)} + 2H_2O_{(l)} + 4\ e^- \rightarrow 4OH^-$

Overall reaction : $2H_{2\ (g)} + O_{2\ (g)} \rightarrow 2H_2O_{\ (l)}$

Potential of H_2 - O_2, fuel cell = 0.9 V

- **Advantages**

Non polluting, highly efficient and long lasting.

Other examples : Methane – O_2, Methanol – O_2, fuel cells

- **Corrosion**

  The slow destruction of a metal by the conversion of it into oxides, sulphides etc on exposure to atmospheric air and moisture. Corrosion is an electrochemical phenomenon,

- **Rusting of Iron**

  One part of metal acts as anode and the oxidation reaction is

  $$2Fe_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + 4e^-$$

  Another part where moisture and atmospheric oxigen are present acts as cathode and the reduction is $4H^+_{(aq)} + O_{2(g)} + 4e^- \rightarrow 2\,H_2O_{(l)}$

  The Fe^{2+} ion formed undergo further oxidation; $2Fe^{2+}_{(aq)} + 2H_2O_{(l)} + ½\,O_{2(g)} \rightarrow Fe_2O_{3(s)} + 4H^+_{(aq)}$

  Hydrated ferric oxide, $Fe_2O_3.\,xH_2O$ is called rust.

  Corrosion of a metal can be prevented by - Barrier protection (Eg. painting etc) or sacrificial protection (Eg. galvanisation of ion) or by cathodic protection (connecting with a more active metal)

***

Chapter 4

Chemical Kinetics

Chemical kinetics deals with rates of chemicals reactions and factors influencing rate. Rate is a measure of speed or velocity of a chemical reactions. Rate is usually expressed in decrease in concentration of any one of the reactants or increase in concentration of any one of the products.

$$A + B \rightarrow C + D$$

$$\text{Average rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t} = +\frac{\Delta[D]}{\Delta t}$$

We cannot express the rate of reaction in terms of average rate because the rate of reaction is not uniform through out the reaction. So rate is expressed instantaneously called instantaneous reaction rate.

$$\text{i.e } \underset{\Delta t \rightarrow 0}{Lt} -\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}$$

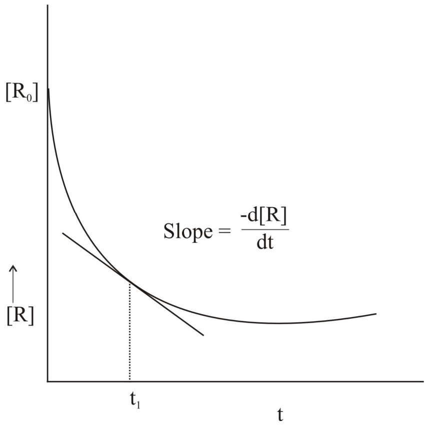
Consider R → Products

rate at time t_1

= slope of the tangent

Corresponding to the point in graph

$$\text{at } t_1 = \text{slope} = -\frac{d[R]}{dt}$$



Always rate is expressed for 1 mole

For aA + bB → cC + dD

$$\text{rate} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{+1}{c}\frac{d[C]}{dt} = \frac{+1}{d}\frac{d[D]}{dt}$$

For expressing the rate of the following reaction in terms of NO_2

$$2\,N_2O_{5(g)} \rightarrow 4\,NO_{2(g)} + O_{2(g)}$$

We can write

$$\text{rate} = \frac{+1}{4}\frac{d[NO_2]}{dt}$$

Factors influencing rate

1. **Concentration :** According to collision theory reaction rate depends on collision of reactants. So increase in concentration increases the rate of reaction.

According to law of mass action for

$$aA + bB \rightarrow cC + dD$$

$$\text{rate} = K\,[A]^a\,[B]^b$$

$$\text{i.e} = \frac{-1}{a}\frac{d[A]}{dt} = K\,[A]^a\,[B]^b \quad \text{[differential rate law]}$$

Differential rate law is a differential equation relating rate and concentration of reactants. This reaction is ‘a’ order with respect to [A] and ‘b’ order. w.r.to [B] and overall order is a + b.

For R → products

$$\text{rate} = \frac{-d[R]}{dt} = K\,[R]^n \quad \text{for } n^{th} \text{ order reaction}$$

$$\text{Unit of K} = \left(\frac{rate}{[R]_n}\right) = \frac{\frac{mol\ L^{-1}}{S}}{(mol\ L^{-1})^n} = (mol\ L^{-1})^{1-n}S^{-1}$$

$$\boxed{\text{i.e Unit of K} = mol^{\,1-n}\,L^{n-1}S^{-1}}$$

Order is an experimental value

For $aA + bB \rightarrow cC + dD$

$\text{rate} = K\,[A]^x\,[B]^y$ $\qquad x = \neq a$,

$\text{order} = x + y$ $\qquad y = \neq b$

Order	Molecularity
1. Sum of powers of concentration terms in the rate law expression $(x + y)$	1. No of molecules (ions or atoms) collide simultaneously to bring about the reaction $(a + b)$
2. Order is an experimental value	2. Theoretical value
3. Can be zero, fractional or whole number	3. Always whole number (Cannot be zero or fractional)
4. Mechanism of certain reactions can be predicted from order	4. Say nothing about mechanism

Decomposition of acetaldehyde

$$CH_3CHO_{(g)} \xrightarrow{\Delta} CH_{4(g)} + CO_{(g)}$$

$$\text{rate} = K\,[CH_3CHO]^{3/2} \quad \text{is 3/2 order}$$

Decomposition of NH_3 over gold catalyst

$2NH_3\,_{(g)} \xrightarrow[\Delta]{Au} N_2\,_{(g)} + 3\,H_{2(g)}$

rate = K $[NH_3]^{\circ}$, zero order. For this rat depend only on the surface area of the catalyst 'Au'. For multistep reaction lowest step is the rate determining step (rate can be written from slowest step)

For $2\,H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2\,H_2O + O_2$ rate $= k\,[H_2O_2]^1\,[I^-]^1$

Mechanism

$H_2O_2 + I^- \xrightarrow{Slow} H_2O + IO^-$

$H_2O_2 + IO^- \xrightarrow{fast} H_2O + I^- + O_2$

- **Integrated rate equations**

Zero order

Consider R → Products

$$\frac{-d[R]}{dt} = K\,[R]^{\circ}$$

Rearranging and integrating

$$\int -d(R) = \int K\,.dt$$

$$\int x^n\,.dx = \frac{x^{n+1}}{n+1}$$
$$\int kx^n\,.dx = k\int x^n\,dx$$
$$\int dx = x$$

$-[R] = Kt + C$ where C integration constant

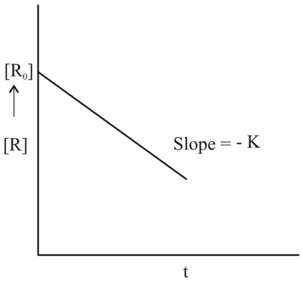
substituting the value of C as $-[R_0]$

at t = 0

[R] becomes $[R_0]$

i.e $-[R_0] = K x O + C$

$$-[R] = Kt - [R_0]$$
$$[R_0] - [R] = kt$$
$$K = \frac{[R_0]-[R]}{t}$$
$$[R = -[R_0] = -Kt$$
$$[R] = -Kt + [R_0]$$
$$y = mx + c$$
$$\text{Slope} = -K$$



Half life period

$$t_{½} = \frac{[R_0]-{[R]}/{2}}{k}$$
$$t_{½} = \frac{[R_0]}{2k}$$

First order

R → Products

$$\frac{-d[R]}{dt} = K\,[R]^1$$

Rearranging and integrating

$$\int \frac{-d[R]}{[R]} = \int K\,.dt$$

$$-\text{Ln}\,[R] = Kt + C$$

$$\int \frac{1}{x}dx = \text{lin}\,x,$$

at t = 0, [R] becomes $[R_0]$

$-\ln[R_0] = k \times O + C$

$\therefore C = -\ln[R_0]$

Substituting the values of C as $-\ln[R_0]$ we get

$$-\ln[R] = Kt - \ln[R_0]$$
$$\ln[R_0] - \ln[R] = Kt$$
$$\ln\frac{[R_0]}{[R]} = Kt$$

$$ln\,m - ln\,n = ln\,\frac{m}{n}$$
$$\ln x = 2.303\log x$$
$$t_{½} = \frac{2.303}{k}\log\frac{[R_0]}{{[R_0]}/{2}}$$
$$= \frac{2.303}{k}\log 2$$
$$t_{½} = \frac{0.693}{k}$$

$$2.303 \log \frac{[R_0]}{[R]} = \text{Kt}$$

$$\boxed{K = \frac{2.303}{t} \log \frac{[R_0]}{[R]}}$$

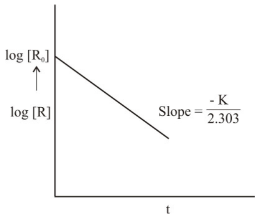
$$\log \frac{[R_0]}{[R]} = \frac{Kt}{2.303}$$

$$\log [R_0] - \log [R] = \frac{Kt}{2.303}$$

$$\therefore \log [R] - \log [R_0] = \frac{-Kt}{2.303}$$

$$\log [R] = \frac{-Kt}{2.303} + \log [R_0]$$

$$y = mx + c$$



Half life period of a reaction ($t_{½}$) is the time required for the reactants to reduced to half of its initial concentration.

Pseudo order reaction is appear to be of higher order but actually follows lower order kinetics.

Eg : Hydrolysis of ester and cane sugar.

$$\underset{\text{ethyle acetate}}{CH_3COOC_2H_3} + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5 - OH$$

$$\text{rate} = K\,[CH_3COOC_2H_5]^1$$

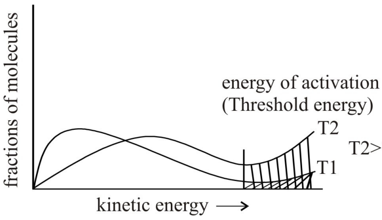
We expect 2nd order kinetics but actually Ist order under experimental conditions (Special conditions that is water is taken in excess.

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\text{rate} = K\,[C_{12}H_{22}\,O_{11}]^1$$

2. Temperature

For every 10° raise in temperature reaction rate almost doubled. For increase in the temperature average kinetic energy of the reaction increases most of the collisions become effective and reaction rate increases.



Area – under the curve after threshold energy represents no of products. On increasing the temperature area under the curve after threshold energy also increases.

Arrhenius equation $K = Ae^{-Ea/RT}$

Where K – rate constant

A – Arrhenius factor or frequency factor

Number of binary molecules collisions per second per litre.

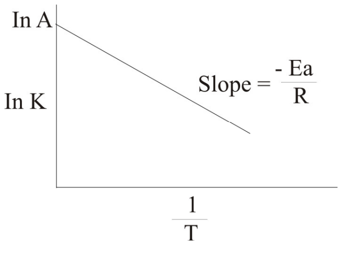
Kinetic energy of maximum fractions of molecules called most probable kinetic energy.

$e^{-Ea/RT}$ - fraction of molecules having kinetic energy greater than Ea

Taking natural logarithms on both side

$$\text{In } k = \text{In } A + \text{In } e^{-Ea/RT}$$

$$\text{In } k = \text{In } A - \frac{Ea}{RT}$$



$e^x = m$

Logarithm of m

$\text{In}_e\ m = x$

$e^x = e^x$

logarithms of $e^x = x$

Let K_1 at T_1 and K_2 at T_2

$$\text{In } K_2 = \text{In } A - \frac{Ea}{RT_2} \quad \text{......... (1)} \qquad \text{In } K_1 = \text{In } A - \frac{Ea}{RT_1} \quad \text{......... (2)}$$

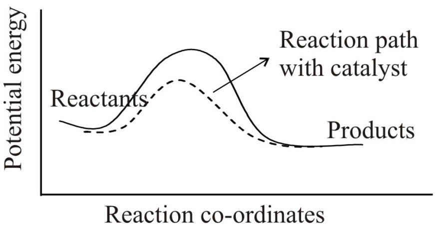
$$(1) - (2) \ = \text{In } K_2 - \text{In } K_1 = \frac{-Ea}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\text{In } \frac{K_2}{K_1} = \frac{Ea}{R_1}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad 2.303 \log \frac{K_2}{K_1} = \frac{Ea}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

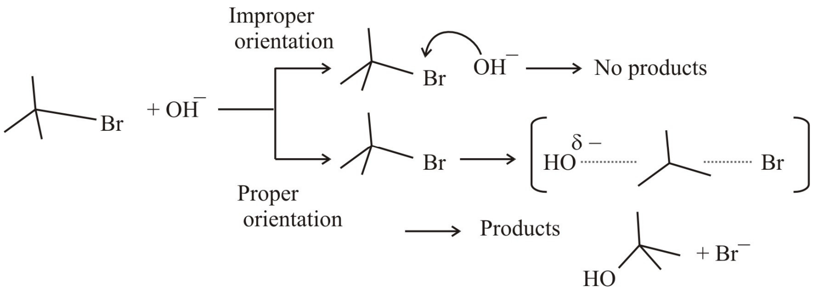
$$\boxed{\log \frac{K_2}{K_1} = \frac{Ea}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]}$$

3. Catalyst

Catalyst provide another path for chemical reaction. So that activation energy is lowered.



In collision theory not only the activation energy but also proper orientation decides the products.



To account proper orientation, probability factor or sterric factor P is introduced in equation

$$\text{Rate} = P\, Z_{AB}\, e^{-Ea/RT}$$

Where Z_{AB} – collision frequency.

***

Chapter 5

Surface Chemistry

Surface chemistry deals with nature of surfaces and reactions on surface.

- **Adsorption**

The phenomenon of accumulation of substances on the surface of another substance is called *adsorption*.

Adsorbing bulk substances is called adsorbent. The substance being adsorbed on the surface is called adsorbate.

Eg : Adsorption of SO_2 by charcoal; moisture by silica gel etc.

- **Absorption**

If the substance is uniformly distributed throughout the substance, it is called absorption.

If adsorption and absorption take place simultaneously it is called sorption.

- **Mechanism of adsorption**

  Adsorption is due to unbalanced van der waals forces of the surface.

- **Heat of adsorption**

  Adsorption is exothermic (ΔH is negative). The amount of heat energy released when 1 mole of an adsorbate is adsorbed on an adsorbent is called heat of adsorption, it varies from 20- 400 $kJmol^{-1}$.

- **Physical adsorption (Physisorption)**

  If the forces of attraction between adsorbent and adsorbate are van der waal's forces, it is called Physisorption.

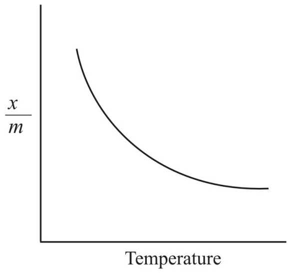
- **Chemical adsorption (Chemisorption)**

  If the forces of attraction between adsorbent and absorbate is chemical bonds, it is called chemisorption.

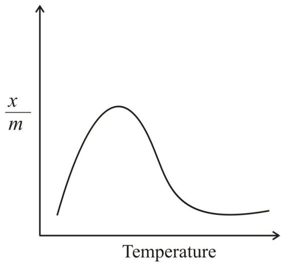
Physisorption	Chemisorption
1. Adsorbate is held on the surface by weak van der waal's forces.	1. Adsorbate is held on the surface by chemical bonds.
2. It is reversible	2. It is irreversible
3. It is not specific	3. It is highly specific
4. It forms multimolecular layers	4. It forms monomolecular layers
5. Low enthalpy of adsorption (20-40 $kJmol^{-1}$)	5. High enthalpy of adsorption(40-400 $kJmol^{-1}$)
6. It decreases with temperature	6. It increases first and then decreases

- **Adsorption isobar**

  Since adsorption is exothermic, rate of adsorption decreases with increase in temp. A graph between amount of substance adsorbed ($\frac{x}{m}$) against temperature at constant pressure is called Adsorption isobar.



(Kobar of physisorption)

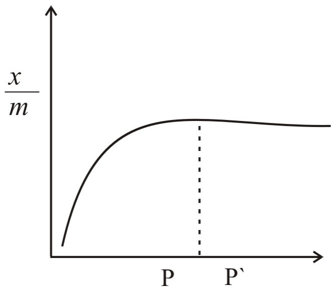


(Isobar of physisorption)

- **Adsorption isotherm (Freundlich adsorption isotherm)**

  The gaseous adsorption various with pressure. The variation of adsorption with pressure is given by an equation.

$$\frac{x}{m} = kP^{1/n} \text{ or } \frac{x}{m} \propto P^{1/n}$$



A graph between amount of adsorption ($\frac{x}{m}$) against pressure at constant temperature is called Freumdlich Adsorption isotherm.

Applications of Adsorption

1. Activated charcoal is used in gas masks to absorb poisonous gases in mines.
2. Silica gel and alumina are used as drying agents.
3. Heterogeneous catalysis is due to adsorption.
4. Froth floatation in metallurgy and chromatography are based on adsorption.
5. Decolorisation of sugar by animal charcoal.
6. Adsorption is used in softening and deionising of water by permutit method.

Catalysis

The substances which alter the reaction rate without undergoing any chemical change are called catalysts

Homogeneous and Heterogeneous catalysts

- When the catalysts and reactants are in same physical state, it is called Homogeneous catalyst.

Eg : Lead chamber process of H_2SO_4 manufacture.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO_{(g)}} 2SO_{3(g)}$$

- When the catalysts and reactants are in difference physical state, it is called heterogeneous catalysts (Solid catalysts)

Eg : $N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe_{(s)}} 2NH_{3(g)}$ (Haber process)

Positive and negative catalysts

- The substance which increases the rate of reaction is called positive catalyst.

Eg : $N_2 + 2H_2 \xrightarrow{Fe} 2NH_3$

- The substance which decreases the rate of reaction is called negative catalyst.

Eg : $2H_2O_2 \xrightarrow{dil\,H_2SO_4} 2\,H_2O + O_2$

Promoters and Poisons

- The substances which enhance the activity of catalysts are called promoters.

Eg : MO is used as promoter for Fe catalyst in Haber process.

- The substances which inhibit the activity of catalysts are called catalytic poisons.

Eg : As acts as a poison for Pt catalyst in H_2SO_4 manufacture.

Mechanism of Heterogeneous catalysis

The mechanism of heterogeneous catalysis involves the following steps.

1) Diffusion of the reactants to the catalysts surface.
2) Adsorption of the reactants in the active sites of the catalyst surface.
3) Occurrence of reactions on catalysts surface.
4) Desorption of the product from the catalyst surface.

5) Diffusion of the products away from catalyst surface

- ***Features of Heterogeneous catalysts :*** Two important features of heterogeneous catalysis are activity and selectivity.

  a) Activity : It is the ability of the catalyst to accelerate a chemical reaction. Catalysts can increase the reaction rate upto 10^{10} times than uncatalysed reactions.

  b) Selectivity : If is the ability of the catalyst to direct a reaction to yield only a particular product.

  Eg : Carbon monoxide and hydrogen react to form different products in the presence of different catalysts.

  $CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$

  $CO + 2\,H_2 \xrightarrow{ZnO–Cr_2O3} CH_3 - OH$

  $CO + H_2 \xrightarrow{Cu} HCHO$

Zeolites (Shape selective catalysts)

Zeolites are hydrated micropores aluminosilicates. The catalytic action of zeolites depends on the size and shape of cavities in them. Therefore, they are called shape selective catalysts. Reactants of a particular shape and size only can enter their cavities and hence adsorbed.

Eg : ZSM –5, which convert alcohol directly into petrol (Gasolene).

Alcohol $\xrightarrow{ZSM-5}$ hydrocarbon (petrol)

Enzyme catalysts

Enzymes are biological catalysts produced by living cells. They catalyse bio-chemical reactions in organisms. Most of enzymes are globular proteins.

Eg : Starch $\xrightarrow{Amylase}$ Glucose

Urea $\xrightarrow{Ilrease} CO_2 + NH_3$

Characteristics of Enzymes

1) Enzymes are highly specific. Each enzyme catalyse only one reaction.
2) They are highly efficient. They increase the speed upto 10^7 times.
3) They are active only at moderate temperature (29 –37°C) moderate pH . (7 –7.5)
4) They are required in very small amounts.
5) Their activity is increased in the presence of co-enzymes and decreased in presence of enzyme inhibitors.

Mechanism of enzyme action (Lock and Key Mechanism)

Catalytic action is due to the presence of some specific sites on their surface called active sites. Active sites have a characteristic shape and only those substrate with suitable shape can fit into it, in the same way as one key can fit into a particular lock. Various steps in enzyme catalysis are:

$$E + S \rightarrow ES \rightarrow EP \rightarrow E + P$$

Colloidal state (Colloids)

Colloids are heterogeneous mixture containing particle size between 1 to 1000 nm. They passes through filter paper but not through semipermeable membrane. Eg: Starch sol, creams, jellies, gelatin milk etc.

The medium in which the particles are dispersed is called dispersion medium. The particles dispersed are called dispersed phase.

Eg : In starch sol, starch is dispersed phase and water is dispersion medium.

- **Classification of colloids.**

A) Based on physical state : Based on physical state of dispersed phase and dispersion medium, colloids are classified into 8 types. (Refer text)

B) Based on interaction force : Colloids are classified into lyophilic colloids and lyophobic colloids depending on the interaction force between dispersion medium and dispersed phase.

- In lyophilic colloids, there is strong interaction between phase and medium particles.

  Eg : Natural sols like starch, gelatin etc...

- In lyophobic colloids, there is weak interaction between phase and medium.

  Eg : Colloidal gold, $Fe(OH)_3$ sol, As_2S_3 sol, etc...

Lyophilic Colloids	Lyophobic colloids
1. Strong interaction between phase and medium	1. Weak interaction between phase and medium
2. Reversible	2. Irreversible
3. More stable	3. Less stable
4. The particles are highly hydrated	4. The particles are not hydrated
5. They are prepared by direct method	5. They are prepared by indirect methods.

C) Based on size of particles : Based on particles colloids are classified into multimolecular, macromolecular and associated colloids.

a) Multimolecular colloids : In multimolecular colloids, particle size is less than 1 nm, but they aggregate to form particles of colloidal state.

Eg : Sulphur sol, gold sol, etc.

b) Macromolecular colloids : In macromolecular colloids, the particles are high molecular mass compounds having colloidal size.

Eg : Starch, cellulose, proteins etc.

c) Associated colloids (Micelles) : These are colloids which behaves as normal electrolytes at low concentration, but have as colloids at high concentration. (they associate together to form colloidal size at high concentration)

Eg : Soap solution

- **Cleansing action of soap (Cleaning Action)**

Soaps are sodium or potassium salts of higher fatty acids.

Eg : Sodium stearate ($C_{17}H_{35}COONa$)

Sodium stearate ionises in water to form stearate ion and Na^+

$C_{17}H_{55} - COONa \rightarrow C_{17}H_{35} - COO^- + Na^+$

Stearate ion has a hydrophobic tail and hydrophilic head. Cleansing action of soap is based on micelle formation. Dirt particles surrounded by stearate ions forming soap micelle, which detaches from the cloth when rinsed with soap water.

Preparation of colloids

A) Condensation methods

1) By oxidation : $2H_2S + SO_2 \rightarrow 3S_{(sol)} + 2H_2O$
2) By reduction : $2AuCl_3 + 2SnCl_2 \rightarrow 2Au_{(gold\ sol)} + 3SnCl_4$
3) By hydrolysis : $FeCl_3 + 3H_2O \rightarrow Fe(OH_3)_{(Sol)} + 3HCl$
4) By double decomposition : $As_2O_3 + 3H_2S \rightarrow As_2S_3 + 2H_2O$

B) Dispersion methods

1) Mechanical dispersion : In this method, dispersed phase particles are mixed with dispersion medium and grinded to colloidal size in ‘Colloid mill’. The mill consists of two metal discs rotating at high speed in opposite directions. Large particles are grinded to colloidal size.
2) Electrical dispersion (Bredig’s arc method) : In this method two metal rods are immersed in dispersion medium and electric arc is produced between the electrodes. The arc vapourises metal atoms which condense together to form products of colloidal size.

   Eg: Gold sol, platinum sol, Ag sol,...
3) Peptization : The process of converting a precipitate into colloid by shaking with dispersion medium in presence of an electrolyte is called peptization. The electrolyte used for this purpose is called peptizing agent.

   Eg : A precipitate of $Fe(OH)_3$ can be converted to colloidal $Fe(OH)_3$ sol by addition of little $FeCl_3$ (Peptizing agent)

Purification of colloids

1) ***Dialysis :*** Dialysis is based on the fact that colloids do not pass through semi- permeable membrane. Colloidal solution is taken in a bag made up of semi- permeable memberane like cellophane or parchment. It is then suspended in fresh water. The impurities are slowly diffused out, leaving pure colloids.
2) ***Ultra filtration :*** Colloidal particles pass through ordinary filter papers. But the pore size of the filter papers can be reduced by dipping in collodion. (4% solution of nitrocellulose in alcohol). When the colloids are filtered using this modified filters, only impurities passes through it.
3) ***Ultra centrifugation :*** In this method, the impure colloid is taken in an ultra centrifuge. The centrifuge is then rotated at very high speed. Colloidal particles settle down at the bottom, leaving impurities.

Properties of colloids

1) ***Colligative properties :*** Colloids show colligative properties like Relative lowering of vapour pressure, Elevation of Boiling point, Depression of freezing point and osmotic pressure. But their molecular mass are large and hence their colligative property values

are relatively low. Since Osmotic pressure gives relatively large value, this colligative property is used for the determination of molecular mass of colloids.

2) ***Mechanical properties (Brownian motion) :*** The irregular or zig-zag movement of colloidal particles is called Brownian motion. It is due to continuous collition between dispersed phase and dispersion medium particles.
3) ***Optical properties (Tyndall effect) :*** When light beam is passed through a colloidal sol, its path become visible. the visibility of light through colloids is called Tyndall effect. It is due to scattering of light by colloidal particles.
4) ***Electrical properties (Electropheresis) :*** The migration of colloidal particles under the influence of electric field is called electrophoresis. It is due to charge on colloidal particles.

   Eg : 1) Brown coloured $Fe(OH)_3$ sol migrate towards negative electrode because it carries positive charge. 2) Red coloured As_2S_3 sol migrate towards positive electrode because it carries negative charge.

- **Zeta potential**

Colloidal particles are surrounded by two layer of charges – fixed layer and diffused layer. The potential difference between fixed layer and diffused layer around a colloidal particle is called Zeta potential (Electrokinetic potential)

- **Coagulation or Flocculation**

The process of setting of colloids by addition of electrolytes or by heating is called **coagulation** or **flocculation**.

Eg : 1) Coagulation of milk by acetic acid (Vinegar) 2) Boiling of egg.

- **Hardy – schulze rule**

This rule states that coagulating power of an electrolyte is directly proportional to the valency of ion carrying opposite charge to that of colloidal particles.

Eg : 1) For coagulating positive $Fe(OH)_3$ sol, the power of electrolytes are in the order.

$NaCl < Na_2SO_4 < Na_3PO_4 < K_4 [Fe(CN)_6]$

2) For coagulating As_2S_3 sol (negative), the power of electrolysis are in the order.

$NaCl < CaCl_2 < AlCl_3 < SiCl_4$

- **Protective colloids**

Lyophilic colloids can be used to protect lyophobic colloide from coagulation. Such lyophilic colloids used to protect lyophobic colloids from coagulation are called protective colloids.

- **Emulsions**

Liquid – liquid colloids are called emulsions

Eg : Milk, butter etc...

The substance which stabilise the emulsion are called emulsifying agent (Emulsifiers)

Eg : Soaps, gums etc...

- **Emulsions are of two types**

1) Oil in water type – In which oil is the dispersed phase and water is the dispersion medium.

Eg : milk

2) Water in oil type – In which water is the dispersed phase and oil is the dispersion medium

   Eg : Butter

- **Application of colloids**

1) Medicines in colloidal form are more effective. Eg : Milk of magnesia (Gelucil)
2) Clouds, mist, fog etc... are colloids, artificial rain can be produced by spraying AgI on clouds (Coagulation).
3) Blood is a colloidal sol, bleeding from wounds can be presented by applying $FeCl_3$, which is a coagulating agent.
4) Cleansing action of soap is due to the formation of colloid micelle.
5) Water purification by adding alums – coagulation.
6) Sewage dispersal – colloidal particles of dirt, mud, sewage particles etc. Carry, charge. When waste water is passed through two electrodes, high potential coagulation takes place and sewage particles settle down.
7) Smoke precipitation (Cottrell precipitator – refer test).
8) Food items like milk, butter ice creams etc are colloids.

***

Chapter 6

General Principles and Processes of Isolation of Elements

- **Occurrence of elements**

1. Free state : Low reactive elements like N_2, O_2, Au, Pt, Pd, S, Ag
2. Combined state : Reactive elements like Na, K, Ca, Al, Fe, Zn, Cu.

- **Minerals & Ores**

The naturally occurring solid compounds of metals are called minerals.

Eg : NaCl, KCl, $CaCO_3$, ZbS etc.

Minerals in which metals are sufficiently concentrated and from which metals can be profitably extracted are called Ores.

Some important Ores are :

1. Aluminum – Bauxite (Al_2O_3 $2H_2O$), Corundum (Al_2O_3).
2. Iron – Hematite (Fe_2O_3), Magnetite (Fe_3O_4), Siderite ($FeCO_3$), Iron pyrites (FeS_2).
3. Copper – Copper pyrites ($CuFeS_2$), Cuprites (Cu_2O), Copper glance (Cu_2S).
4. Zinc – Zinc blende (Zns), Calamine ($ZnCO_3$).

- **Metallurgy**

The process of extraction of metals from their ore is called **metallurgy**.

Steps in metallurgy are;

I Ore concentration/Ore benefaction/Ore dressing

a) *Hydraulic washing/Levigation/gravity separation*

This method is based on the difference in densities or solubility's of ore and impurities. The powdered ore is washed in a current of water. Lighter impurities are washed away leaving heavier are particles.

Eg : Purification of Haematite, gold, etc...

b) *Magnetic separation*

This is used when either the ore or impurity is magnetic in nature. The powdered ore is dropped over a belt moving over two rollers, one of which is magnetic. The magnetic compound is attracted by this magnetic roller and fall as a separate heap leaving non-magnetic impurities.

eg : Magnetite, Pyrolusite (MnO_2) etc are purified from non-magnetic impurities by this method.

c) *Froth Floatation*

This method is based on preferential wetting of the ore particles than impurities. This is used for the concentration of sulphide ores. The powdered ore is mixed with water and pine oil in a tank. The mixture is agitated by blowing air. Ore particles are wetted by pine oil and rise to the surface along with the foam. The foam is collected and ore particles are recovered.

- Depressants used – KCN, NaCN
- Activators used – $CuSO_4$

d) *Leaching*

Leaching is a chemical method of ore concentration. The impure ore is treated with suitable chemical reagent which dissolves the ore but not the impurities. Eg : Leaching of bauxite, i.e $\underset{\text{(impure baurite)}}{Al_2O_3 \cdot 2H_2O} + 2NaOH + H_2O \rightarrow \underset{\text{(sodium aluminate) (soluble)}}{2Na[Al(OH)_4]}$

$$2Na[Al(OH)_4] + CO_2 \rightarrow Al_2O_3 \cdot xH_2O + 2NaHCO_3$$

$$Al_2O_3 \cdot xH_2O \rightarrow \underset{\text{(pure alumina)}}{Al_2O_3} + xH_2O$$

II Calcination & Roasting

Calcination - Heating of ore in absence of air.

Roasting - Strong heat of an ore in the presence of air or O_2

Eg : Calcination

i) $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$ ii) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

Eg: Roasting

1) $2PbS + 3O_2 \xrightarrow{\Delta} 2PO + 2SO_2$ 2) $2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnS + 2SO_2$

III Extraction of Metals

a) *Reduction with C and CO (smelting)*

C and CO are most common reducing agents. Less reactive metals can be prepared from their oxide ores by smelting.

Eg : $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$ $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

- **Thermodynamic principles of metallurgy**

For any process, change in free energy is given by the equation,

$\Delta G = \Delta H - T\Delta S$ or $\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ_f$

i) If ΔG of process is negative, it becomes spontaneous.

ii) If ΔG of process is positive, it becomes non-spontaneous.

iii) A reaction with positive ΔG can be made to occur by coupling with another reaction having large negativeΔG. So that the net ΔG of the coupled reaction is negative.

Such coupling can be easily predicted from Ellingham diagram.

- **Ellingham Diagram**

A graph of standard free energy of formation (ΔG°_f) against temperature T is called **Ellingham** diagram. At any temperature, a metal lying below in Ellingham diagram act as a reducing agent.

eg : ΔG°_f (Fe, FeO) at 800° is –300 kJ. ΔG°_f (C, CO) at 800° is – 450 kJ.

Therefore, 'C' can be used as reducing agent at 800° C. But 'C' cannot be used as reducing agent below 400°f. But below 400°C, ΔG°_f(CO, CO_2) his below ΔG°_f (Fe, FeO)

Therefore, 'CO' can be used as reducing agent at low temperature.

So, in Iron manufacture, CO is reducing agent at low temperature and C is the reducing agent at higher temperature.

The intersection point of ΔG°_f (Al, Al_2O_3) and ΔG°_f (Mg, MgO) is around 1600K. Therefore, below 1600K, Mg acts as reducing agent, which can reduce Al_2O_3 into Al. But, above 1600K, Al acts as reducing agent, which can reduce MgO into Mg.

b) ***Reduction with Aluminium : (Thermite Process)***

Al and Mg are used as reducing agents. Reduction with Al power is called thermite reduction/Thermite process.

Eg : $Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 2Cr$

c) ***Electroreduction***

Most reactive metals like Na, K, Ca, Al, Mg, etc. are prepared by electrolysis of their fused salts. During electrolysis, metals are formed at cathode and non-metals are formed at anode.

Eg : $2NaCl \xrightarrow{electrolysis} \underset{(cathode)}{2Na} + \underset{(anode)}{Cl_2}$

d) ***Autoreduction***

Sometimes, when sulphide ores are heated, a part of it is oxidised to oxide, which reduces the unreacted sulphide into metal.

Eg : $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$ $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$

e) ***Cyanide process (Hydrometallurgy)***

Metals like gold/silver, etc. are prepared by leaching their ores with KCN or NaCN solution. The metal dissolves as cyanides from which the metal is precipitated by adding zinc.

f) ***Electrochemical displacement (Displacement method)***

A less reactive metal (lying above in electrochemical series) can be prepared by displacement with a more reactive metal (lying below in electrochemical series)

Eg : Cu from low grade ores can be prepared by adding scrap iron or by passing H_2

$$\underset{\text{(blue)}}{CuSO_4} + Fe \rightarrow \underset{\text{(green)}}{FeSO_4} + Cu$$

g) ***Preparation of Non-metals (By oxidation)***

Non-metals are usually prepared by oxidation. During electrolysis, non-metals are liberated at anode.

Refining of Metals

The process of removing impurities from crude metal is called **refining.** Important refining techniques are;

a) ***Liquation :*** Easily fusible metals like Pb, Sn etc are purified by this method

b) ***Distillation :*** Volatile metals like Hg, Zn etc.. are purified by this method.

c) ***Electro refining :*** Noble metals like Au, Pt, Cu etc are purified by this method. The impure metal is taken as anode, and a thin sheet of pure metal is taken as cathode. During the passage of electricity metals dissolves from anode and deposited on cathode. The impurities are left at the bottom of anode called **anode mud**. From anode mud of Cu purification, metals like Antimony, selenium, Telurium, Gold, Silver etc. are obtained.

d) ***Zone refining :*** For semiconductor elements like Silicon, Germanium, gallium, etc...

e) ***Vapour phase refining :*** In this method, the impure metal is converted into a volatile compound at lower temperature and then decomposed back into pure metal at higher temperature. It is of two types.

i) Van- Arkel Method (For titanium & zirconium)

$$\underset{\text{(impure)}}{Zr + 2I_2} \xrightarrow[\Delta]{700k} \underset{\substack{\text{(volatile)}\\ \text{(zirconium tetraiodide)}}}{ZrI_4} \xrightarrow[\Delta]{1200k} \underset{\text{(pure)}}{Zr + 2I_2}$$

ii) Mond's process (For Nickel)

$$\underset{\text{(impure)}}{Ni + 4CO} \xrightarrow[\Delta]{350k} Ni(CO)_4 \xrightarrow[\Delta]{450k} Ni + 4CO$$

(Nickel tetracarbonyl) (pure)

e) ***Chromatography : Based on selective adsorption***

Extraction of Iron

The powdered ore (Haematite) is mixed with coke and limestone and dropped from the top of blast furnace. The furnace is heated by a blast of hot air from the bottom.

The reactions are:

- ***Upper portion*** (500 – 900k), CO is the reducing agent.

  $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$ $Fe_2O_3 + CO \rightarrow 2FeO + Co_2$

- ***Middle portion*** (900 – 1500k), CO is the reducing agent

  $C + CO_2 \rightarrow CO$; $FeO + CO \rightarrow CO_2$

The flux $CaCO_3$ decomposes to give CaO, which react with gangue, SiO_2 do from slag ($CaSiO_3$)

$CaCO_3 \rightarrow CaO + CO_2$; $CaO + SiO_2 \rightarrow \underset{\text{(slag)}}{CaSiO_3}$

○***Bottom portion*** (1500 – 2200k), C is the reducing agent

$FeO + C \rightarrow Fe + CO$; $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

Molten iron is collected at the bottom and cooled in moulds to get pig iron.

- Pig iron : It is the impure form of iron. It contains 4% carbon.
- Cast iron : It contains 3% carbon.
- Wrought iron : At is the purest form of iron. It contains less than 0.5% carbon. It is prepared by heating cast iron with haematite.
- Steel : 0.5 – 1.5% carbon.

- **Extraction of copper**

The chief ore is copper pyrites ($CuFeS_2$). It is concentrated by froth floatation.

The purified ore is heated strongly in a Reverberatory furnace in which $CuFeS_2$ split into Cu_2S and FeS.

$2CuFeS_2 + O_2 \xrightarrow{\Delta} Cu_2S + 2FeS + SO_2$

This mixture is roasted in a blast furnace, where FeS is oxidised to FeO, which combine with flux SiO_2 to form slag $FeSiO_3$.

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$ $FeO + SiO_2 \rightarrow FeSiO_3$ (thomas slag)

After roasting, the remaining mixture contains Cu_2S and slight unreacted FeS. This mixture is called copper matte : This copper matte is heated strongly with air/O_2 in Bessemer furnace. A part of Cu_2S is oxidised to Cu_2O, which act as reducing agent, which reduce the unreacted Cu_2S into Cu.

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$ $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$ (Auto reduction).

The impure copper thus obtained is called 'blister copper' due to blisterly appearance of SO_2 escape. It is purified by electro refining.

- **Extraction of Aluminium**

The ore used is Bauxite and it is concentrated by leaching. Aluminium is manufactured by electro reduction of molten alumina (Hall – Heroult process)

Leached Alumina is mixed with Cryolite (Na_3AlF_6) and Fluospar (CaF_2). The fused mixture is electrolysed in a steel tank lined with carbon, which act as cathode. Anode consists of graphite carbon rods dipped in molten electrolyte. During electrolysis, Aluminium is deposited at the bottom of the tank (cathode). The O_2 formed at anode burns the graphite rods into CO_2 and hence graphite rods are replaced periodically.

Reactions are; $2\,Al_2O_3 \rightarrow 4Al^{3+} + 6O^{2-}$
at cathode; $4Al^{3+} + 12e^- \rightarrow 4Al$
at anode ; $6O^{2-} \rightarrow 3O_2 + 12e^-$
net reaction; $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$

- **Extraction of Zinc**

Zinc is extracted from ZnS. After froth floatation, the ore is roasted at 1173K to give ZnO. It is then mixed with coke and heated at 673K.

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

$2ZnO + C \xrightarrow{673K} 2Zn + CO_2$

***

Chapter 7

The p- Block Elements

The Elements of group 14 to 18 in the periodic table. Outer electronic configuration ns^2np^{1-6}.

Group 15 Elements

The Nitrogen family includes Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth.

- Nitrogen occurs as N_2 gas (78% by volume of earth's atmosphere) and as nitrate minerals like Chile Saltpetre ($NaNO_2$) and Indian Saltpetre (KNO_2). Phosphorus occurs as Flora apatite ($Ca_2(PO_4)_6$. CaF_2 and also present in bones, eggs etc.
- Electronic configuration : **ns^2np^3**
- Atomic size increases down the group but from As to Bi the increase is small due to the presence of filled *d* and/or *f* orbitals which are inefficient in screening.
- Ionisation enthalpy decreases down the group but greater than that of group 14 due to the presence of stable half filled electronic configuration in outer p –subshell
- Electro negativity decreases down in the group.
- Nitrogen is a diatomic gas while others are poly atomic solids. Except Nitrogen others show allotropy. Metallic character increases down the group.
- Common oxidation states are -3, +3 and +5. Nitrogen shows +1, +2, +3, +4, +5 and -3 oxidation states.
- Down the group the stability of +5 oxidation is less compared to +3 due to inert pair effect.

Chemical properties

With hydrogen, they form trihydrides of the formula EH_3. Basic characters of hydrides decreases down the group and reducing character increases. With halogens, they from halides of the formula, EX_3 (Predominantely ionic), EX_5 (covalent) and with oxygen, oxides of the formula, E_2O_3 (less acidic) and E_2O_5 (more acidic). Nitrogen forms a variety of oxides having oxidation states +1 to +5.

They react with metals to form compounds in which they show –3 oxidation states.

Anomalous properties of Nitrogen

Nitrogen differs in many properties from the rest of the elements of the group due to its small size, high electro negativity, high ionisation enthalpy and non availability of d- orbitals in its valence shell. Eg: Due to its ability to form pπ –pπ multiple bonds with itself (and with C & O). It exists as diatomic molecule where as other are tetra atomic Nitrogen does not form pπ- dπ multiple bonds and tendency for catanation is less. It does not form penta-halides due to the absence of d-orbital.

- **Dinitrogen (N_2)**

  Laboratory preparation

  $NaNO_2 + NH_4Cl \rightarrow NaCl + 2H_2O + N_2$

  ○ N_2 is a colourless odourless gas which reacts with metals and non metals at high temperature, eg. $3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$; $N_2 + O_2$ 🕓 $\overset{\Delta}{2NO}$

- **Ammonia; NH_3**

  It is prepared on the laboratory by the reaction

  $(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2NH_3 + 2\ H_2O$

  ○ Manufactured by Haber process.

  $N_2 + 2H_2 \xrightleftharpoons{FCl\ ,\ 700\ K,\ 200\ atm} 2NH_3$; $\Delta_f H = -46.1\ kJ\ mol^{-1}$

  According to Le Chatelier's principle high pressure and low temperature favour the formation ammonia, but high yield is obtained at optimum conditions of pressure and temperature (700 K and 200 atom) catalysts is FeO/Fe with small amount of K_2O and Al_2O_3 (Promoters).

  ○ Ammonia is colourless, pungent smelling gas which is associated through hydrogen bonding in liquid and solid states. The molecules is triagonal pyramidal in shape.

  ○ Highly soluble in water to form a weakly basic solution due to formation of OH^- ions.

  ○ It is a lewis base and reacts with acids to from salts like NH_4Cl, $(NH_4)_2SO_4$. It precipitates metal hydroxides of many metals from their salt solution.

  ○ It acts as ligands to form complex compounds with metal ions such as Cu^{2+}, Ag^+ etc and therefore used to detect these ions from salt solutions.

  <u>Uses</u>

  ○ Ammonia is used to produce nitrogenous fertilizers and inorganic nitrogen compounds like nitric acid. Liquid NH_3 is used as a refrigerant.

- **Oxides of Nitrogen**

  Because of the ability of nitrogen to form $p\pi - p\pi$ multiple bond with itself and with oxygen, it forms a number of oxides in which the oxidation state of nitrogen varies from +1 to +5. They are N_2O, NO, N_2O_3, NO_2, N_2O_4 and N_2O_5. Most of them can be prepared from nitrates, nitrites or nitric acid

  Eg : $2Pb\ (NO_3)_2 \xrightarrow{673K} 2PbO + 4NO_2 + O_2$

  $2NO_2 \xrightleftharpoons[heat]{cool} N_2O_4$

- **Nitric Acid (HNO_3)**

  ○ Prepared in laboratory by heating sodium or potassium nitrate with sulphuric acid

  $NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaH_2SO_4$

  ○ Manufactured by Ostwald process

  $4NH_3 + 5O_2 \xrightarrow[500\,K,\,9\,bar]{pt\,/\,Rh\ gauze\ catalyst} 4NO_{(g)} + 6H_2O_{(g)}$

  $2NO + O_2$ 🕓 $2NO_2$

  $3\ NO_2 + H_2O \rightarrow 2HNO_3 + NO$ The NO formed is recycled

- In gaseous states nitric acid is a planer molecule.
- It is a strong monobasic acid and therefore reacts with bases.
- It is a strong oxidizing agent. It oxidizes S to H_2SO_4 and C to CO_2
- It reacts with metals to form corresponding metal nitrates and oxides of nitrogen. Reactions of dilute and concentrated nitric with metals give different products.
- Presence of nitrate ions in solution is detected by brown ring test.

  Nitric acid is used in the manufacture of nitrate fertilizers, explosives such as nitroglycerin, TNT and as a common laboratory reagent.

  A mixture conc. HNO_3 and conc. HCl in the ratio 1:3 is called **aqua-regia.**

Phosphorous P

Allotropes – white phosphorus which consists of discrete P_4 molecules and is highly reactive and poisonous. It is stored under water. When it is heated to 573K in an inert atmosphere red phosphorus is formed which is less reactive and non poisonous. Red Phosphorus is heated to 803 K to get α black phosphorous and white P is heated to 473 K to get β – black P.

Phosphine – PH_3

Prepared by following reaction

$$P_4 + 3\,NaOH + 2H_2O \rightarrow 2NaH_2PO_2 + PH_3$$

$$Ca_3P_2 + 6H_2O \rightarrow 3\,Ca\,(OH)_2 + 2PH_3$$

PH_3 is a poisonous gas, and weaker box than NH_3. It has pyramidal structure in which P atom is sp^3 hybridised. It is used in Holme's signals.

Phosphorus trichloride – (PCl_3)

- Prepared by following reactions; $P_4 + 6Cl_2 \rightarrow 4\,PCl_3$

  $$P_4 + 8\,SOCl_2 \rightarrow 4\,PCl_3 + 4SO_2 + 2\,S_2Cl_2$$

- It has pyramidal shape and undergo hydrolysis in presence of moisture giving fumes of HCl.

  $$PCl_3 + 3\,H_2O \rightarrow H_3PO_3 + 3\,HCl$$

- Reacts with organic compounds containing OH giving chloro derivatives

  $$3\,ROH + PCl_3 \rightarrow 3\,RCl + H_3PO_3$$

Phosphorus penta chloride PCl_5

- Prepared by following reactions

  $$P_4 + 10\,Cl_2 \rightarrow 4\,PCl_5$$

  $$P_4 + 10\,SO_2Cl_2 \rightarrow 4\,PCl_5 + 10\,SO_2$$

- It dissociates into PCl_3 and Cl_2 on heating and hydrolysed to $POCl_3$ and finally to H_3PO_4 in presence of moisture. If has triagonal bipyramidal shape with sp^3d hybridised p atom.

Oxoacids of Phosphorus

The important oxoacids of P are Hypophosphorus acid or phosphonic acid (H_3PO_2) ortho phosphorus acid or phosphonic acid (H_3PO_3), orthophosphoric acid (H_3PO_4) , pyrophosphoric acid ($H_4P_2O_7$). Hypophosphoric acid ($H_4P_2O_8$), Cyclotrimeta phosphoric acid $(HPO_3)_3$ and polymetaphosphoric acid$(HPO_3)_n$. In all of these oxo acids P is tetrahedrally surrounded by four other atoms or groups. All these acids contain one P = O and at least one P–OH bond.

The hydrogen atom of P–OH groups are ionisable and number of P–OH groups decide the basicity of the oxoacids.

Group 16 Elements – Oxygen Family (Chalcogens)

- This group includes Oxygen, Sulphur, Sclenium, tellurium and polonium. Their general electronic configuration is ns^2np^4.
- Lower ionisation enthalpy than gp 15 elements.
- Due to the small size and consequent inter electronic repulsion electron gain enthalpy of O is less than S.
- Oxygen is the second most electronegative element in periodic table.
- Oxygen shows – 2 oxidation states (except in OF_2). Other elements show +2, +4 and +6 oxidation states. (+4 and +6 are common)
- They react with H to form hydrides of the formula H_2E – Acidic character of hydrides increases from H_2O to H_2Te, and thermal stability decreases from H_2O to H_2Te.
- H_2O has high boiling point due to inter molecular hydrogen bonding.
- They form oxides of the formula EO_2 and EO_3.
- The form halides of the formula EX_2, EX_4 and EX_6

Anomalous properties of oxygen

- Oxygen is diatomic gas while others are solids.
- Oxygen usually shows an oxidation state of −2 (except in puroxide, super oxides and OF_2) other elements show oxidation states of +2, +4 and +6.
- Among hydrides, H_2O alone is a liquid(due to- H-bonding) at room temperature while others are gases.

Dioxygen- O_2

- Prepared by decomposition of chlorides, permanganates, nitrates etc.

  Eg : $2KClO_3 \xrightarrow[MnO_2]{700K} 2\,KCl + 3O_2$
- Industrially O_2 is prepared by electrolysis of water.
- Oxygen is a colourless odourless gas, slightly soluble in water. If reacts with other elements to form oxides.

Uses : Essential for respiration and combustion, oxyacetylene torch is used in welding and liquid O_2 is used as an oxidiser in rocket propellants.

- Oxygen reach with metals and non metals to form oxides.

Acidic oxides

Acidic oxides give acids with water. Eg : SO_2, SO_3, CO_2, N_2O_5, P_4O_8 etc.

$SO_2 + H_2O \rightarrow H_2SO_3$ (Sulphurous acid)

- Oxides that give bases with water are called basic oxides. Eg: Na_2O, CaO, BaO etc.
- Oxides which show both oxidise and basic properties as called amphoteric oxides

  Eg : Al_2O_3, ZnO, PbO etc.

- There are neutral oxides such as CO, NO, N_2O etc.

Ozone, O_3

- It is formed in the upper atmosphere by photochemical reaction involving O_2. This layer called Ozone layer, which protect the earth's surface from UV radiations from the Sun.
- O_3 is prepared in laboratory by the following reaction

  $3O_2 \xrightarrow{\text{Silent electric discharge}} 2O_3$. This reaction is carried out in an apparatus called ozoniser.
- O_3 is a pale blue gas having diamagnetic property.
- O_3 is a powerful oxidising agent due to the formation of nascent oxygen. Eg : Oxygen oxidises black PbS to white $PbSO_4$

  Eg : $PbS + 4\,O_3 \rightarrow PbSO_4 + 4O_2$

Uses : Used as a germicide and disinfectant during purification of water.

Bleaching agent for vegetable colouring matter, starch etc...

Powerful oxidising agent

Allotropes of sulphur

Yellow rhombic – or α sulphur and monoclinic or β sulphur

α Sulphur (insoluble in water) prepared by evaporating a solution of roll sulphur in carbon disulphide (CS_2), β - Sulphur is prepared by melting α - sulphur and then cooling .

Above 369 K β- sulphur changes into α - sulphur. α and β sulphur have S_8 molecules having crown shape.

Sulphur dioxide (SO_2)

- Prepared by burning sulphur in air or treating a sulphite salt with dilute acids.

  Eg : $Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$
- SO_2 is a colourless gas which forms sulphurous acid when dissolved in water.
- Reacts with chlorine to form SO_2Cl_2 (Sulphuryl chloride)
- SO_2 is a reducing agent in presence of moisture.
- If reduces Ferric salts to ferrous and decolourises acidified $KMnO_4$.
- SO_2 has an angular structure.

Uses : - A bleaching agent for wool, silk etc.

- An antichlor and a preservative

- Used for the manufacture of H_2SO_4

Oxoacids of Sulphur

- Oxoacids of S contain at least one S = O bond and S – OH bond.
- Important oxoacids of S are sulphurous acid H_2SO_3, sulphuric acid (H_2SO_4), Oleum or pyrosulphuric acid ($H_2S_2O_7$) and peroxo disulphuric acid $H_2S_2O_8$.

Sulphuric acid H_2SO_4

- H_2SO_4 is manufactured by contact process. In this process SO_2 gas is prepared by burning sulphur; $S + O_2 \rightarrow SO_2$.
- SO_2 is catalytically oxidised to SO_3 with atmospheric oxygen

V_2O_5

$$2SO_2 + O_2 \rightleftharpoons 2\,SO_3 \qquad \Delta H = -196.6\ kJmol^{-1}$$

According to Le Chatelier's principle low temperature and high pressure should give maximum yield of SO_3 since the catalyst V_2O_5 is active at a slightly higher temperature, an optimum temperature of 720 K and 2 bar pressure are used.

The SO_3 gas produced is absorbed on 98% sulphuric acid to get oleum or forming sulpuric acid which is then diluted to sulphuric acid.

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (Oleum)

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

Properties

It is a strong diabasic acid. It dissociates in water as follows.

$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^{\,-}$

$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{\,2-}$

- Sulphuric acid forms two series of salts namely normal sulphates (Eg. Na_2SO_4) and acid sulphates (Eg. $NaHSO_4$)
- Sulpuric acid is a good dehydrating agent
- It is an oxidising agent and can oxidises S to SO_2, C to CO_2 etc.

Group 17 Elements – Halogen Family

Halogen family includes, Fluorine, Cholrine, Bromine, Iodine and Astatine.

Main source of chlorine is NaCl (Rock salt) Fluorine occurs as Fluorspar (CaF_2) fluorapatite $Cag(PO_4)_3$. CaF_2 etc.

- General electronic configuration is $\mathbf{ns^2np^5}$
- They are all non metal F_2 & Cl_2 are gases, Br_2 is liquid and I_2 is solid
- They have very high ionisation enthalpy showing that they have little tendency to lose electrons.
- They have high electronegativity, fluorine is the highest electronegative element in the periodic table.
- They show maximum electron gain enthalpy (ΔH). Due to the smaller size of fluorine its electron gain enthalpy is less negative compared to chlorine. – The order of electron gain enthalpy is, $F < Cl > Br > I$
- The bond dissociation enthalpy of F_2 is very less due to the relatively large electron - electron repulsion among the lone pairs of electrons in F_2 molecule where they are much closer compared to Cl_2
- Halogens are highly reactive, of which fluorine is the most reactive.
- Halogens are powerful oxidising agents and show strong tendency to take up electron. F is the strongest oxidising agent.
- A smaller halogen oxidises a larger halide ion.

  $F_2 + 2X^- \rightarrow 2F^- + X_2$ (X = Cl, Br or I)
- All the halogen show −1 oxidation state and fluorine shows only −1 oxidation state. Cl, Br and I shows +1, +3, +5 and +7 oxidation states also.

F_2 oxidises water to oxygen.

$2\ F_2 + 2H_2O \rightarrow 4HF + O_2$

- Halogens combines with hydrogen to form covalent hydrides called hydrogen halides. Aqueous solutions of hydrogen halides are acidic and are called hydrohalic acid.

  The orders of acidity of hydrohalic acids is as follows;

  $HF < HCl < HBr < HI$ H –X bonds strength decides acidity
- They react with metals and nonmetals to form halides

  Eg : $2Na + Cl_2 \rightarrow 2\ NaCl$, $2\ P_4 + 6Cl_2 \rightarrow 4\ PCl_3$

Anomalous behaviour of fluorine

- Ionisation enthalpy, electronegativity and oxidising power are higher than other group members.
- Form only one oxoacid
- HF is low boiling liquid (due H – bonding) but hydrides of other halogen are gases.
- The anomalous properties of fluorine are attributed to small size, highest electro negativity, low F –F bond dissociation enthalpy and non availability of d – orbitals in its valence shell.

Chlorine

- Prepared by heating MnO_2 or $KMnO_4$ with conc. HCl

  Eg : $MnO_2 + 4\ HCl \rightarrow MnCl_2 + 2\ H_2O + Cl_2$
- Manufactured by;

  i) Deacon's process $4HCl + O_2 \xrightarrow[72K]{CuCl_2} 2\ Cl_2 + 2\ H_2O$

  iii) Electrolytic process – Elctrolysis of sodium chlorides solution produces Cl_2 at anode.
- Chlorine is a greenish yellow gas
- Combines with metals and non metals to form their chlorides

  $2\ Al + 3Cl_2 \rightarrow 2\ AlCl_3$; $P_4 + 6Cl_2 \rightarrow 4\ PCl_3$
- Reacts with cold dilute alkali to form mixture of chloride and hypochlorite (Eg. NaOCl)
- With hot conc. alkali gives mixture of chloride and chlorate (Eg. $NaOCl_3$)
- Chlorine gas is passed through dry slaked lime to get bleaching powder.

  $2\ Ca(OH)_2 + 2\ Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$
- Composition of bleaching powder is

  $Ca(OCl_2).CaCl_2.\ Ca(OH_2).2H_2O$
- Chlorine oxidises ferrous salts to ferric, SO_2 to H_2SO_4 and Iodine to iodic acid.
- Chlorine is a good bleaching agent

  $Cl_2 + H_2O \rightarrow HCl + O$. The nascent oxygen formed here is responsible for bleaching.
- Chlorine reacts with excess NH_3 to form NH_4Cl and N_2. However when excess chlorine is taken the products are NCl_3 and HCl

Uses : i) For bleaching cotton wool pulp etc.

ii) For preparing chloroform, DDT etc

iii) in the manufacture of dyes and drugs

iv) for sterilising water.

- **Hydrogen chloride (HCl)**
  - Prepared by the following reaction

    $NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$
  - HCl is a gas highly soluble in water.

    A mixture of conc. HCl and conc. HNO_3 in 3:1 ratio in known as aqua regia, used for dissolving inert metals such as gold, platinum etc.
  - HCl reacts with carbonates and bicarbonates to form CO_2 gas.

  Uses : Used in laboratory as reagent, in medicines and in the manufacture of NH_4Cl, Cl_2 etc.

- **Oxoacids of Halogens**

Fluorine form only one oxoacid hypofluorous acid or fluoric (I) acid (HOF). Other halogens can form hypohalous, (Eg. hypochlorines acid HOCl), halous, (Eg. Chlorous acid $HClO_2$) halic (Chloric acid $HClO_3$) and perhalic (perchloric acid- $HClO_4$) acids.

- **Interhalogen compounds**
  - The combination of two different halogens yield interhalogen compounds having the general for much XX', XX'_3, XX'_5 and XX'_7 where X is larger halogen and X′ in a smaller one. Eg. ClF, BrF_3, BrF_5, IF_7 etc.
  - Prepared by direct combination two halogens

    $Cl_2 + F_2 \rightarrow 2\,ClF$ $\qquad$ $Br_2 + 3F_2 \rightarrow 2BrF_3$
  - Inter halogen compounds are more reactive than corresponding halogens (except F_2) because $X-X'$ bond is weaker than $X-X$ bond.
  - Interhalogen compounds undergo hydrolysis.

    $ClF + H_2O \rightarrow HOCl + HF$

Group 18, The Noble Gases

- Group members are Helium (He) Neon (Ne), Argon (Ar), Krypton(Kr), Xenon(Xe) and Radon (Rn)
- Except radon all elements are present in very minute quantities in atmosphere hence called rare gases. All are mono atomic gases. He is present in natural gas.
- General electronic configuration is $ns^2\,np^6$ (except He which has $1s^2$ configuration).
- Due to completely filled outer shell, they are less reactive and hence called inert gases.
- They have very high ionisation enthalpy due to stable configuration in their valence shell.
- No tendency to accept additional electrons, therefore their electron gain enthalpies are large positive values.

- **Physical properties**
  - All are monoatomic gases.
  - They have very low melting and boiling points because of weak interatomic interaction

- ○ He has the lowest boiling point (4.2 K of any known substance).

- **Chemical properties**
  - ○ Among noble gases Xe forms a large number compounds.

Fluorides : Xenon form di, tetra and hexafluorides on direct reaction with fluorine.

Eg. $Xe + F_2 \xrightarrow[1bar]{673K} XeF_2$; $Xe + 2F_2 \xrightarrow[1bar]{673K}$, XeF_4

They are readily hydrolysed even by traces of water.

Eg. $2XeF_2 + 2\ H_2O \rightarrow 2Xe + 4HF + O_2$

- **Xenon Oxygen compounds**

Hycholysis of XeF_4 and XeF_6 give XeO_3, a colourless explosive solid having pyramidal structure.

Eg : $XeF_6 + 3\ H_2O \rightarrow XeO_3 + 6HF$

$6XeF_4 + 1_2\ H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

- ○ Partial hydrolysis of XeF_6 forms oxyfluorides

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

$XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

- **Uses of group 18 elements**

He is used for filling airships and balloons. Liquid He is used as cryogenic agent for carrying out various experiments.

Due to its low solubility in blood He is used as a diluent for oxygen in diving apparatus.

Argon is used to provide an inert atmosphere in high temperature metallurgical process and for filling electric bulbs.

***

Chapter 8

The ‘d’ and ‘f’ Block Elements

The transition element may be defined as the element whose atom or ion contains partially filled ‘d’ orbitals. Zn, Cd and Hg have fully filled ‘d’ orbitals in their ground state as well as in their common oxidation states and hence are not regarded as transition elements. However, being the end members of the series their chemistry is studied along with that of ‘d’ block elements.

There are three complete series of transition elements and the fourth series is incomplete.

1. 3d series [Sc to Zn]
2. 4d series [Y to Cd]
3. 5d series [La to Hg]
4. 6d series [Begins with Ac is still incomplete]

General Characteristics

1. Electronic Configurations

The general outer electronic configuration of these elements is $(n-1)d^{1-10} ns^{1-2}$

Exceptional configuration of Cu and Cr

Cr (24) → $[Ar]\ 3d^5, 4s^1$

Cu (29) → $[Ar]\ 3d^{10}, 4s^1$

This is because half filled and completely filled orbitals are more stable.

2. Melting and boiling points

Transition metals, have very high melting and boiling points due to the presence of strong metallic bonding present in them. (Exception to Zn, Cd and Hg)

The melting points of transition elements rise to a maximum at d^5 (except for anomalous values of Mn and Tc) and fall regularly as the atomic number increases. Tungsten possess the highest melting point among transition elements. Zn, Cd and Hg have low melting and boiling points due to the presence of completely filled 'd' orbitals with no unpaired electrons.

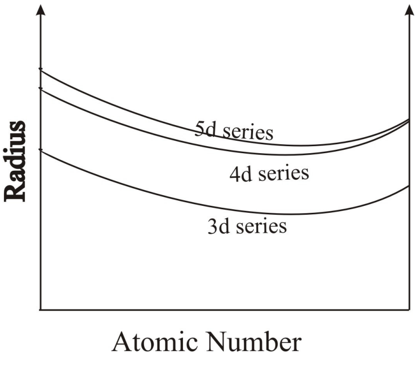
The transition elements have high enthalpies of atomisation (Enthalpy change takes place when one mole of a metallic solid is converted into its vapour atoms) and maximum values occur around the middle of each series [Greater the number of valance electrons stronger the resultant bonding]

The metals with high enthalpy of atomisation tend to be noble in their reactions. The metals of second and third transition series have greater enthalpies of atomisation than first series due to frequent metal-metal bonding in compounds of heavy transition metals.

3. Variation in atomic and ionic sizes

The atomic and ionic radi of transition elements on a particular series first decreases till the middle, becomes almost constant and then increases towards the end of the period. The decrease in size in the beginning is due to the increase in nuclear charge. When the increased nuclear charge and increased screening effect balance each other in the middle portion and the atomic radi becomes almost constant in the middle portion. The increase in atomic radi at the end of the series is due to the electron-electron repulsion as a result of pairing of electrons in the 'd' orbitals.

Down the group atomic size shown an increase from the 3d series to 4d series but the size of 4d and 5d series remains almost same due to lanthanide contraction.



The decrease in metallic radi coupled with increase in atomic mass results in a general increase in the density of the elements

4. Ionisation enthalpies

The ionization enthalpy of transition elements are higher than those of S – block elements but lower than P- block elements. There is an increase in ionization enthalpy along each series due to increase in nuclear charge. The elements of 5d series possess higher ionization enthalpies than 3d and 4d series due to the ineffective shielding of inner 4f electrons.

The smaller the ionization enthalpy of the metal the more stable will be its compound. Eg : The Ni (II) compounds are more stable than Pt (II) compounds.

This is because the sum of the first two ionization enthalpies of nickel is smaller than the sum of the first two ionization enthalpies Pt.

5. Oxidation states

Transition elements show variable oxidation states due to the involvement of both ‘ns’ and ‘(n-1)d’ electrons in chemical reactions. The lower oxidation states are shown when ‘ns’ electrons participate in bonding and higher oxidation states are shown when ‘ns’ and ‘(n-1)d’ electrons take part in the bonding.

The elements which give the greatest number of oxidation states occur in the middle of the series. The highest oxidation state shown by transition elements is +8 (shown by Ru and Os). For the elements of 3d series +2 oxidation state is the most common (except Sc)

$Sc \rightarrow [Ar]\ 3d^1, 4s^2$

The transition elements in the lower oxidation states (+2 and +3) generally form ionic bonds. In the higher oxidation states the bonds formed are essentially covalent.

Eg: MnO_4^{-1} (The oxidation state of Mn is +7)

Some transition metals show zero oxidation in their compounds Eg. $[Ni(CO)_4]$ $[Fe(CO)_5]$

6. Electrode potentials

It may be noted that there is no regular variation of reduction potentials because the ionization enthalpy and sublimation energy do not exhibit any regular trend. The electrode potentials are the measure of the values of total enthalpy change, which is equal to the sum of enthalpy of sublimation, ionization energy and enthalpy of hydration.

The E^o value of Cu is +ve because the high energy of transform Cu(s) to Cu^{2+} (aq) is not balanced by its hydration enthalpy.

Disproportionation reaction

Reactions in which a single substance undergoes change to produce products, one of which is in higher oxidation state and the other in the lower oxidation state are called disproportionation reactions. Disproportionation reaction takes place when a particular oxidation state of the element becomes less stable than the other oxidation states.

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

7. Magnetic Properties

Due to the presence of unpaired electrons in the ‘d’ orbitals most of the transition metals are paramagnetic. The magnetic moment is related to number of unpaired electrons according to the equation (Spin only formula)

$$\mu = \sqrt{n(n+2)}\ \text{Bm}$$

where ‘n’ is the number of unpaired electrons

8. Formation of Coloured ions

The transition elements form coloured compounds due to the presence of unpaired electrons in the 'd' orbitals and the ability of electrons to promote from one orbital to another within the same d-subshell. (d-d transition) The atoms or ions having d^0 and d^{10} configurations are generally colourless.

Eg:- $Sc^{3+} \rightarrow 3d^0$ colourless
$Zn^{2+} \rightarrow 3d^{10}$ colourless

9. Formation of Complex Compounds

The transition metals form a large number of complexes

Eg: - $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$

This is due to the comparatively smaller size of the metal ions, their high ionic charges and the availability of 'd' orbitals for bond formation.

10. Catalytic Properties

The transition elements and many of their compounds are used as catalysts. This is due to their ability to adopt multiple oxidation states and to form the complexes.

Eg : -
1. Iron is used in Haber process
2. V_2O_5 is used in Contact process
3. Ni, Pt and Pd are used in the hydrogenation of alkenes
4. Zeigler – Natta catalyst ($TiCl_4$ + $(C_2H_5)_3Al$) used in the polymerization of alkenes.
5. Fe^{3+} oxidises I^- ions to iodine

11. Formation of interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N one trapped inside the crystal lattices of metals.

Eg Fe_3H, Mn_4N, etc.

12. Alloy Formation

Transition metals form a large number of alloys. Such alloys are hard and have high melting points. The transition metals are quite similar in size and, therefore, the atoms of one metal can easily take up the position of the atoms of other metals in its crystal lattice.

Eg:- Brass [Cu – Zn]
Bronze [Cu – Sn]

Some important compounds of transition elements

I Potassium dichromate [$K_2Cr_2O_7$]

Preparation

$K_2Cr_2O_7$ is prepared from chromite are $FeCr_2O_4$. The different steps involved in the preparation of $K_2Cr_2O_7$ are.

1) Preparation of sodium chromate

$$4FeCr_2O_4 + 8\,Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8\,CO_2$$

2) Conversion of sodium chromate into sodium dichromate

$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

3) Conversion of sodium dichromate into Potassium dichromate

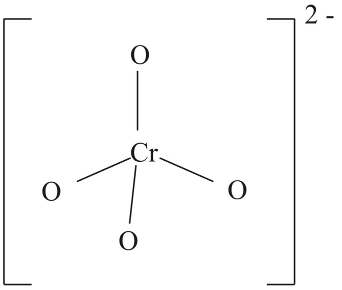
$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

The chromates and dichromates are inter convertible in aqueous solution depending upon the pH of the solution.

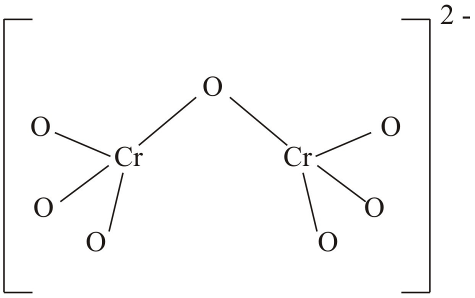
$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O.$

Structure :



Chromate Ion



Dichromate ion

Chemical Properties

1) Oxidising Properties

$K_2Cr_2O_7$ is a powerful oxidising agent in acidic medium

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Eg : a. It oxidises iodides to iodine

$6I^- \rightarrow 3I_2 + 6e^-$

b. It oxidises Fe^{2+} to Fe^{3+}

$6Fe^{2+} \rightarrow 6Fe^3 + 6e^-$

c. It oxidises H_2S to sulphur

$3H_2S \rightarrow 6H^+ + 3S + 6e^-$

d. It oxidises Sn^{2+} to Sn^{4+}

$3Sn^{2+} \rightarrow 3Sn^{4+} + 6e^-$

II. Potassium Permanganate [$KMnO_4$]

Preparation

$KMnO_4$ is prepared from pyrolusite ore (MnO_2).

The preparation involves the following steps.

1. Conversion of pyrolusite into potassium manganate

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

2. Conversion of potassium manganate in potassium permanganate

$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by electrolysis

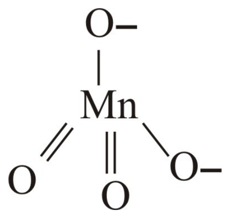
$MnO_2 \xrightarrow{KOH/O_2} MnO_4^{2-}$

At anode : $MnO_4^{2-} \rightarrow MnO_4^- + e^-$

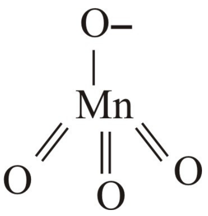
In the laboratory, a manganese (11) ion salt is oxidised by peroxodisulphate to permanganate

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^{-} + 10\ SO_4^{2-} + 16\ H^{+}$$

Structure:



Tetrahedral MnO_4^{2-} ion



Tetrahedral MnO_4^{-} ion

Chemical properties

1. Action of heat

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$$

2. Oxidising properties

$KMnO_4$ is a powerful oxidising agent in alkaline or acidic medium.

Acidic medium

$$MnO_4^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O$$

Alkaline medium

$$MnO_4^{-} + 2H_2O + 3e^{-} \rightarrow MnO_2 + 4OH^{-}$$

Eg :- In acidic solutions,

a. It oxidises oxalic acid to CO_2

$$5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^{-}$$

b. It oxidises Fe^{2+} to Fe^{3+}

$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^{-}$$

c. It oxidies nitrites to nitrates

$$5NO_2^{-} + 5H_2O \rightarrow 5NO_3^{-} + 10H^{+} + 10e^{-}$$

d. It oxidises iodides to iodine

$$10I^{-} \rightarrow 5I_2 + 10e^{-}$$

e. It oxidies H_2S to sulphur

$$5S^{2-} \rightarrow 5S + 10e^{-}$$

f. It oxidises sulphurous acid to sulphate

$$5SO_3^{2+} + 5\ H_2O \rightarrow 5\ SO_4^{2-} + 10H^{+} + 10e^{-}$$

ii) In alkaline solutions,

a) It oxidises iodine to iodate

$$I^{-} + 6\ OH^{-} \rightarrow IO_3^{-} + 3\ H_2O + 6\ e^{-}$$

b) It oxidises thiosulphate to sulphate

$$8MnO_4^{-} + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^{-}$$

c) It oxidises manganous salt to MnO_2

$$2MnO_4^- + 3\,Mn^{2+} + 2H_2O \rightarrow 5\,MnO_2 + 4H^+$$

Permanganate titrations in presence of HCl are unsatisfactory since this is oxidised to Cl_2

Uses: It is used

1. as an oxidizing agent
2. as a disinfectant and germicide
3. as Bayers reagent which is used in organic experiments.

The Inner transition elements (f- block)

The elements in which the last electrons enter the f-orbital of the atoms are culled f-block elements (Inner transition elements). They consists of two series of elements placed at the bottom of periodic table.

Lanthanoids (Lanthanides)

The 14 elements placed after La form the lanthanides or 4f series.

1. Electronic configurations

The lanthanides involve the gradual filling of 4f orbitals

2. Atomic and ionic sizes

There is a regular decrease in the size of atoms and ions with increase in atomic number as we move across form La to Lu. This slow decrease in size is known as **lanthanide contraction.**

The steady decrease in atomic and ionic sizes of lanthanide elements with increase in atomic number is called lanthanide contraction

Cause of lanthanide contraction

As we move along the lanthanide series the nuclear charge increases by one unit and the new electron is added to the same inner subshell namely 4f. The electrons in 4f orbitals cannot effectively screen the nucleus from the outermost electron. Hence the increased nuclear charge attracts the electron cloud more and there will be a steady contraction in size

Consequences of lanthanide contraction

1. Because of the similarity in radi, the chemical properties of lanthanides are similar. This make it difficult to separate the elements in the pure state.
2. Because of lanthanide contraction the elements of second and third transition series resemble each other much more than the elements of first and second transition series. Eg: Atomic radi of Zr and Hf are nearly the same [Zr- 160pm; Hf– 159 pm]
3. As the size of lanthanide ions decreases from La^{3+} to Lu^{3+}, the covalent character of the hydroxides increases and hence the basic strength decreases. Thus $La(OH)_3$ is most basic while $Lu(OH)_3$ is least basic

3. Oxidation states

All the lanthanides exhibit a common oxidation state +3 some of them show +2 and +4 oxidation states also. These are shown by those elements which by doing so attain the stable f^0,f^7 and f^{14} configurations.

Eg : Ce and Tb exhibit + 4 oxidation states

Ce^{4+}; [Xe] $4f^0$

Tb^{4+} ; [Xe], $4f^7$

Eu and Yb attain f^7 and f^{14} configuration in +2 oxidation states.

4. Colour of ions

Many trivalent lanthanide ions are coloured a due the excitation of unpaired electrons from one 4f orbital to another by absorbing visible light.

5. Magnetic properties

The lanthanide ions other than f^0 type (La^{3+} and Ce^{4+}) and f^{14} type ($Yb^{2+}$and Lu^{3+}) are paramagnetic.

Lanthanides combine with hydrogen form hydrides. When heated with carbon, they form carbides also. They mainly form oxides of the type M_2O_3 and hydroxides of the type $[M(OH)_3]$.

Uses of lanthanides

1. A well known alloy 'mischmetall' consists of 95% lanthanide and 5 % iron and traces of S,C Ca of Al which is used to produce bullets, shell and lighter flint
2. Mixed oxides of lanthanides are used as catalyst in petroleum cracking

Actinides [Actinoids]

The 14 elements that follow actinium are the actinides or 5f series. The actinides are radioactive and so their study is limited.

1. Electronic configuration

The actinides involve the gradual filling of 5f subshells.

2. Oxidation states

Actinides show different oxidation states such as +2, +3, +4, +5, +6 and + 7. However, +3 oxidation state is common among all the actinides.

3. Ionic sizes

The size of atoms or M^{3+} ions decreases across the series. This steady decrease in ionic radi with increase in atomic number is called **actinide contraction.** The contraction is however greater from element of element in this series because of poor shielding by 5f electrons. Due to imperfect shielding of 5f orbitals, the effective nuclear charge increases along the series causing contraction in size.

Comparison of Lanthanides and Actinides

Similarities

1. Both exhibit +3 oxidation state predominantly
2. In both series, f orbitals are being progressively filled.
3. Like lanthanide contraction, actinide shows actinide contraction
4. Both exhibit magnetic and spectral properties
5. Both are electropositive and very reactive.

Differences

1. Lanthanide compounds are less basic but actinide compounds are more basic

2. Except Promethium all elements of lanthanides are non radioactive. But all actinides are radioactive.

3. Besides common oxidation state +3, some of the lanthanids show +2 and +4 oxidation states. But actinides show higher oxidation state of +4, +5 +6 and + 7 also.

4. 4f electrons have greater shielding effect than 5f electrons. Therefore the contraction in ionic radi is less as compared to actinides

Application of 'd' and 'f' block elements.

1. Iron and steel are the most important construction materials.
2. TiO is used in pigment industry.
3. Zn, Ni, Cd are widely used in batteries.
4. The coinage metals (Cu, Ag, Au) form collection items and coins.
5. 'd' and 'f' block metals and many of their compounds serve as catalysts in chemical industry.
6. Photography is based on the light sensitive qualities of AgBr.
7. Nickel is used as hydrogenation catalyst.

***

Chapter 9

Co-Ordination Compounds

- **Double salt and Complex salt**

A salt that keeps its identity only in solid state is called a double salt. In solution they dissociate into component ions. Eg: Mohr's Salt[$FeSO_4.(NH_4)_2SO_4.6H_2O$], Carnalite [$KCl.MgCl_2.6H_2O$], Potash alum [$K_2SO_4.Al_2(SO_4)_3.24H_2O$].

The salt that keeps its identity both in solid and solution states is called a complex salt.

Eg: Potassium ferrocyanide $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$, $K_2[PtCl_4]$, $[Ni(CO)_4]$ etc.

- **Some definitions**

1. ***Co-ordination entity:*** The central metal atom or ion and ligands form a co-ordination entity. For example, $[CoCl_3(NH_3)_3]$ is a co-ordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are $[Ni(CO)_4]$, $[PtCl_2(NH_3)_2]$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$.
2. ***Central atom/ion:*** In a co-ordination entity, the atom/ion to which a fixed number of ions/neutral molecules are attached is called the central atom or ion. For example, the central atom/ion in the co-ordination entities: $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$ are Ni^{2+}, Co^{3+} and Fe^{3+} respectively. These central atoms/ions are also referred to as Lewis acids, since they accept electron pairs from ligands.
3. ***Ligands:*** The ions or neutral molecules bound to the central atom/ion in the coordination entity are called ligands. For a species to act as ligand, it can donate atleast one pair of electron to the central atom. The atom of the ligand which is directly bonded to the central

atom or ion is called co-ordinating atom or donor atom. Examples for ligands are Cl^-, Br^-, F^-, I^-, OH^-, CN^-, NC^-, CNO^-, NCO^-, SO_4^{2-}, NO_3^-, CNS^-, H_2O, NH_3, CO etc.

- **Types of ligands**

Based on the number of donor atoms of the ligand that binds to a metal ion or atom, the ligands are classified as follows:

a) ***Monodentate or unidentate ligand:*** A ligand that binds to the central atom/ ion through a single donor atom, is said to be unidentate ligand. Eg: Cl^-, Br^-, I^-, OH^-, H_2O, NH_3, CN^-, NC^-, SCN^- etc.

b) ***Bidentate (Didentate) ligands:*** A ligand that binds to the central atom through two donor atoms is called a bidentate ligand. Eg: Ethane–l,2–diamine or ethylenediamine ($H_2NCH_2CH_2NH_2$) notated as 'en' and oxalate ion ($C_2O_4^{2-}$).

c) ***Polydentate ligand:*** A ligand that binds to the central atom through more than two donor atoms is called polydentate ligand. Eg: Triethylamine ammonia [$N(CH_2–CH_2–NH_2)_3$], Ethylenediamine tetraacetate ion ($EDTA^{4-}$) etc. Ethylenediamine tetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

- **Ligands are also classified as:**

I) Ambidentate ligands: They are unidentate ligands which contain more than one donor atoms. They can coordinate through two different atoms. Examples of such ligands are the NO_2^-, CN^-, SCN^-, CNO^- etc. NO_2^- ion can coordinate either through nitrogen or through oxygen atom to the central metal atom/ion.

II Chelating Ligands: Di- or polydentate ligands can bind to the central atom through two or more donor atoms and form ring complexes. Such complexes are called chelates and such types of ligands are said to be chelating ligands.

4. ***Denticity:*** The number of donor atoms of a particular ligand that are directly bonded to the central atom is called denticity. For unidentate ligands, the denticity is 1, for didentate ligands it is 2 and so on.

5. ***Co-ordination number:*** The co-ordination number (C.N) of a metal in a complex can be defined as the total number of ligand donor atoms to which the metal is directly bonded.

6. ***Co-ordination sphere:*** The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the co-ordination sphere. The ionisable groups are written outside the bracket and are called simple ions or counter ions.

7. ***Co-ordination polyhedron:*** The spatial arrangemgnt of the ligands around the central atom/ion defines a coordination polyhedron about the central atom.

8. ***Oxidation number of central atom:*** The oxidation number of the central atom in a complex is defined as the residual charge on it, if all the ligands are removed along with their electron pairs that are shared with the central atom.

9. ***Homoleptic and Heteroleptic complexes***: Complexes which contain only one type of ligand are called homoleptic complexes. Complexes which contain more than one type of ligands are called Heteroleptic complexes.

IUPAC Nomenclature of Co-ordination Compounds

The following rules are used while naming co-ordination compounds:

i) The cation is named first in both positively and negatively charged co-ordination entities

ii) The ligands are named in alphabetical order before the name of the central atom/ion.

iii) Names of the anionic ligands end in-o, those of neutral and cationic ligands are the same except 'aqua' for H_2O, 'ammine' for NH_3, 'carbonyl' for CO and 'nitrosyl' for NO.

iv) Prefixes mono, di, tri, etc., are used to indicate the number of individual ligands in the co-ordination entity. When the names of the ligands include a numerical prefix, then the terms bis (for 2 such ligands), tris (for 3), tetrakis (for 4) are used. Here the name of the ligand is placed in simple bracket.

v) Oxidation state of the metal is indicated by Roman numeral in simple bracket.

vi) If the complex ion is a cation, the central atom is named same as the element. If the complex ion is an anion, the name of the metal ends with the suffix -ate. For example ferrate for iron, cobaltate for cobalt, zincate for In etc.

vii) The neutral complex molecule is named similar to that of the cationic complex.

Isomerism in Co-ordination Compounds

Compounds that have the same molecular formula but different structural formula or spatial arrangement of atoms are called isomers and the phenomenon is called isomerism. Isomers differ in physical or chemical properties. The isomerism shown by co-ordination compounds are broadly divided into two - structural isomerism and stereo isomerism.

I) Structural Isomerism

These are isomers which differ in the structural arrangement of ligands around the central atom. They are of four types:

1) ***Ionisation Isomerism:*** It arises due to the inter change of ions between the inside and outside of co-ordination sphere. They give different types of ions in aqueous solution. In order to show this isomerism, the ion outside the coordination sphere can also act as ligand. An example is $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

2) ***Linkage isomerism:*** It arises in a co-ordination compound containing ambidentate ligand, which can bind to the central atom through more than one donor atoms. For example complexes containing thiocyanate ligand, SCN^-, may bind either through nitrogen to give M-NCS or through sulphur to give M-SCN. Another e.g. is $[Co(NH_3)_5(ONO)]Cl_2$, in which the ligand is bound through oxygen (–ONO), and $[Co(NH_3)_5(NO_2)]Cl_2$ in which the ligand is bound through nitrogen ($-NO_2$).

3) ***Co-ordination Isomerism:*** If both anionic and cationic parts are complexes, the isomerisrn arises due to the interchange of ligands between cationic and anionic entities. This type of isomerism is called co-ordination isomerism. An example is $[Co(NH_3)_6][Cr(CN)_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+} and $[Cr(NH_3)_6)[Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+}.

4) ***Solvate isomerism:*** This form of isomerism is also known as 'hydrate isomerism' if water is involved as the solvent. This is similar to ionisation isomerism. Solvate isomers differ in the no. of solvent molecule which are directly bonded to the metal ion as ligand. An example is $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

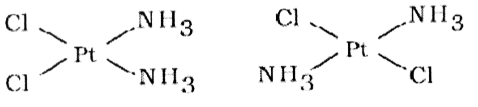
II) Stereoisomerism

These are isomers which differ only in the spatial arrangement of ligands around the central atom. These are of two types:

i) Geometrical isomerism ii) Optical isomerism

i) ***Geometrical Isomerism:*** This type of isomerism is shown by heteroleptic complexes. It arises due to the different possible geometric arrangements of the ligands around the central atom. It is mainly found in co-ordination complexes with co-ordination numbers 4 (square planar complexes) and 6 (octahedral complexes). Geometrical isomer in which the same ligands are on the same side of the central metal atom is called *cis isomer* and the isomer in which the same ligands are on the opposite side is called *trans isomer*.

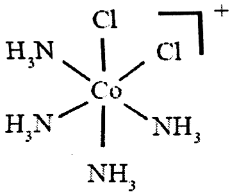
Square planar complexes with formula $[MX_2L_2]$ (X and L are unidentate ligands) can show this isomerism. E.g.: $[Pt(NH_3)_2CI_2]$

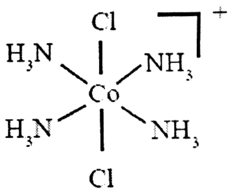

cis *trans*

Square planar complexes of the type MABXL (where A, B, X, L are unidentate ligands) show three geometrical isomers-two c/s and one trans.

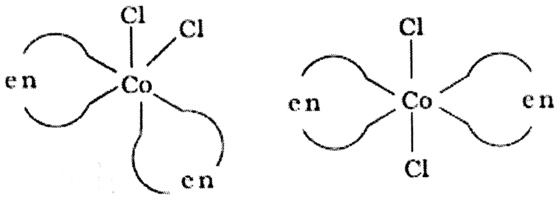
Octahedral complexes with formula $[MX_2L_4]$ can also show this type of isomerism. Here the two ligands X may be oriented cis or trans to each other.

eg: $[Co(NH_3)_4Cl_2]$

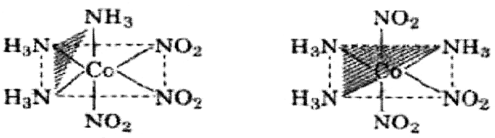

cis isomer $[Co(NH_3)_4Cl_2]$


trans $[Co(NH_3)_4Cl_2]$

This type of isomerism also arises when bidentate ligands (L–L) are present in complexes with formula $[MX_2(L–L)J$ eg: $[Co(en)_2Cl_2]^+$


cis *trans*

Fac-mer isomerism: It is a type of geometrical isomerism occurs in octahedral co-ordination entities of the type $[Ma_3b_3]$. If similar ligands occupy three adjacent positions of an octahedral face, it is called ***facial (fac) isomer***. When the positions are around the meridian of the octahedron, it is called ***meridional (mer) isomer***. Eg. $[Co(NH_3)_3(NO_2)_3]$.


fac *mer*

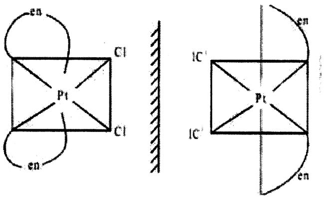
Tetrahedral complexes do not show geometrical isomerism because in a tetrahedron all the positions are equivalent. So the relative positions of the ligands attached to the central metal atom are the same with respect to each other.

ii) *Optical Isomerism*

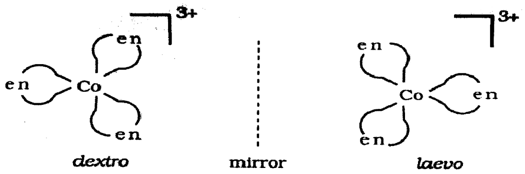
Optical isomers are mirror images that cannot be superimposed on one another. These are also called enantiomers. The molecules or ions that cannot be superimposed are called ***chiral***.

There are two forms of optical isomers - *dextro* (d) and laevo (*l*) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, *l* to the left). Optical isomerism is common in octahedral complexes involving bidentate ligands.

In a co-ordination entity of the type $[PtCl_2(en)_2]^+$, only the cis-isomer shows optical activity. The trans- isomer has a plane of symmetry and is optically inactive.



Another e.g. is $[Co(en)_3]^{3+}$



Theories of Co-ordination Compounds

1. *Werner's Co-ordination Theory*

It was Alfred Werner who first proposed a theory for co-ordination compounds.

1) Every metal has two types of valencies - primary (1°) valency and secondary (2°) valency. Primary valency is ionisable, while secondary valency is non-ionisable.
2) Primary valency is denoted by doted lines, while secondary valency is denoted by thick lines.
3) Primary valency gives the oxidation state of the metal, while secondary valency gives the co-ordination number of the metal.
4) Primary valency is always satisfied by -ve ions, while secondary valency may be satisfied by –ve ions or neutral molecules.
5) Every metal has a fixed number of secondary valencies.
6) The primary valencies are non-directional, while the secondary valencies are directional, i.e. they are directed to some fixed positions in space.
7) Since secondary valencies are directional, co-ordination compounds have a definite geometry and they show isomerism.

Demerits: Werner could not explain why only certain elements form co-ordination compounds. Also he could not explain the directional nature of bonds in co-ordination compounds and their magnetic and optical properties.

2. *The Valence Bond Theory (VBT)*

This theory was put forward by Linus Pauling. The important postulates of this theory are:

1) In co-ordination compounds, the central metal atom/ion provides some vacant orbitals in order to accommodate the electrons donated by the ligands. The number of vacant orbitals formed is equal to the co-ordination number of the metal atom.

2) The vacant orbitals of the metal undergo hybridisation to form a set of new orbitals called hybrid orbitals. The type of hybridisation gives the shape of the compound.

3) Tetrahedral, square planar and octahedral complexes are formed as a result of sp^3, dsp^2 and d^2sp^3 (sp^3d^2) hybridisation respectively.

4) Each ligand should contain at least one pair of electron.

5) The vacant hybrid orbitals of the metal overlap with the filled orbitals of the ligands to form ligand - metal coordinate bond.

6) If a complex contains unpaired electron, it is paramagnetic and if it contains only paired electron, it is diamagnetic.

- **Applications of VBT**

It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory.

Eg: **1) $[Fe(CN)_6]^{3-}$**

Here the central atom Fe is in +3 oxidation state.

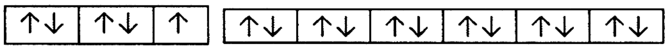
$_{26}Fe$ – $[Ar]3d^6 4s^2$
Fe^{3+} – $[Ar]3d^5 4s^0 4p^0$

Fe^{3+}

In this complex, the co-ordination number of Fe is 6 and hence the no. of vacant orbitals required = 6. In presence of the ligand CN^-, the electrons in 3d level get paired.

Now the two 3d orbitals, one 4s orbital and three 4p orbitals undergo d^2sp^3 hybridization to form 6 new orbitals. Six pairs of electrons, one from each CN^- ions, occupy these six hybrid orbitals. Thus, the complex has octahedral geometry and is paramagnetic because of the presence of one unpaired electron.

In the formation of this complex, since the inner d orbitals (3d) are used for hybridization, the complex is called an ***inner orbital*** or ***low spin*** or ***spin paired complex***.



2) $[FeF_6]^{3-}$

Here the central atom Fe is in +3 oxidation state.

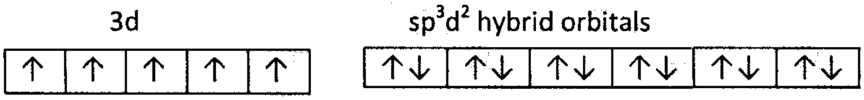
$_{26}Fe$ – $[Ar]3d^6 4s^2$

Fe^{3+} – $[Ar]3d^5 4s^0 4p^0$

Fe^{3+}

In this complex the co-ordination number of Fe is 6 and hence the no. of vacant orbitals required = 6. In presence of the ligand F^-, the electrons in 3d level do not get paired.

Now the one 4s orbital, three 4p orbitals and two 4d orbitals undergo sp^3d^2 hybridization to form 6 new orbitals. These hybrid orbitals overlap with the filled orbitals of the ligand to form ligand- metal co-ordinate bond.



Since the hybridization is sp^3d^2, the shape of the molecule is octahedral and due to the presence of 5 unpaired electrons, it is *highly paramagnetic*. In the formation of this complex, since the outer orbitals (4*d*) are used for hybridisation (sp^3d^2), it is called *outer orbital* or *high spin* or *spin free complex.*

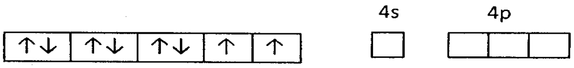
3) $[Ni(CN)_4]^{2-}$

Here the central atom Ni is in +2 oxidation state.

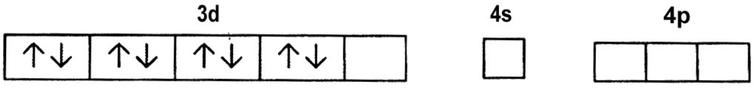
$_{28}Ni$ – $[Ar]3d^8 4s^2$

Ni^{2+} – $[Ar]3d^8 4s^0 4p^0$

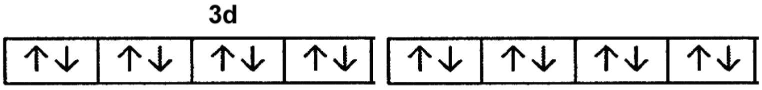
Ni^{2+}



In this complex the co-ordination number of Ni is 4 and hence the no. of vacant orbitals required = 4. Even though it contains 4 orbitals, in presence of the ligand CN^-, the electrons in 3d level get paired.



Now the one 3d orbital, one 4s orbital and two 4p orbitals undergo dsp^2 hybridization to form 4 new orbitals. Four pairs of electrons, one from each CN^- ions, occupy these four hybrid orbitals. Thus, the complex has square planar geometry and is diamagnetic, because of the absence of unpaired electron.

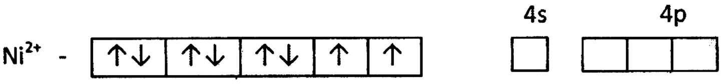


4) $[NiCl_4]^2$

Here the central atom Ni is in +2 oxidation state.

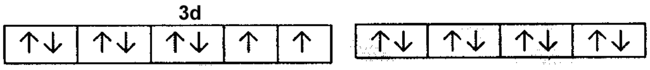
$_{28}Ni$ – $[Ar]3d^8 4s^2$

Ni^{2+} -[Ar]3d84s°4p°



In this complex the co-ordination number of Ni is 4 and hence the no. of vacant orbitals required = 4. In presence of the ligand Cl^-, the electrons in 3d level do not get paired.

Now the one 4s orbitals and three 4p orbitals undergo sp^3 hybridization to form 4 new orbitals. These four hybrid orbitals are occupied by the four electron pairs from each Cl^- ligands. Thus, the complex has tetrahedral geometry and is paramagnetic because of the presence of unpaired electron.



- **Magnetic Properties of Co-ordination Compounds**

By knowing the magnetic moment, we can predict the geometry of complexes. For eg: $[Mn(CN)_6]^{3-}$ has magnetic moment of two unpaired electrons while $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired electrons. $[Fe(CN)_6]^{3-}$ has magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ is diamagnetic.

- **Limitations of Valence Bond Theory**

i) It involves a number of assumptions

ii) It does not give quantitative interpretation of magnetic data.

iii) It does not explain the colour exhibited by co-ordination compounds.

iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of co-ordination compounds

v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-co-ordinated complexes

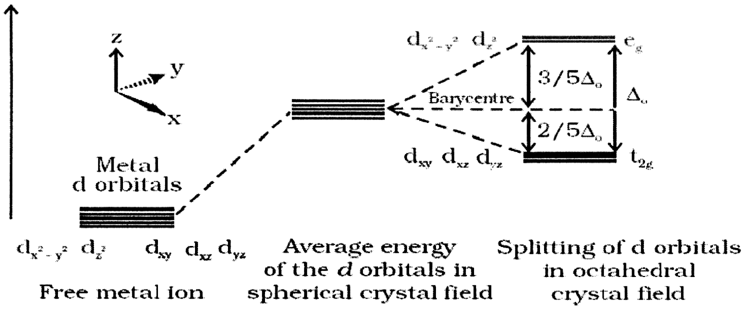
vi) It does not distinguish between weak and strong ligands.

3. Crystal Field Theory

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond as purely ionic. Here the ligands are treated as point charges in case of anions or as dipoles in case of neutral molecules. The five d orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. But when this negative field is due to ligands in a complex, the degeneracy of the d orbitals is lost. It results in splitting of the d orbitals. This splitting of d-orbitals is termed as Crystal field splitting and it depends on the nature of the field.

a) Crystal field splitting in octahedral co-ordination entities (octahedral field)

In an octahedral co-ordination entity there are six ligands surrounding the metal atom/ion and they are along the axis of the octahedron. So the repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands is greater for the dx^2-y^2 and dz^2 orbitals, which are pointing towards the axes, than the dxy, dyz and dxz orbitals, which are directed between the axes. So the energy of the dx^2-y^2 and dz^2 orbitals (called e_g orbitals) will be raised and that of the dxy, dyz and dxz orbitals (called t_{2g} orbitals) will be lowered. Thus, the degeneracy of the d orbitals has been removed. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_0 (the subscript o is for octahedral). Thus, the energy of the two e_g orbitals will increase by (3/5) Δ_0 and that of the three t_{2g} orbitals will decrease by (2/5) Δ_0.



Strong field ligands produce large splitting whereas weak field ligands produce small splitting of d orbitals.

Filling of electrons

For d^1, d^2 and d^3 coordination entities, the d electrons occupy the t_{2g} orbitals singly in accordance with the Hund's rule. For d^4 ions, two possible patterns of electron distribution arise:

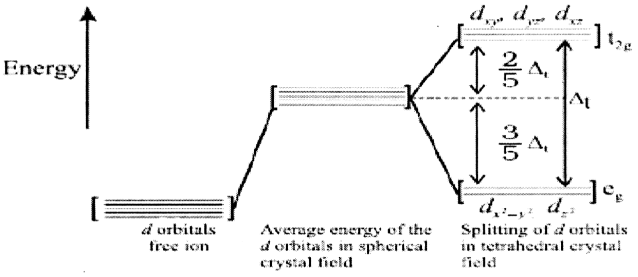
i) the fourth electron could either enter the t_{2g} level and pair with an existing electron, or

ii) it could enter into the eg level.

Here the electron distribution depends on the relative magnitude of the crystal field splitting (Δ_0) and the pairing energy (P). If $\Delta_0 < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.

If $\Delta_0 > P$, the fourth electron occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands for which $\Delta_0 < P$ are known as strong field ligands and form low spin complexes.

a) Crystal field splitting in Tetrahedral coordination entities (tetrahedral field)



The splitting in tetrahedral field is less than that in octahedral field. It is found that $\Delta t = 4/9\ \Delta_0$. This is because in tetrahedral field, there are only four ligands (but in octahedral field, the number of ligands is six) and there is no direct interaction between the ligands and the d-orbitals.

Spectrochemical series

It is a series in which the ligands are arranged in the increasing order of their field strength. The series is: $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$. It is an experimentally determined series based on the absorption of light by complexes with different ligands.

Colour in Coordination Compounds

Most of the complexes of transition metals are coloured. This can be explained in terms of the crystal field theory. In presence of the ligands, the crystal field splitting occurs. So the electrons from lower d level (t_{2g} level) can excite to higher d level (e_g level). For this some energy is required, which is absorbed from the white light. The colour of the complex is complementary to that which is absorbed. Thus **according to crystal field theory the colour of the coordination compounds is due to d-d transition of the electron**.

Limitations of Crystal Field Theory

1. From the assumptions, that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. But the anionic ligands actually are found at the low end of the spectrochemical series.
2. It does not take into account the covalent character of bonding between the ligand and the central atom.

Stability of Coordination Compounds

The stability of a complex in solution refers to the degree of association between the metal ion and ligands in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability.

For a reaction of the type:

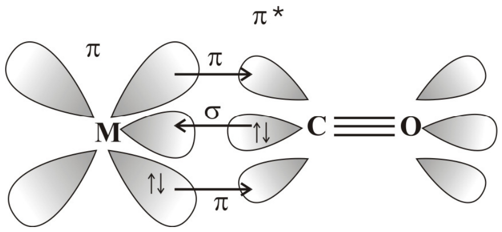
$M + 4L \rightarrow ML_4,\ \beta = [ML_4]/[M][L]^4$

As the value of the stability constant increases, the stability of the complex also increases. The stability of a complex depends on the following factors.

1. ***The nature of the metal ion:*** Greater the charge to radius ratio of the metal ion, greater will be the stability of the complex.
2. ***Nature of the ligand:*** The greater the basic strength of the ligand, the greater will be the stability of the complex.
3. ***Presence of chelating ligands:*** increases the stability of the complex.

Bonding in Metal Carbonyls

The metal-carbon bond in metal carbonyls possess both s and p character. The M –Cσ a bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–Cπ bond is formed by the donation of a pair of electrons from a filled *d* orbital of metal into the vacant anti-bonding π* orbital of carbon monoxide. Thus the metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.



Synergic bonding

Application of Co-ordination Complexes

1) In Qualitative & Quantitative Analysis
2) In water treatment
3) In Metallurgy
4) Biological Applications
5) In Catalysis
6) In etectroplating
7) In Photography

8) In medicine

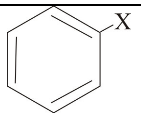
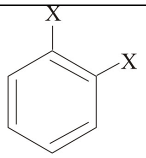
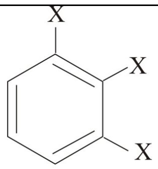
***

Chapter 10

Haloalkanes And Haloarenes

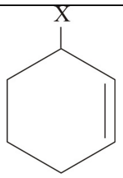
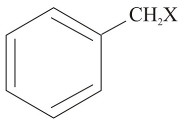
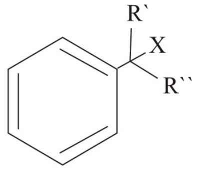
Classification

- On the Basis of Number of Halogen Atoms

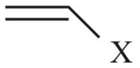
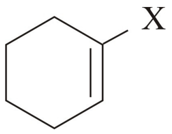
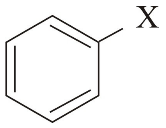
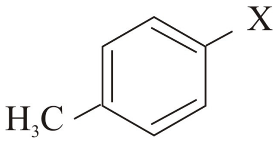
C_2H_5X Monohaloalkane	CH_2X I CH_2X Dihaloalkane	CH_2X I CHX I CH_2X Trihaloalkane	 Monohaloarene  Dihaloarene  Trihaloarene

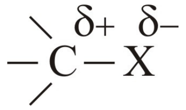
Monohalocompounds may further be classified according to the hybridisation of the carbon atom to which the halogen is bonded.

- **Compounds Containing $_{sp3}$ C – X Bond (X = F, Cl,** Br, I)

a) Alkyl halides or haloalkanes (R –X)	**b) Allylic halides**	**c) Benzylic halides**
H I R′ –C – X I H Primary (1°) R′ I R″ –C – X I H Secondary (2°) R′ I R″ –C – X I R‴ Tertiary (3°)	 	 (1°)  R′ = CH_3, R″= H(2°) R′ = R″= CH_3(3°)

- **Compounds Containing $_{Sp2}$ C–X** Bond:

a) Vinylic halides	**b) Aryl halides**
 	 

Nature of C-X Bond: The carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.	

- **Methods of Preparation**

The hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride. Thionyl chloride is preferred because the other two products are escapable gases. Hence the reaction gives pure alkyl halides.

$$R - OH + HX \xrightarrow{ZnCl_2} R - X + H_2O$$

$$R - OH + NaBr + H_2SO_4 \rightarrow R - Br + NaHSO_4 + H_2O$$

$$3R - OH + PX \rightarrow 3R - X + H_3PO_3 \ (X = Cl, Br)$$

$$R - OH + PCl_5 \rightarrow R - Cl + POCl_3 + HCl$$

$$R - OH \xrightarrow[X_2 = Br_2,\ I_2]{redP/X_2} R - X$$

$$R - OH + SOCl_2 \rightarrow R - Cl + SO_2 + HCl$$

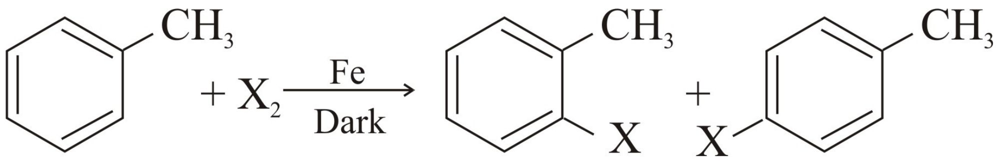
The order of reactivity of alcohols with a given haloacid is 3° >2° >1°.

- **From Hydrocarbons:**

a) By free radical halogenations:

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/UV\ \text{light}} CH_3CH_2CH_2\ CH_2Cl + CH_3CH_2CHClCH_3$$

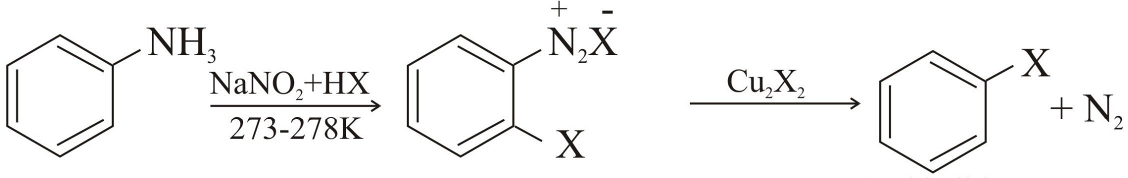
b) By electrophilic substitution



o- Halotoluene p - Halotoluene

c) **Sandmeyer's reaction :**

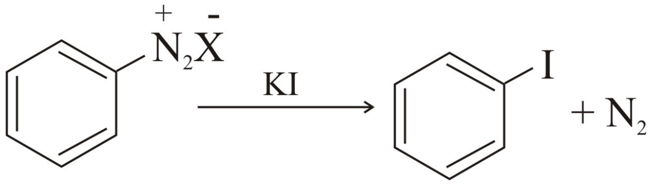
Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by –Cl or –Br.



Benzene diazonium halide

Aryl halide
X = Cl Br

- **Preparation of iodo benzene**

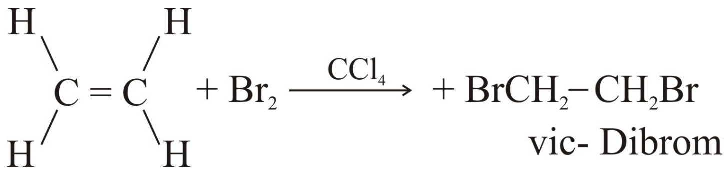


d) **From alkenes**

i) ***Addition of hydrogen halides***: An alkene is converted to corresponding alkyl halide by reaction with hydrogen chloride, hydrogen bromide or hydrogen iodide.

$$CH_3CH = CH_2 + H\text{–}I \rightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CH1CH_3}$$

ii) Addition of halogens: An important method for the detection of double bond in a molecule. Colourless *vic*-dibromide is the product.



vic- Dibromide

- **Physical Properties**

Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives. That is why the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

For the same alkyl group, the boiling points of alkyl halides decrease in the order:

RI > RBr > RC1 > RF.

The boiling points of isomeric haloalkanes decrease with increase in branching.

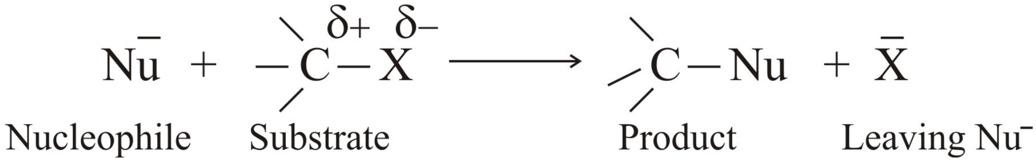
Boiling points of isomeric dihalobenzenes are very nearly the same. Where as melting point is of the order Para > Ortho = meta.

- **Chemical Reactions**

Reactions of Haloalkanes

i) Nucleophilic substitution ii) Elimination reactions iii) Reaction with metals

i) Nucleophilic substitution reactions



-- H_2O→ ROH + HX
--NaOR'→ROR'+NaX **(Williamson's synthesis)**
RX——--NaI → RI + NaX **(Finkelstein Reaction)**
--NH_3→ RNH_2 + HX
--R'NH_2→ RNHR' +HX

--R_2NH→ R_3N + HX

- **Mechanism:**

a) Substitution nucleophilic bimolecular (SN^2)

i) The rate depends upon the concentration of both the reactants.

Rate = k [RX] [Nu^-]; Order = 2

ii) Inversion of Configuration takes place.

iii) Order of Reactivity

Primary Halide > Sec.Halide > Tertiary Halide

b) Substitution nucleophilic uniniolecular (SN^1)

i) The rate of reaction depends upon the concentration of only one reactant, Rate = k [RX]; Order = 1.

ii) Carbocation Intermediate

iii) Order of Reactivity

Tertiary Halide > Sec. Halide > Primary Halide

- **Halogen Exchange**

Finkelstein reaction; When alkyl chlorides/bromides are treated with Nal in dry acetone Alkyl iodides are prepared. This reaction is known as Finkelstein reaction.

- **Swarts reaction**

When an alkyl chloride/bromide in the presence of AgF or Hg_2F_2 or CoF_2 or SbF_3. Alkyl Fluorides are obtained.The reaction is termed as Swarts reaction.

$H_3C-Br + AgF \rightarrow H_3C-F + AgBr$

- **Elimination reaction**

$CH_3CHBrCH_2CH_2CH_3 \xrightarrow{alc.\ KOH} CH_3-CH=CH-CH_2-CH_3$ (major)

Reaction with metals

$RX + Mg \xrightarrow{dry\ ether} RMgX$

Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols, amines are sufficiently acidic to convert them to corresponding hydrocarbons.

$RMgX + H_2O \rightarrow RH + Mg(OH)X$

It is therefore necessary to avoid even traces of moisture from a Grignard reagent. On the other hand, this could be considered as one of the methods for converting halides to hydrocarbons.

Wurtz reaction

Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide. This reaction is known as Wurtz reaction.

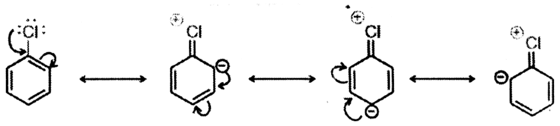
$2RX + Na \rightarrow RR + NaX$

Reactions of Haloarenes

l. Nucleophilic substitution

Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

i) Resonance effect:



ii) Difference in hybridisation of carbon atom in C–X bond:

iii) Instability of phenyl cation: SN^1 mechanism is ruled out.

iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

2. Elimination reactions

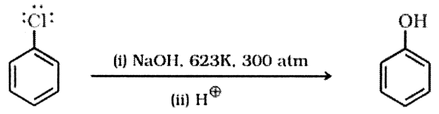
When a haloalkane with β-hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from β-carbon and a halogen atom from the α-carbon atom. As a result, an alkene is formed as a product.

$CH_3\text{-}CH_2Br \xrightarrow{alc.\ KOH} CH_2{=}CH_2 + KBr + H_2O$

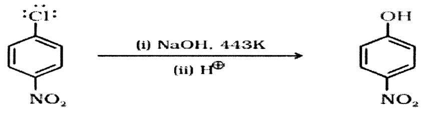
Saytzeff Rule : *"in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number ofalkyl groups attached to the doubly bonded carbon atoms."*

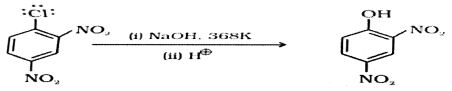
Replacement by hydroxyl group

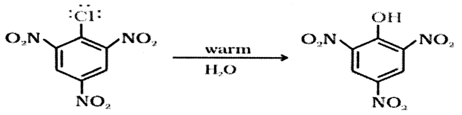
Dow's Process



The presence of an electron withdrawing group ($-NO_2$) at ortho- and para-positions increases the reactivity of haloarenes.

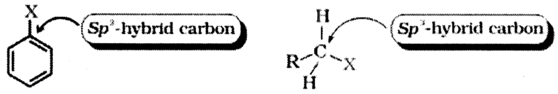






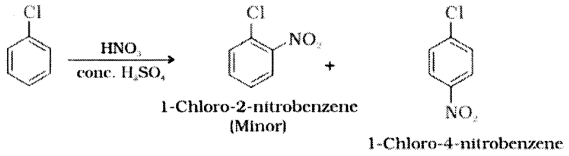
- **Electrophilic substitution reactions**

Halogenation

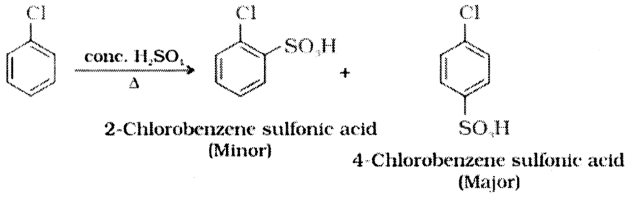


Thus, C – Cl bond length in haloalkane is 177pm while in haloarene is 169 pm. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

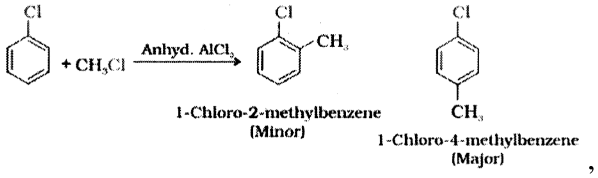
- **Nitration**

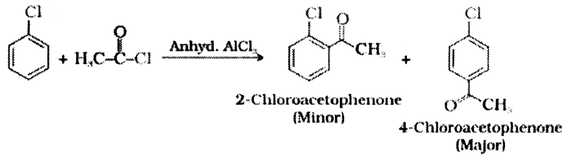


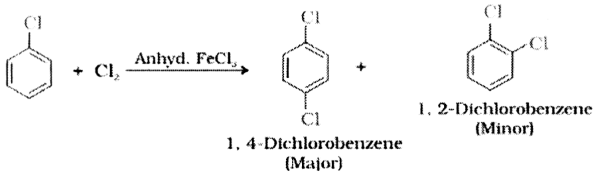
- **Sulphonation**



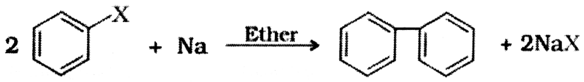
- **Friedel-Crafts reaction**



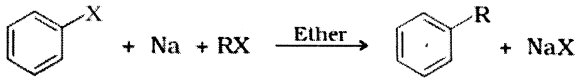




- **Fitting reaction**



- **Wurtz – fitting reaction**



***

Chapter 11

Alcohols, Phenols and Ethers

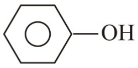
- **Alcohols**

  Compounds having one or more hydroxyl (–OH) group(s) attached to alkyl group.

  Eg. $CH_3CH_2–OH$

- **Phenols**

  Compounds containing hydroxyl (OH) group(s) directly attached to carbon atoms of aromatic ring. Eg.



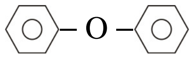
(Phenol)

- **Ethers**

  Compounds containing two alkyl or aryl groups attached to an oxygen

  R – O – R or R – O –

or



- **Classification of alcohols**

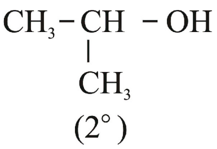
Classified into mono, di, tri or polyhydric alcohols depending on whether their molecules contain one, two, three or many hydroxyl groups respectively.

Eg : CH_2CH_2OH $CH_2OH–CH_2OH$ $CH_2OH–CHOH–CH_2OH$

Also classified into primary(1°), secondary (2°) and tertiary (3°) alcohols depending on whether the –OH group is attached to primary (1°), secondary (2°) and tertiary (3°) carbon atoms.

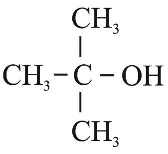
$CH_3 – CH_2 – OH$

(1°)



$CH_3–CH(CH_3)–OH$

(2°)



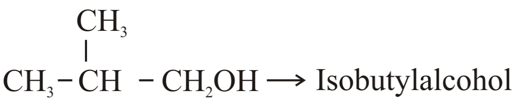
$CH_3–C(CH_3)_2–OH$

(3°)

- **Nomenclature of alcohols**

  - In common system alcohols are named as alkyl alcohols.

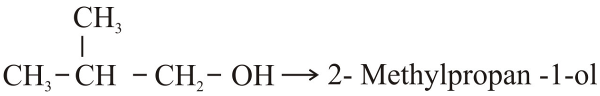
    Eg : $CH_3 – CH_2 – CH_2\ OH \rightarrow$ n – propyl alcohol



$CH_3–CH(CH_3)–CH_2OH \longrightarrow$ Isobutylalcohol

  - In IUPAC system they are named as Alkanol.

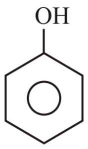
    Eg : $CH_3\ CH_2 – CH_2\ OH \rightarrow$ Propanol



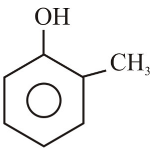
$CH_3–CH(CH_3)–CH_2–OH \longrightarrow$ 2- Methylpropan -1-ol

- **Nomenclature of phenols**

  Common and IUPAC names of some phenols are given below

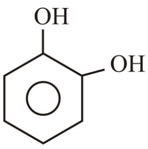


Phenol



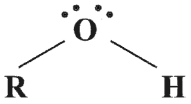
2- Methyl Phenol
(O-Cresol)

4 - Methylphenol
(P- Nitrophenol)



Benzene -1, 2- diol
(Catechol)

- **Structure of Alcohol**



Preparations of alcohols

- Alcohols are formed when alkyl halides are heated with aqueous NaOH or KOH

  $CH_3CH_2 - Br + KOH \rightarrow CH_3\ CH_2OH + KBr$

- Reduction of aldehydes give corresponding primary alcohols.

  $CH_3CHO \xrightarrow[orNaBH_4orLiAlH_4]{H_2/Ni/Pt/Pd} CH_3CH_2OH$

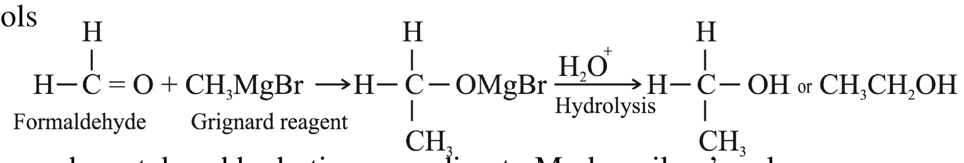
- Ketones are reduced to corresponding secondary alcohols.

- ***Using Grignard reagents.***

  Aldehydes and Ketones react with Grignard reagents to form addition products which on hydrolysis give alcohols.

  Formaldehyde with Grignard reagent give primary alcohol and other aldehydes react with Grignard reagents to give secondary alcohol. Ketones react with Grignard reagent to give tertiary alcohols

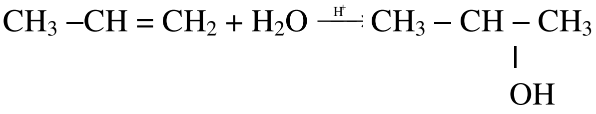
  Eg :



$$H-\overset{H}{\overset{|}{C}}=O + CH_3MgBr \longrightarrow H-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OMgBr \xrightarrow[Hydrolysis]{H_2O^+} H-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH \text{ or } CH_3CH_2OH$$

Formaldehyde Grignard reagent

- From alkenes by catalysed hydration according to Markovnikov's rule



$$CH_3-CH=CH_2 + H_2O \xrightarrow{H^+} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$$

- By hydroboration – oxidation – according to anti Markovnikov's rule

  $CH_3-CH=CH_2 \xrightarrow{(BH_3)_2} (CH_3-CH_2-CH_2)_3B \xrightarrow{H_2O_2/OH^-} CH_3CH_2-CH_2-OH$

- From carboxylic acids by reduction

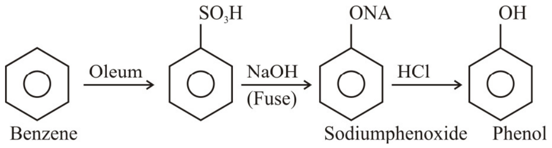
  $CH_3COOH \xrightarrow[ii)H_2O]{i)LiAlH_4} CH_3-CH_2-OH$ (1° alcohol)

- From esters by reduction

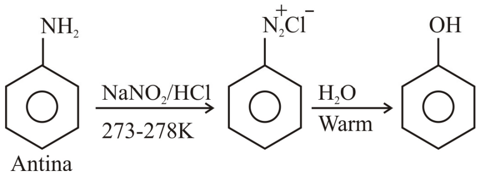
  $CH_3-CH_2COOC_2H_5 \xrightarrow{H_2/Ni} CH_3CH_2-CH_2OH + C_2H_5OH$

Preparation of Phenol

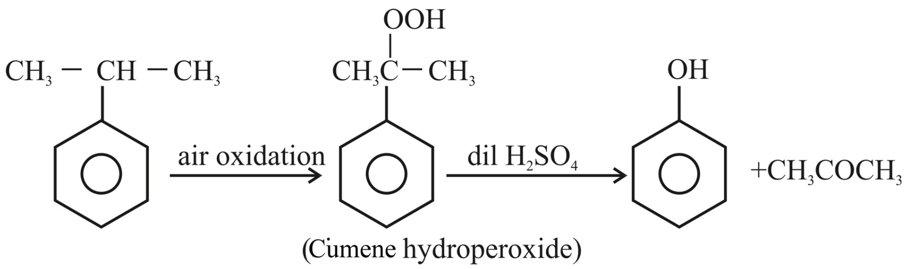
- From benzene sulphonic acid



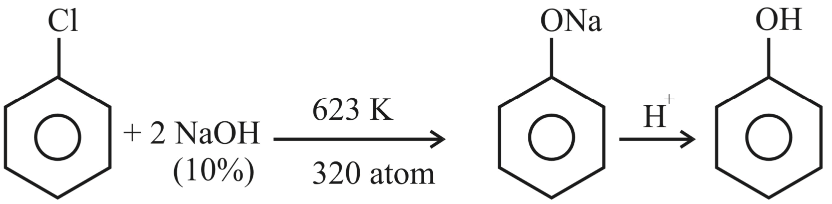
- From diazonium salt



- Industrially prepared from Cumens



- From chlorobenzene by Dow's process



Properties of alcohols

Physical properties : Lower members are soluble in water due to the ability to form hydrogen bonds with water.

Boiling points of alcohols are higher than hydrocarbons, haloalkanes or ethers of comparable molecular mass due to the ability to form Intermolecular hydrogen bonding

Reactions of Alcohols

1) Involving C–OH bond cleavage

- Reaction with halogen acids to form alkyl halides.

$CH_3CH_2-OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2-Cl$

Here order of reactivity is 3° > 2° > 1°

- Reactions with PCl_5 and PCl_3

$CH_3CH_2OH + PCl_5 \rightarrow CH_2CH_2Cl + POCl_3$

$3CH_3CH_2OH + PCl_3 \rightarrow 3CH_3CH_2Cl + H_3PO_3$\

- With thionylchloride

$SO_2Cl + CH_3CH_2OH \rightarrow CH_3CH_2Cl + SO_2 + HCl$

2) Reactions involving O–H bond cleavage

- With metals

$2CH_3CH_2OH + 2Na \rightarrow CH_3CH_2ONa + H_2$

This reaction indicates acidic nature of alcohols and the order of acidity is 1° > 2°> 3°. They are weaker acids than water.

- **Esterification**

$$\underset{\text{Carboxylic acid}}{CH_3COOH} + \underset{\text{alcohol}}{CH_3CH_2OH} \xrightarrow[\text{(fewdrops)}]{ConcH_2SO_4} \underset{\text{ester (with fruity smell)}}{CH_3COOCH_2CH_3}$$

This reaction is used to distinguish alcohols from other organic compounds.

- With acids chlorides or acids unhydrides give esters

$CH_3COCl + CH_3CH_2OH \xrightarrow{Pyridine} CH_3COOCH_2CH_3$

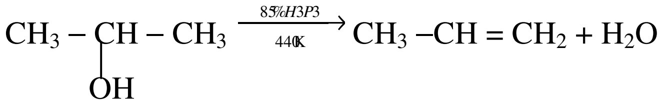
This reaction involving introduction of RCO – group is called acylation.

Reactions involving both alkyl and hydroxyl groups

1) Dehydration – Using H_2SO_4

$$CH_3CH_2–OH \xrightarrow[443K]{Conc\,H_2SO_4} CH_2 = CH_2 + H_2O$$

2) Using H_3PO_3



$$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3 \xrightarrow[440K]{85\%H3P3} CH_3 -CH = CH_2 + H_2O$$

Ease of dehydration of alcohols follows the order 3° > 2° > 1° alcohols

- **Oxidation of alcohols**

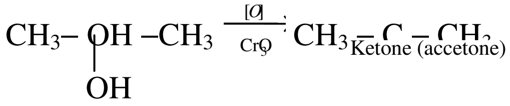
Primary alcohol : On using strong oxidising agents such as acidified or alkaline $KMnO_4$ gives carboxylic acid as final product.

$$\underset{\text{alcohol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{aldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{carboxylic acid}}{CH_3COOH}$$

Pyridinium Chloro Chromate (PCC) in Methylene chloride is a mild oxidising agent which oxidises alcohols to aldehydes and ketones. Carbon – Carbon double bond is also not got affected

$$CH_3CH_2 = OH –CH_2OH \xrightarrow{PCC} CH_3CH = CH – CHO$$

Secondary alcohol is oxidised to Ketone.



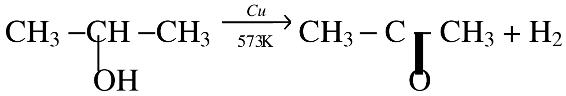
$$CH_3– \underset{\displaystyle OH}{\underset{|}{OH}} –CH_3 \xrightarrow[CrO_3]{[O]} CH_3 – C – CH_3$$

Ketone (accetone)

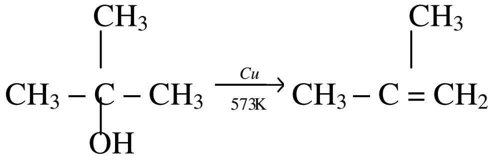
Prolonged action of oxidising agents, ketones are oxidised to acids containing fewer number of carbon atoms.

- **Dehydrogenation**

$$CH_3 – CH_2OH \xrightarrow[Cu]{573K} CH_3CHO + H_2$$



$$CH_3 –\underset{\displaystyle OH}{\underset{|}{CH}} –CH_3 \xrightarrow[573K]{Cu} CH_3 – \underset{\displaystyle O}{\underset{\|}{C}} – CH_3 + H_2$$



$$CH_3 – \underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} – CH_3 \xrightarrow[573K]{Cu} CH_3 – \overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2$$

- **Reactions of Phenol**

  ○ Acidic character

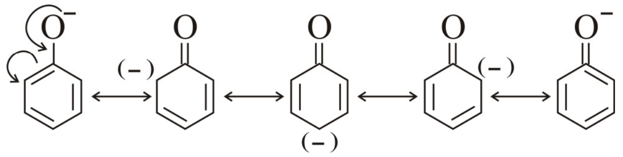
$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

They are weakly acidic and therefore they do not decompose carbonates and bicarborates giving CO_2 gas. But they are better acids than alcohol and water

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$$

Since the equilibrium is shifted in favour of phenoxide ion ($C_6H_5O^-$) phenol is acidic.

The negative charge on phenoxide ion delocalised as follows.



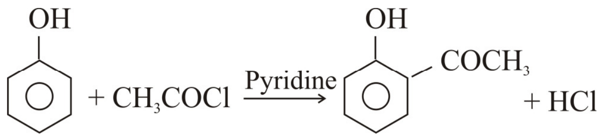
Due to this greater resonance stabilisation phenoxide ion is more stable than phenol.

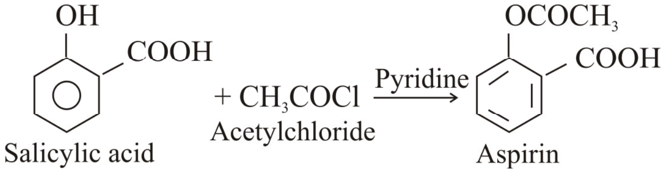
The acidity of phenol increases if an electron withdrawing group present in the benzene ring and electron releasing group decreases its acidity.

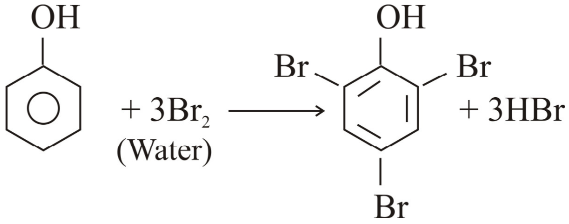
- **Action with zinc dust**

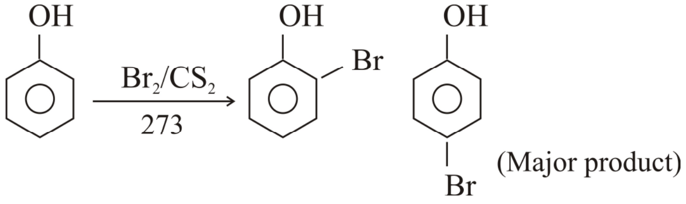
$C_6H_5OH + Zn \xrightarrow{distil} C_6H_6 + ZnO$

- **Acetylation**

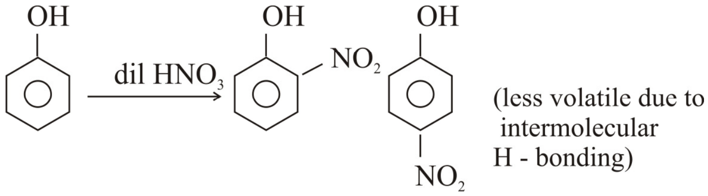


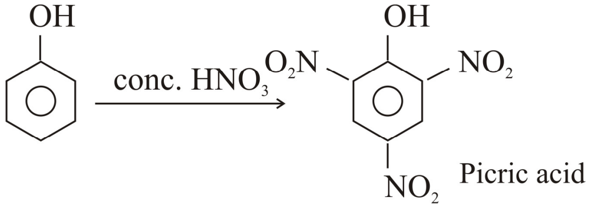




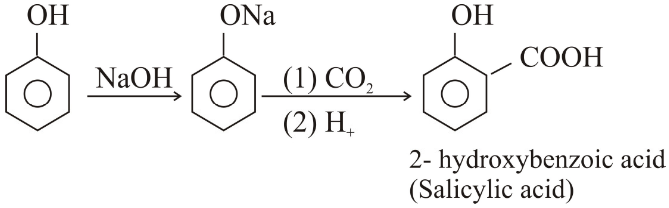


- **Nitration**

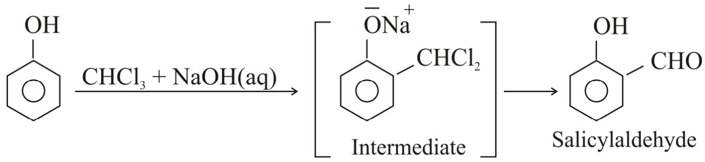




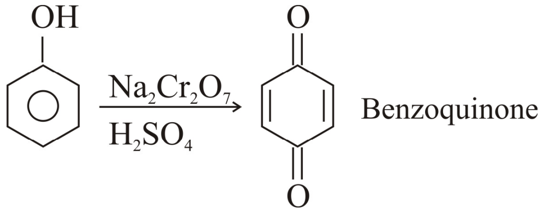
- **Kolb's reaction**



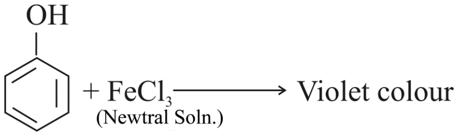
- **Reimer – Tiemann reaction**



- **Oxidation**



- **Test for phenol**



- **Commercially important alcohols**

1) Methanol – Manufacture

$$CO + 2H_2 \xrightarrow[573-673\ K\ (200-300\ K)]{ZnO-Cr_2O_3} CH_3OH$$

Methanol can also be obtained by destructive distillations of wood.

Methanol is poisonous in nature, ingestion of which causes blindness and even death. It is used as a solvent for paints varnishes. It is used for making formaldehyde.

2) Ethanol – $CH_3CH_2\ OH$

Manufactured by fermentation of molasses. Sugar present in molasses is acted upon by enzymes Invertase and Zymase supplied by yeast to form ethanol.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} \underset{glueou}{C_6H_{12}O_6} + \underset{fructose}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2CH_3CH_2OH + 2CO_2$$

95.6 % alcohol is called rectified spirit. Commercial alcohol is made until for drinking by adding methanol (Poisonous), copper sulphate (to give colour) and pyridine (to give a foul smelling). It is known as denaturation of alcohol and the alcohol is called denatured spirit.

Ethanol is also manufactured by the following reaction.

$$CH_2 = CH_2 + H_2O \xrightarrow[(Catalyst)]{acid} CH_3CH_2OH$$

- **Distinguishing test for 1°, 2° and 3° alcohols – Lucas test**

In this test Lucas reagent (a mixture of concentrated hydrochloric acid and anhydrous zinc chloride) is added to alcohol. 3° tertiary alcohol gives a turbidity immediately. 2° alcohol gives turbidity in a give minutes while primary (1°) alcohol dose not gives turbidity at room temperature. Turbidity is formed by the formation of alkylchloride which is immiscible with water.

$$R - OH + HCl \xrightarrow{ZnCl} R - Cl + H_2O$$

- **Ethers** - General formula R –O –R′

Simple or symmetric ethers

Alkyl groups attached to oxygen atom are same. Eg. $CH_3 - O - CH_3$

When R and R′ are different we get mixedor unsymetric ethers.

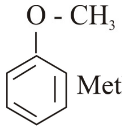
Eg: $CH_3 - O - CH_2 - CH_3$

- **Nomenclature**

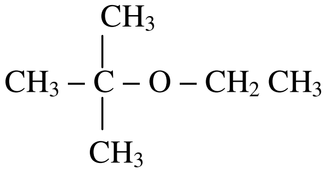
They are named in IUPAC as **alkoxyalkanes.**

(Etherial oxygen considered with smaller alkyl group). In common system they are named as *alkyl alkyl* ethers. (Alkyl groups are listed in alphabetical order)

$CH_3 - O - CH_3$	Methoxy methane (Dimelthyl ether)
$CH_3 - O - CH_2CH_3$	Methoxy ethane (Ethyl methy ether)



Methoxybenzene (Anisole or Methylphenyl ether)



$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - O - CH_2\,CH_3$$

2-Ethoxy 2- Methylpropane

- **Preparation**

By dehydration of alcohols

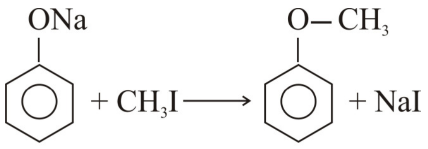
$$2\,CH_3\,CH_2\,OH \xrightarrow[413K]{H_2SO_4} CH_3 - CH_2 - O - CH_2 - CH_3$$

The reaction involves the removal of one water molecule from 2 molecules of alcohol. Only symmetric ethers can be prepared by this method.

- By Williamson’s synthesis from alkyl halides

  An alkyl halides is treated with sodium alkoxide or sodiumphonoxide to form ethers.

  $CH_3\,CH_2\,ONa + CH_3 - CH_2 - I \rightarrow CH_3\,CH_2 - OCH_2\,CH_3 + NaCl$



The reaction takes place by SN_2 mechanism and therefore the alkyl halide used should be primary.

- **Physical properties**

Boiling points of ethers are lower than those of isomeric alcohols – lower member are soluble in water due to the formation of H – bonds with water.

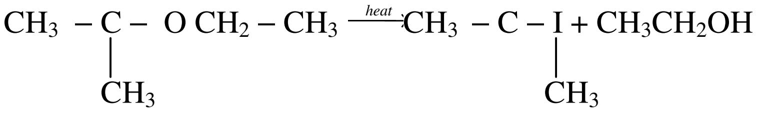
- **Chemical Properties**

Reaction with H I :

$$CH_3\,CH_2 - OCH_3 \xrightarrow{+HI} CH_3\,CH_2\,OH + CH_3I$$

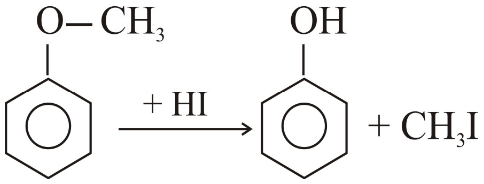
This reaction proceeds through SN_2.

When one of the alkyl groups is a tertiary groups reaction proceeds through SN_1 and the halide formed will be tertiary.



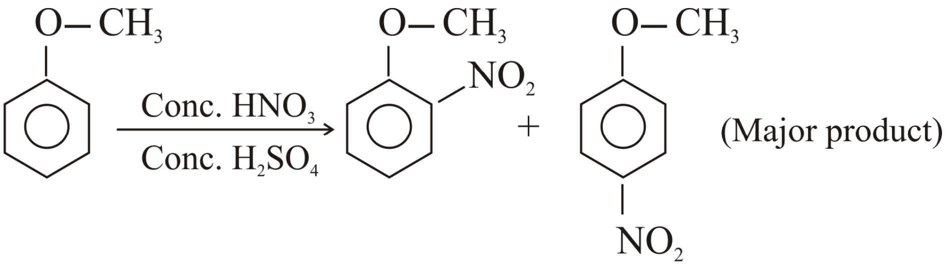
$$CH_3-\underset{\underset{CH_3}{|}}{C}-OCH_2-CH_3 \xrightarrow{heat} CH_3-\underset{\underset{CH_3}{|}}{C}-I + CH_3CH_2OH$$

In aryl ethers cleavage occurs to form phenol and alkyl halide due to double bond character of O –C (of benzene ring) bond.

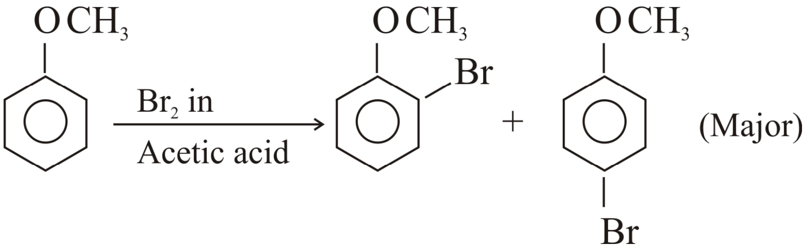


Ring Substitution in aromatic ethers. Aromatic ethers undergo electrophilic substitution at ortho and positions, because – O–CH_3 group is an electron releasing group.

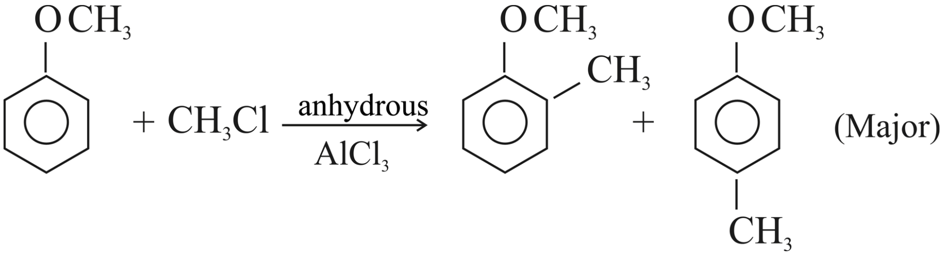
- **Nitrations**



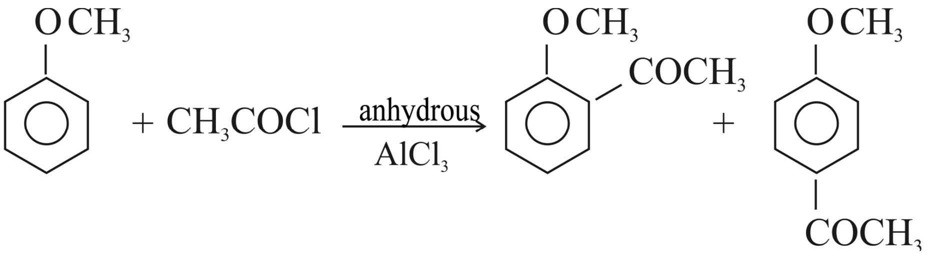
- **Halogenation**



- **Friedel – Crafts reaction – alkylation**



- **Acylation**



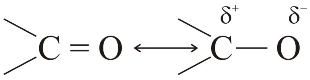
***

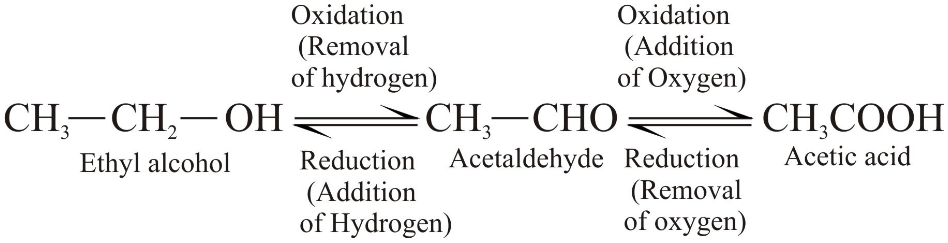
Chapter 12

Aldehydes ketones and carboxylic acids

Common name		Common name	IUPAC name
Carboxylic acid	$CH_3 - COOH$	Acetic acid	Ethanoic acid
Aldehyde	$CH_3 - CHO$	Acetaldehyde	Ethanol
Salt	$CH_3 - COONa$	Sodium Acetate	Sodium ethanoate
Ester	$CH_3C - COOC_2H_5$	Ethyl acetate	Ethyl ethanoate
Anhydride	$(CH_3\ CO)_2O$	Acetic anhydride	Ethanoic anhydride
Acid chloride	$CH_3\ COCl$	Acetyl Chloride	Ethanoyl Chloride
Cyanides	$CH_3 - CN$	Methyl cyanide Acetonitrite	Ethane nitrilie
Ketone	$CH_3 - CO- CH_3$	Acetone	Propanone
Amide	$CH_3 - CO- NH_2$	Acetamide	Ethanamide

Carboxyl carbon is sp^2 hydridised





$$CH_3-CH_2-OH \rightleftharpoons CH_3-CHO \rightleftharpoons CH_3COOH$$

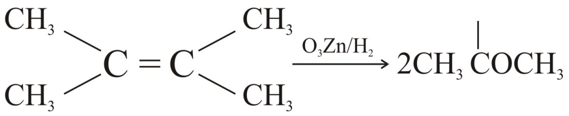
Preparation

i) $1°\ \text{alcohol} \xrightarrow{\text{oxidation}} \text{aldehyde} \xleftarrow[\text{heated Cu at 573 K}]{\text{dehydrogenation}} 1°\ \text{alcohol}$

$2°\ \text{alcohol} \xrightarrow{\text{oxidation}} \text{ketone} \xleftarrow[\text{heated Cu at 573 K}]{\text{dehydrogenation}} 2°\ \text{alcohol}$

ii) Ozonolysis (addition of O_3 followed by hydrolysis in the presence of Zn) of alkene

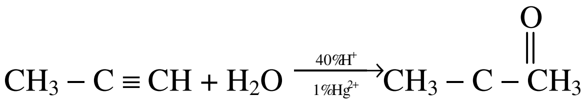
$CH_3 - CH = CH - CH_3 \xrightarrow{O_3/Zn/H_2O} 2\ CH_3CHO$



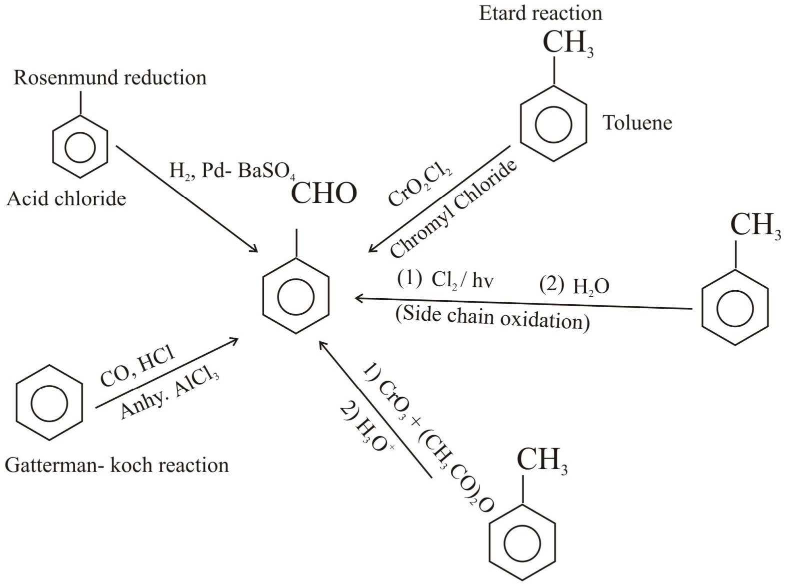
$$(CH_3)_2C = C(CH_3)_2 \xrightarrow{O_3Zn/H_2} 2CH_3COCH_3$$

iii) Hydration

$HC \equiv CH + H_2O \xrightarrow[1\%HgSO_4]{40\%H_2SO_4} H_3C - CHO$



$$CH_3 - C \equiv CH + H_2O \xrightarrow[1\%Hg^{2+}]{40\%H^+} CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$$



$$CH_3 - CH = CH - CH_2 - CH_2 - CN \xrightarrow[2)\ H_2O]{1)\ DiBAL\text{-}H} H_3C - CH = CH - CH_2 - CH_2 - CHO$$

(Disobutyl aluminium hydride)

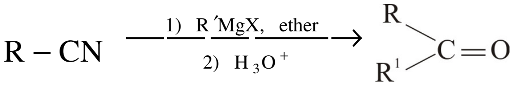
Stephen reaction

$R - CN + SnCl_2 + HCl \xrightarrow{H_3O^+} RCHO$

$\text{ester} \xrightarrow[2)\ H_2O]{1)\ DiBAL\text{-}H} \text{aldehyde}$

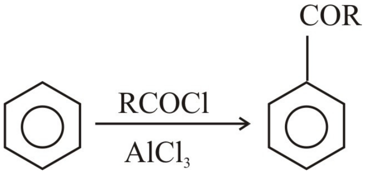
$2\ RCO\text{–}Cl + R'_2\ Cd \rightarrow 2\ RCOR' + CdCl_2$

(acid chloride) (ketone)

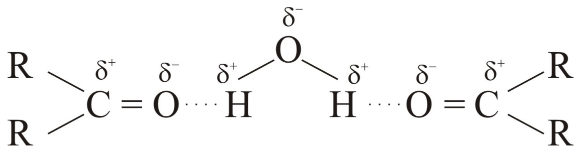


$$R - CN \xrightarrow[2)\ H_3O^+]{1)\ R'MgX,\ ether} \begin{matrix} R \\ R^1 \end{matrix}\!\!>C=O$$

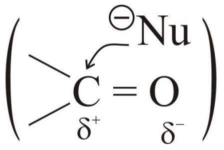
Field crafts acylation



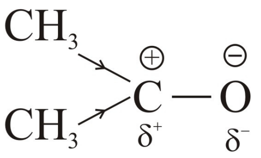
Due to the presence of hydrogen bond in alcohols have greater boiling points than aldehydes and ketones (only dipole interactions). Lower members (HCHO, CH_3CHO, CH_3COCH_3) are soluble in water due to H- bond



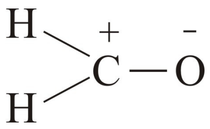
Chemical reactions

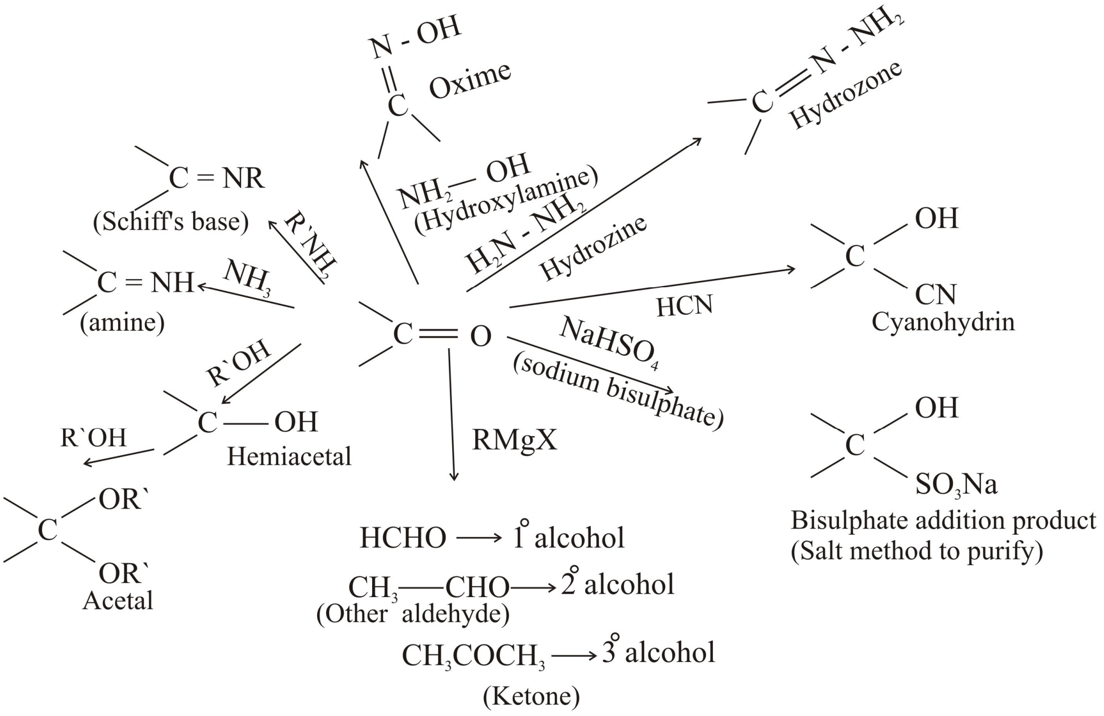


In nucleophilic substitution reaction aldehydes are more reactive than ketones [due to sterric and electronic (+I effect of alkyl groups)] Reasons.

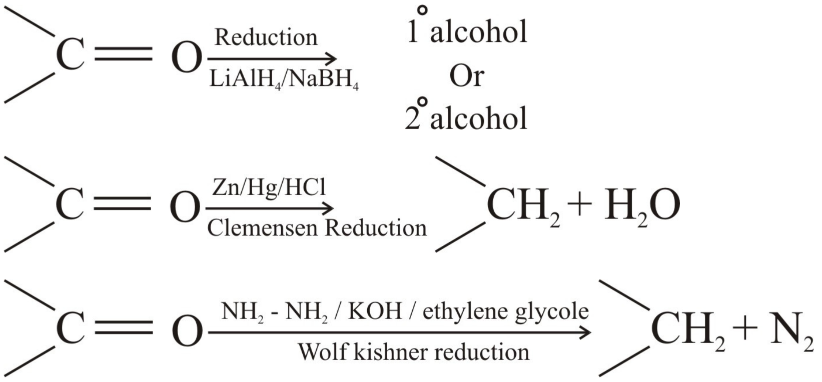


and





- **Reduction**



- **Oxidation**

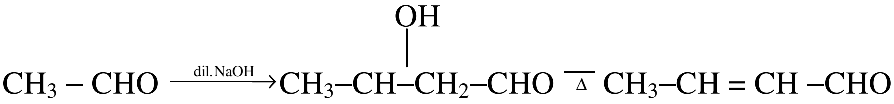
$RCHO \xrightarrow{\text{Oxidation}} RCOOH$

$R-CO-CH_2-R` \xrightarrow{\text{Oxidation}} RCOOH + R`\ CH_2COOH$

$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \left(\xrightarrow[\text{Ammoniacal Silver nitrite}]{\text{Tollens test}}\right) RCOO^- + 2Ag + 2H_2O + 4\ NH_3$

$RCHO + 2Cu^{2+} + 5OH^- \xrightarrow{\text{Feblingtest}} RCOO^- + \underset{\text{red ppt}}{Cu_2O} + 3H_2O$

- **Aldol condensation** (Aldehydes and ketones having α - hydrogen)



$$CH_3-CHO \xrightarrow{\text{dil.NaOH}} CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-CHO \xrightarrow[\Delta]{} CH_3-CH=CH-CHO$$

- **Cannizzaro reaction** (Aldehydes and ketones without α - hydrogen)

$HCHO \xrightarrow{\text{conc. NaOH}} CH_3-OH + HCOONa$

$C_6H_5-CHO \xrightarrow{\text{conc. NaOH}} C_6H_5-CH_2OH + C_6H_5COONa$

self recution and oxidation

Carboxylic acids

$HCOOH$ – formic acid (formica –ant) CH_3COOH (Acetic acid – vinegar)

Methods of preparation

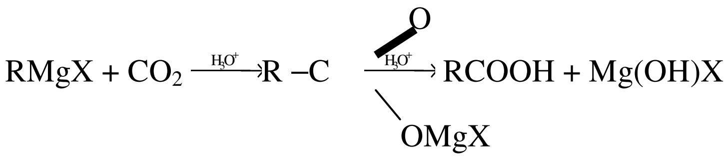
1) By Oxidation of alcohols – aldehydes and ketons

$RCH_2OH \xrightarrow{KMnO_4/OH^-} RCHO \xrightarrow{KMnO_4/OH^-} RCOOH$

2) By hydrolysis of nitriles (Cyanides)

$RCN \xrightarrow{H_3O^+} RCO\,NH_2 \xrightarrow{H_3O^+} RCOOH + NH_3$

3) From Grignard Reagents



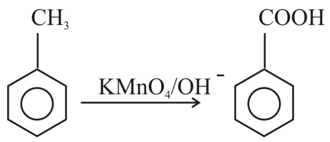
$$RMgX + CO_2 \xrightarrow{H_3O^+} R-C\begin{matrix}\diagup O \\ \diagdown OMgX\end{matrix} \xrightarrow{H_3O^+} RCOOH + Mg(OH)X$$

4) By hydrolysis of Acid chlorides/ Esters

$RCOCl \xrightarrow{H_3O^+/OH^-} RCOOH + HCl$

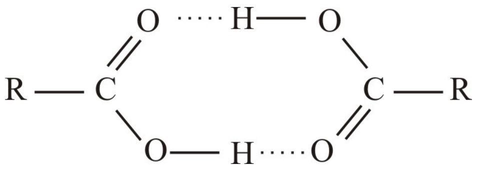
$RCOOR` \xrightarrow{H_3O^+/OH^-} RCOOH + R`OH$

5) By Side chain oxidation



Physical properties

Carboxylic acids dimerise even in gaseous state due to strong intermolecular hydrogen bonding. Due to this strong hydrogen bonding they have very high boiling point.



Chemical properties

1) Acidity : Carboxylic acids are strongly acidic due to following ionisation

$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$

$$\therefore\ Ka = \frac{[RCOO^-][H_3O^+]}{[H_2O]}$$

Greater the value of Ka [smaller the value of p^{Ka}], grater the acids strength.

Electron with drawing group (EWG) increases the acid strength. Electron donating groups decrease the acid strength.

Electron withdrawing groups = Cl, F, NO_2, COOH, CHO etc.

Electron donating groups = CH_3, C_2H_5 etc.

Chemical properties

1) Reduction

$$RCOOH \xrightarrow[B_2H_6]{LiAlH_4/Ether} \underset{\text{(aldehyde)}}{RCHO}$$

2) Dehydration

$$RCOOH \xrightarrow[\Delta]{P_2O_5 H_2SO_4} \underset{\text{(anhydride)}}{(RCO)_2O}$$

3) Estrification

$$RCOOH + R`OH \xrightarrow[\Delta]{H_2SO_4} \underset{\text{(Ester)}}{RCOOR` + H_2O}$$

4) Ammonolysis

$$RCOOH + NH_3 \rightarrow \underset{\text{(Amide)}}{RCONH_2} + H_2O$$

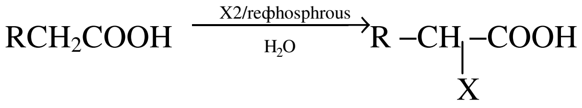
5) Halogination

$$RCOOH + PCl_5 \rightarrow \underset{\text{(Acid chloride)}}{RCOCl} + POCl_3 + HCl$$

6) De-Carboxylation

$$CH_3COONa \xrightarrow[\text{Soda lime}]{NaOH+CaO} \underset{\text{(Methane)}}{CH_4} + Na_2CO_3$$

7) HVZ reaction (Hell – Volhard – Zelinsky reaction)



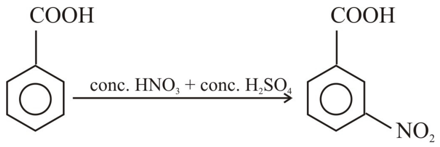
$$RCH_2COOH \xrightarrow[H_2O]{X2/\text{red phosphrous}} R-\underset{\underset{X}{|}}{CH}-COOH$$

(α - haloaicd)

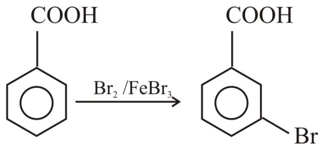
8) Ring Substitution (Electrophilic substitution)

– COOH group is meta directing (de-activating)

a) Nitration



b) Halogination (Bromination)



Uses

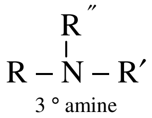
HCOOH is used in rubber, textile, dyeing, leather and electroplating industries. CH_3COOH (vinegar) is used as solvent, ester of benzoic acid in perfumery, sodium benzoate as food preservative, higher fatty acids used as the preparation of soap, Hexane dioicacid is used for preparing nylon 6, 6.

***

Chapter 13
Amines

Amines are organic bases. They are considered to be the derivatives of Ammonia, because they are considered to be formed from ammonia by replacement of H atoms by alkyl groups (Aryl groups). One by one

Eg : $\underset{\text{Ammonia}}{NH_3,}$ $\underset{1^\circ \text{ amine}}{R - NH_2,}$ $\underset{2^\circ \text{ amine}}{R - NH - R'}$



$$\underset{3^\circ \text{ amine}}{R - \overset{\overset{\displaystyle R''}{|}}{N} - R'}$$

- **Classification**

Amines are classified in to primary (1°) amine, secondary amines (2°) and Teritiary amines (3°). In 1° amines one H atom of NH_3 is replaced by alkyl group. In 2° - two H atoms are replaced by alkyl or aryl groups and in 3° amine, three H atoms are replaced by alkyl groups.

- **Nomenclature**

According to IUPAC, amines are named by replacing 'e' of the alkane name by amine. If more than one amino group is present, prefixes such as di, bi etc are used in front of the name amines. In the case of 2° and 3° amines N – alkyl, N, N – dialkyl etc are used.

Eg : $CH_3 - NH_2$	Methanamine
$CH_3 - CH_2 - NH_2$	Ethanamine
$H_2N - CH_2 - CH_2 - NH_2$	Ethane -1, 2- diamine
$CH_3 - NH - CH_3$	N-methyl methanamine

- **Methods of preparation**

1. ***By reduction of Nitro compounds***

Reduction of aliphatic & aromatic nitro compounds with reducing agents H_2/Pt, Pt, Ni, Sn+ HCl or Fe + HCl, give amines. Fe + HCl is preferred because the by product FeCl hydrolysed back to form HCl. Thus only small amount of HCl is required.

i.e $R - NO_2 \xrightarrow{H_2/Pt} R - NH_2$

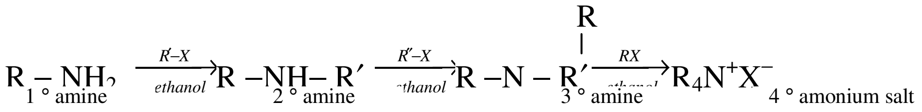
$$NO_2 \xrightarrow[or\ Fe + HCl]{H_2/Pt} NH_2$$

2. By Ammonolysis of alkyl halides

Decomposition of a compound by ammonia is called ammonolysis. Replacement of 'X' by NH_2 group take place to give 1° amines.

i.e $R - X + NH \xrightarrow{ethanol} R - NH_2 + HX$

I° amine formed again react with R –X to form 2° amines, then 3° amines and finally quaternary ammonium salt.



$$\underset{1^\circ\ amine}{R - NH_2} \xrightarrow[ethanol]{R'-X} \underset{2^\circ\ amine}{R - NH - R'} \xrightarrow[ethanol]{R''-X} \underset{3^\circ\ amine}{R - \overset{\overset{\large R}{|}}{N} - R'} \xrightarrow[ethanol]{RX} \underset{4^\circ\ amonium\ salt}{R_4N^+X^-}$$

3. By Reduction of Nitrile (cyanides)

Cyanides on reduction with reducing agents like H_2/Pt, Pd, Ni, $LiAlH_4$, $Na/C_2H_5^-OH$ give 1° amines.

i.e $\underset{Cyanides}{R - C \equiv N} \xrightarrow[or\ LiAlH_4]{H_2/Pt,Pd,Ni} \underset{1^\circ\ amine}{R - CH_2 - NH_2}$

But isocyanides one reduction gives 2° amines.

i.e $R - N \equiv C \xrightarrow[or\ LiAlH_4]{H_2/Pt,Pd,Ni} \underset{2^\circ\ amine}{R - NH - CH_3}$

4. By Reduction of amides

Reduction of 1° amides with $LiAlH_4$ give 1° amines

i.e $R - CO - NH_2 \xrightarrow{LiAlH_4} R - CH_2 - NH_2$

5. By Hoffman bromanide reaction (Hoffman degradation)

When an amide is treated with Bromine in alkali (NaOH/KOH), a primary amine containing one C atom less than the amide is formed.

i.e $R - CO - NH_2 + Br_2 + 4NaOH \rightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

- **Physical properties**

Amines have fishy odour they are soluble is water because they can form H – bonds with water.

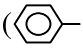
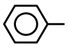
They can form intermolecular H- bonding with each other. Their BP are relatively higher than alkanes, halo alkanes, ethers etc but lower than alcohol.

- **Chemical properties**

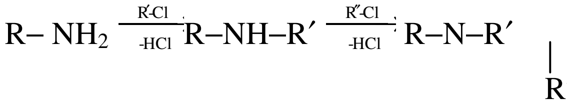
1. Basic character : Amines are basic like ammonia due to the pressure of lone pair of electrons.

$$NH_3,\quad R-\ddot{N}H_2 \quad R-\ddot{N}H-R \quad R-\underset{\underset{\large R}{|}}{\ddot{N}}-R$$

Alkyl group (R) is +I group (electron donating). i.e presence of R group increases the availability of electron pair on N atom. i.e Alkyl amines are generally stronger than ammonia. 3° amines contains three +I R – groups. i.e 3° amines are expected to be most basic and the basicity order is 3°>2°>1° . But in aquous state, the posibility of hydration is in the order. 1°>2°>3°. Due to this opposing effect, secondary amines are the most basic amoung aliphatic amines.

Aromatic amines ($-NH_2$) are weaker than ammonia because phenyl group ($-$) is electron withdrawing. i.e phynyl group decreases the availability of lone pair electrons, which decreases the basicity.

2. ***Alkylation :*** Undergo alkylation – when treated with alcoholic solutions of alkyl halide to form 2° amines and 3° amines.



$$R-NH_2 \xrightarrow[-HCl]{R'Cl} R-NH-R' \xrightarrow[-HCl]{R''Cl} R-\underset{\displaystyle R''}{\underset{|}{N}}-R'$$

3. ***Acylation :*** Amines react with acid chlorides, anhydrides and esters to form substituted amides.

i.e $R-NH_2 + R'COCl \xrightarrow[-HCl]{} R-NH-CO-R'$ (Acylation)

$R-NH_2 + C_6H_5-COCl \xrightarrow[-HCl]{} R-NH-CO-C_6H_5$ (Bezoyltion)

4. ***Carbylamine reaction :*** Alliphatic and aromatic 1° amines react with chloroform and alkali (NaOH/KOH) to form isocyanides or Carbylamnes. This is called carbylamine reaction. Carbylamine are foul smelting substances and hence this is used as a test to distinguish 1° amines.

Eg : $R-NH_2 \xrightarrow{CHCl_3/KOH} R-NC + 3KCl + 3H_2O$

(Carbylamine)

2° and 3° amines do not give this test.

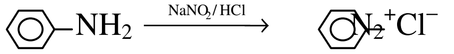
5. ***Reaction with Nitrous acid (HNO_2) :*** HNO_2 is unstable and produced in the reaction site by reaction between $NaNO_2$ & HCl.

$$(NaNHO_2 + HCl \rightarrow HNO_2 + NaCl)$$

Aliphatic 1° amines react with HNO_2 to form aliphatic diazonium salt which is unstable and hence decomposes to give alcohols.

i.e $R-NH_2 \xrightarrow{NaNO_2/HCl} R-N_2^+Cl \xrightarrow{H_2O} R-OH + N_2 + HCl$

But aromatic 1° amines react with HNO_2 to form aromatic diazonium salt, which are stable. (This reaction is called diazotisation)



Anilinic Benzene diazonium chloride

6. ***Hinsberg's test*** (Reactions with benzene sulphonyl chloride)

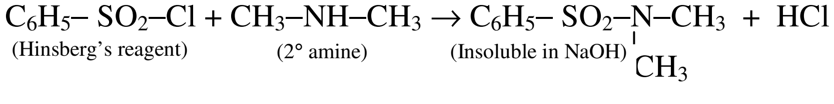
Benzene sulphonyl chloride is called Hinsberg's reagent. It is used to distinguish 1°, 2° and 3° amines.

- 1° amines react with Hinsberg's reagent to form N –alkylbenzene sulphonamide which dissolve in NaOH to form a clear solution.

  $C_6H_5-SO_2-Cl + CH_3-NH_2 \rightarrow C_6H_5-SO_2-NH-CH_3+HCl$

  (Hinsberg's Reagent_ (1° amine) (Soluble in NaOH)

- 2° amine react with Hinsberg's reagent to form N, N–dialkyl benzene suphonamide, which is in soluble in NaOH

  $$C_6H_5-SO_2-Cl + CH_3-NH-CH_3 \rightarrow C_6H_5-SO_2-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3 + HCl$$

  (Hinsberg's reagent) (2° amine) (Insoluble in NaOH)

- 3° amines do not react with Hinsberg's reagent.

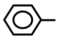
- **Diazonium salts**

  Organic compounds with general formula Ar– $N_2^+X^-$ are called diazonium salts. (Ar – Aromatic group) Eg: $C_6H_5-N_2^+Cl^-$ is called benzene diazonium chloride.

- **Preparation (Diazotisation)**

  Aromatic 1° amines on treatment with Nitrous acid (HNO_2) or ($NaNO_2$/HCl)give aromatic diazonium salts. This is called diazotisation.

  $$\underset{\text{Aniline}}{C_6H_5-NH_2} \xrightarrow[(HNO_2)]{NaNO_2/HCl} \underset{\text{(Benzene diazonium chloride - BDC)}}{C_6H_5-N_2^+Cl^-}$$

- **Chemical properties** **(Ar =**  **)**

1. Sandmeyer's reaction

   $$Ar-N_2^+Cl^- \xrightarrow{CuCl/HCl} Ar-Cl + N_2$$

   $$Ar-N_2^+Cl^- \xrightarrow{CuCN/HCN} Ar-CN + N_2$$

2. Gatterman reaction

   $$Ar-N_2^+\,Cl^- \xrightarrow{Cu/HCl} Ar-Cl + N_2 + Cu$$

3. Replacement reactions

   a) $Ar-N_2^+\,Cl^- \xrightarrow{KI} Ar-I + K + N_2$

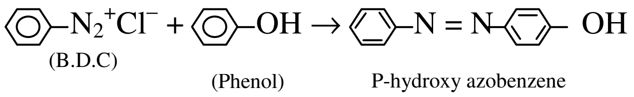
   b) $Ar-N_2^+\,Cl^- \xrightarrow{HBF} Ar-F + BF_3 + N_2$

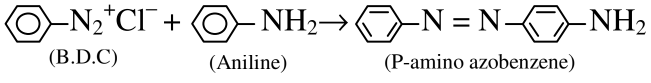
   c) $\underset{\text{(B.D.C)}}{Ar-N_2^+\,Cl^-} \xrightarrow{H_3PO_2/H_2O} \underset{\text{Benzene)}}{Ar-H}$

   d) $\underset{\text{(B.D.C)}}{Ar-N_2^+\,Cl^-} \xrightarrow{H_2O} \underset{\text{(Phenol)}}{Ar-OH} + N_2 + HCl$

   e) $Ar-N_2^+Cl^- \xrightarrow{HBF_4/NaNO_2} Ar-NO_2$

4. Coupling reactions





(Both p –hydroxy azobenzene and p – amino azo benzene are dyes)

***

Chapter 14

Biomolecules

Living systems are made up of various complex molecules such as carbohydrates proteins, nucleic acids, lipids etc are called biomolecules.

Carbohydrates- most of the carbohydrates have the general formulae $C_x(H_2O)_y$, and were considered as hydrates of carbon from where the name carbohydrate is derived.

Eg : $C_6H_{12}O_6$ (glucose) fits into this general formula $C_6(H_2O)_6$. Acetic acid (CH_3COOH), formaldehyde ($HCHO$) fits into this general formula but is not a carbohydrate the carbohydrate rhamnose $C_6H_{12}O_5$ not fit in this definition.

Carbohydrate (Saccharides) are optically active polyhydroxy aldehydes or ketones or the compounds which are obtained during hydrolysis.

Carbohydrates which are sweet in taste called sugars [Sucrose, milk sugar (lactose)]

Classification based on hydrolysed products

1) Monosaccharides which can not be hydrolysed further.

   Eg : Glucose, fructose, ribose.

2) Oligosaccharides yields 2 to 10 monosaccharides on hydrolysis sucrose (disaccharide) give glucose and fructose

3) Polysaccharides yields a large number of monosaccharides.

   Eg : Starch, cellulose, glycogen (animal starch), gum. They are non sugars.

   All carbohydrates which reduce Fehling's solution and Tollens reagent are called reducing, sugars. Eg : A monosaccharides maltose, Lactose (Functional groups are free)

   In non reducing sugars (sucrose) all the functional group aldehyde or Ketonic are bonded.

   Monosaccharides are classified based on no of carbon atoms and functional groups present in them, glucose is aldohexose, fructose is ketohexose, ribose is aldopentose.

Glucose (dextrose)

1) Hydrolysis of cane sugar (Sucrose) by dil. HCl or H_2SO_4 in alcoholic solution.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

2. $$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393K,2\ -3\ atom]{H^+} \underset{\text{glucose}}{nC_6H_{12}O_6}$$

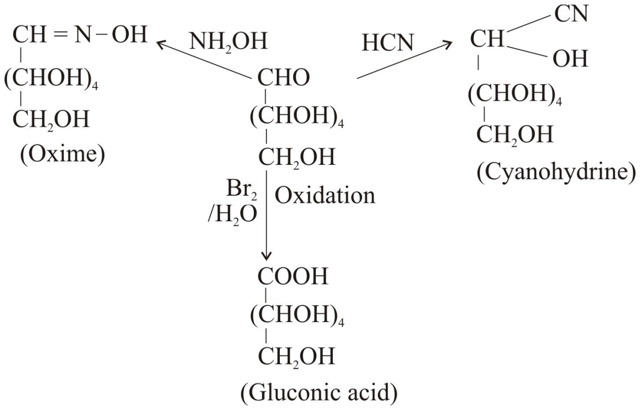
Structure

1) Molecular formula, $C_6H_{12}O_6$

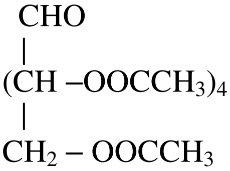
2) On prolonged heating with HI gives n-hexane suggesting that all the six carbon atoms in glucose are linked in a straight line.

$$\text{Glucose} \xrightarrow[\Delta]{HI} \text{n-hexane}$$

3) Reaction with hydroxylamine (form oxime) and HCN (form cyanohydrine) confirms the presence of $>C=O$ group and oxidised by Br_2 water indicates $-$ CHO groups.



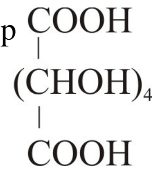
4) Acetylation gives stable glucose penta acetate indicates 5 – OH groups at 5 different carbon atoms.



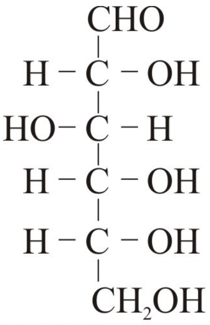
$$\begin{array}{l} CHO \\ | \\ (CH-OOCCH_3)_4 \\ | \\ CH_2-OOCCH_3 \end{array}$$

glucose penta acetate

5) Oxidation of glucose and gluconic acid by HNO_3 gives saccharic acid (dicarboxylic acid) Indicates the presence of 1° alcoholic group



$$\begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{array}$$



$$\begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ CH_2OH \end{array}$$

D(+) Glucose (Fischer)

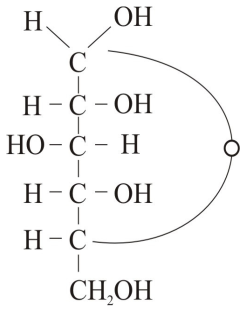
All isomer co-related to (+) Glyceraldehyde belongs to D-configuration and to (–) Glyceraldehyde L- configuration. For glucose the –OH group present in the asymmetric carbon farthest from most oxidised carbon is on the right hand side as in (+) glyceraldehyde. So it is assigned D-Configuration.

a) Eventhough glucose contains –CHO group. It does not give schiff's test not add $NaHSO_3$.

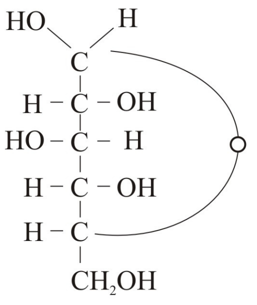
b) Even though glucose penta acetate contains –CHO group. It does not react with hydroxylamine.

c) Glucose exist in 2 different crystalline form (α and β). All the above 3 facts can be explained only by Cyclic structure.

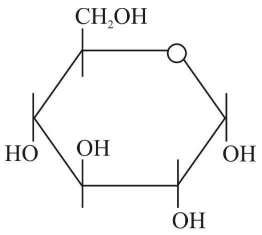
Cyclic hemiacetal formation (addition of –OH at C-5 to –CHO group) leads to α and β form and acetal formation (further addition of – H group) leads to dimerisation or polymerisation.



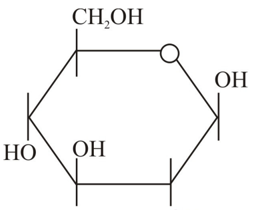
α – D(+) Glucose



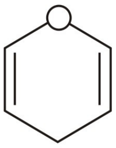
β – D(+) Glucose



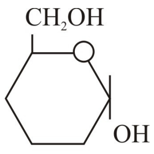
α – D(+) Glucopyranose



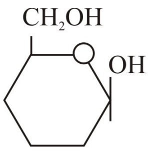
β – D(+) Glucopyranose



Pyran



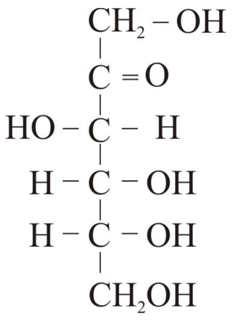
(α)



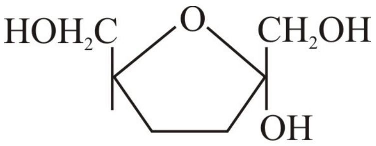
(β)

α and β glucose are anomers which differ only on the position of –OH group on Ist asymmetric carbon atom.

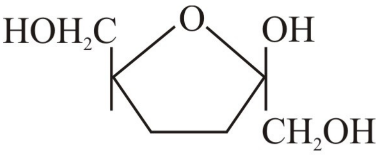
Fructose - ketohexose



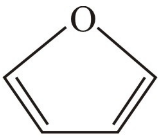
D(-) Fructose



α–D (–) Fructofuranose



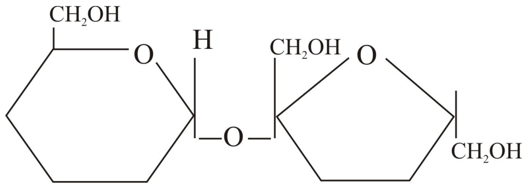
β–D (–) Fructofuranose



furan

Disacharide

Sucrose



α – D(–) glucose β – D(–) fructose

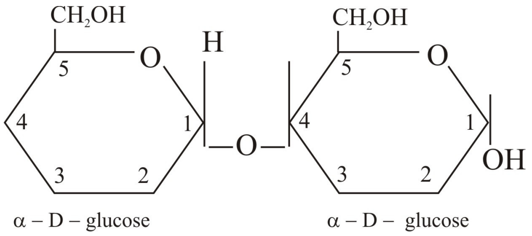
(C_1 of α glucose and C_2 of β- fructose. Glycosidic linkage) Since reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non – reducing.

Sucrose $\xrightarrow{hydrolysis}$ glucose + fructose

(dextro) + 52.5 ° – 92.4°

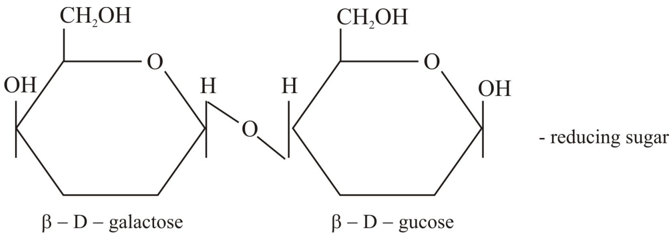
(mixture is laevorotatory invert sugar)

Maltose



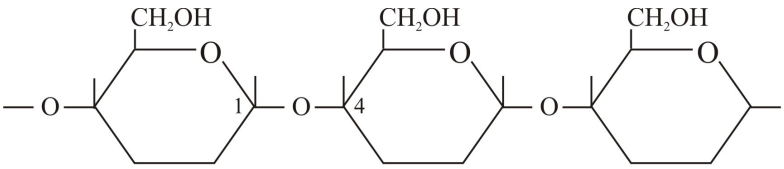
Since free aldehydic group can be produce at C of 2nd glucose unit, in solution it is reducing.

Lactose

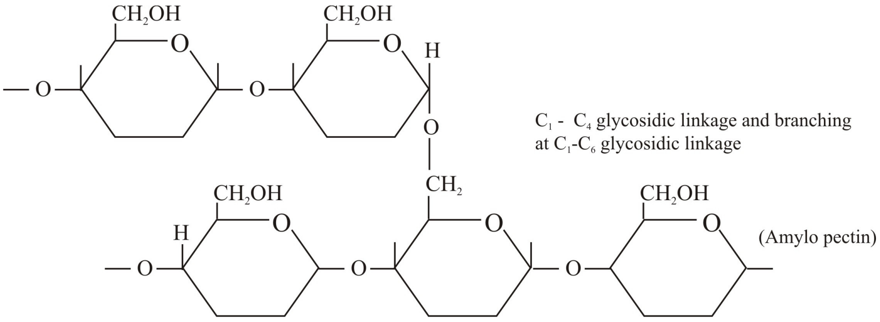


Poly saccharides

Starch is a polymer of α - glucose. It consist of water soluble amyllose (long unbranched chain) and water insoluble Amylopectin units (branched chain)

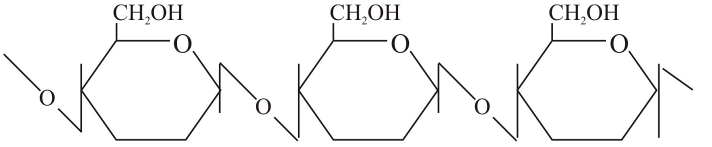


C_1 - C_4 glycosidic linkage (amylose)



C_1 - C_4 glycosidic linkage and branching at C_1-C_6 glycosidic linkage

Cellulose is a polymer of β - glucose



C_1 - C_4 linkage

Glycogen (animal starch)

Structure similar to amylopectin. It is present in liver muscles and brain.

Uses of carbohydrates – Food, structural material of cell wall

D (–) ribose and 2 – deoxy D (–) ribose present in Nucleic acids.

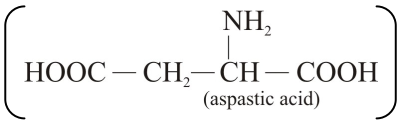
Proteins

Proteins are polymer of α - amino acids.

(Simplest α - amino acids is glycine H_2N –CH_2 – COOH

Which is optically inactive)

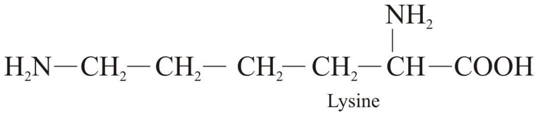
Amino acids are acidic



$$\left(HOOC-CH_2-\underset{}{\overset{NH_2}{\overset{|}{CH}}}-COOH \right)$$

(aspastic acid)

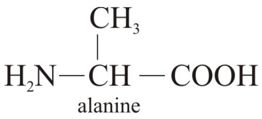
Basic



$$H_2N-CH_2-CH_2-CH_2-CH_2-\overset{NH_2}{\overset{|}{CH}}-COOH$$

Lysine

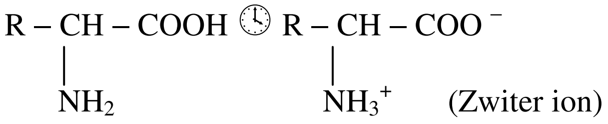
and neutral



$$H_2N-\overset{CH_3}{\overset{|}{CH}}-COOH$$

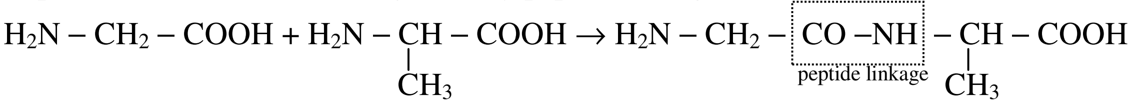
alanine

Acidic amino acids contains more –COOH groups than $-NH_2$ groups. Essential amino acids cannot be synthesised by our body, so it should be supplied through food. In aqueous solution amino acids forms zwitter ion (dipolar ion or internal salt) and shows amphoetric behaviour.



$R-\underset{NH_2}{\underset{|}{CH}}-COOH$ 🕓 $R-\underset{NH_3^+}{\underset{|}{CH}}-COO^-$ (Zwiter ion)

In proteins α - aminoacids are joined by peptide linkage.



$$H_2N-CH_2-COOH+H_2N-\underset{CH_3}{\underset{|}{CH}}-COOH \rightarrow H_2N-CH_2-\underbrace{\boxed{CO-NH}}_{\text{peptide linkage}}-\underset{CH_3}{\underset{|}{CH}}-COOH$$

Dipeptide (Gly – Ala) contains one peptide bond and 2 α - amino acids. A polypeptide contains more than 100 amino acid residues called protein.

On the basis of molecular shapes proteins are two types

a) Fibrous proteins are fibre – like in which polypeptide chains run parallel and held together by hydrogen and disulphide bonds and are insoluble in water.

Eg : Keratin (hair, wool, silk) myosin (muscles)

b) Globular proteins are spherical shape and formed by coiling of polypeptides and are soluble in water. Insulin egg albumins.

There are 4 levels of structural organisations for proteins.

Primary (1°) structure - Sequence of α - amino acids in a protein chain.

Secondary (2°) structure - relative arrangements of one poly peptide segments with respect to another poly peptide segment. Polypeptide chains coiled up to form spiral structure like right handed α - helix by intramolecular hydrogen bond ($>C=O\ldots.\ HN-$) called α - helical structure. They can be stretched.

Intermolecular hydrogen bonds of different poly peptide chains laid side by side forms β - pleated type – which resembles pleated folds of drapery and can not stretched but bended.

3° - The overall folding of secondary structured protein by hydrogen bonds, disulphide linkages van der waals and electrostatic forces of attraction leads to fibrous and globular type proteins.

4° - The inter coiling of subunits (poly peptide chains) by further folding of 3° structured proteins to perform actual function of proteins called quaternary structure.

Native protein: has unique three –dimensional structure with a particular biological activity. Denaturation of proteins can be done by changing the temperature and pH and during this hydrogen bonds are disturbed. During denaturation 2° and 3° structures are destroyed but 1° structure remains intact. Eg: coagulation of egg albumin on boiling, curdling of milk by lactic acid.

Enzymes are biological catalysts and are globular proteins. Eg : maltase helps the hydrolysis of maltose. They are highly selective and active.

Vitamins are required in small amounts to perform specific biological function for normal growth and health of organism.

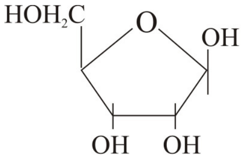
Vitamin A, D, E and K are fat soluble and B and C are water soluble.

Vitamin		***Deficiency diseases***
A (Retinol)	–	Xerophthalamia night blindes
D (Sunshine)	–	Rickets
E (Anti sterility)	–	Sterility
K	–	Increased blood clotting time
C (Ascorbic acid)	–	Scurvy
B_1 (thiamine)	–	Beri-beri
B_2 (Riboflavin)	–	Cheilosis, digestive disorders
B_6 (Pyridoxine)	–	Convulsions
B_{12} (Cynocobalamine)	–	Pernicious anaemia

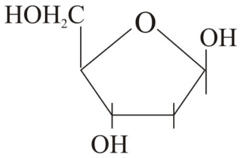
Nucleic acids are responsible for hereditory transmission chromosomes are made up of proteins and nucleic acids. Nucleic acids are poly nucleotides. (Eg. RNA and DNA)

D.N.A	R.N.A.
2 – deoxy D (–) Ribose	D (–) Ribose
Adenine, Thymine (A⋯T)	Adenine, uracil (A ⋯ U)
Cytosine, Guanine (G ⋯C)	Guanine Cytosine (G⋯C)
Double stranded	Single stranded
Present in nucleous of cell	Present every where in the cell
Directs protein synthesis	Done protein synthesis

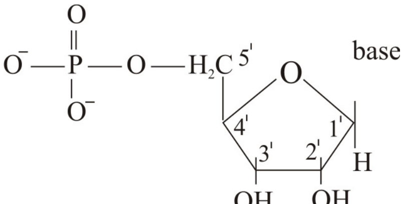
Nucleotide consist of Sugar, base and phosphate units.



β–D–ribose

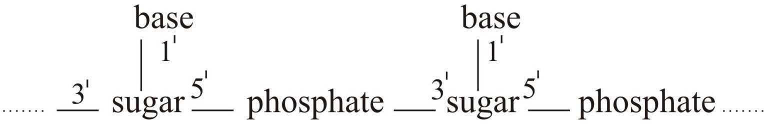


2 - deoxy β– D(–) ribose



(base at 1\` and phosphate unit at 5′ positions)

Sugar containing only base at 1′ positions is called nucleoside. Nucleotdes are linked together at 3′ , 5′ positions.



$$\cdots\cdots \overset{3'}{—} \overset{\overset{\text{base}}{|\,1'}}{\text{sugar}} \overset{5'}{—} \text{phosphate} \overset{3'}{—} \overset{\overset{\text{base}}{|\,1'}}{\text{sugar}} \overset{5'}{—} \text{phosphate} \cdots\cdots$$

In DNA two strands are complementary to each other. Specificity in base pairing (A = T, G C) helps the heredity transaction. During cell division identical DNA strands are formed (self duplication or replication). Preparation of messenger RNA by DNA is called transcription and changing genetic code in m-RNA to corresponding amino acids and proteins is called translation. Ribosomal RNA provides sites for protein synthesis. Transfer RNA carries amino acids to ribosomal site. Messenger RNA carries the message of DNA for specific protein synthesis to ribosomal site.

***

Chapter 15

Polymers

Polymers are very large molecules having high molar mass and are formed by the combination of a large number of simple molecules called monomers. The process of formation of polymers from respective monomers is called *polymerisation.*

The word 'polymer' is derived from two Greek words - poly (means many) and mer (means unit or part). Polymers are also called *macromolecules.*

Eg. polythene, polypropene, polystyrene, polyesters, polyamides, synthetic fibres, synthetic rubbers etc.

Classification of Polymers

The following are some of the common classifications of polymers:

I) **Classification Based on Source:** Based on this, polymers are classified into three:

1. ***Natural polymers:*** These polymers are found in nature. Examples are proteins, cellulose, starch, natural fibres and natural rubber.
2. ***Semi-synthetic polymers:*** Cellulose derivatives such as cellulose acetate (rayon) and cellulose nitrate are the examples of this category.
3. ***Synthetic polymers:*** These are man-made polymers.

Eg. plastics like polythene, poly styrene, PVC etc. Synthetic fibres like nylon 6,6 and synthetic rubbers like Buna–S

II) Classification Based on Structure of Polymers: Based on this polymers are divided into three:

1. ***Linear polymers:*** They contain long and straight chains of polymers.

   Eg. high density polythene, polyvinyl chloride, etc

2. ***Branched chain polymers:*** These polymers contain linear chains having some branches.

   Eg. low density polythene.

3. ***Cross linked or Network polymers:*** These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains. Eg. bakelite, melamine, etc.

Ill) Classification Based on Mode of Polymerisation: Based on this polymers are classified into two:

1. ***Addition polymers:*** These are polymers formed by addition polymerisation reaction. Here the monomer molecules should possess double or triple bonds. Addition polymers are now known as chain growth polymers.

   Eg. polythene, polypropene, polystyrene, polyvinyl chloride etc.

$$\underset{\text{Etheric}}{nCH_2 = CH_2} \rightarrow \underset{\text{Polythene}}{\left(CH_2 - CH_2 \right)_n}$$

2 ***Condensation polymers:*** These are polymers formed by condensation polymerisation reaction. In this polymerisation reaction, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc take place. Here the monomers should be bifunctional or polyfunctional. Condensation polymers are now known as step growth polymers.

Eg. Nylon – 6,6, Nylon – 6, terylene, glyptal etc.

IV) Classification based on the type of monomers: Based on this, polymers are of two types:

1. ***Homopolymers:*** These are polymers containing only one type of monomer unit.

   Eg: polythene, polystyrene, polypropene etc.

2. ***Copolymers:*** These are polymers containing different types of monomer units.

   Eg: Polyesters like glyptal, terylene etc. poly amides like Nylon-6, Nylon-6,6 etc.

V) Classification based on the Molecular Forces: Based on this, polymers are of 4 types:

1. ***Elastomers:*** These are rubber - like solids with elastic properties. In these polymers, the polymer chains are held together by the weakest intermolecular forces (van der Waal's force). So they can be stretched. A few 'cross links' are formed in between the chains, which help the polymer to regain to its original position after the force is released.

   Eg. buna-S, buna-N, neoprene, etc.

2. ***Fibres:*** Fibres are the thread forming solids which possess high tensile strength and high modulus. Here the different polymer chains are held together by strong intermolecular forces like hydrogen bonding. So they have close packed structure and are crystalline in nature. Eg. Nylon-6,6, Nylon-6, terylene etc.

3. ***Thermoplastic polymers:*** These are the linear or slightly branched long chain molecules. They can be repeatedly softening on heating and hardening on cooling. On heating a physical change occurs. These polymers possess intermolecular forces of attraction in between that of elastomers and fibres. Some examples are polythene, polystyrene, polyvinyls, etc.
4. ***Thermosetting polymers:*** These polymers are cross linked or heavily branched molecules. On heating, they undergo extensive cross links and become infusible. These cannot be reused. There occurs a chemical change on heating. Some common examples are bakelite, urea-formaldelyde resins, glyptal, terylene etc.

Types of Polymerisation Reactions

There are two types of polymerisation reactions - addition or chain growth polymerisation and condensation or step growth polymerisation.

I) Addition Polymerisation or Chain Growth Polymerisation

Here the monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds like alkenes, alkadienes and their derivatives. This type of polymerisation leads to an increase in chain length or chain growth. So it is also called chain growth polymerisation.

This type of polymerisation mainly takes place through *free radical mechanism*. In this mechanism, the reaction takes place in presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide etc.

For example the polymerisation of ethene to polythene is carried out by heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide initiator.

The process consists of three steps:

1. Initiation step
2. Propagation step
3. Termination step

Preparation of some important addition polymers

1. ***Polythene:*** There are two types of polythene - Low density polythene and high density polythene
   - *i)* ***Low density polythene (LDP):*** It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 to 570 K in the presence of an organic peroxide (catalyst).

     It is chemically inert, tough, flexible and a poor conductor of electricity. Hence, it is used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes.
   - *ii)* ***High density polythene (HDP):*** It is formed when addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres.

     It consists of linear molecules and has a high density due to close packing. It is also chemically inert and more tough and hard. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

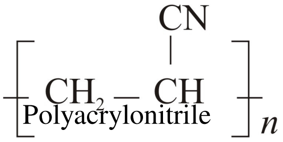
2. ***Teflon:*** It is manufactured by heating tetrafluoroethene with a free radical or persulphate catalyst at high pressures.

$$nCF_2 = CF_2 \xrightarrow[\text{High Pressure}]{\text{Catalyst}} [\, CF_2 - CF_2 \,]_n \quad -$$

Tetrafluoroethene *Teflon*

It is chemically inert and resistant to attack by corrosive reagents. It is used in making oil seals and gaskets and also used for non - stick surface coated utensils (non-sticky pans).

3. ***Polyacrylonitrile (PAN):*** It is prepared by the addition polymerisation of acrylonitrile in presence of a peroxide catalyst. It is used as a substitute for wool in making commercial fibres as orlon or acrilan.



$$nCH_2 = CHCN \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerisation}} \left[CH_2 - \overset{\overset{\Large CN}{|}}{CH} \right]_n$$

Acrylonitrile Polyacrylonitrile

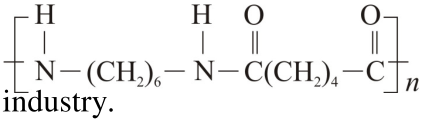
II) Condensation Polymerisation or Step Growth polymerisation

This type of polymerisation involves a repetitive condensation reaction between two bi-functional monomers. It results in the loss of some simple molecules like water, alcohol etc., and lead to the formation of high molecular mass condensation polymers.

In these reactions, the product of each step is again a bi-functional species. Since, each step produces a different functionalised species and is independent of each other; this process is also called as step growth polymerisation. Some examples of condensation polymers are:

1. ***Polyamides :*** These polymers possess amide linkages. They are also known as nylons.

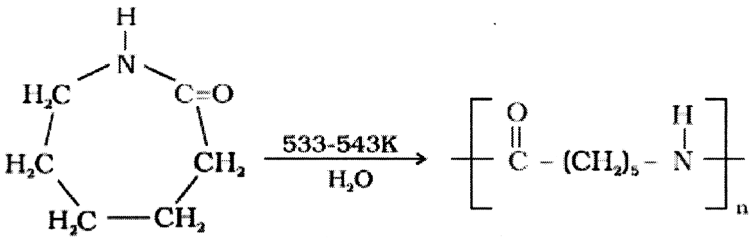
   a) ***Nylon 6,6:*** It is prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.



$$nHOOC(CH_2)_4COOH + nH_2N(CH_2)_6NH_2 \xrightarrow[\text{High pressure}]{553K} \left[\overset{\overset{H}{|}}{N} - (CH_2)_6 - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{\|}}{C}(CH_2)_4 - \overset{\overset{O}{\|}}{C} \right]_n$$

It is used in making sheets, bristles for brushes and in textile industry.

   b) ***Nylon 6:*** It is obtained by heating caprolactum with water at a high temperature.



Caprolactam Nylon 6

It is used for the manufacture of tyre cords, fabrics and ropes.

2. **Polyesters:** These are the polycondensation products of dicarboxylic acids and diols.

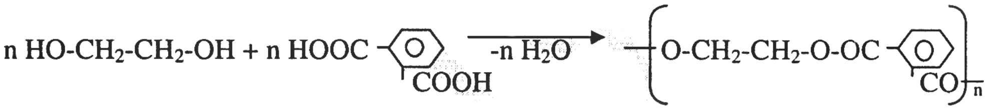
   Some eg: are;

   a) ***Terylene (Dacron):*** It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetate - antimony trioxide catalyst.

Ethylene glycol *[Ethane -1, 2-diol]* *Terephthalic acid* *[Benzene -1, 4-di carboxylic acid]* *Terylene or dacron*

Dacron fibre (terylene) is used in blending with cotton and wool fibres and also as glass reinforcing materials in safety helmets, etc.

b) ***Glyptal :*** It is a polymer of ethylene glycol and phthalic acid.



3. ***Phenol - formaldehyde polymer (Bakelite and related polymers):***

These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst. Initially o-and p-hydroxymethylphenol derivatives are formed, which further react with phenol to form a linear product called Novolac. It is used in paints.

Novolac on heating with formaldehyde undergoes cross linking to form infusible solid mass called *bakelite*.

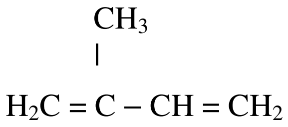
It is used for making combs, phonograph records, electrical switches and handles of various utensils.

4. **Melamine - formaldehyde polymer:** It is formed by the condensation polymerisation of melamine and formaldehyde. It is used in the manufacture of unbreakable crockery.

Rubber

1. **Natural rubber:**

It is a linear polymer of isoprene (2-methyl-l, 3-butadiene) and is also called as cis-1, 4 - polyisoprene.



$$H_2C = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH = CH_2$$

The various cis-polyisoprene chains are held together by weak van der Waals forces and has a coiled structure. Thus, it can be stretched like a spring and exhibits elastic properties.

- **Vulcanisation of rubber**

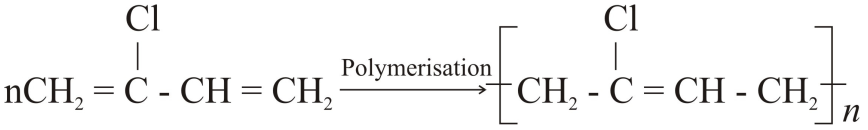
To improve the physical properties of natural rubber, it is heated with sulphur and an appropriate additive at a temperature of 373 to 415 K. This process is called vulcanisation. On vulcanisation, sulphur forms cross links between the different poly isoprene units and thus the rubber gets stiffened.

2. **Synthetic rubbers**

These are either homopolymers of 1, 3 - butadiene derivatives or copolymers of 1, 3 - butadiene or its derivatives with another unsaturated monomer.

Some examples are:

a) **Neoprene (polychloroprene):** It is formed by the polymerisation of chloroprene.



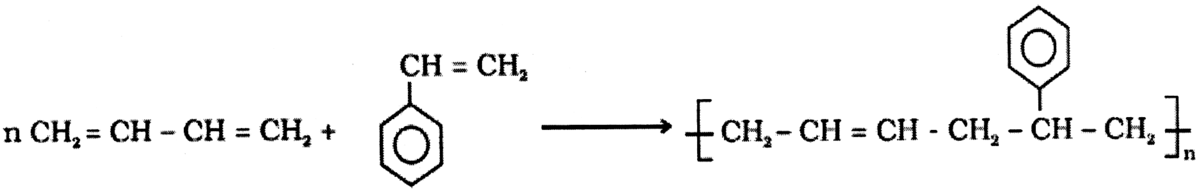
$$nCH_2 = \overset{Cl}{\overset{|}{C}} - CH = CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2 - \overset{Cl}{\overset{|}{C}} = CH - CH_2 \right]_n$$

Chloroprene Neoprene

2-Chloro-1, 3- butadiene

It is used for manufacturing conveyor belts, gaskets and hoses.

b) ***Buna - S:*** It is formed by the co-polymerisation of 1,3-butadiene with styrene.



1,3- Butadiene Styrene Butadiene – styrene copolymer

It is quite tough and is a good substitute for natural rubber. It is used for the manufacture of autotyres, floor tiles, footwear components, cable insulation, etc.

c) ***Buna - N:*** It is obtained by the copolymerisation of 1, 3 - butadiene and acrylonitrile in the presence of a peroxide catalyst.

$$n\,CH_2{=}CH{-}CH{=}CH_2 + nCH_2{=}\overset{CN}{\overset{|}{C}H} \xrightarrow{\text{Copolymerisation}} \left[CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{CN}{\overset{|}{C}H} \right]_n$$

1,3 – Butadiene Acrylonitrile Buna –N

It is used in making oil seals, tank lining, etc.

- **Biodegradable Polymers**

These are polymers which can be decomposed by micro organisms. They contain functional groups similar to the functional groups present in biopolymers like starch, cellulose etc.

Aliphatic polyesters are one of the important classes of biodegradable polymers.

Some important examples are:

1. ***Poly β - hydroxybutyrate - co-β-hydroxy valerate (PHBV):*** It is obtained by the copolymerisation of 3-hydroxybutanoic acid (β-hydroxy butyric acid) and 3 – hydroxy pentanoic acid (p-hydroxy valeric acid)

   It is used in speciality packaging, orthopaedic devices and in controlled release of drugs.

2. ***Nylon 2-nylon 6:*** It is a copolymer of glycine (H_2N-CH_2-COOH) and amino caproic acid [H_2N-$(CH_2)_5$-COOH]

***

Chapter 16

Chemistry in every day life

The treatment of diseases using chemicals called chemotherapy

Classification based on

1) Pharmacological effect – Analgesic reduce pain
2) Drug action – Antihistamines inhibit histamines (Inflammation in the body)
3) Structure – Sulphadrugs are derivatives of sulphonamides.
4) Molecular target – Drugs possessing some common.

   Structural features may have the same mechanism of action on targets.

- **Drug – Target interaction**

A Enzymes as Drug target

1) Competitive inhibitors - Drug compete with natural substrate for their attachment on the active sites of enzymes
2) Some drugs binds to different site (allosteric site) so that it changes the shape of active site so that substrate can not recognise it

B Receptors as Drug target

1) Antagonists are drugs which bind to the receptor site (to transfer message) and inhibit natural function.
2) Agonists mimic the natural messenger by switching on the receptor. These are useful when there is lack of natural chemical messenger.

- **Based on therapeutic Action**

Antacids reduces acidity in the stomach $NaHCO_3$, $Al(OH)_3$, $Mg(OH)_2$

Cimetidine (tegamet) and ranitidine (Zantac) prevents the interaction of histamine with receptors so that it reduces the production of HCl

Antihistamines : Bromopheniramine (Dimetapp) and terfenadine (seldane). They interact with the natural actions of histamine (Contract smooth muscles in bronchi responsible for nasal congestion associated with cold and allergy)

Antiallergic and antacid drugs work on different receptors **Tranquilizers** (Stress and mental diseases)

Antidepressants drugs such as Iproniazid and phenelzine inhibit the enzyme which catalyse the degradation of noradrenalin (neurotransmitter) Equanil is used in controlling depression and hypertension. Barbiturates such as verenal, amytal, nembutal, luminal, seconal are hypnotic (Sleep producing agents). Valium and serotoxin are others.

- **Analgesics** reduces or remove pain with out causing mental confusion

Aspirin and paracetamol are non – narcotic type. Aspirin inhibits synthesis of prostoglandins which stimulate inflammation in the tissue to cause pain. Aspirin is also antipyretic and prevent platelet coagulation (Used to prevent heart attacks). Morphine, heroine, codeine (habit forming drugs are narcotic type.

- **Antimicrobials**

a) **Antibiotics** are chemicals produced by microorganisms (bacteria, fugi and molds) that inhibit the growth or even destroy micro organisms. Salvarsan (arsphenamine) is used for treatment of syphilis. Other examples are prontosil and sulphadrugs (Sulphapyridine)

Bactericidal (Killing)	Bacteriostatic (Inhibit)
Pencilline (by Alexander Fleming), Aminoglycosides, ofloxacin	Erthromycin Tetracycline, Chloramphenicol

Antibiotics which kill or inhibit wide range of gram positive or gram negative bacteria are **broad spectrum**. Antibiotics (Ampicillin, Amoxycillin, Chloram phenicol, Vancomycin ofloxacin). If effective against a single organism or disease are **narrow spectrum** antibiotics (dysidazirine o-is toxic for certain type of cancer cells, pencillin – G)

Antiseptics and **disinfectants** are also the chemicals. Which kill or prevent the growth of micro organisms. Antiseptics are not harmful to human tissues (applied to living tissues).

Dettol (mixture of chloroxylenol and terpinol in a suitable solvent) 2-3 Iodine in alcohol – water mixture (TinctureIodine) CHI_3 (Iodoform, wound powder). Bithional (in sopas) Boric acid (for eyes), Soframycine, 02% pehonol disinfectants are used for in animate objects (are harmful for human tissues) 1% phenol, Aqueous Cl_2 (0.2- 0.4 ppm) dilute SO_2 solution Antitertility drugs (birth control) eg : norethindrone (Progesterone derivative) Novestrol (ethynyl estradiol) is estogen derivative.

Chemicals in food

- **Artificial sweeteners**

  Saccharin (ortho – sulpho benzimide) 550 times as sweet as cane sugar. It is excreted from the body in urine unchanged (taken by diabetic patients)

  Aspartame (100 times) used in cold foods, Alitame (22800 times) Sucrolose (600 times, thermally stable)

- **Food preservatives** (sodium benzoate, salts of sorbic acid and propionic acid salt, sugar, CH_3COOH etc...
- **Anti oxidants** (retarding the action of oxygen in food

  BHT (butylated hydroxy toluene) and BHA (Butylated hydroxy anisole)

- **Cleaning agents**

  Soaps : Mixture of sodium salt of higher fatty acids, prepared from oils and fats by treating with aqueous NaOH (Saponification). Soap is precipitated by adding salt (Salting out of soap).

  $C_{17}H_{35}COONa$ (Sodium stearate)

  Potassium soaps are more soft, transparent soaps are made by dissolving the soap in ethanol and then evaporating the excess solvent, shaving soaps contains glycerol to prevent rapid drying and rosin which produce more lather. Laundry soap contains fillers like sodium carbonate, borax, sodium silicate and sodium rosinate Ca^{2+} Mg^{2+} cause precipitation of soap as corresponding salt Eg: $(C_{17}H_{35}COO)_2Ca$.

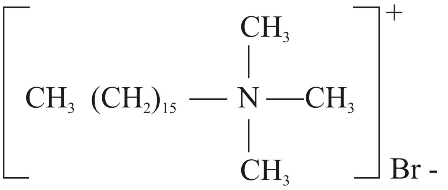
  Synthetic detergents : they can be used both in Soft and hard water.

Anionic detergents : Anionic part involved in cleansing action.

$CH_3(CH_2)_{10}CH_2OSO_3^- Na^+$ (Sodium lauryl sulphate)

$CH_3(CH_2)_{11}$  $SO_3^- Na^+$ (sodium dodecyl benzene sulphonate) they are used in toothpastes and other house hold work.

Cationic detergents : Cationic parts are involved in cleansing action



$$\left[CH_3(CH_2)_{15} - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}} - CH_3 \right]^+ Br^-$$

Cetyl trimethyl ammonium bromide

If has germicidal properties and used in hair conditioners.

Non ionic (Liquid dish washing detergents)

Its cleansing action is due to micelle formation. Bacteria cannot degrade this due to highly branched hydrocarbon chain.

$CH_3 (CH_2)_{16} COO (CH_2CH_2O)_n CH_2CH_2OH$

formed by stearic acid reacts with ethylene glycol

$[CH_3 (CH_2)_{16} COOH + nHO - CH_2–CH_2–OH]$

***