Annamacharya Institute of Technology and Sciences, Tirupati
(Autonomous)
<u>Chemistry Material</u>
Subject Code: 20ABS9904
(AK20 Regulations)
(Common to CSE, ECE, CIC and EEE)

UNIT—1

STRUCTURE AND BONDING MOLECULES

Introduction:

All atoms except hydrogen atom are composed of three fundamental particles namely electron, protons and neutrons. A bonding model is a theoretical model used to explain atomic bonding structure, molecular geometry properties and reactivity of physical matter.

Plank's quantum theory:

1. Different atoms and molecules can emit or absorb energy in discrete quantities only. The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum or photon.

2. The energy of the radiation absorbed or emitted is directly proportional to the frequency of radiation

$$E = h\nu = \frac{hc}{\lambda}$$

Where E =energy of the radiation

h =planks constant (6.626*10^-34 J.S)

c =velocity of light

λ =wavelength

1/λ =v   E =hcv

v=wavenumber

Dual nature of matter:

Einstein had suggested that light has dual character, i.e as wave and also as particle. Lewis de-broglie proposed that electrons also a dual character, as a wave and as a particle.

De-broglie equation: If a particle of mass 'm' moving with velocity 'v', then the wave length of this moving particle is given by

$$\lambda = h/mv$$

where   h = planks constant

m = mass of particle

v = velocity of particle

According to planks quantum theory

$$E = h\nu \qquad\qquad\qquad equation(1)$$

According to einsteins energy mass relation, the energy E of the photon is given by

$$E = mc^2 \qquad\qquad\qquad equation(2)$$

Where   m = mass of photon

C = velocity of light

From equation (1) and equation (2)

$$h\nu = mc^2$$

$$hc/\lambda = mc^2$$

$$h/\lambda = mc$$

$$\lambda = h/mc = h/p \qquad\qquad \text{equation(3)}$$

where p = mc is the momentum of photon having mass 'm' and travelling with velocity 'c' . The above equation is known as the de-broglies wave equation.

Uncertainty principle :

The wave nature of particle is further explained by Heisenbergs uncertainty principle. It is impossible to measure exactly and simultaneously both position and momentum of a particle and momentum respectively when they are simultaneously measured.

$$\Delta x.\Delta p \geq \hbar/2 \qquad\qquad \text{where } \hbar = h/2\pi$$

An attempt to reduce Δx will raise Δp and vice-versa.

This is the consequence of diffraction of electron.

Schrodinger Wave Equation:

Schrodinger derived a mathematical equation to derive the dual nature of matter waves.

Definition: The mathematical equation that describes the wave of a particle is known as schrodinger wave equation

Schrodinger time independent wave equation:

If a particle of mass 'm' moving with a velocity 'v' is associated with a group of waves , let Ψ be the wave function of the particle. Also let us consider a simple form of progression wave like the one represented by equation

$$y = A\sin(\omega t - kx) \qquad\qquad (1)$$

$$\Psi = \Psi_o \sin(\omega t - kx) \qquad (2) \qquad$$

Where $\Psi = \Psi(x, t)$ and

Ψ_o is amplitude

And ω = angular frequency

K = angular wave number, $k = 2\pi/\lambda$

y = displacement

A = Amplitude

So, $\Psi = \Psi_o \sin(\omega t - kx)$

Differentiating with respect to x

$\partial \Psi / \partial x = \Psi_o \cos(\omega t - kx)(-k)$

Again differenciating with respect to x

$\partial^2 \Psi / \partial x^2 = -\Psi_o \sin(\omega t - kx)(k^2)$

$\qquad = -k^2 \Psi_o \sin(\omega t - kx)$

$\qquad = -k^2 \Psi$

And since $k = 2\pi/\lambda$

$\partial^2 \Psi / \partial x^2 = -4\pi^2/\lambda^2 \ \Psi$

From de-broglie wavelength expression

$\lambda = h/mv$

By substituting

$\partial^2 \Psi / \partial x^2 = -4\pi^2 . m^2 v^2 / h^2 \ \Psi$

We know total energy of a particle is sum of kinetic energy (k) and

 Potential energy (v)

 i.e. E=k+V

    E-V=k

    E-V=1/2mv²

    2(E-V)=mv²

    2m(E-v)=m²v²   (by multiplying with m)

 So by substituting

$\partial^2\Psi/\partial x^2 = -8\pi^2 m(E-V)/h^2.\Psi$

In quantum mechanics, the value h/2π occurs most frequently. Hence

We denote ħ =h/2π   Where ħ=reduced plank constant

 Using this notation, we have

 $\partial^2\Psi/\partial x^2+2m(E-V)/\hbar^2\Psi=0$

For simplicity, we considered only one dimensional wave extending
equation for three dimensional wave

 $\partial^2\Psi/\partial x^2+\partial^2\Psi/\partial y^2+\partial^2\Psi/\partial z^2+2m(E-V)/\hbar^2.\Psi=0$ Where Ψ=Ψ(x,y,z)

Here, we have considered only stationary states of Ψ, after separating
the time dependence of Ψ

 Using laplacian operator

 i.e. $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$

Equation can be written as

$$\Delta^2\Psi + 2m(E - V)/\hbar^2\ \Psi = 0$$

∇This is schrodinger wave equation. Since time factor doesn't appear, it is called time independent wave equation

(b) schrodingers time dependent wave equation:

Let us consider a particle of mass 'm' moving with a velocity 'v'.Let ψ be the wave function of a particle along x-direction at anytime.

The classical differencial equation of wave motion is given by

$$\partial^2\Psi/\partial x^2 = 1/V^2 \cdot \partial^2\Psi/\partial t^2 \qquad \text{------------------(1)}$$

The solution for equation (1) is assumed to be

$$\Psi = \Psi_o e^{-i\omega t} \qquad \text{------------------(2)}$$

Differentiating equation (2) with respect to "t"

$$\partial\Psi/\partial t = \Psi_o e^{-i\omega t}(-i\omega)$$

$$= -i\omega\Psi \qquad \text{--------------------(3)}$$

But $E = h\nu = h(\omega/2\pi)$

$$= (h/2\pi)\omega$$

E= ℏω

i.e ω=E/ℏ   -----------------(4)

 Substituting (4) in (3)

$\partial\Psi/\partial t = -(iE/ℏ)\Psi$

       $= (E/iℏ)\Psi$

 ie. $E\Psi= iℏ. \partial\Psi/\partial t$ --------------(5)

Substituting eq (5) in schrodinger time independent one dimensional wave equation, we get

 $\partial^2\Psi/\partial x^2+2m/ℏ^2(E-V)\Psi=0$ --------------(6)
 $\partial^2\Psi/\partial x^2+2m/ℏ^2(E\Psi-V\Psi)=0$

 $\partial^2\Psi/\partial x^2+2m/ℏ^2(iℏ(\partial\Psi/\partial t)-V\Psi)=0$

 Multiplying ℏ/2m on both sides

 ie. $ℏ^2/2m(\partial^2\Psi/\partial x^2)+(i.(\partial\Psi/\partial t)-V\Psi=0$

$ℏ^2/2m(\partial^2\Psi/\partial x^2)-V\Psi= -iℏ.(\partial\Psi/\partial t)$ ----------------(7)
$- ℏ^2/2m(\partial^2\Psi/\partial x^2)+V\Psi=iℏ.(\partial\Psi/\partial t)$

This equation(7) is known as schrodinger time dependent one dimensional wave equation.   or $H\Psi=E\Psi$

Where $H= -ℏ^2/2m\ \partial^2/\partial x^2+v$ is called hamilton operator and $E=iℏ\partial/\partial x$ is called energy operator.

→ Significance of Ψ and Ψ^2:

 The wave equation Ψ associated with a moving particle is not observable quantities and does not have any direct physical meaning. It is a complex quality. This can represent the probability density of locating the particle at a place in a given instant of time. In all wave equation the square of the wave function is the property which has physical significance. In case of light wave, square of the amplitude of the wave at a point is proportional to the intensity of the light wave. Similarly in electron wave maltron Ψ^2 should represent intensity. According to uncertainty principle greater is the probability of locating the electron at the point. Thus Ψ^2 may be interpreted as being proportional to electron density. The wave function Ψ may be positive, negative or imaginary but the probability density Ψ^2 will always be positive and real. The probability of finding the electron is finite, which means $\Psi^2 dt$ must gives real values.

$\Psi = a + ib$ $\qquad\qquad$ (where a, b are real numbers)

$\Psi^* = a - ib$

$\Psi\Psi^* = |\Psi|^2 = a^2 + b^2$

(b) Applications of schrodinger wave equation:

For multi electron system schrodinger wave equation does not give exact solution, but may be exactly solved with reason able accuracy using some approximation.

 The hydrogen atom is the simplest atom consisting of electron and a proton, is a two particles around their centre of mass is equivalent to the motion of the single particle with a reduced mass. The reduced

particle is located at T. r is the distance between proton and electron in terms of cartesian coordinates its position is (x,y,z) while in terms of spherical symmetry and cartesian units can't measure directly, so it is better to use polar coordinates to solve schrodinger wave equation. The schrodinger wave equation for the hydrogen atom

$$\hat{H}(r,\theta,\phi)\ \Psi(r,\theta,\phi)=E\Psi(r,\theta,\phi)\qquad \text{---------------(1)}$$

For hydrogen atom the distance 'r' between the two particles can vary the hydrogen atom hamiltanian also contain a potential energy term $\hat{v}$ to describe the attraction between proton and electron. This term is coulomb potential energy.

$$\hat{V}(r)= -e^2/4\pi\varepsilon_o r \qquad \text{where r is the distance between proton and electron}$$
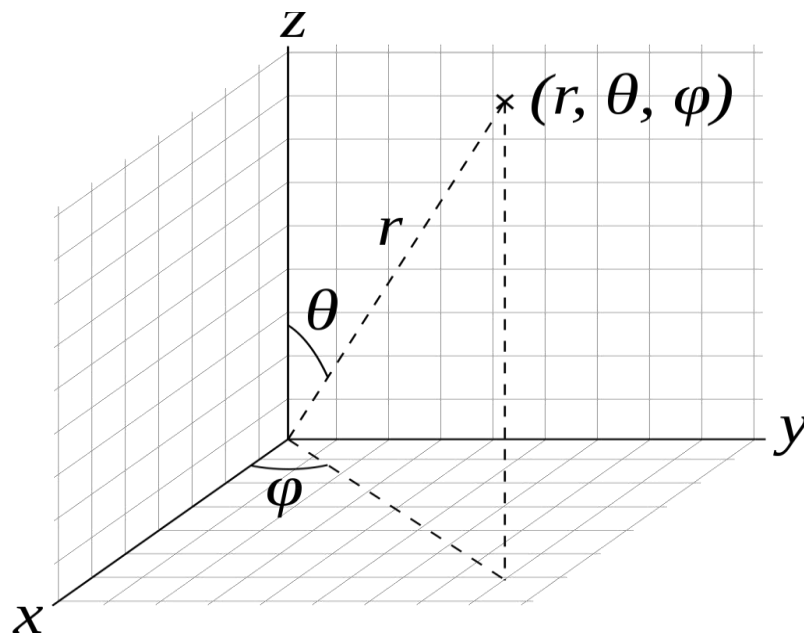
The coordinates are related to each other, r is measured between 0 and π and φ is measured between 0 to 2π

$$X = r\sin\theta\cos\phi$$

$$\cos\phi = x/r\sin\theta$$

Y = rsinɵsinø

Sinø = y/rsinɵ

Z = rcosɵ

$r^2 = x^2+y^2+z^2$

The schrodinger time independent wave equation for an element around a positively charged nucleus is then

$\{-\hbar^2/2\mu r^2 [\partial/\partial r(r^2.\partial/\partial r)+1/sin\theta.(\partial/\partial\theta)+1/sin^2\theta.\partial^2/\partial\phi]-e^2/4\pi\varepsilon_\circ r\}\Psi(r,\theta,\phi)$
r=radical variable, ɵ, φ are angular momentum variable since the angler momentum variable does not involve the radical variable 'r' we can separate variable in the above equation by using a product wave function.

$\Psi n,l,m(r,\theta,\phi)= Rn,l(r) yl,m(\theta,\phi)$

Ψ-atomic orbital

R value represent radical part of momentum.

Y-angular part of the momentum

The spherical harmonic y(ɵ, φ)function provides information about where the electrons is around the proton, and the radial function R(r) describe show for electron is away from proton.

The hydrogen atom wave function, Ψ(r,ɵ,φ) are called atomic orbital is a function that describes one electron in an atom. The wave function with n=1, l=0 is called the 1s orbital, and an electron that is described by this function is said to be in the "1s" orbital.

When n=1   l=0   m=0

n=2   l=1   m=-1, 0, 1

n=3   l=2   m= -2,-1, 0, 1, 2

The constraints on n, l, m that are imposed during the solution of hydrogen atom schrodinger equation.

Applications of Schrodinger's wave equation:

→ lt helps us to know Bohr quantum number (i.e. principle Quantum number)

→ It helps us for finding a particle in one dimensional box .

→ It is also used for calculation of energy level.

→ It also explains band theory(semiconductors, conductors and insulators)

a) Particle in an infinite potential well (or) potential box:

Consider a particle of mass 'm' moving back and forth between the walls of a one dimensional box separated by a distance 'a' as shown in figure. Let the particle travel along the x–axis and is confined between x=0 and x=a by two infinitely hard walls so that the particle has no chance of penetrating them. Thus it doesn't lose energy and it is total energy remains constant. This box is represented by a potential box of width 'a' with potential box of width 'a' with potential walls of infinite height at x=0and x=a, so that the potential energy 'v' of the particle is infinitely high on both sides of the box inside it 'v' is uniform.
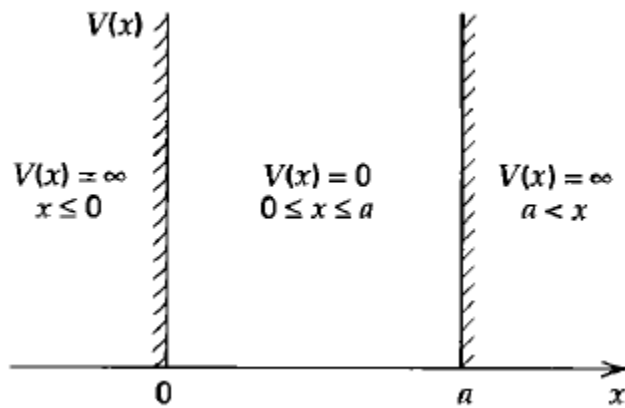
Let us assume that v = 0 inside the box

$$V(x) = 0 \qquad \text{for } 0 < x < a$$

$$V(x) = \infty \qquad \text{for } x \leq 0 \text{ and } x \geq a$$

Then the wave function Ψ(x) of the particle in the region $0 < x < a$ where v=0 is described by Schrodinger's one dimensional time independent wave equation i.e,

$\partial^2\psi/\partial x^2 + [2m(E-v)\psi(x)]/\hbar^2 = 0$

$\partial^2\psi/\partial x^2 + [2m(E-V)/\psi(x)]/\hbar^2 = 0$

Since v=0 by substituting " v=0" in the above equation
$\partial^2\psi/\partial x^2 + 2mE\psi(x)/\hbar^2 = 0$

i.e. $\partial^2\psi/\partial x^2 + k^2\psi(x) = 0$ ---------→ ①

Where $k^2 = 2mE/\hbar^2$ or $K = \sqrt{2mE}/\hbar^2$

The solution of above equation is given by

$\psi(x) = A\sin(kx) + B\cos(kx)$ ----------→ ②

When A and B are arbitrary constants applying the first boundary condition

i.e. at x=0 and ψ(x)=0

ψ(x)=Asin(0)+BCos(0)

0=0+B

B=0

New when x=a, ψ(x)=ψ(a)=0

ψ(x) = Asin(ka)   (SinceA≠0)

sin(ka)=0

We know that k=nπ/a

Sin(nπ/a)a=0   Where n value is equal to 1,2,3…………….

 We cannot take n=0 because for n=0, k=0, E=0 here ψ(x)=0 everywhere in the box. Thus the particle with zero energy cannot be present in the box i.e. a particle in the box cannot have zero energy. The wave function for the motion of the particle in the region 0<x<a are given by

$$ψ_n(x) = AsinKx$$

$$ψ_n(x) = Asin(nπx/a)$$

Eigen values of energy:

We know that $K^2 = (2m/ℏ^2)E$

$$E = K^2ℏ^2/2m$$

$$But\ K = n^2π^2/a^2$$

$$E = (n^2\pi^2/a^2) \qquad\qquad (\hbar = h/2\pi)$$

$$E = [n^2\pi^2/a^2][h^2/8\pi^2 m]$$

$$E_n = n^2 h^2/8ma^2$$

From the above equation it is clear that

i. The lowest energy of the particle obtained by putting $n=1$
i.e. $E_1 = h^2/8ma^2$ and $E_n = n^2 E_1$

This is known as zero point energy of the system

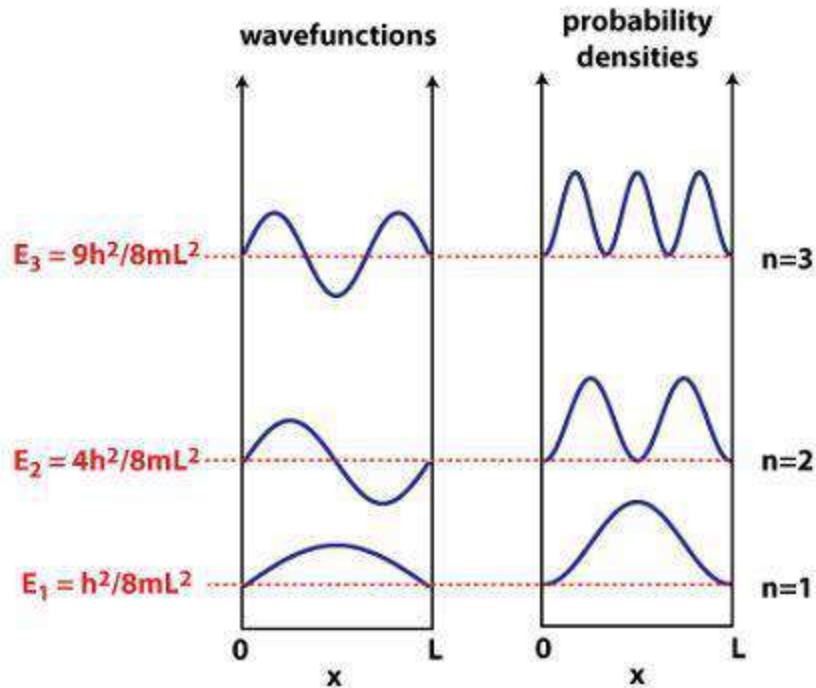ii. For $n=1, 2, 3$ we get discrete energy values of the particle in the
box $\qquad E_1 = h^2/8ma^2 \qquad\qquad E_2 = 2^2 h^2/8ma^2 = 4E_1$

$$E_3 = 3^2 h^2/8ma^2 = 9E_1$$

The spacing between then the energy level and next higher level
increases as $(n+1)^2 E_1 - n^2 E_1 = (2n+1) E_1$

iii. These values of E_n are known as Eigen functions of the particle.
The integer 'n' is the quantum number of energy.

iv. In the figure given below shows us the energy level diagram for
the particle

wavefunctions

probability densities

$E_3 = 9h^2/8mL^2$

$E_2 = 4h^2/8mL^2$

$E_1 = h^2/8mL^2$

n=3

n=2

n=1

0 L

x

0 L

x

Eigenfunctions:-

The eigen wave function for the motion of the particle in the region 0<x<a   is Ψn(x) = Asin(nπx/a)

Ψn(x) = 0   in region x≤0 and x≥a

The total probability that the particle is some in the box must be unity

$$\int Pxdx = \int |\Psi(x)|^2 dx = 1$$

$$\int A^2 \sin^2(n\pi x/a)dx = 1$$

$$A^2 \int 1/2[1-\cos 2n\pi x/a]dx = 1$$

$$A^2/2[x-a/2\pi m \sin(2\pi nx/a)] = 1$$

The second term becomes zero at both the limits

Therefore, $A^2a/2=1 \rightarrow A=\sqrt{2}/a$

The wave functions are shown in above figure

The wave function ψ_1 has two nodes at x=0 and x=a.The wave function ψ_2 has three nodes at x=0, x=a/3, x=2a/3 and x=a

Thus $\psi_n(x)$ has (n+1) nodes.

Schrodinger equation application to conjugated molecule:

The π electrons in a conjugated molecule to be constructed according to the aufbau principle. for example if the conjugated molecule shown below is considered the orbital energy diagram become energy
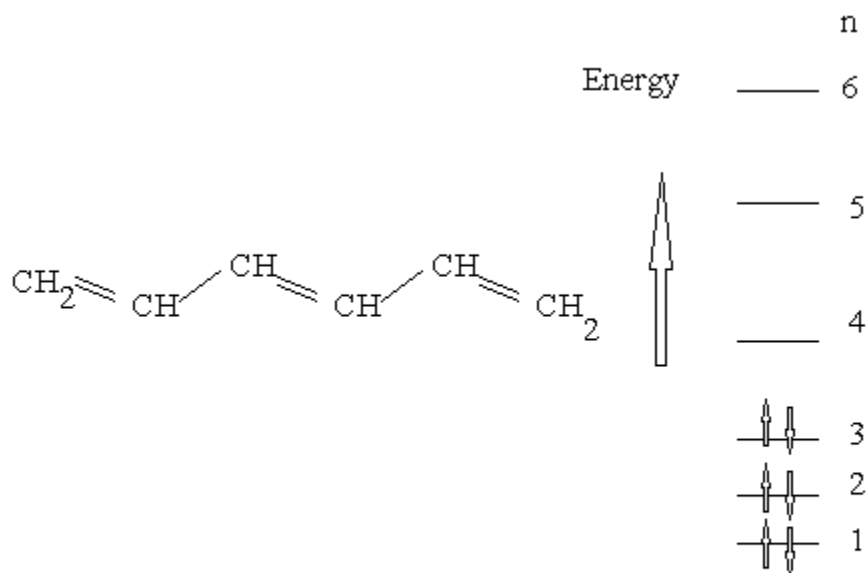
Here in this case there are 6π electrons. Where eau carbon is sp² hybridized and thus contributes a p orbital and one π electron to the system. The lowest energy configuration called the electronic ground state, corresponds to the 6e⁻ beingin the lowest three orbitals. Higher energy configurations are constructed by promoting an electron from (for example) the highest filled orbital (HFO) to a higher vacant orbital. This higher energy arrangement is called an electronically excited state. The lowest or first electronically excited state, is achieved by promotion of an electron from the HFO to the lowest unfilled orbital (LVO).The energy difference between these states is simply given by the following expression

$$\Delta E = E_{LVO} - E_{HFO} = h^2/8mL^2(n^2_{LVO} - n^2_{HFO})$$

The energy required for this electronic transition can be supplied by a photon of the appropriate frequency, given by the plank relation.

$$E = h\nu = hc/\lambda$$

Where h is plank's constant, ν is frequency, c is the speed of light λ is the wavelength.

CRYSTAL FIELD THEORY

Crystal field theory was first developed by physicists BETH and vanvleck in the year 1930 and explain the colour and magnetic properties ceystalline solid. In 1951 several chemists used the crystal field theory to interpret the spectral of transition metal complex.

Sailent features:

1. The bond between metal and ligand in a metal complex is assumed to be 100% ionic.

2. The interaction between metal and igands are consider as ion-ion attraction Or ion-dipole attraction.

3. The metal ligand bond energy can be calculated by the following expression

   Bond energy = -q1q2/2.

4. The theory mainly concerns with the metal orbital and their electrons.

5. The interaction between metal and the ligand is repulsive.

6. The d-orbital is free metal will have same ground state. They are degenerate in free state Or ground state. In the presence of ligands these degenerate d-orbital of transition metal splits into various sets depending on the orientation of ligands around the metal. This type of splitting of d-orbitals and the metal into different sets in the presence ligands approaching the metal is termed as crystal field splitting. The crystal field splitting is the basis for crystal field theory.

   In order to understand the crystal field theory. It is necessary to have a clear idea about the special orientation of the d-orbital of the transition metal.

        The transition metal has the degenerate d-orbital dxy, dyz , dxz , dx^2-dy^2 , dy^2. In this case of three d-orbitals dxy, dyz, and dxy the electrons cloud is oriented in the form of double dumbbell shape between the axis.

- In the other two orbital $dx^2\text{-}dy^2$ and dy^2 the electro cloud is oriented in the form of double dumbbell along the axis. These two orbital are designatd as eg or dz orbital. The shapes of five d-orbital is as shown below
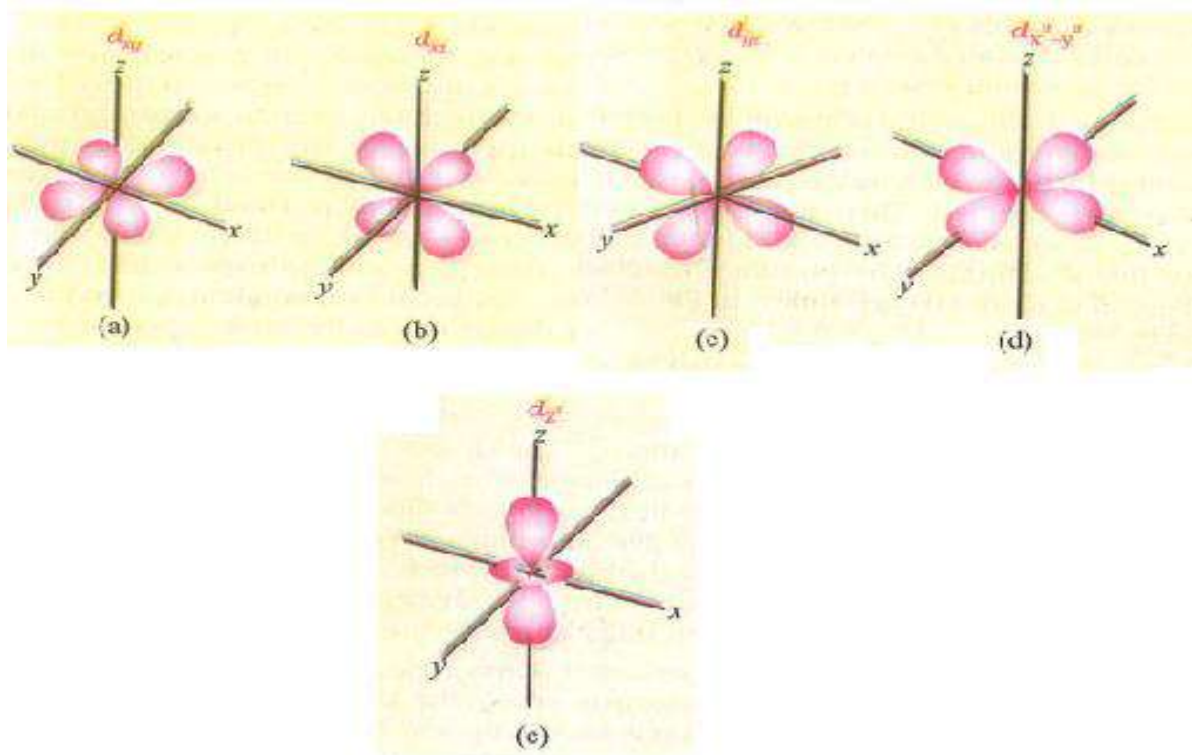
6. The number of ligads and the arrangements about metal ion will predict the crystal field the metal ion will predict the crystal field .If there are six ligands octahedral crystal fieldis formed.

- Four ligands – Tetrahedral Or Square planer.
- Five ligandsv – Square pyramidal Or trigonal.
- Three ligands – Trigonal planer.
- Two ligands – Linear crystal field.

7. It consists of electro static aattraction forces between metal ion and ligand.

8.The metal complexes is positively charged metal is

surrounded by the ligand molecular with their negative ends.

MERITS OF CRYSTAL FIELD THEORY

1. It explains the formation of complex having different geometrics.
2. It explains the formation of high-spin or spin free and low-spin or spin-paired octahedral complexes.
3. This theory explains the magnetic properties of complexes.
4. Crystal field theory explains the inertness and also lability of complexes.
5. This theory explains colours associated with complexes.
6. Crystal field theory explains the spectral properties of compound based on d-d transitions.
7. It helps in predicting the structure of spi.
8. It explains why certain complexes are distortion.
9. It explains certain kinetic and thermodynamic properties of complexes.

## DRAWBACKS OF CRYSTAL FIELD THEORY

1. Ligands are considered as point charge .Due to importance is not given to ligands as chemical species. Only the effect of ligands on the metal orbital is considered.
2. The covalent nature of metal-ligands bonds in complex is totally ignored even though there is an evidence for covalent bond contribution.

   EX: ESR spectrum of $Ircl6^{2-}$.

3. This theory does not consider the formation of π-bonding in complex.
4. This theory fails to explain the relative strengths of ligands CO,CN->NO2>CN >C5H6N>NH3>H2O>C2O>4^{2-}>OH>F>Scn>cl>Br>I. Crystal field theory gives no explanation why the negatively charged oH- is a weaker ligand than natural ligand H2o.
5. It does not explain the charge transfer bond and the intensities.

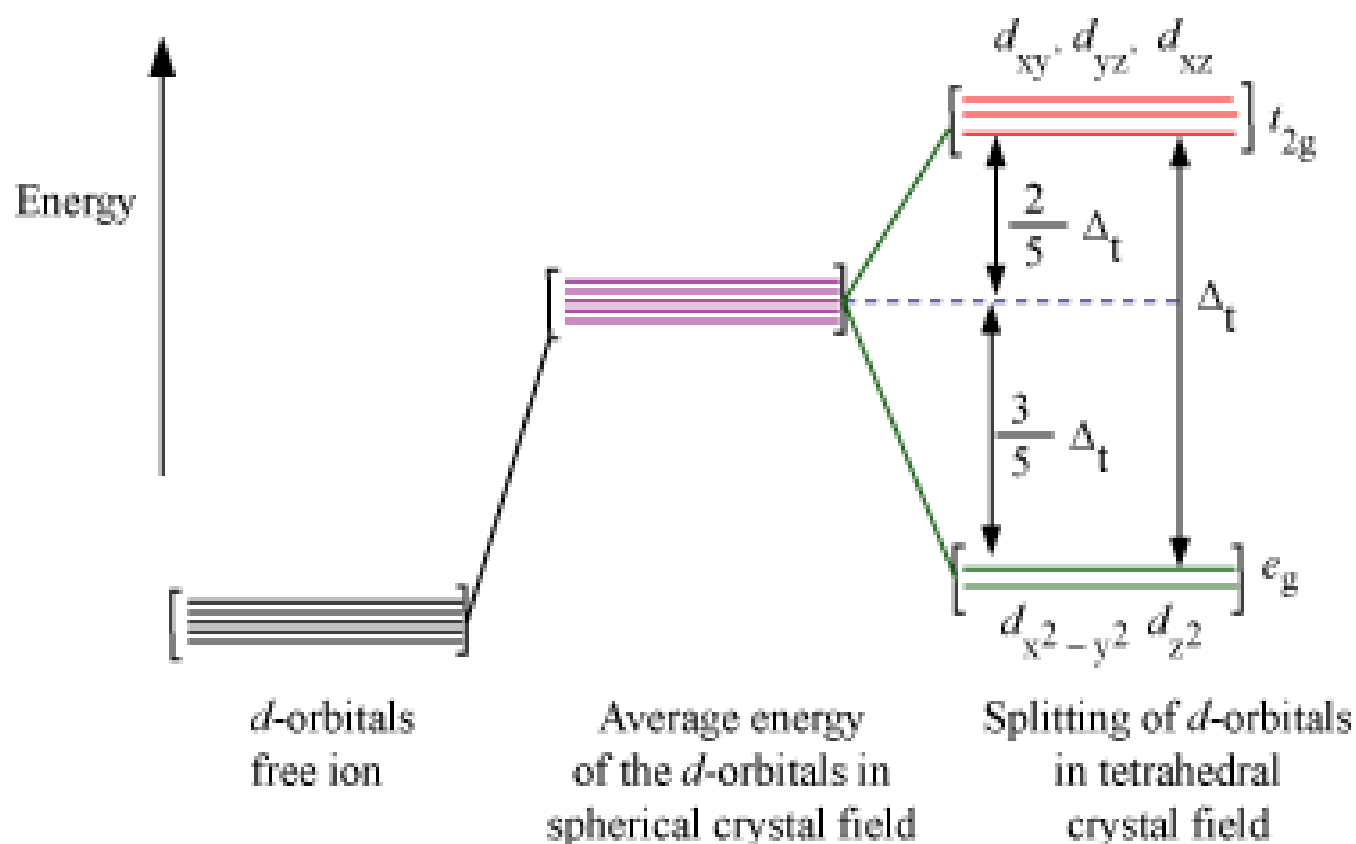## CRYSRAL FIELD SPLITTING OF METAL ORBITAL IN OCTAHEDRAL FIELD

The co-ordination number of an octahedral complex is six. In octahedral complex the metal ion is at the central and six ligand at the six corner of an octahedral as shown below
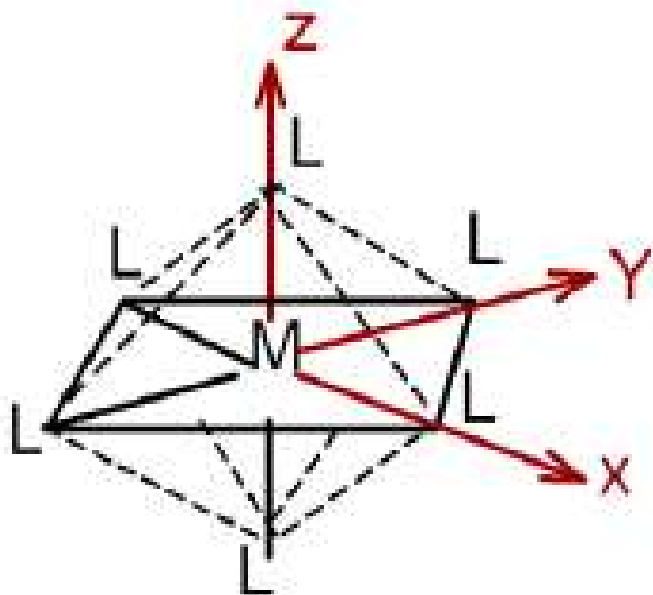
octahedral geometry
having central metal M &
six ligands at vertices

Six ligands at the corner of an octahedron surround the metal ion.

In octahedral geometry the six ligands approach the central metal ion along x,y and z axis, two ligand along x-axis, two along y-axis and two along z-axis. Under these conditions the ligands undergo strong repulsive interaction with two eg orbital's of metal/metal ion (i.e. $dx^2 - y^2$, dz^2) which are present in the same path as ligands are approaching the metal ion. As a result eg orbital are stabilized and occupy high energy (3/5*10=6Dq) the other three t2g orbital of metal ion. In which in between the axis will receive less repulsion. So these three t2g orbital we stabilized by occupying lower energy 0.4Δ

d-orbitals free ion	Average energy of the d-orbitals in spherical crystal field	Splitting of d-orbitals in tetrahedral crystal field

The energy difference between the split up orbital sets t2g and eg is called crystal field splitting energy .It is denoted by $\Delta°$. It value is equal to 10Dq. D is the polarizability of the metal 'q'is the ligand field strength

The above mentioned crystal field denotes that each electron occupying t2g orbital decreases the energy of d-orbital by $0.4Dq$ each electron occupying eg orbital increases the energy of d-orbital by 6Dq

Crystal field theory of an octahedral complex can be calculated by the following expression

C.F.S.E = nt2g(-0.42Δ)+neg(0.6Δ)tmp

Or

C.F.S.E=nt2g(4Dq)-neg(6Dq)temp

nt2g,neg denotes the number of electron present in t2g and eg orbital respectively

m=Number of paired electron

p= pairing energy

## CRYSTAL FIELD SPLITTING OF METAL d-ORBITAL IN TETRAHEDRAL FIELD

The splitting of d-orbital in a tetrahedral complex can be understand by inserting tetrahedron inside a cube as shown below. The coordination number of metal in tetrahedral complex is 4. In the tetrahedral complex the metal is at the centre of a cube and four ligand occupy four corner of a cube out of eight corner

(a)   (b)
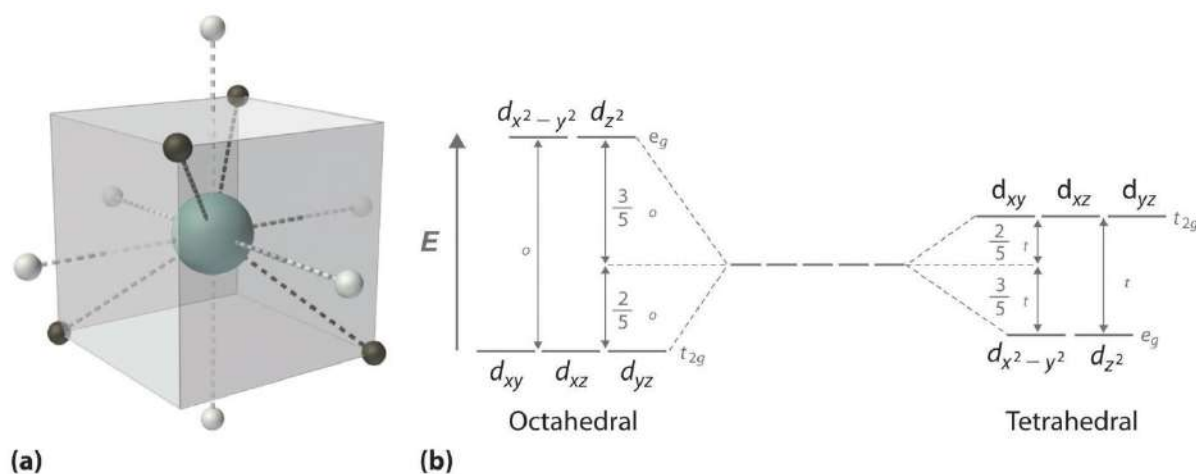
(TETRA HEDRAL INSIDE A CUBE)

The above mentioned tetrahedral arrangement reveals that no d-orbital of the metal directly interact with ligand. It so become that the t2g orbital of metal which are present in between axis are nearer to the ligand as they lie in an angle 35°16 with the ligands then the eg orbital present along the axis which lie on angle of half tetrahedral angle(i.e.109°28=54°44) with the ligand

Hence the t2g orbital receive greater repulsive interaction and occupy the higher energy level similarly the eg orbital are stabilized by occupying lower energy level as they receive less repulsive interaction with the ligands . The energy difference between eg and t2g orbital sets in tetrahedral is denoted notation Δt. The magnitude of 10Dq in tetrahedral complexes is considerably 4/9 times less than the half of octahedral complexes. The splitting of d-orbital of metal in tetrahedral field is shown below
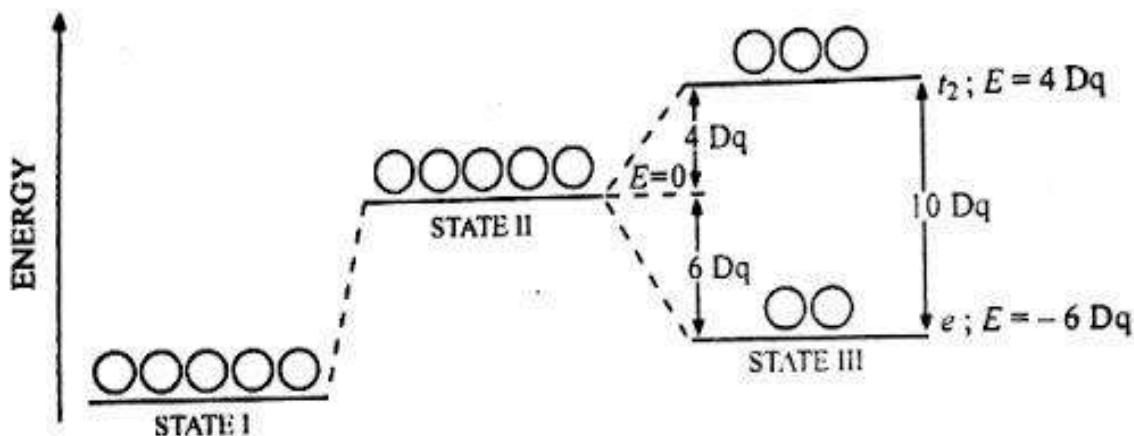
The magnitude of 10Dq in tetrahedral complex is considerably 4/9 times less than that of octahedral complexes due to following reason

1. The coordination number of ratio between tetrahedral complexes and octahedral complexes is 4/6=2/3. Hence the C.F.S.E in tetrahedral field is lowered by 2/3 of octahedral due to the less number of ligands.
2. In the tetrahedral field , the direction of the d-orbital of metal does not coincide with the direction of the ligand just in the octahedral field. Hence this component also will reduce tetrahedral C.F.S.E by 2/3 of octahedral energy .Hence in tetrahedral complexes the CFSE of octahedral complexes as shown below

$$\Delta t=(2/3)(2/3)=4/9\Delta.$$

COLOUR OF TRANSITION METAL COMPLEXES

C.F.T provides an explanation for color exhibition by transition metal complexes. When light radiation of specific wavelength is supplied to a complex, a part of it is absorbed by the complex and rest of light radiation is transmitted by the complex as its complementary

color. This transmitted color is in fact the color of the complex concerned. This phenomenon will occur due to d-d transition.

EX:

COMPLEX	COLOUR
[Ti(H2o)6]cl3	Purple Or Violet
[cu(H2o)4]So4	Blue
[Cr(H2o)6]cl3	Violet
[Co(NH3)5No2]	Yellow
[Co(NH3)5ONO]	Red

UNIT-2

Electrochemistry and Applications

Electro chemistry: -

Electrochemistry is a branch of science that deals with conversion of chemical energy into electrical energy and vice versa.

Electrolyte: -

A substance, which decomposes as a result of passing of electric current is called 'Electrolyte' and the phenomena of decomposition of electrolyte through passage of electricity is called 'electrolysis'.

Concepts of electrolysis: -

(1). A conductor used to electrical contact as a non-metallic part of a circuit.

(2). An element in a semi conductor device (such as a transistor) That emits or collects electrons or holes containing their movement.

Electrode are:-(1) Cathode (+)

(2) Anode (-)

Reference electrodes: -

The electrodes of standard potential with which one can compare the potentials of another electrodes of interest is called reference electrode. The standard hydrogen electrode is used as reference electrode for determined single electrode potential whose potential arbitrarily taken as zero.

Hydrogen electrode: -

It is the primary electrode. It consists of a small platinum strip coated with platinum black to absorb hydrogen gas. A platinum wire welded to the electrode and sealed through a glass tube makes contact with the outer circuit. The platinum strip is surrounded by an outer glass tube which has an inlet for hydrogen at the top and number of holes at the base for the escape of excess gas. The electrode is placed in a dilute solution of an acid. Pure hydrogen gas is then passed into it at one atmosphere pressure. A part of hydrogen gas absorbed by the platinised electrode, while the excess is escapes through the lower holes. Then result an equilibrium between the adsorbed hydrogen on the electrode surface and hydrogen ions in the solution.

$H_2 \rightarrow 2\ H^+ + 2e^-$
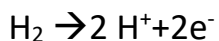
By the potential of the standard hydrogen electrode when hydrogen at one atmosphere pressure is bubbled through a solution of hydrogen ions of unit concentration is arbitrarily fixed as zero. The hydrogen electrode may be used to find the PH of a solution.
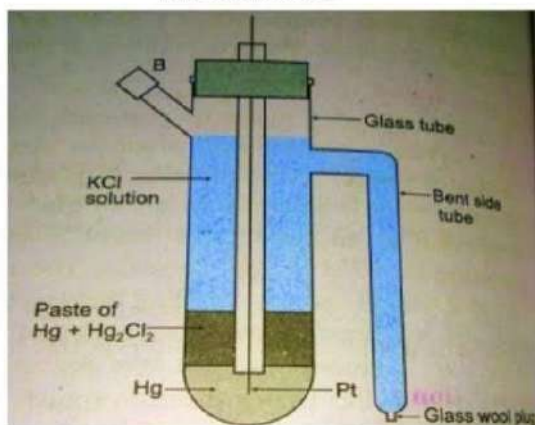
Hydrogen Electrode
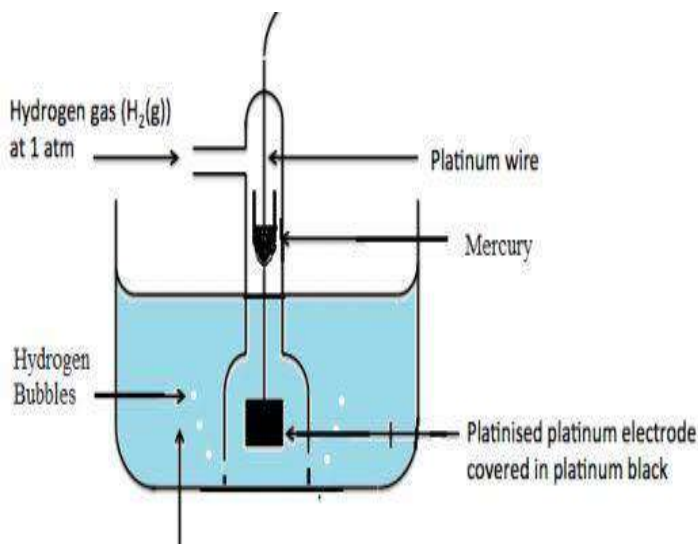
(B). Calomel electrode: -

It is a secondary consists of a glass tube having a side tube on each side mercury of high degree is placed at the bottom of the tube and is connected to the other circuit by means of platinum wire sealed in a glass tube. The surface of chemistry covered with a paste of mercurous chloride (calomel) and mercury in KCL solution. The electrode is also a solution of KCL. The electrode is connected with the help of side tube on the loft through a salt bridge with the other electrode, the potential of which is to be determined.

Calomel electrode:

Secondary electrode or calomel electrode

- The potential of calomel electrode depends upon the concentration of the potassium chloride solution. It has been very accurately determined by connecting it to a

standard hydrogen electrode and the results are obtained for reduction potential of the electrode (Hg/Hg2Cl2) for different concentration of KCL at $24°C$ are given below.

- For 0.1N KCL solution E=+0.3338V

- For 1.0N KCL solution E=+0.2800V

- For saturated KCL solution E=+0.2415V

The positive value indicates that when combined with standard hydrogen electrode, reduction takes place at the electrode.

(C). <u>Silver-silver chloride electrode: -</u>

The silver- silver chloride electrode has recently been employed as a reference electrode in connection with accurate determination of standard potential due to reversible and stable, which can combine with cells containing chlorides without inserting liquid junctions.

For an effective functioning of the electrode, it is necessary that the solution immediate contact with the silver surface is properly saturated by providing a coating of Agcl on the silver. This is done by using the silver electrode as an anode in a chloride solution (KCL or HCL) at low current density for about LaH an hour. The electrode is represented as:
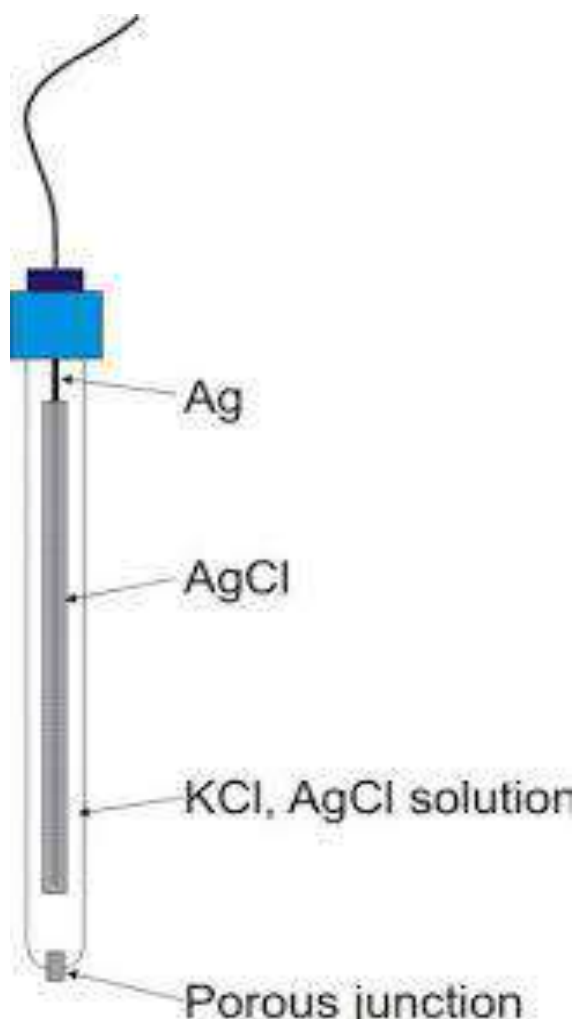
Ag/Agcl(s), H^+Cl^-/H_2 (1atm)
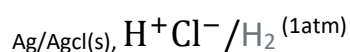
On the hydrogen scale, it is standard reduction potential is found to be +0.2224 Volts at   25°c.

Ag/Agcl (s)cl-;

E°=+0.2224Volts at 25°C.

<u>Silver -silver chloride electrode: -</u>

Ag

AgCl

KCl, AgCl solution

Porous junction

GLASS ELECTRODE:

Glass electrode is a hydrogen-ion responsive electrode usually consisting of a bulb or suitable form of special glass attached to a stim of high resistance glass complete with internal resistance electrode and internal filling solution system.

Glass electrode is also available for the measurement of sodium ions.

The glass electrode which consists of a thin wall glass bulb has an extremely high electrical resistance. The membrane of a typical glass electrode(with a thickness of 0.03mm to 0.1mm)has an electrical resistance of 30Ω to 600Ω.The surface of a glass membrane must be hydrated before it will be function as PH electrode .When a glass surface is immersed in a aqueous solution then a thin solvated layer(gel layer) is formed on

the glass surface in which the glass structure is softer. This applied to both the outside and inside of the glass membrane.
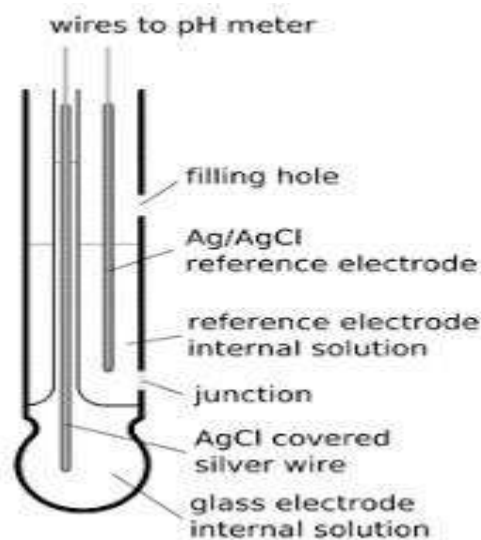
The simplest explanation for the working of the thin glass electrode is that the glass acts as a weak acid.

$$Glass\text{-}H \rightleftharpoons Glass^- + H^+$$

The hydrogen ion activity of the internal solution is held constant. When a solution of different PH forms the inside in contact with the outside of the glass membrane. The glass is either deprotonated or protonated relative to the inside of the glass. The difference in PH between solution inside and outside the thin glass membrane creative electromotive force in proportion to this difference in PH.

Advantages:

i)Used for PH values between 2-10.   ii)Equlibrium is

established quickly.   iii)It is immune to poison.

wires to pH meter

filling hole

Ag/AgCl reference electrode

reference electrode internal solution

junction

AgCl covered silver wire

glass electrode internal solution

BASIC CONCEPTS:

A filter studying this Unit, you will be able to describe an electrochemical cell and differentiate between galvanic and electrolytic cells; apply Nernst equation for Chemical reactions can be used to produce electrical energy, conversely, electrical energy can be used to carry out chemical reactions that do not proceed spontaneously. Calculating the emf of galvanic cell and define standard potential of the cell.

•   Derive relation between standard potential of the cell, Gibbs energy of cell reaction and its equilibrium constant.

•   Define resistivity (ρ), conductivity (κ) and molar ionic solutions; conductivity ($¥$)

•   differentiate between ionic (electrolytic) and electronic conductivity.

- Describe the method for measurement of conductivity of electrolytic solutions and calculation of their molar conductivity.
- Justify the variation of conductivity and molar conductivity of solutions with change in their concentration and define $\Lambda°m$ (molar conductivity at zero concentration or infinite dilution);
- Enunciate Kohlrausch law and learn its applications.
- Understand quantitative aspects of electrolysis.
- Describe the construction of some primary and secondary batteries and fuel cells.
- Explain corrosion as an electrochemical process.

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations. The subject is of importance both for theoretical and practical considerations. A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods. Batteries and fuel cells convert chemical energy into electrical energy and are used on a large scale in various instruments and devices. The reactions carried out electrochemically can be energy efficient and less polluting. Therefore, study of electrochemistry is important for creating new technologies that are eco-friendly. The transmission of sensory signals through cells to brain and vice versa and communication between the cells are known to have electrochemical origin. Electrochemistry, is therefore, a very vast and interdisciplinary subject. In this Unit, we will cover only some of its important elementary aspects.

ELECTROCHEMICAL CELL:

An electrochemical cell is a device in which redox reaction is utilised to get electrochemical energy. This type of cell is commonly known as voltaic or galvanic cell. The electrode where oxidation occurs is called anode, while the electrode where reduction occurs is called cathode. In redox chemical reaction, oxidation can take place only if reduction can also take place at the sometime.

EXAMPLE: -

Zn- C uSO4 solution in a beaker. Oxidation of zinc metal by Cu2 +ions. If a zinc rod is placed in a solution of C uSO4 .The foll owing observation will be made.

$$Zn(s) \rightarrow Zn2 + + 2e- \text{ (oxidation half reaction) ------------(1)}$$ At the same time starts to precipitate out from the solution.

$$Cu2+ + 2e- \rightarrow Cu(s) \text{ (reduction half reaction)------------(2)}$$

The reaction 1 and 2 are called half reactions. The overall reaction is a redox reaction and obtained by adding two half reactions.

$$Zn(s) + Cu2 +(aq) \rightarrow Zn2 +(aq) + Cu(s)$$
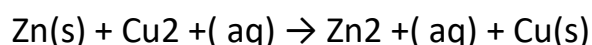
Zn metal can be oxidised by Cu2+ ions. Copper metal cannot be oxidised by Zn2 + Ions.

NERNST EQUATION: The Nernst equation provides a relation between the cell potential of an electrochemical cell, the standard cell potential, temperature, and the reaction quotient. Even under non-standard conditions, the cell potentials of electrochemical cells can be determined with the help of the Nernst equation.

The Nernst **equation is often used to calculate the cell potential** of an electrochemical cell at any given temperature, pressure, and reactant concentration. The equation was introduced by a German chemist Walther Hermann Nernst.

The General Nernst Equation

The general Nernst equation correlates the Gibb's Free Energy ΔG and the EMF of a chemical system known as the galvanic cell. For the reaction
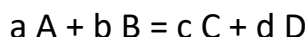
a A + b B = c C + d D

and

$$Q = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

It has been shown that

$$\Delta G = \Delta G° + R\ T \ln Q$$
and
$$\Delta G = -\ n\ F\Delta E.$$

Therefore

$$-\ n\ F\ \Delta E = -\ n\ F\ \Delta E° + R\ T \ln Q$$

where $R,\ T,\ Q$ and F are the gas constant (8.314 J mol^{-1} K^{-1}), temperature (in K), reaction quotient, and Faraday constant (96485 C) respectively. Thus, we have

$$R\ T \quad [C]^c\ [D]^d$$

$$\Delta E = \Delta E° - \frac{}{n\,F} \ln \frac{}{[A]^a\,[B]^b}$$

This is known as the **Nernst equation**. The equation allows us to calculate the cell potential of any galvanic cell for any concentrations. Some examples are given in the next section to illustrate its application.

It is interesting to note the relationship between equilibrium and the Gibb's free energy at this point. When a system is at **equilibrium**, $\Delta E = 0$, and $Q_{eq} = K$. Therefore, we have,

$$\Delta E° = \frac{R\,T}{n\,F} \ln \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}, \quad \text{(for equilibrium concentrations)}$$

Thus, the equilibrium constant and $\Delta E°$ are related.

The Nernst Equation at 298 K

At any specific temperature, the Nernst equation derived above can be reduced into a simple form. For example, at the standard condition of 298 K (25°), the Nernst equation becomes
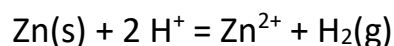
$$\Delta E = \Delta E° - \frac{0.0592\ V}{n} \log \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Please note that log is the logrithm function based 10, and ln, the natural logrithm function.

For the cell

$$\text{Zn} \mid \text{Zn}^{2+} \mid\mid \text{H}^+ \mid \text{H}_2 \mid \text{Pt}$$

we have a net chemical reaction of

$$\text{Zn(s)} + 2\,\text{H}^+ = \text{Zn}^{2+} + \text{H}_2\text{(g)}$$

and the standard cell potential $\Delta E° = 0.763$.

If the concentrations of the ions are not 1.0 M, and the H_2 pressure is not 1.0 atm, then the cell potential ΔE may be calculated using the Nernst equation:

$$\Delta E = \Delta E° - \frac{0.0592\ \text{V}}{n} \log \frac{P(H_2)\,[Zn^{2+}]}{[H^+]^2}$$

with $n = 2$ in this case, because the reaction involves 2 electrons. The numerical value is 0.0592 only when T = 298 K. This constant is temperature dependent. Note that the reactivity of the solid Zn is taken as 1. If the H_2 pressure is 1 atm, the term $P(H_2)$ may also be omitted. The expression for the argument of the log function follows the same rules as those for the expression of equilibrium constants and reaction quotients.

Indeed, the argument for the log function is the expression for the equilibrium constant K, or reaction quotient Q.

When a cell is at equilibrium, $\Delta E = 0.00$ and the expression becomes an equilibrium constant K, which bears the following relationship:

$$\log K = \frac{n\,\Delta E°}{0.0592}$$

where $\Delta E°$ is the difference of standard potentials of the half cells involved. A battery containing any voltage is not at equilibrium.

The Nernst equation also indicates that you can build a battery simply by using the same material for both cells, but by using different concentrations. Cells of this type are called **concentration cells**.

Applications of Nernst equations

1. Nernst equation is used to calculate electrode potential of unknown metal.
2. Corrosion tendency of metals can be predicted.

Electrochemistry problems

1. Calculate the standard emf of the cell; cd(s)/cd^{+2}(aq)//cu^{+2}(aq)/cu and determine the cell reaction ($E°_{cu+2}$/cu= 0.34;$E°_{cd+2}$/cd=-0.40)

    Sol.

    $$E°_{cell} = E°_{cell}(Right) - E°_{cell}(Left)$$

    $$= E°_{cu+2}/cu - E°_{cd+2}/cd$$

    $$= 0.34 - (-0.40)$$

    $$= 0.74\ \text{volts}$$

Cell reaction: $cd \leftrightarrow cd^{+2} + 2e^-$ (oxidation)

$$cu^{+2} + 2e^- \rightarrow cu \text{ (Reduction}$$

$$\underline{Cd + cu^{+2} \leftrightarrow cd^{+2} + cu}$$

2. Calculate the emf of the cell represented the cell as as $Zn/Zn^{+2}// H^+/H_2$ at $[E_{zn}^{+2}(Zn = -$
   (0.7618v)

   Sol: $\qquad\qquad E^0_{cell} = E^0_{Right} - E^0_{Left}$

   $\qquad\qquad =0-(-0.7618V)$

   $\qquad\qquad =+0.7618V$

3. Calculate the emf of the cell $Cd/Cd^{+2}//Cu^{+2}/Cu$ at 25^0c. The standard reduction
   potential of cadmium and copper electrodes are -0.40 and 0.34volts respectively

   Sol: $\qquad\qquad\qquad\qquad E^0_{cell} = E^0_{Right} - E^0_{Left}$

   $\qquad\qquad\qquad\qquad = 0.34-(-0.40)$

   $\qquad\qquad\qquad\qquad =0.34+0.40$

   $\qquad\qquad\qquad\qquad = 0.74volt$

4. Calculate the standard emf of Ni-Ag cell whose E^0_{Ni} and E^0_{Ag} are –o.25 and 0.83 v Also
   write cell representation.

   Sol:

   $$Anode = Ni \rightarrow Ni^{+2}+2e^- \text{ (-0.25v)}$$
   $$\underline{Cathode=2Ag^++2e^- \rightarrow 2Ag \text{ (+0.83v)}}$$
   $$Ni +2Ag^2 \leftrightarrow Ni^{+2} + 2Ag$$
   $$E^0_{cell} = E^0_{Ag} - E^0_{Ni}$$
   $$= 0.83-(-0.25)$$
   $$=1.08v$$

5. Calculate the emf of the Zinc=silver all at 25^0c when $[Zn^{+2}]=0.10$ M &
   $[Ag^+]=10.0M[E^0_{cell}$ at $25^0c =1.56v]$

   S0l.

   $$2Ag^+ + Zn \leftrightarrow 2Ag +Zn^{+2}$$
   $$E^0_{cell} = E^0_{cell} + \frac{RT}{nf} \ln\frac{[Ag^+]^2}{[Zn^{+2}]}$$
   $$1.56 + \frac{0.0592}{2} \log \frac{[10]^2}{[0.1]}$$
   $$=1.56 + \frac{0.0592}{2} \log 100*10$$
   $$= 1.56+0.0888$$
   $$= 1.6488 \text{ volts}$$

6. The emf of a cell, $mg/mg^{+2}(0.01//cu^{+2}/cu$ is found to 2.78 volts at 300K. The standard
   electrode potential of mg electrode is -2.371v. what is electrode potential of copper
   electrode

$$E_{mg} = E^0{}_{mg}{}^{+2}/mg + \frac{0.0591}{n} \text{Log } [mg^{+2}]$$

$$= -2.37 + \frac{0.0591}{2} \log (0.01)$$

$$= -2.37 - 0.0591$$

$$= -2.4290v$$

$$E_{cell} = E_{cu} - E_{mg}$$

$$2.78 = E_{cu} - (-2.4290)$$

$$E_{cu} = 2.78 + 2.4290$$

$$E_{cu} = +0.3509V$$

7. Calculate the electrode potential of Zinc electrode dipped in 0.1M $ZnSo_4$ solution at 25^0c [$E^0 \ Zn^{+2}/Zn = -0.763v$]

   sol:

$$E = E^0 + \frac{0.0591}{n} \log(0.1)$$

$$= -0.763 + \frac{0.0591}{2} \log(0.1)$$

$$= -0.763 - 0.02955$$

$$= -0.79255v$$

8. Find the oxidation potential of $Zn/Zn^{+2} = 0.2M$ electrode at 25^0c standard reduction potential of Zn/Zn^{+2} is 0.763v

   Sol:

$$[Zn^{+2}] = 0.2M$$

$$E^0{}_{Zn/Zn}{}^{+2} = 0.763$$

$$E = E^0 - \frac{0.0591}{n} \log [Zn^{+2}]$$

$$= 0.763 - \frac{0.0591}{2} \log [0.2]$$

$$= 0.763 - (0.02955 - 0.69897)$$

$$= 0.763 + 0.02065$$

$$= 0.78365v$$

Concepts of P^H :

- Negative logarithm of H^+ ion concentration is called P^H

$$P^H = -log \ [H^+]$$

- P^H stands for potential of Hydrogen, which measure the acidity or alkalinity of water-soluble substance.
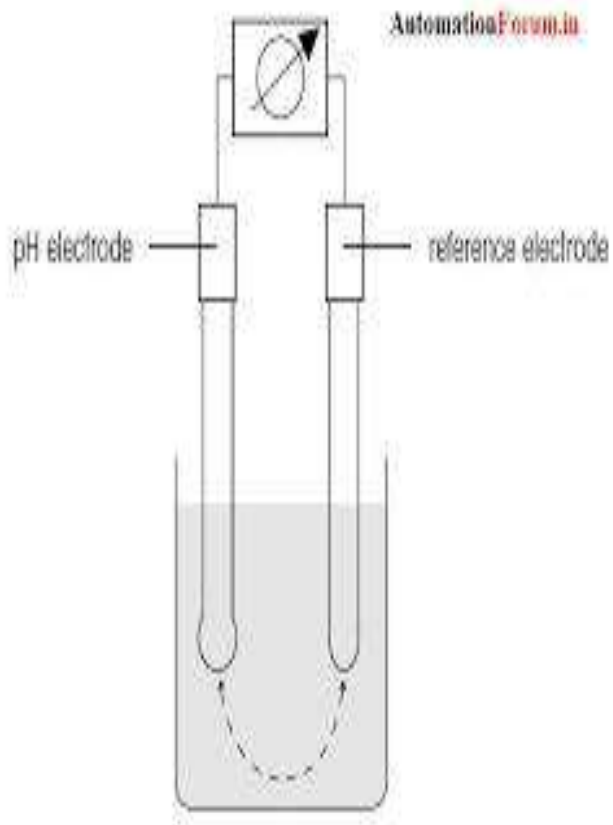
P^H meter:

An electric device used to measure hydrogen ion activity in solution. It consists of *P^H* response electrode usually glass electrode and reference electrode (calomel electode). These two electrodes placed in electrolyte and connected to voltmeter, which measures the potential difference between the glass and reference electrodes.

Application of P^H metry (Acid-Base Titrations)

- In acid-base titration, equivalence point has to be determined.

- Equivalence point can be determined by titrating unknown molarity of acid solution against known molarity of base in the burette.

- The P^H of the solution will change dramatically at equivalence point.

Calibration:

- Calibration should be performed with at least two standard buffer solutions that span the range of P^H values to be measure.

For general purpose buffers at P^H 4 and P^H 10 are acceptable.

- ☐ The P^H meter has one control (calibrate) to set the meter reading equal to the value of the first standard buffer and a second control (slope) which is used to adjust the meter reading to the value of the second buffer.

- ☐ A third control allows the temperature to be   electrode maintenance

set.   guide

- ☐ Materials : PH meter calibration and

P^H meter with standard buffer of P^H 4.0 and P^H 7.0 , Burette, Burette stand, Stirrer, Beaker, HCl and NaOH.

Procedure :

- ▢ Take 20 ml of Hcl in a clean beaker

- ▢ Standardise the P^H meter and place the electrodes in Hcl and record the initial P^H of Acid solution.

- ▢ Fill the burette with NaOH solution whose concentration is known.

- ▢ Add 0.5 ml of NaOH solution from burette to Hcl in beaker and stir the solution with stirrer and record the P^H of the solution.

- ▢ Continue adding NaOH in 0.5 ml increments until you have obtained a P^H reading greater than 12.

☐ Remove and clean the P^H electrodes and the solutions may be discarded.

Calculations:

☐ Plot a graph between volume of NaOH on X-axis and P^H on Y-axis.

- There should be a region on your graph where the slope is very steep.

- Determine the mid point of this region.

- This is the equivalence point.

- Record the volume of NaOH added at equivalence point as determined from the graph.

- Use the relationship

$$MAVA = MBVB \text{ to determine molarity of acid.}$$

Graph :
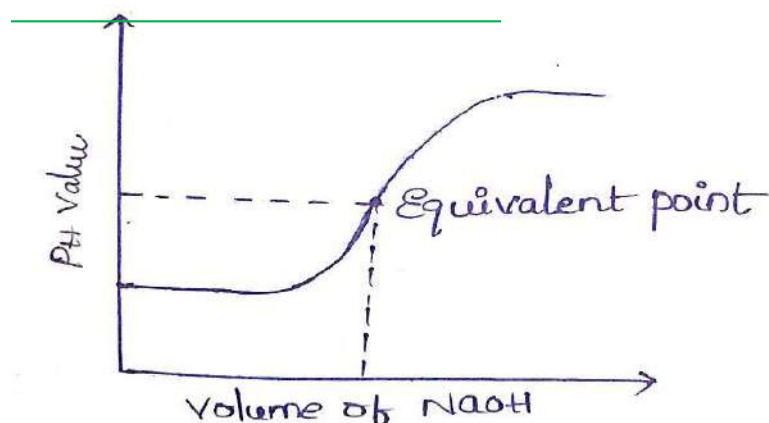
General Applications of P^H Meter:

- The rate and outcome of chemical reactions taking place in water of ten depends on the acidity of the water, and it is therefore useful to know the acidity of the water, typically measured by means of a P^H meter.

- Knowledge of P^H is useful or critical in many situations, including chemical

laboratory analyses.

- P^H meters are used for soil measurements in agriculture.

- Water quality for municipal water supplies and swimming pools.

- Environmental remediation.

- Brewing of wine or beer.

- Manufacturing, healthcare and clinical applications such as blood chemistry, and many other applications.

Potentiometric Titrations:

A titration in which the end for equivalance point is estimated with the help of measurement of the potentials of the reaction mixture is called a potentiometric titration.

Without using indicator, we can determine the end point.

Potentiometry Principle:

When the pair of electrodes are placed in the sample solution or analyte it shows the potential difference between two electrodes by addition of the titrant or by the change in the concentration of ions.

Potentiometric titration is of three types.

i)   Acid – base titrations

ii)   Redox titrations

3)Precipitation titration

Redox titrations:

Potentiometric titration was first used for redox titration by Crotogino. He titrated hali

ions with KMnO4 using a platinum electrode and calomel electrode.

In this titration, it will be observed that at the end point, there is a sharp increase in PH for the addition for a very small quantity K2Cr2O7. The variation of P^H value can be measured potentiometrically by immersing a bright platinum working electrodes. The emf of the electrode is measured by activity ration of the substance being oxidized or reduced.
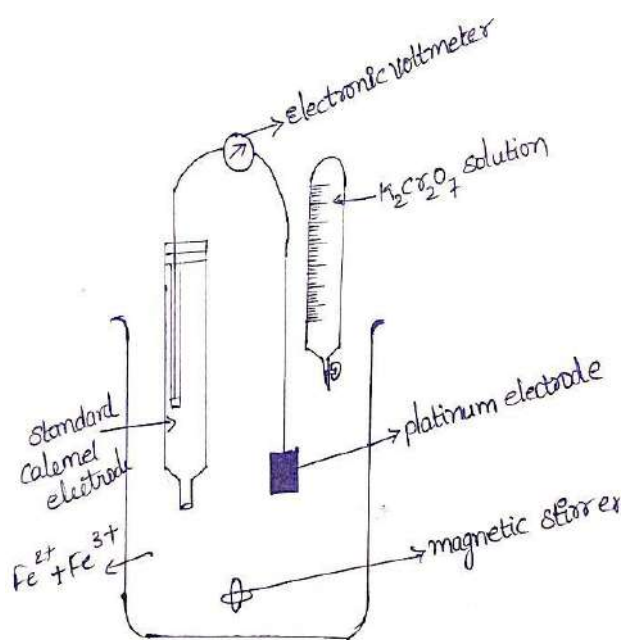

Calibration:

Let us consider the titration of ferrous ammonium sulphate against potassium dichromate.

A known volume of ferrous salt solution is placed in the beaker and transferred to 100 ml of distilled water and 10 ml of dilute H2SO4. Then a bright platinum electrode is dipped in the solution and connected with a saturated Calomel reference electrode with the help of a salt bridge.

The emf of the cell is observed for each addition of K2Cr2O7 solution from the burette is noted. The observed value of E(emf) is then plotted against 'V' and the steepest portion of the curve indicates its equivalence point. If there is difficulty in finding the end point, in such cases, for obtaining a sharp end point, plot $\delta E/\delta v$ instead of 'E' against the volume of base. At the volume corresponding to the equivalence point of the titration, the differential curve shows a maximum

Applications:

 It is used in clinical chemistry for analysis of metals.

  It is used for analysis of cyanide, ammonia etc. in water or wastewater.

  It is used in agriculture for detection of different elements in soils, fertilizers etc.
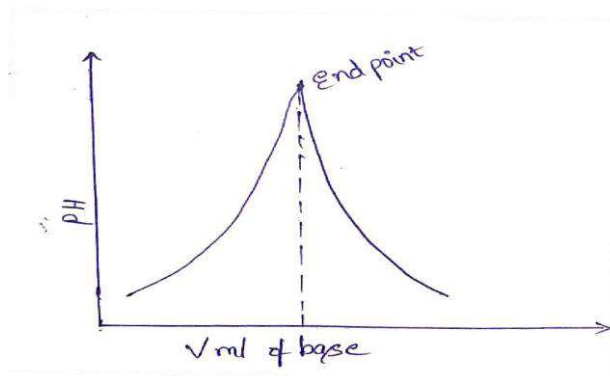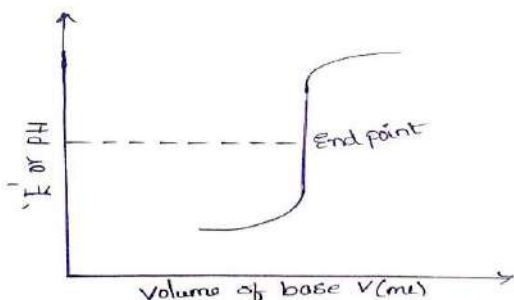
It is used in detergent manufacturing, food processing etc.

Conductivity of electrolytes: -

(1) Specific conductance: -

The resistance of conductor is directly proportional to its length and inversely proportional to its cross-sectional area.

$R \propto R/A$ R=resistance in ohms.

$R = \rho \, l/A$ ρ= specific resistance.

l=length in cm.

A=Area of cross section.

If l=1and A=1 $[\![cm]\!]$ ^2.

Then $R = \rho$

Resistivity of specific resistance of a conductor the resistance between two opposite faces of a centimeter cube.

 Units --ohm-cm.

(2)Specific conductivity:-

It is reciprocal of specific resistance an electrolytic solution.

$k = 1/p = l/AR$

Units=ohm^(-1) cm^(-1)

(3)Equivalent conductivity:-

The conductivity of all the ions present in equivalent of the electrolyte in solution.

1equivalent of electrolyte is contained in then

~~^eq = v × specific conductance~~

=v×k

If the normality of electrolytic solution is

V=(1/N)L=1000/N ml

V^eq =1000/N k

Units=ohm^(-1) cm^2 〚eq〛 ^(-1)

(4). Molar conductivity: -

The conductance of all ions presents in one mole of electrolyte in the solution.

^m=1000k/M

Units=ohm^(-1) cm^2 mol^(-1)

Classification of electrolytes: -

Electrodes like NaOH. NaCl, HCL, KCL have value of conductance even at low dilution and there is no rapid change or increasing in their equivalent conductance on dilution. Such electrolytes are called as strong electrodes.

Electrolytes like acetic acid have a low value of equivalent conductance even at higher concentrations and there is rapid increase in the conductance of dilution. Such as weak electrolytes

Conductometric Titrations:

It is a method of volumetric analysis based on the change in conductance of the solution, at equivalence point during titration. The conductance of an electrolyte mainly

depends on

- No.of free ions in the solution

- Charge on the free ions

- Mobility of the ions

During the course of titration, the number of free ions in the solution changes and also the identity of the ions also changes. As a result, conductance of the solution also changes.

Conductometric titrations are four types.

i) Acid-base titrations

ii) Redox titrations

iii) Precipitation titrations

iv) Complex titrations

i) Acid –Base titration:

a) Strong acid with strong base:

$$[H^+cl^-] + [Na^+OH^-] \longrightarrow [Na^+cl^-] + H2O$$
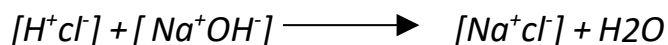
The acid is taken into the conductivity vessel and the alkali in the burette. Before base is added, the conductivity of acid solution is high due to high mobile hydrogen ions. As alkali is added, the hydrogen ions are replaced by slowly moving sodium ions. This will result in the decrease conductivity rapidly. The solution at neutralization point containing only sodium and chloride ions will have minimum conductivity.

Any subsequent addition of NaOH will cause introduction of fast moving hydroxide ions will result in increase of conductivity on plotting the conductance against the volume of NaOH added, the points will ie on two straight lines AB & CD. The point of intersection

of two lines 'X' gives the end point and will give volume of alkali required for the neutralization.
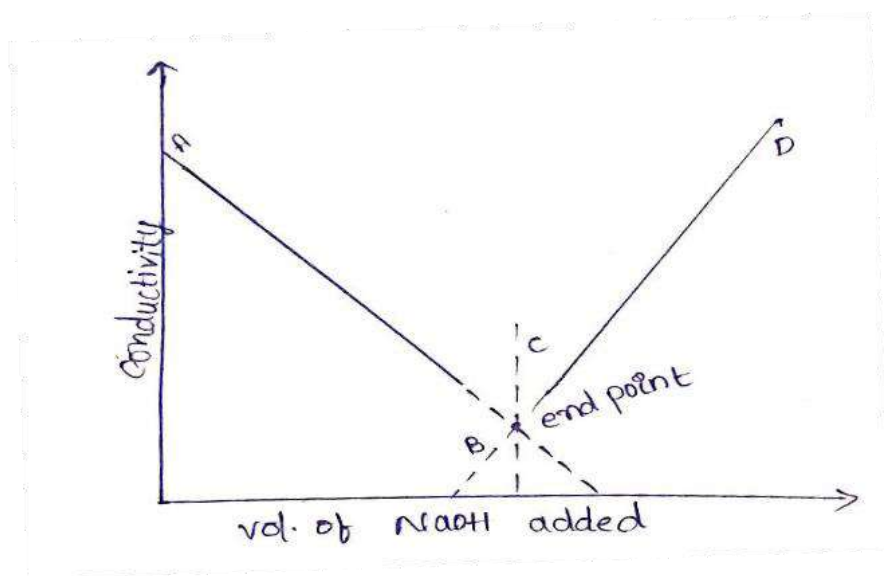
b)Strong acid with a weak base:

Let us consider titration of HCl with NH4OH. When NH4OH is added to Hcl, the conductivity decreases because of the replacement of the fast-moving H+ ions by slow moving NH_4^+ ions.

$$[H^+cl^-] + [NH_4^+OH^-] \longrightarrow [NH_4^+Cl^-] + H2O$$
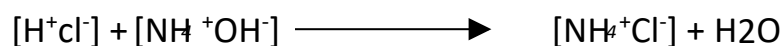
The addition of NH4OH after the end point, does not change the conductance because NH4OH, a weakly ionized electrolyte has a very small conductivity with acid or its salt.
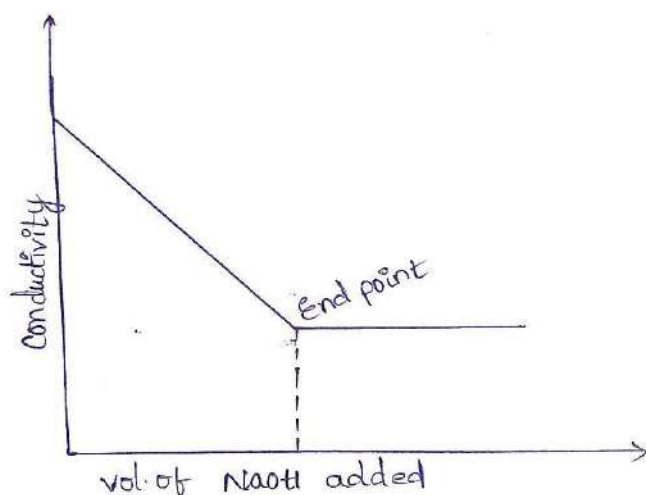
c) **Weak acid with a strong base:**

Let us consider the titration of CH3COOH with a NaOH. The conductance of acid will be low on account of its poor dissociation. When a small amount of NaOH is added to CH3COOH, the conductivity decreases initially the increases with the further addition of NaoH.

$$[CH3COO^-H^+] + [Na^+OH^-] \longrightarrow [CH3COO^-Na^+] + H2O$$
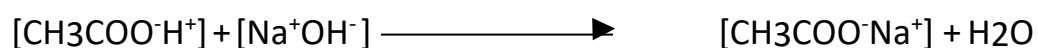
When the neutralization of acid is completed, further addition of alkali produces excess of OH⁻ ions. The conductance of solution therefore begins increasing rapidly.
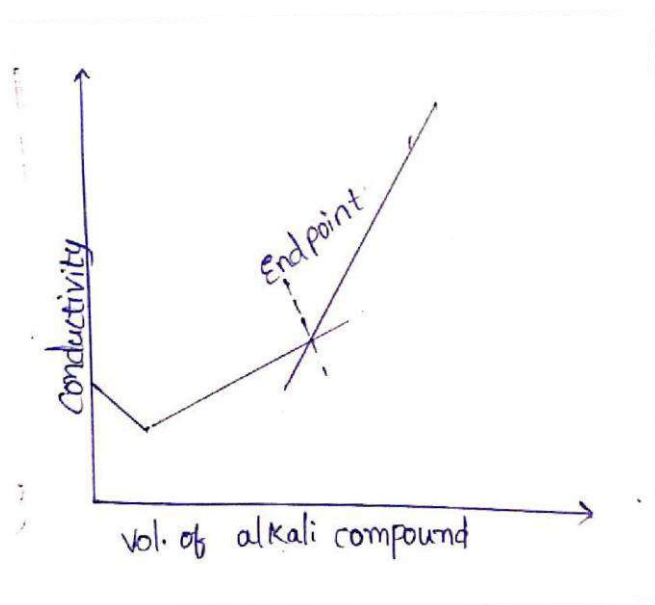
d)Weak acid with weak base:

Let us consider the titration of CH3COOH with NH4OH, the addition of NH4OH may cause decrease in conductance in the beginning, because the common ions formed depresses the dissociation of their respective electrolyte.

$$CH3COOH + NH4OH \longrightarrow NH_4^+ CH3COO^- + H2O$$
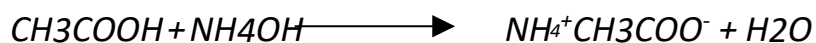
On further addition of NH4OH, an increase in the conductivity of the solution results, because the conductance of highly ionized salt exceeds the conductance of the weak acid it replaces. After the neutralization of the acid, further addition of NH4OH does not cause any change in the conductance.

$$NH4^+ + CH3COO^- \underline{\quad NH4OH \quad} \blacktriangleright \quad No\ change\ in\ conductance.$$

A conductometric titration curve of conductivity ($1/R$) versus volume of NaOH solution, showing the regions labelled $HAc + NH_4^+ Ac^-$, $NH_4^+ Ac^- + NH_4OH$, and the equivalence point.
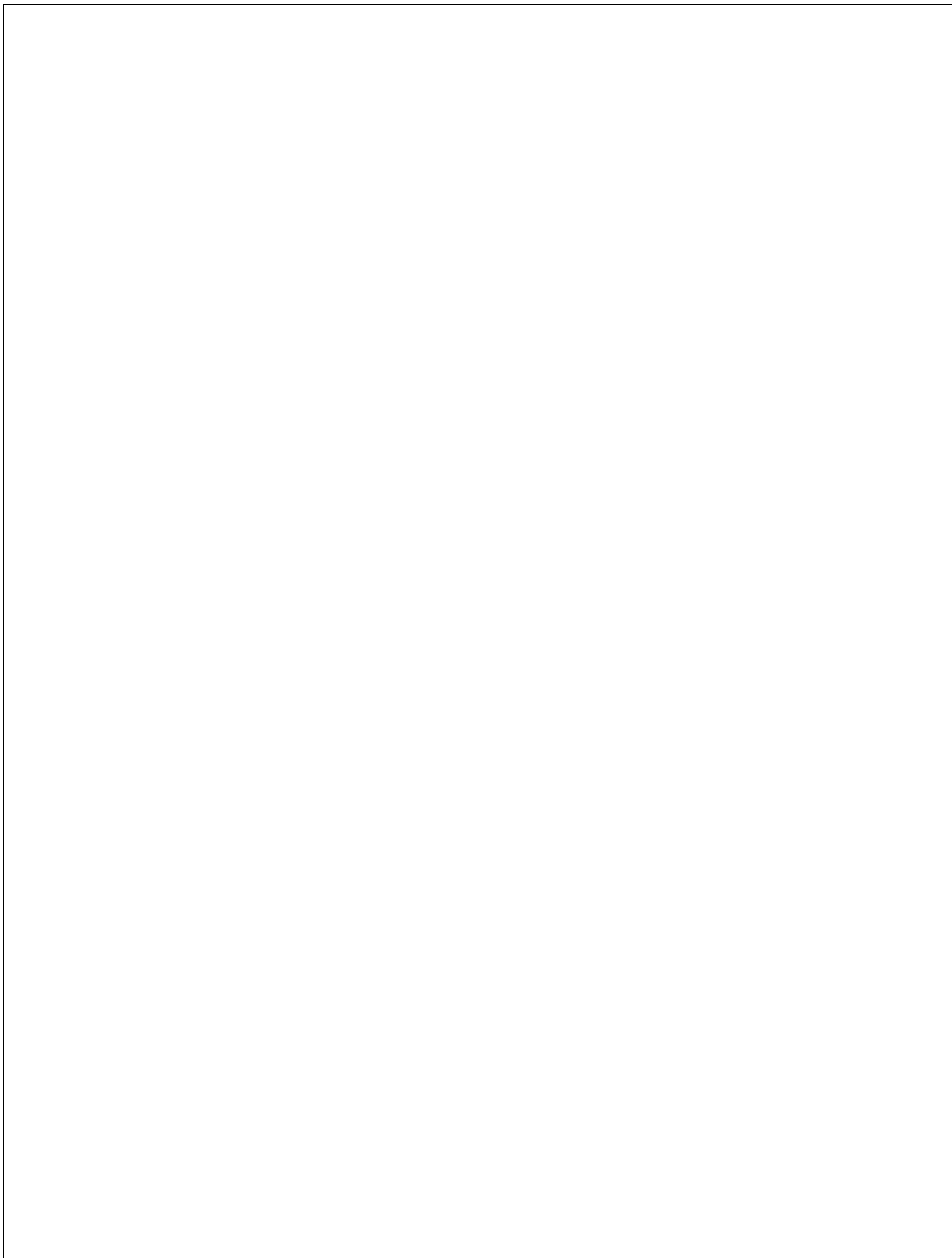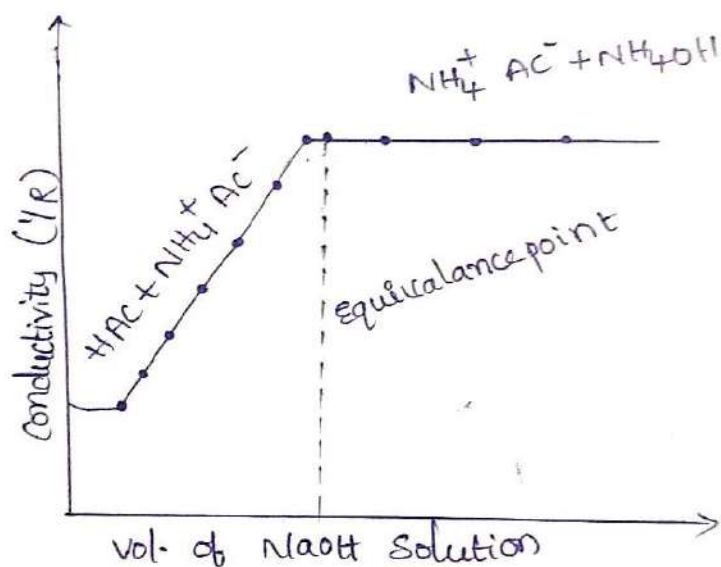
Applications:

▪ Check water pollution in rivers and lakes

▪ Alkalinity of fresh water

▪ Salinity of sea water (oceanography)

▪ Deuterium ion concentration in water – deuterium mixture.

▪ Food microbiology – for tracing micro organisms

▪ Tracing antibiotics.

▪ Estimate ash content in sugar juices

▪ Purity of distilled and de – ionized water can determine

▪ Solubility of sparingly soluble salts like AgCl, BaSO4 can be detected

▪ Determination of atmospheric SO2, estimation of vanillin in vanilla flavor.

Photovoltaic cells:

A solar cell or photovoltaic cell is an electrical that converts the energy of light directly into electricity by the photovoltaic effect, which is a physical and chemical phenomenon. It is a form of photoelectric cell, defined as a device whose electrical characteristics such as current, voltage or resistance vary when exposed to light. Solar cell is the building block of photovoltaic molecules, otherwise known as solar panels.

The operation of a photovoltaic cell requires 3 basics

1. The absorption of light, either electron-hole pairs or excitations
2. The separation of charge carriers of opposite types
3. The separation extraction of those carriers to an external circuit

Construction:

It essentially consists of a silicon PN junction diode with a glass window on top surface layer of p material is made extremely thin. so, that incident light photons may easily reach the PN junction.
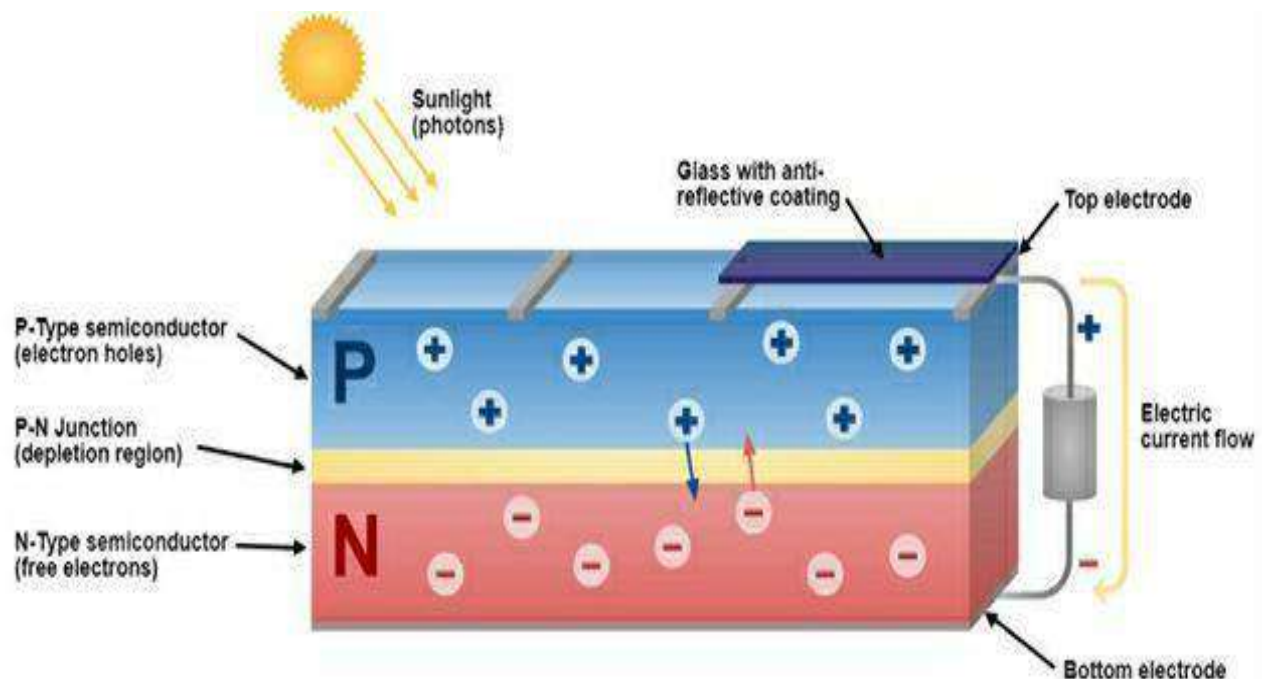
$$EG = h = hc/\lambda = 1.24$$

Application:

- Concentrator photovoltaics
- Photovoltaic thermal hybrid solar collector
- Power station
- Rural electrification
- Floatavoltaics
- In transport
- Spacecraft application
- Specialty power system

❖ **PHOTO GALVANIC CELL**

Introduction:

A galvanic cell is an electro - chemical cell that derives electrical energy from spontaneous redox reactions takes place within the cell .

THEORY:

The energy from a battery comes from a spontaneous redox reaction In which the electron transfer is forced to take place through a wire . The apparatus that provides electricity through redox reaction is called galvanic cell .

A galvanic cell is made up of two half cells i.e

❖ **Zinc electrode:**

A zinc(Zn) electrode dips into a solution of znso4 on the left.

❖ **Copper electrode:**

A copper(Cu) electrode dips into a solution of cuso4 on to the right.

❖ The two electrodes are connected by an external electrical circuit.
❖ Two solutions are connected by salt bridge.

When the circuit is completed by closing switch, the reduction of Zn2+ to Zn occurs. Spontaneously in the half cell on the left oxidation of Cu to Cu2+ occurs in the half cell in the right.

REACTIONS:

Zn2+ + 2e- --------→ Zn(reduction)

Cu(s)   ----------→Cu2+ +2e- (oxidation)

Total equation :

Zn2 + + Cu --------→Zn + Cu2+ (Cell reaction)
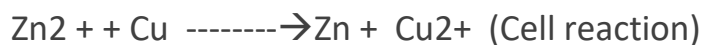
When electron appear as reactant , the process is reduction, when they appear as a product ,it is Oxidation.

When these reactions takes place ,electrons left behind by oxidation of the copper, travel through an external circuit to the other electrode where they are transferred to the Zn2+ is reduced to the Zinc metal .
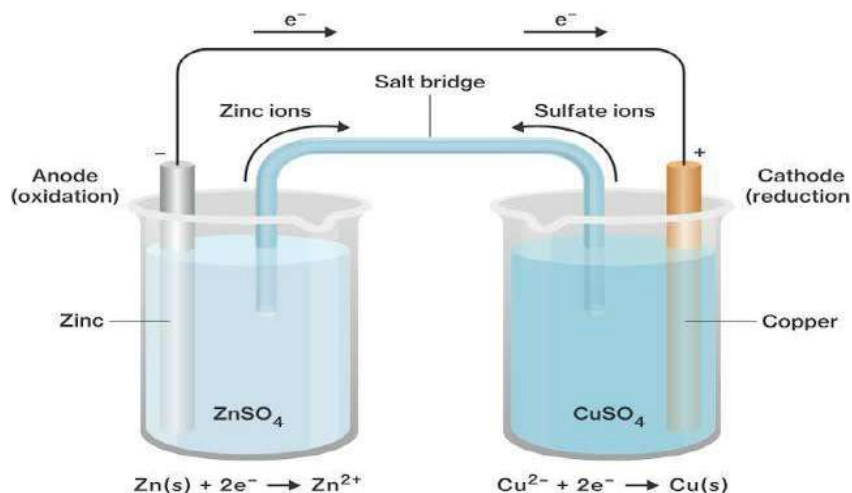
Fig: photo galvanic cell

Electric current flows from negative electrode to positive electrode. The flow of electricity from one electrode to another electrode in a galvanic cell indicates that the two electrodes have different potentials. The difference of potentials which causes the flow of current from one electrode, which is at higher potential to another electrode which is at lower potential is called the "Electro motive force" of the cell.

APPLICATIONS:

- Electronic cell
- Electronic calculations
- Space vehicles
- Power stations

Electro chemical sensors:

History: -

The history of electro chemical sensors starts basically with the development of glass electrode by Cremer in 1906.

Definition: -

Electro chemical sensors are devices that extracts information about sample from measurement of some electrical parameters.

SCHEMATIC REPRESENTATION OF ELECTROCHEMICAL SENSORS:

The electrochemical sensors mainly consist of outer frame containing an electrolyte gel and three electrodes. At the top of the frame it should have gas permeable membrane. The electrodes are carefully constructed with high sensitivity, long life and allow large surface area. Each cell shall construct with special filter electrodes and electrolytes for high specificity as possible. This will helpful for allowing of larger signal   immediate response and even a smaller volume of electrolyte sensor.

Block diagram of electro chemical sensors

Classification of electro chemical sensors:

Electro chemical sensors are devices that extract information about sample from measurement of some electrical parameters.

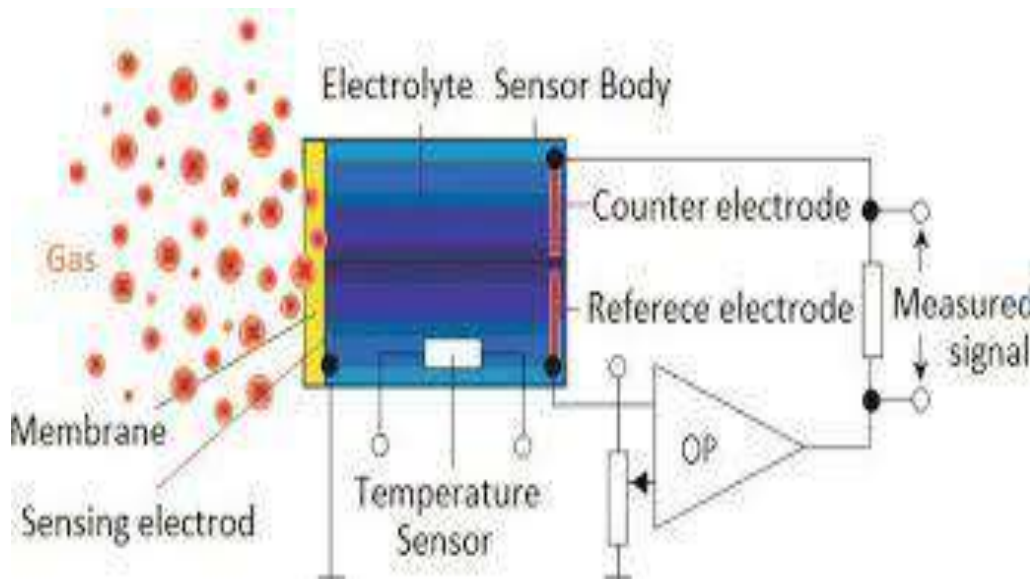Sensors are divided into three kinds.they are:

1. Potentiometric sensors(if we measure difference of two potentials)
2. Amperometric sensors(if the parameters of intrest is current)
3. Chemiresistors [or]conductometric sensors(if we measure resistance or conductance)

These three kinds of sensors are working based on the basic principle of ohms law stating that the potential difference in a circuit is equal to the product of the current and the resistance i.e volt =amphere times ohm.

They all have two things in common.First,the measurement must be done with closed electrical circuit, meaning that a hypothetical (test) charge can be passed through the electrical circuit and return to it's origin.Second electrical neutrality must be preserved.Example a postive charge(+ve)is added at one place of the closed circuit another positive charge must be taken out(or negative charge added)somewhere else.

Potentiometric sensors:

Ion-selective electrode is electrode with a potential that is dependent on the concentration of an ionic species in the last solution and is used for electro analysis. Most common ion-selective electrode are often membrane type electrode. Ion-selective electrode the reorganization of hydrogen ion is done by the glass electrode sensing element . Here develops a potential between ISE and reference electrode and the sensor measures the potential differences between these two electrodes. Since the electrode is selective for one ion. The mother of all ions selective electrode is the glass electrode which is selectively sensitive to hydrogen ions.

Working principle of potentiometric sensors:

The working principle of glass electrode is similar and common to all ISE's.

The glass electrode may be represented as

Ag Agcl/1m Hcl/H^+

When placed in a solution, the potential of glass electrode depends on like concentration of H^+ ions in the solution. The potential develop across glass membrane as the result of a concentration differences of H^+ ions on its two sides of membrane.

Glass, it has been exposed to water   adsorbs and develops a very thin film gel like layers at its surface. Hydrogen ion available in the solution likes to be

in this gel layers, more so then in its solutions. The charges have been separated and when that happens an equilibrium potential is formed. This potential is detected by the p ^{H} sensors.

Eg: For reference electrode are Agcl , calomel and electrodes.

These sensors are used to measure the acidity/ alkalinity of solutions, a parameter protection, agriculture, biology , medicine and many chemical processes.
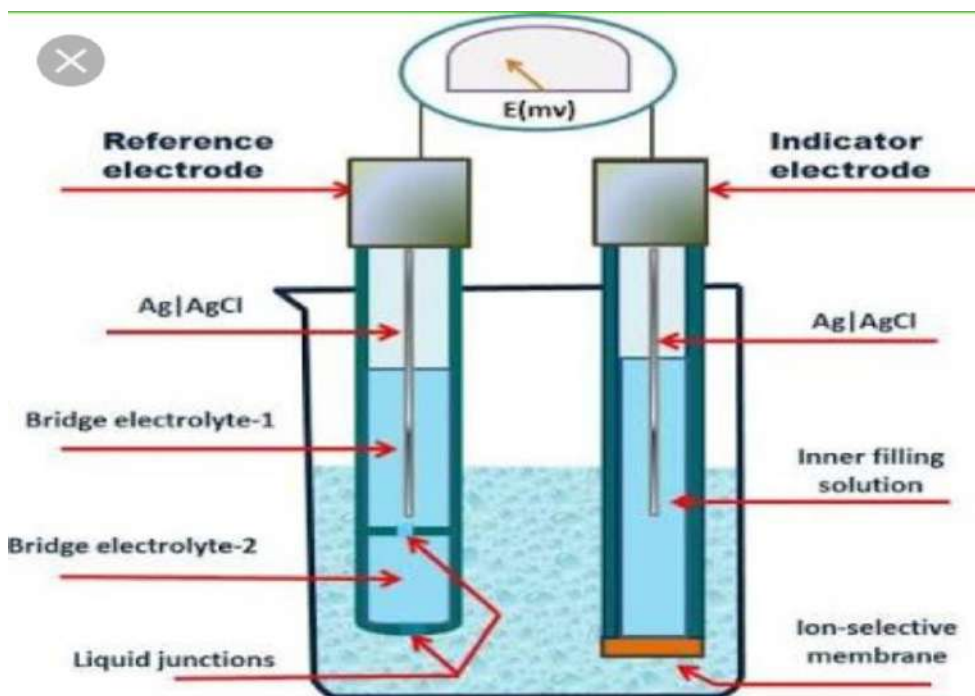
Working of potentiometric sensors

Glucose – potentiometric sensors:

Glucose is an electrically neutral molecule. Hence, it does not produce signal. The neutral glucose molecule bas to be converted into ions, which are then selectively

detected. Enzymatic oxidation of glucose to gluconic acid and the subsequent measurement of this liberated hydrogen ions.

D-glucose + O_2 + H_2O --$\rightarrow$ D- gluconic acid + H_2O_2

H_2O_2----$\rightarrow$ $2H^+$ +O_2 + 2 e$-$

When glucose de-hydrogenase (GDH) was applied, the electro chemical reactions using electron transfer mediator in the glucose sensors.

GDH(oxi) + D-glucose---$\rightarrow$GDH(red)+ ………….

- In presence of glucose and oxidase

Mediator(oxi) + GDH(red)-$\rightarrow$ mediator(red) + GDH(oxi)

Mediator(red)--$\rightarrow$mediator(oxi) +e$-$

Amperometric sensors {or}Voltametric sensors

The principle of Amperometric is based on the measurement of the current between the working and counter electrode which is induced by a redox reaction at the working electrode. The signal or response is with respective to the diffusion current , i.e in Amperometric sensors

Estimation of uric acid:

Uric acid is a major nitrogenous compound in urine , is the product of urine metabolism in the human body and is related to many clinical disorders . One of the major problems in biological determinations of UA comes from electro chemical interferences such as ascorbic acid which has similar oxide potential. There are two methods for the measurement of UA i.e enzymatic and non-enzymatic.

The enzymatic procedures using uricase

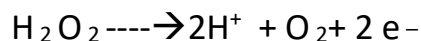Uric acid $+O_2$ + $2H_2O$ --$\rightarrow$ Allantoin + H_2O_2 + CO_2
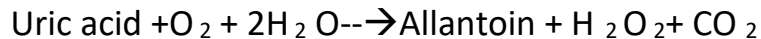
- In presence of uricase

H_2O_2 ----$\rightarrow$ $2H^+$ + O_2 + $2e^-$

Other enzymatic procedures are based on electron transfer mediators

Uric-acid + mediator(oxi) + H_2O -$\rightarrow$ Allantoin + mediator(red) + CO_2 + $2H^+$

Mediator(red) --$\rightarrow$ mediator(oxi) + $2e^-$

Advantages:

- These can be used for non optically active compounds.
- Many inorganic ions .
- Electro chemically not active anions.

Some more applications:

- Detection of O_2 and toxic gases like NO_2, SO_2 , CO_2 and H_2S.
- For checking the race level construction of fertilizers, pesticides, drugs etc.

Button cells

It is a small single cell battery shaped as a squat cylinder like a button on a garment.

A metal can forms the bottom body and positive terminal of the cell. A insulated top cap is the negative terminal. Button cells are single cells. These are disposable primary cells. Anode materials are zinc or lithium. Cathode materials are manganese dioxide, silver oxide, oxygen from the air. Mercuric oxide cells are common.

Ex: Mercury button cells

In mercury batteries mercuric oxide (MgO) with MnO2 acts as cathode. Mercuric oxide is a non-conductor, so some graphite is mixed with it.

At cathode: HgO+H2O+2e- ---→Hg+2oH-

The anode is made of zinc and separated from the cathode with a layer of paper or the other porous material soaked with electrolytes, this is known as salt bridge.

At Anode: Zn+2OH ----→Zn (OH)2 +2e-

At Cathode: HgO+H2O+2e- -----→Hg+2oH

Overall reaction: Zn+HgO -------→ZnO+Hg
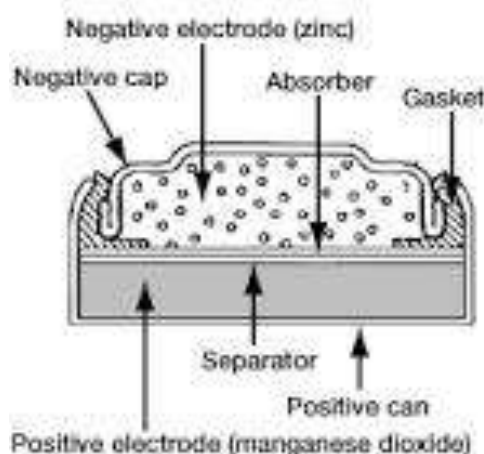
Applications: -

- These are used in watches, hearing aids, cameras, calculators.

BATTERY:

It is a device consisting of 100 galvanic cells connected in series of parallel or both.

PRINCIPLE COMPONENT:

- A anode oxidation occurs
- A cathode reduction occurs
- An electrolyte, which is ironically conducting
- A separator to separate anode and cathode compartment.

CLASSIFICATION OF BATTERIES:

Batteries are of two types:

- Primary Batteries
- Secondary Batteries

Primary batteries

These are batteries where the redox reactions proceed in only one direction. The reactants in these batteries are consumed after a certain period of time, rendering them dead. A primary battery cannot be used once the chemicals inside it are exhausted. An example of a primary battery is the dry cell – the household battery that commonly used to power TV remotes, clocks, and other devices. In such cells, a zinc container acts as the anode and a carbon rod acts as the cathode. A powdered mixture of manganese dioxide and carbon is placed around the cathode. The space left in between the container and the rod is filled with a moist paste of ammonium chloride and zinc chloride. The redox reaction that takes place in these cells is:

At Anode

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

At Cathode

$2e^- + 2 NH_4^+ (aq) \rightarrow 2 NH_3 (g) + H_2 (g)$

2 NH3 (g) +Zn2+ (aq) –> [Zn (NH3)2] 2+ (aq)

H2 (g) +2Mno2(s) ▯ Mn2o3(s)+H2O(I)
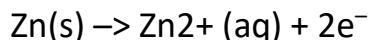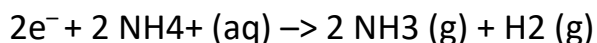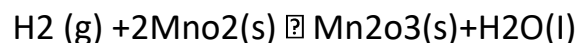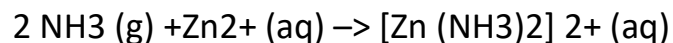
THUS, THE OVERALL CELL EQUATION IS

Zn(s)+2NH4+(aq)+2Mno2(s)▯[Zn(NH3)2] 2+(aq)+Mn2O3(s)+H2O(I)
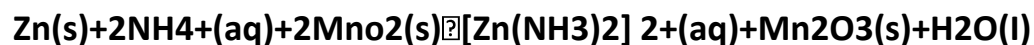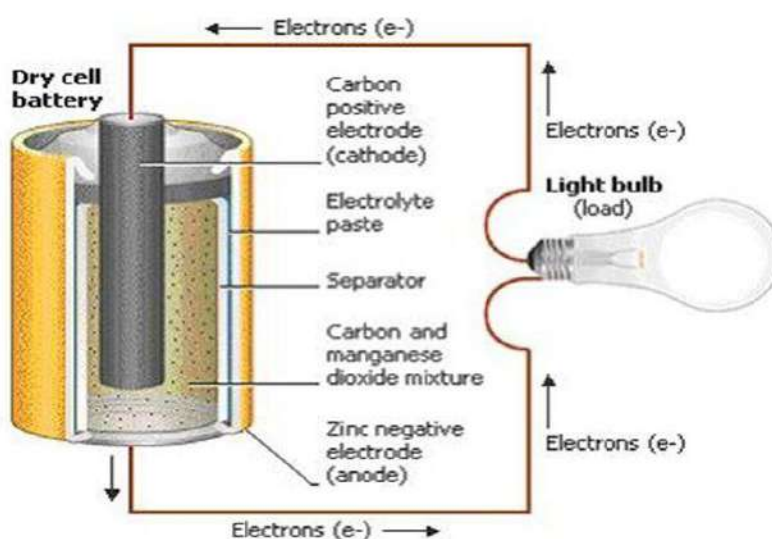
Another example of the primary cell is the mercury cell, where a zinc-mercury amalgam is used as an anode and carbon is used as a cathode. A paste of HgO is used as an electrolyte. These cells are used only in devices that require a relatively low supply of electric current (such as hearing aids and watches).

1. ZINC AIR BATTERIS

Figure 1
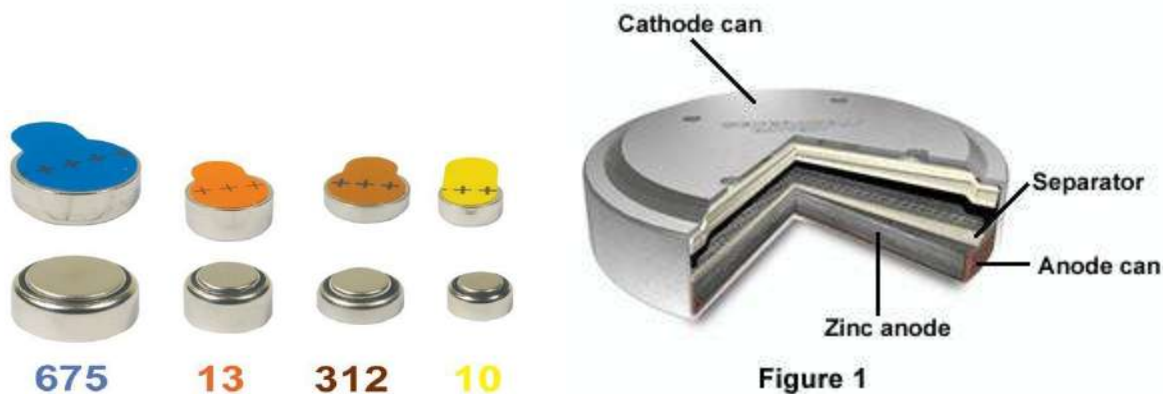
These are non-rechargeable batteries and zinc-air fuel cells (mechanically rechargeable) are metal-air batteries powered by oxidizing zinc with oxygen from the sir. These batteries have high energy densities and are relatively inexpensive to produce. Sizes range from very small button cells for hearing aids.

During discharge, a mass of zinc particles from a porous anode, which is saturated with an electrolyte. Oxygen from the air reacts at the cathode and forms hydroxyl ions which migrate into the zinc paste and form zincate (Zn (OH) 42−) releasing electrons to travel to the cathode. The zincate oxidized to zinc oxide and water returns to the electrolyte. The water and hydroxyl from the anode are recycled at the cathode, so the water is not consumed. The reactions produce a theoretical 1.65v.

Location	HALF CELL REACTION	VOLTAGE
ANODE	*Zn2+ + 2OH- —> Zn(OH)2*	1.25
CATHODE	*1/2 O2 + H2O + 2e —> 2 OH-*	0.4
OVERALL	*2Zn +O2 +2H2O —> 2Zn(OH)*	1.65
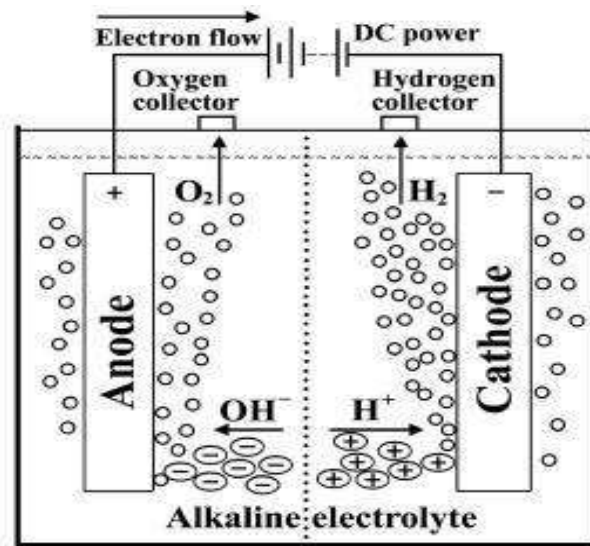
Figure 3. Basic scheme of a water electrolysis system

Applications

1. Used as power source in hearing aids
2. Used in electronic pagers
3. Used in military radio receivers
4. Used in voice transmitters

2. Alkali metal Sulphide batteries

These are of two types
   a) Sodium-sulphur battery
   b) Lithium-sulphur battery

Sodium-sulphur battery

It is a type of molten-salt battery constructed from liquid sodium and sulphur. This type of battery has high energy density, high efficiency of charge or discharge and long cycle life and is fabricated from inexpensive materials. The operating temperatures are 300°-350°.

Construction:

It has a solid electrolyte membrane between the anode and cathode compared with liquid metal batteries. The cell is made with a cylindrical configuration. The entire cell is protected by chromium and molybdenum from corrosion. This outside container serves as the positive electrode, while liquid sodium serves as the negative electrode; the container is sealed at the top with an airtight alumina lid. An essential part of the cell is the pressure of 13- alumina solid electrolyte (BASE) membrane, which selectively conducts Na+.

BASE is a good conductor of Na+ ions but a poor conductor of electrons and thus avoid self-discharge. When Na gives off electron, the Na+ ion migrates to the sulphur container. The electron drives an electric current through the molten. Sodium to the contact, through the electrical load and back to the sulphur container. Here another electron reacts with sulphur to form sodium polysulfide powder.

As the cell discharges, the sodium level drops. During the charging, the reverse process takes place.

$$2Na + 4s \rightarrow Na_2S_4 \text{ (discharging process)}$$

Applications:

1. Space
2. Transport and heavy machinery
3. Grid and standalone system

Sodium–sulfur battery

https://en.wikipedia.org/wiki/File:Galvanic_Cell.svg
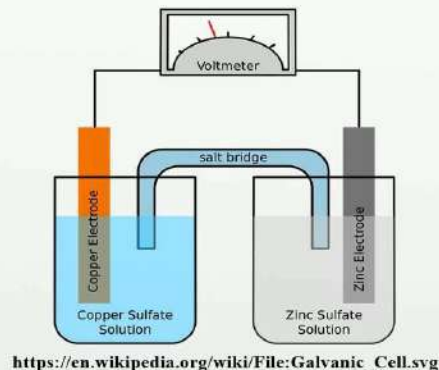
Lithium-sulphur batteries:

It is a type of rechargeable batteries, for its high specific energy. The low atomic weight of lithium and moderate atomic weight of sulphur means that Li-s batteries are relatively light.

Lithium-sulphur batteries may Precede Li+ cells because of their high energy density and reduced cost due to the use of sulphur.

In Li-s cell includes lithium dissolution from the anode surface during discharge and reverse lithium plating to the anode while charging. Each sulphur atom can host two lithium ions. It possesses high lithium storage density.

Discharging:

S_8◻Li_2S_8◻Li_2S_6◻Li_2S_4◻Li_2S_3 **Charging:**

Li_2s◻Li_2S_2◻Li_2S_3◻Li_2S_4◻Li_2S_6◻Li_2S=◻S=

Application

These are used on the longest and highest altitude solar - powered Aeroplane flight.

Discharge · e⁻ · Li⁺ · Li⁺ · Li⁺ · Li⁺ · Li⁺ · Li⁺ · separator · current collector · Li (-) · S₈ (+)
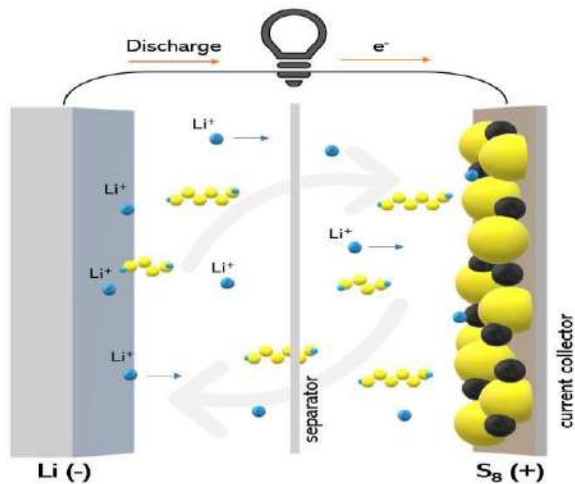
SECONDARY CELL:

These chemical reactions are reversed by passing direct electric current in opposite directions. The cell is designed for repeated use and they are able to the rechargeable.

e.g.: ni-cd storage cell, lithium batteries.

LEAD ACID STORAGE CELLS:

A cell that can operate both as a voltaic cell and as an electrochemical cell is called lead acid storage cell. A number of lead plates (-ve) are connected in parallel will act as Anode and pb02 plates (+ve) will act as cathode, which were also connected in parallel.

The lead plates are fitted in between the lead dioxide plates. These plates are separate from the adjacent ones by insulating with strips of wood or rubber or glass fibre. The entire combination is immersed in 20 to 21 dil H2s04.

DISCHARGING:

When the storage cell is operating as voltaic cell, it is said to be discharging

Pb$\rightarrow$pb^{2+}+2e$^-$ (anode)

Pb^{2+}+ SO$_4$$^{2-}$$\rightarrow$pbso$_4$

PbO$_2$+4H $^+$ +2e$^-$+so$_4$$^{2-}$$\rightarrow$pbso$_4$ +2H$_2$0(cathode)

NET CELL REACTION:
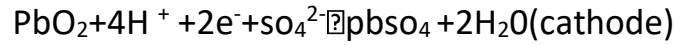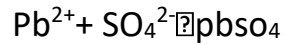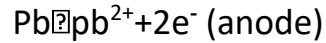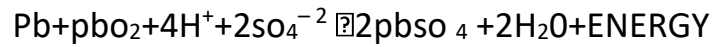
Pb+pbo$_2$+4H$^+$+2so$_4$$^{-2}$ $\rightarrow$2pbso $_4$ +2H$_2$0+ENERGY

CHARGING:

When anode and cathode covered with pbso$_4$, the cell cases to function. In order to recharge, the following reactions takes place.

Pbso$_4$+2H$_2$0+2e$^-$$\rightarrow$ pbo$_2$+4H$^+$+SO$_4$ $^{2-}$(anode)

Pbso$_4$+2e$^-$$\rightarrow$ pb+so$_4$ 2-(cathode)

NET REACTION:

Pbso$_4$+2H$_2$O+energy$\rightarrow$pb+pbo$_2$+4H$^+$+2SO$_4$$^{2-}$
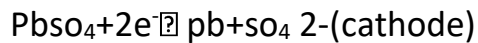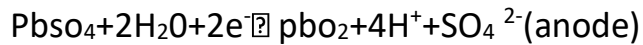
USES:

⮚ Electrical Vehicles, Lab, Hospitals, Telephone Exchange.
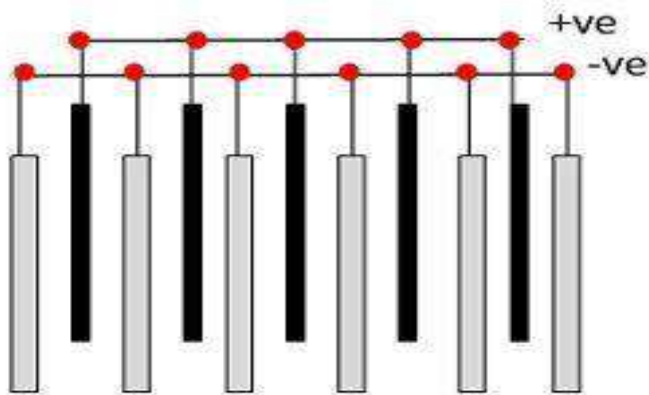
Arrangements of Plates in a Lead-acid-Battery
Circuit GLobe

APPLICATION:

Traction batteries are used in golf carts and other battery electric vehicles.

NICKEL-CADMIUM-HYDRIDE CELL:

This cell is a secondary cell that produces a potential of about 1.4V which is slightly lower than that of zinc – carbon cell.

It consists of cadmium anode and a cathode of a paste of $Nio(OH)_2$. The electrode reactions in the cell during discharge.

$CdH_2(S) +2OH^- \rightarrow cd+2H_2O+2e^-$ (anode)

$Nio(OH)_2+H_2O+2e^- \rightarrow Ni(OH)_2+2OH^-$ (cathode)

_____

$CdH_2(S) +Nio(OH)_2 \rightarrow Ni(OH)_2+cd+H_2O$
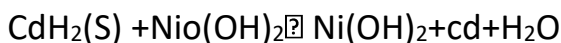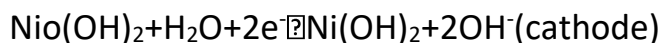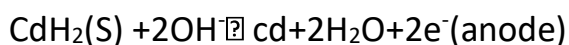
The cell reactions can be readily reversed since the reaction products $NI(OH)_2$ & $cd(OH)_2$ adhere to the electrode surfaces.

seal
core
can
"jelly roll"
insulating washer
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cap
vent ball
cover
positive tab
separators
pressed powdered negative electrode
sintered positive electrode
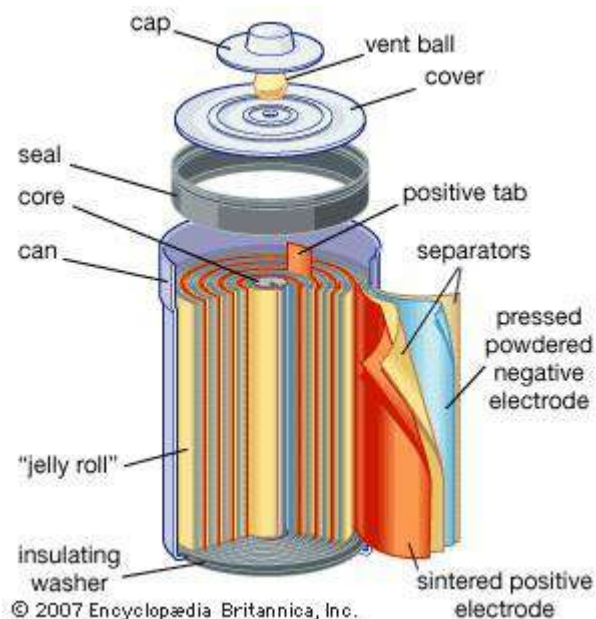
- In portable power tools, cd players, electronic cars, electronic calculators, cordless electronic shavers and transistors.
- Nickal metal hydride is an alloy anode and cathode made up of metal foils belongs to cd and ni.

LITHIUMIONS CELLS: (RECHAREABLE)

These cells do not contain metallic lithium hence they are called as lithium ion cells.

The cell operation does not actually involve oxidation and reduction. But it was the transport of Li+ ions through the electrolyte from one electrode to the other by the transport of electrons through the external circuit to maintain charge balance.

When the cell of Li C_oO_2 and graphite is constructed it is in uncharged state with no Li^+ ions between the layers of carbon atoms in the graphite when the cell Is discharging, lithium ions leave Li C_oO_2 and travel through the electrolyte to the graphite.

- Li C_oO_2+ C6 ▢ Li $_{1-x}$ C_oO_2 +Li $_x$ C_6
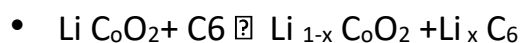
When the cell is spontaneous discharging to provide electrical power, Li^+ ions move track through the electrolyte to the cobalt oxide while the electrons move through external circuit from graphite electrode to the cobalt oxide electrode if we represent amount of Li^+ transferring by 'y'. The charge reaction is

- Li1-x CoO2 +LixC6 ▢ LI1-X+Y Co O2+LiX-Y C6

Negative Current Collector (Cu)   Anode   Separator   Cathode   Positive Current Collector (Al) Li^+
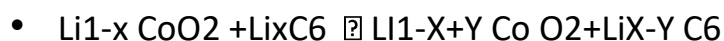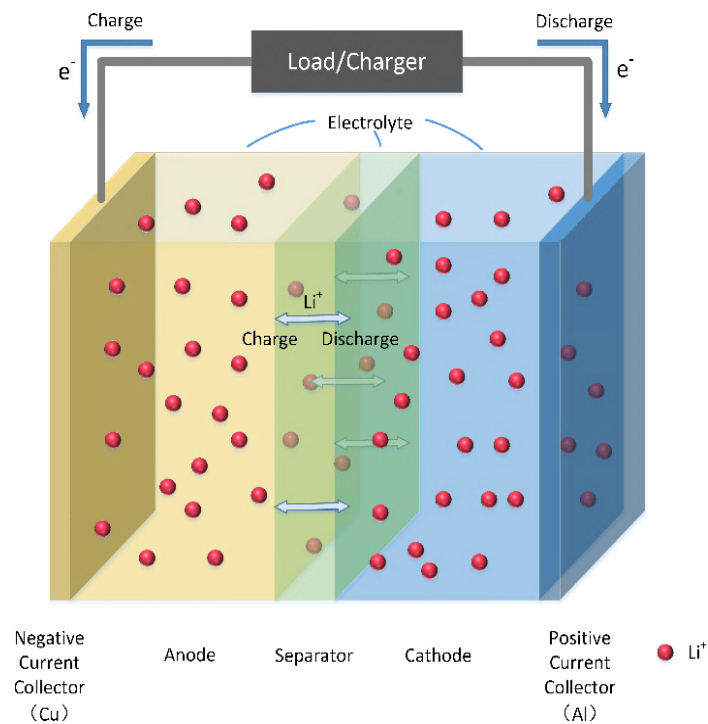
APPLICATIONS:

- Power backups/ ups, Mobile, Laptops, and other commonly used consumer electronic, electric mobility, Energy storage system.

Fuel cells:

The galvanic cell can only produce. Electrical energy for a limited time because the electrode reactant is eventually depleted.

Fuel cells are the electro chemical cells in which electrode reactants are supplied continuously and are able to operate without theoretical limits as long as the apply of reactant is maintained. In fuels cells electrical energy is obtained without combination from oxygen and a gas that can be divided.

A Fuel cells convert the chemical energy of the fuel directly to electricity.

Fule + O$_2$→Oxidation product + Electricity.

Hydrogen-oxygen fuel cell:

It consists of a hot concentrated solution. Of KOH as an electrolyte in the entire compartment which is in contact with two process electrode that contain catalyst to the electrode reactions. Gaseous hydrogen and oxygen under pressure as circuited as to come in contact with the electrode.

O$_2$+2H$_2$o+4e$^-$ →4OH$^-$

2H$_2$+4OH$^-$ →4H$_2$O+4e$^-$

2H$_2$+O$_2$ →2H$_2$O
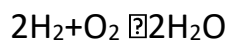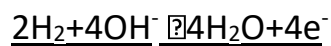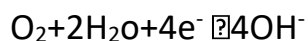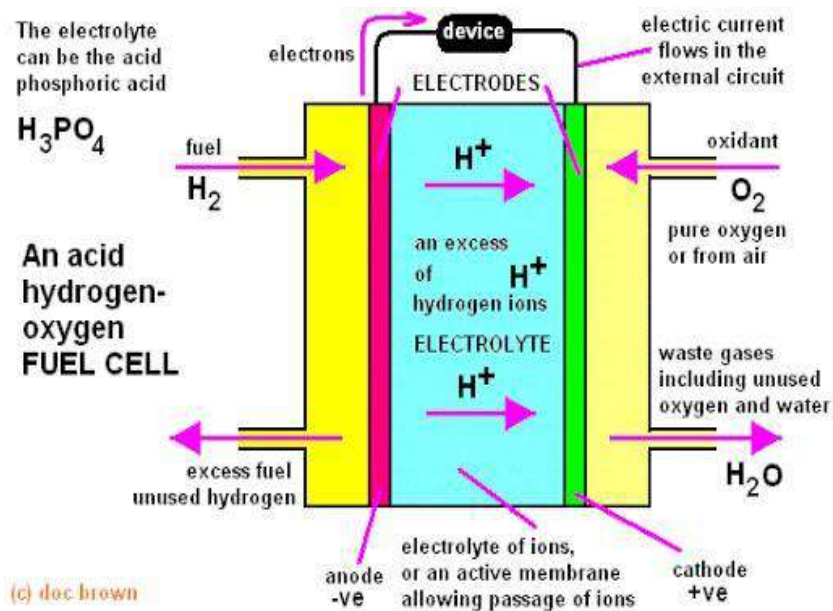
The standard EMF of the cell is

$$E^0 = E^0_{RED} - E^0_{OX}$$

$$=0.83+0.4$$

$$=1.23V$$

Large number of these cells are connected in series to make a battery called fuel call battery of fuel battery. H_2-O_2 fuel cells are an attractive alternative to gasoline pressured only product of the reaction is harmless water. These are thermodynamically efficient converting as much as 75% of available energy to useful work.

Disadvantages:

- Energy cost of generating H2 fuel.
- Problem in storing.
- Availability of alternative fuels.

Application:

- Used as an energy resource in space vehicles submarines, military vehicle.
- The weight of fuel battery for 15 days is about 25kg.
- The product of water pores to be a valuable source of fresh water to the astronauts.

Methanol fuel cell:

It is a subcategory of proton. Exchange fuel cells the oxidation of methanol on catalyst layer to from CO_2 water is consumed at anode which is produced at cathode. The positive ions (H^+) are transformed across. The proton exchange membrane often made from anode to cathode where they react with oxygen to produce water.

Electrons are transacted through an external circuit from anode to cathode. Platinum is used as catalyst in both half reactions.

Methanol or water mixture is circulated through an anode while O_2 or air is circulated at cathode.

$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (anode)

$\underline{3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O\ \text{(cathode)}}$

$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$
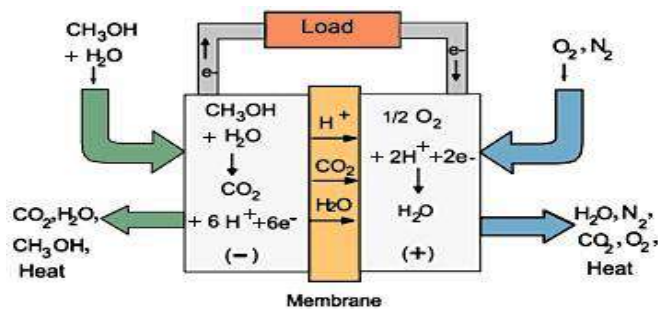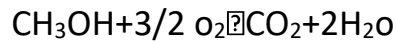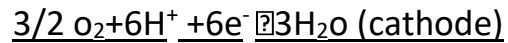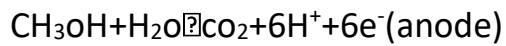
Figure 2. Flow of reactants, water, CO_2 and heat for a Direct Methanol Fuel Cell (DMFC).

The $6e^-$ pass the load resistance of the enter circuit and are consumed at the cathode together with six protons.

For the reaction of molecules of methanol, $3/2$ molecules will be reduced to $3H_2O$. From this, for a $6e^-$ charge transfer a standard cell voltage of 1.21V and energy density of 6 kwh/kg methanol is produced.

POLYMERS

Polymers are the high molecular weight compounds obtained by repeated union of simple molecules. (Monomers). **Ex**: Starch, Polyvinyl chloride, Polyethylene, Nylon 6, 6 and etc.

The word ' *Polymer*' is coined from two Greek words: *poly* means many and *mer* means unit or part. The term polymer is defined as very large molecules having high molecular mass. These are also referred to as *macromolecules*, which are formed by joining of repeating structural units on a large scale. The repeating structural units are derived from some simple and reactive molecules known as *monomers* and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called *polymerization*. The transformation of ethene to polythene and interaction of hexamethylene diamine and adipic acid leading to the formation of Nylon 6, 6 are examples of two different types of polymerisation reactions.
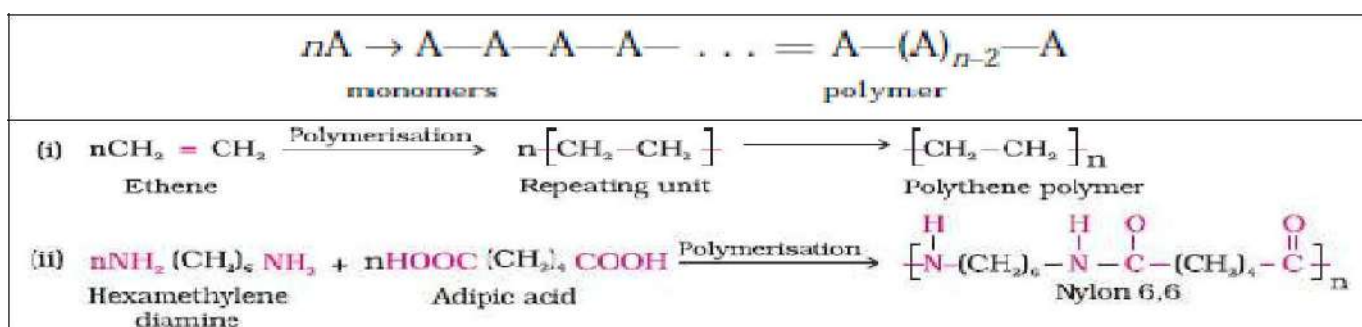
Monomers

Monomer is a simple repetitive unit which when joined together in large numbers which give rise to a polymer. These are the building blocks of Polymer

Ex: Vinyl chloride, ethene, propylene etc.
The number of repeating units (n) in the chain so formed is called the **Degree of polymerization**(DP=n).
Polymers with ahigh degree of polymerization are called **High polymers** and those with low degree of polymerization are called **Oligopolymers**

Degree of polemerization (DP).

Degree of polymerization is a number, which indicates the number of repetitive units (monomers) present in the polymer. By knowing the value of DP, the molecular weight of the polymer can be calculated.

[Molecular wt of the polymer] = DP x Molecular wt of each monomer. DP is represented as 'n'.

Ex: (CH2 – CH2) n Polythene
Here 'n' is the DP.

i) Calculate the molecular weight of the polythene polymer given DP is 100.

Molecular weight of the polythene = DP X Molecular weight of Polethene
$$= 100 \text{ X } 28 = \textbf{2800.}$$

Basic Concepts:

1.Functionality

The *functionality of a monomer* is the number of sites it has for bonding to other monomers under the given

conditions of the polymerization reaction. Thus, a bifunctional monomer, i.e., monomer with functionality two, can link to two other molecules under suitable conditions.

A polyfunctional monomer is one that can react with more than two molecules under the conditions of the polymerization reactions.

Definition: The number of bonding sites (or) reactive sites or functional groups present in the molecule.

Ex: The double bond in vinyl monomers ($CH2 = CHX$) can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination.

$$H_2C=CHX \rightarrow \text{ --- } CH_2 - CHX \text{ ------}$$
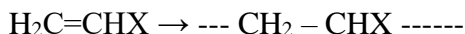
A). When the functionality of monomer is two bifunctional linear (or) straight chain polymer is formed.
   Ex: (a)vinyl monomers (b)adipic acid (c)hexamethylene diamine
   Example for polymer: HDPE (high density polythene)
                          -M-M-M-M-M-M-M-

B). When the functionality of monomer is three (tri-functional), three-dimensional net work polymer is formed. Ex: phenol, glycerol
   Examples for polymers : Urea formaldehyde, phenol formaldehyde.

                          -M-M-M-M-M-M-M-
                          -M-M-M-M-M-M-M-
                          -M-M-M-M-M-M-M-

C). when a trifunctional monomer is mixed in small amounts with a bifunctional   monomer, a branched chain polymer is formed.
    Ex: LDPE (LOW density polyethene)

                       -M-N-M-N-M-N-M-N-
                          M   N
                          N   M
                          M   N
                          N   M
                          M   N

2. Nomenclature of Polymers
 Polymers are classified in to four types
 a) Homo Polymers   b) Hetero polymers c) Homo chain Polymers   d) Hetero chain polymers
 a) Homo Polymers   : Polymers made up of with same type of monomers are called homo polymers
   eg: Poly ethylene, PVC

 b) Hetero polymers : Polymers made up of with different type of monomers are called hetero polymers
    eg: buna-s rubber

   Graft copolymers: If main chain consists of one momomer and branched chain consists of another monomers are called Graft copolymers
                       -M-M-M-M-M-M-M-M
                          N   N
                          N   N
                          N   N
                          N   N

2

N   N

c) Homo chain Polymers : If the main chain consists of only one type of atoms called Homo chain Polymers eg: polyethylene.   –C-C-C-C-C-C-C-C-

d) Hetero chain polymers: If the main chain consists of different type of atoms called Hetero chain Polymers
   eg: Polyester, Nylon-6.   –C-O-C-O-C-O-C-O-

Copolymers

Homopolymer from a single monomer, copolymer from two (or more) monomers
chain copolymerization (different monomers incorporated during the growth of the polymer chain) can
lead to:
          alternating copolymer – ABABABABABABABABABABABA
          block copolymer - AAAAAAAABBBBBBBBBBBBAAA
          random copolymer - BAABBAABABBABABBBAABBAB
          graft copolymer - branches of a different polymer are attached to a polymer chain
                  AAAAAAAAAAAAAAAAAAAAAAAABBBBBBBBBBBBBBBBBB
                  (generate reactive site on existing polymer chain, grow new chain)

3. Tacticity – The difference in configuration due to the orientation of different functional groups with respect to the main chain is called tacticity. It is of three types

a). Isotactic – If all the functional groups are arranged on the same side of main chain is called isotactic

b) .Syndiotactic - If all the functional groups are arranged in the alternative fashion of main chain is

   called Syndiotactic

c). Atactic - If all the functional groups are arranged in random of main chain is called atactic

Basis of Classification		Polymer Type
Origin	-	Natural, Semi synthetic, Synthetic
Thermal Response	-	Thermoplastic, Thermosetting
Mode of formation	-	Addition, Condensation
Line structure	-	Linear, Branched, Cross-linked
Application and Physical Properties	-	Rubber, Plastic, Fibers
Tacticity	-	Isotactic, Syndiotactic, Atactic
Crystallinity	-	Non crystalline(amorphous), Semi-crystalline, Crystalline
Polarity	-	Polar, Non polar
Chain	-	Hetro, Homo-chain

There are several ways of classification of polymers based on some special considerations. The following are some of the common classifications of polymers: [1] by Source [2] by Backbone of the chain [3] by Structure [4] by Compostion [5] by Mode of Polymerization [6] by Molecular force

Classification Based on Source: [1] *Natural Polymers*: These polymers are found in plants and animals. Examples are proteins, cellulose, starch, resins and rubber. [2] *Semi-synthetic Polymers*: Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are the usual examples of this sub category. [3] *Synthetic Polymers*: A variety of synthetic polymers as plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna - S) are examples of man-made polymers.

Classification Based on Backbone of the polymer chain: *Organic and Inorganic Polymers:*
A polymer whose backbone chain is essentially made of carbon atoms is termed as **organic polymer**. The atoms attached to the side valencies of the backbone carbon atoms are, however, usually those of hydrogen, oxygen, nitrogen, etc. The majority of synthetic polymers are organic. On the other hand, generally chain backbone contains no carbon atom is called **inorganic polymers**. Glass and silicone rubber are examples of it.

Classification Based on Structure of Polymers: [1] *Linear Polymers*: These polymers consist of long and straight chains. The examples are high density polythen, PVC, etc.

[2] *Branched Polymers*: These polymers contain linear chains having some branches, *e.g.*, low density polythene.

[3] *Cross-linked Polymers*: These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains, e.g. vulcanized rubber, urea-formaldehyde resins, etc. Cross linked polymers are hard and do not melt, soften or dissolve in most cases.

Linear Polymers	Branched Polymers	Cross-linked Polymers
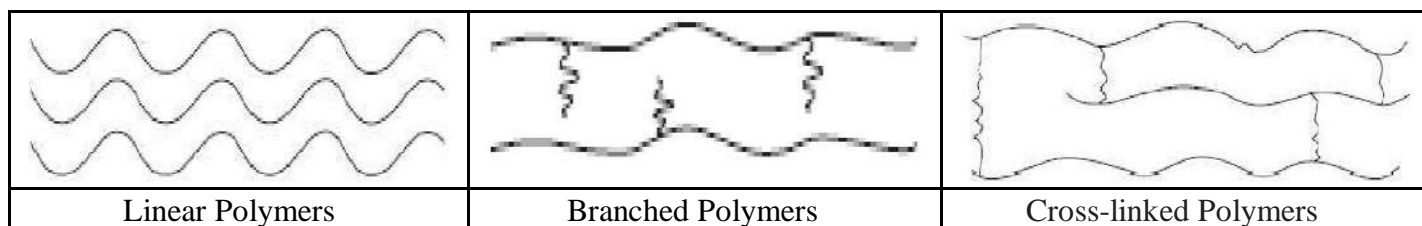
Classification Based on Composition of Polymers: [1] *Homopolymer:* A polymer resulting from the polymerization of a single monomer; a polymer consisting substantially of a single type of repeating unit.
[2] *Copolymer:* When two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer.
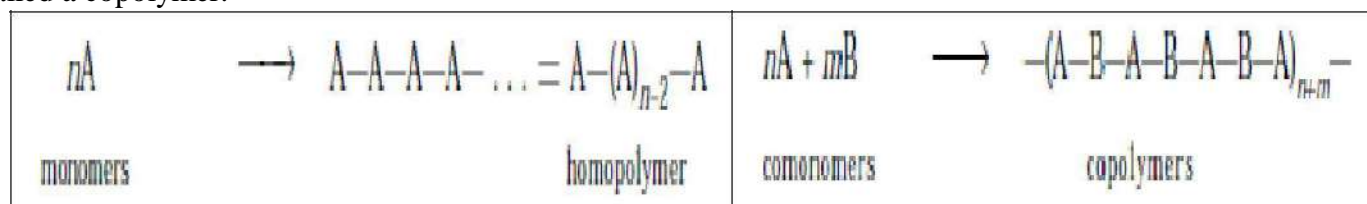
Lets imagine now two monomers(A and B) are made into a copolymer in many different ways
In an **alternating copolymer**, the two monomers are arranged in an alternating fashion
In a **random copolymer** the two monomers may follow in any order.
In a **block copolymer** all of one type of monomers are grouped together , and all of the other are grouped

together

In **graft copolymer**, a block copolymer can be thought of as two homopolymers joined together at the ends: branched copolymers with one kind of monomers in their main chain and another kind of monomers in their side chains.

Alternating	—A—B—A—B—A—B—A—B—A—B—A—B—A—B—
Random	—A—A—B—A—B—B—A—B—A—A—B—B—B—A—
Block	—A—A—A—A—A—A—A—B—B—B—B—B—B—B—
Graft	... —A—A—A—A—A—A—A—A— ... with B—B side chains

Copolymerization: A *heteropolymer* or *copolymer* is a polymer derived from two (or more) monomeric species, as opposed to a homopolymer where only one monomer is used. Copolymerization refers to methods used to chemically synthesize a copolymer. Commercially relevant copolymers include ABS plastic, SBR, Nitrile rubber, styrene-acrylonitrile,

Classification Based on Mode of Polymerisation: Polymers can also be classified on the basis of mode of polymerisation into two sub groups; (a) *Addition Polymers* and (b) *Condensation Polymers*.

Addition Polymers: The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds, *e.g.*, the formation of polythene from ethene and polypropene from propene. However, the addition polymers formed by the polymerisation of a single monomeric species are known as homopolymer, *e.g.*, polythene.

$$n \, CH_2 = CH_2 \longrightarrow -(CH_2 - CH_2)_n \text{ Homopolymer}$$
$$\text{Ethene} \qquad\qquad\qquad \text{Polythene}$$

The polymers made by addition polymerisation from two different monomers are termed as copolymers, *e.g.*, Buna-S, Buna-N, etc.

$$n CH_2 = CH - CH = CH_2 + n \, C_6H_5CH=CH_2 \longrightarrow -(CH_2 - CH = CH - CH_2 - CH_2 - \overset{\overset{\textstyle C_6H_5}{\textstyle |}}{CH})_n$$
$$\text{1, 3-Butadiene} \qquad\qquad \text{Styrene} \qquad\qquad\qquad \text{Butadiene-styrene copolymer}$$
$$\text{(Buna - S)}$$

Condensation Polymers: The condensation polymers are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units. In these polymerisation reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place. The examples are terylene (dacron), nylon 6, 6, nylon 6, etc. For e.g., nylon 6, 6 is formed by the condensation of hexamethylene

diamine with adipic acid.

$$n \ H_2N \ (CH_2)_6 \ NH_2 + n \ HCOC \ (CH_2)_4 \ COOH$$
$$\longrightarrow \ -\!\!\left[NH(CH_2)_6 \ NHCO(CH_2)_4CO\right]\!\!-_n + n \ H_2O$$

Nylon 6, 6

It is also possible, with three functional groups (or two different monomers at least one of which is tri-functional), to have long linkage sequences in two (or three) dimensions and such polymers are distinguished as *cross linked polymers*.

Classification Based on **Molecular Forces:** The mechanical properties of polymers are governed by intermolecular forces, *e.g.*, van der Waals forces and hydrogen bonds, present in the polymer. These forces also bind the polymer chains. Under this category, the polymers are classified into the following groups on the basis of magnitude of intermolecular forces present in them. They are (i) *Elastomers* (ii) *Fibers* (iii) *Liquid resins* (iv) *Plastics* [(a) *Thermoplastic* and (b) *thermosetting plastic*].

Elastomers: These are rubber – like solids with elastic propert ies. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc.

Fibers: If drawn into long filament like material whose length is at least 100 times its diameter, polymers are said to have been converted into 'fibre'. Fibres are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. Examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

Liquid Resins: Polymers used as adhesives, potting compound sealants, etc. in a liquid form are described liquid resins. Examples are epoxy adhesives and polysulphide sealants.
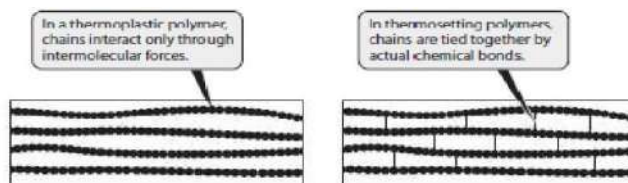
Plastics
: A polymer is shaped into hard and tough utility articles by the application of heat and pressure; it is used as a 'plastic'. Ty pical examples are polystyrene, PVC and polymethyl methacrylate.

They are two types (a) thermoplastic and (b) thermosetting plastic.

Thermoplastic Polymers: Some polymers soften on heating and can be converted into any shape that they can retain on cooling. The process of heating, reshaping and retaining the same on cooling can be repeated several times. Such polymers, that soften on heating and stiffen on cooling, are termed 'thermoplastics'. These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Polyethylene, PVC, nylon and sealing wax are examples of thermoplastic polymers.

Thermosetting Polymers: Some polymers, on the other hand, undergo some chemical change on heating and convert themselves into an infusible mass. They are like the yolk of egg, which on heating sets into a mass, and, once set, cannot be reshaped. Such polymers, that become infusible and insoluble mass on heating, are

called 'thermosetting" polymers. These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.

In a thermoplastic polymer, chains interact only through intermolecular forces.

In thermosetting polymers, chains are tied together by actual chemical bonds.

13.6 Tacticity:-

It may be defined as the geometric arrangement (orientation) of the characteristic group of monomer unit with respect to the main chain (backbone) of the polymers. On the basis of structure, polymer may be classified into three groups:-

A. Isotactic polymer:- It is the type of polymer in which the characteristic group are arranged on the same side of the main chain.

Isotactic Polypropene
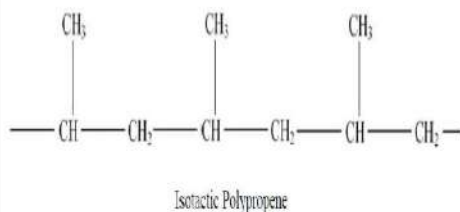
B. Syndiotactic polymer:- A polymer is said to be syndiotactic if the side group (characteristic group) are arranged in an alternate fashion.

Syndiotactic Polypropene
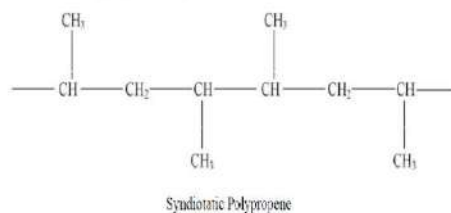
C. Atactic polymer:- A polymer is said to be atactic, if the characteristic groups (side group) are arranged in irregular fashion (randomness) around the main chain. It has proper strength and more elasticity.

Atactic Polypropene
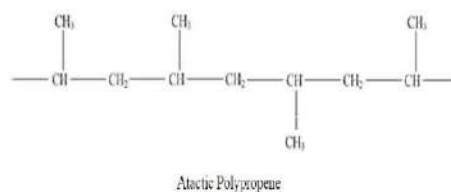
Types of Polymerization

There are four types of polymerisation reactions; (a) *Addition* or *chain growth* polymerisation (b) *Coordination* polymerisation (c) *Condensation* or *step growth* polymerisation and (d) *Copolymerization*

Addition Polymerisation: In this type of polymerisation, the molecules of the same monomer or different monomers add together on a large scale to form a polymer. The monomers normally employed in this type of polymerization contain a carbon-carbon double bond (unsaturated compounds, *e.g.*, alkenes and their derivatives) that can participate in a *chain reaction*. A chain reaction consists of three stages, Initiation, Propagation and Termination.

In the *Initiation step* an initiator molecule is thermally decomposed or allowed to undergo a chemical reaction to generate an "active species." This "active species," which can be a free radical or a cation or an anion, then initiates the polymerization by adding to the monomer's carbon-carbon double bond. The reaction occurs in such a manner that a new free radical or cation or anion is generated. The initial monomer becomes the first repeat unit in the incipient polymer chain. In the *Propagation step*, the newly generated "active species" adds to another monomer in the same manner as in the initiation step. This procedure is repeated over and over again until the final step of the process, termination, occurs. In the *Termination step*, the growing chain terminates through reaction with another growing chain, by reaction with another species in the polymerization mixture, or by the spontaneous decomposition of the active site. Under certain conditions, anionic can be carried out without the termination step to generate so-called "living" polymers.

The following are several *general characteristics of addition polymerization*:
[1] Once initiation occurs, the polymer chain forms very quickly [2] The concentration of active species is very low. Hence, the polymerisation mixture consists of primarily of newly-formed polymer and unreacted monomer [3] Since the carbon-carbon double bonds in the monomers are, in effect, converted to two single carbon-carbon bonds in the polymer, so energy is released making the polymerization exothermic with cooling often required.

The mechanism of addition polymerisation can be divided broadly into two main classes, Free radical and Ionic polymerization and again Ionic is divided into two types Cationic and anionic Polymerisations

Free radical polymerization: A variety of alkenes or dienes and their derivatives are polymerised in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. A free radical may be defined as an intermediate compound containing an odd number of electrons, but which do not carry an electric charge and are not free ions. For example, the polymerization of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide initiator.
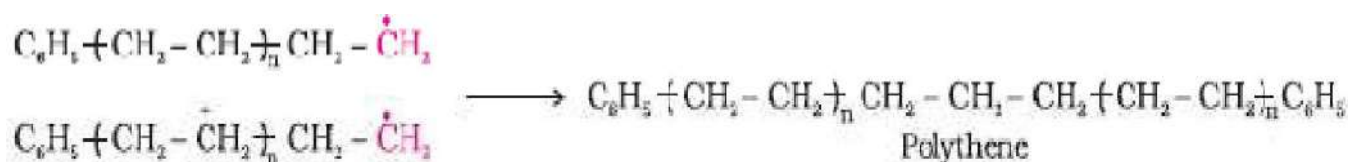
The first stage of the chain reaction is the *initiation process*; this process starts with the addition of phenyl free radical formed by the peroxide to the ethene double bond thus generating a new and larger free radical.
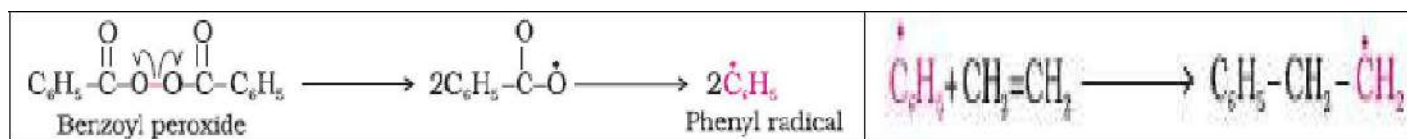
The second stage of the chain reaction is the *propagation process*, the radical reacts with another molecule of ethene, and another bigger sized radical is formed. The repetition of this sequence with new and bigger radicals carries the reaction forward and the step is chain propagating step

$$C_6H_5 - CH_2 - \overset{\bullet}{C}H_2 + CH_2 = CH_2 \longrightarrow C_6H_5 - CH_2 - CH_2 - CH_2 - \overset{\bullet}{C}H_2$$

$$C_6H_5 +CH_2 - CH_2 \}_n CH_2 - \overset{\bullet}{C}H_2$$

The final stage of the chain reaction is the *termination process*; the product radical formed reacts with another radical to form the polymerised product.

$$C_6H_5 +CH_2 - CH_2 \}_n CH_2 - \overset{\bullet}{C}H_2$$
$$C_6H_5 +CH_2 - \overset{\bullet}{C}H_2 \}_n CH_2 - \overset{\bullet}{C}H_2 \longrightarrow C_6H_5 +CH_2 - CH_2 \}_n CH_2 - CH_2 - CH_2 +CH_2 - CH_2 \}_n C_6H_5$$
Polythene

Ionic Polymerisation: The addition polymerization that takes place due to ionic intermediate is called ionic polymerization. Based on the nature of ions used for the initiation process ionic polymerization classified into two types; (a) Cationic polymerization and (b) Anionic polymerization

Cationic polymerization depends on the use of cationic initiators which include reagents capable of providing positive ions or **H⁺** ions. Typical examples are aluminium chloride with water ($AlCl_3+H_2O$) or boron trifluoride with water (BF_3+H_2O). They are effective with monomers containing electron releasing groups like methyl ($-CH_3$) or phenyl ($-C_6H_5$) etc. They include propylene($CH_3CH=CH_2$) and the styrene ($C_6H_5CH=CH_2$).

i) Chain Initiation: Decomposition of the initiator is shown as $BF_3 + H_2O \rightarrow$ **H⁺** $+ BF_3(OH^-)$. The proton (**H⁺**) adds to C – C double bond of alkene to form stabl e carbocation.

$(G = e^-$ donating group. + I effect)
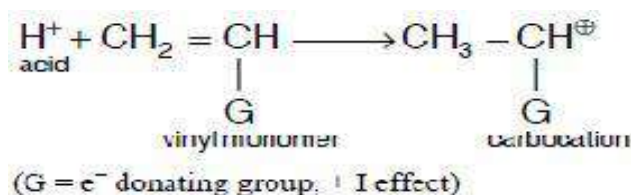
*ii) **Chain Propagation:*** Carbocation add to the C – C double bond of another monomer molecule to from new carbocation.

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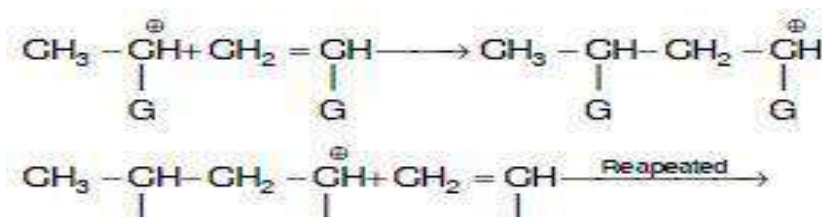
iii) Chain Termination: Reaction is terminated by combination of carbocation with negative ion (or) by loss of proton

$$CH_3 - CH(-CH_2 - CH-)_n\, CH_2 - CH + HSO_4^- \longrightarrow$$

with G substituents below each CH, and the product:

$$CH_3 - CH(-CH_2 - CH)_n - CH = CH + H_2SO_4$$

with G substituents.
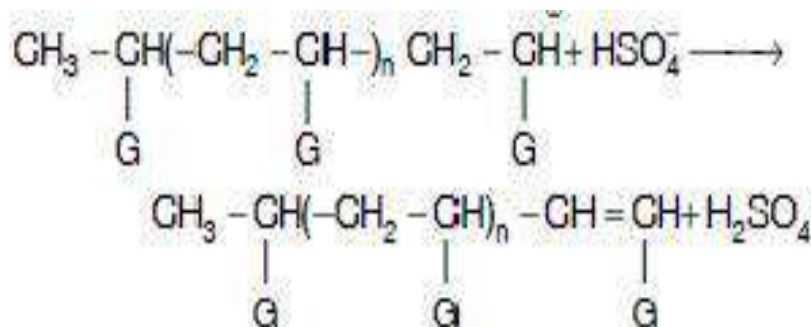
Anionic polymerization depends on the use of anionic initiators which include reagents capable of providing negative ions. Typical catalysts include sodium in liquid ammonia, alkali metal alkyls, Grignard reagents and triphenylmethyl sodium [$(C_6H_5)_3$C-Na].

They are effective with monomers containing electron withdrawing groups like nitrile (–CN) or chloride (-Cl), etc. They include acrylonitrile [CH_2=C(CN)], vinyl chloride [CH_2=C(Cl)], methyl methacrylate [CH_2=C(CH$_3$)COOCH$_3$], etc.

i) Chain Initiation: Potassium amide ($K^+NH_2^-$) adds to C – C double bond of alkene to form stabl e carbanion.

where W is electron withdrawing group

ii) Chain Propagation: Carbanion adds to the C – C double bond of another monomer molecule to from new carbanion.

*iii)* Anionic polymerization has no chain termination reaction. So it is called living polymerization.

Coordination polymerization: It is also a subclass of addition polymerization. It usually involve transition-metal catalysts. Here, the "active species" is a coordination complex, which initiates the polymerization by adding to the monomer's carbon-carbon double bond. The most important catalyst for

coordination polymerization is so-called Ziegler-Natta catalyst discovered to be effective for alkene polymerization. Ziegler-Natta catalysts combine transition-metal compounds such as chlorides of titanium with organometallic compounds [TiCl_3 with Al(C$_2$H$_5$)$_3$]. An important property of these catalysts is that they yield stereoregular polymers when higher alkenes are polymerized, e.g., polymerization of propene produces polypropene with high selectivity. Branching will not occur through this mechanism since no radicals are involved; the active site of the growing chain is the carbon atom directly bonded to the metal.
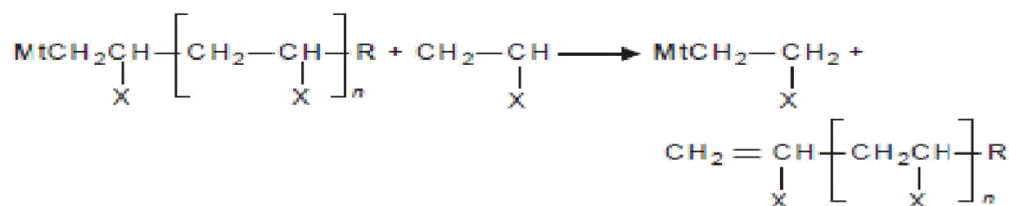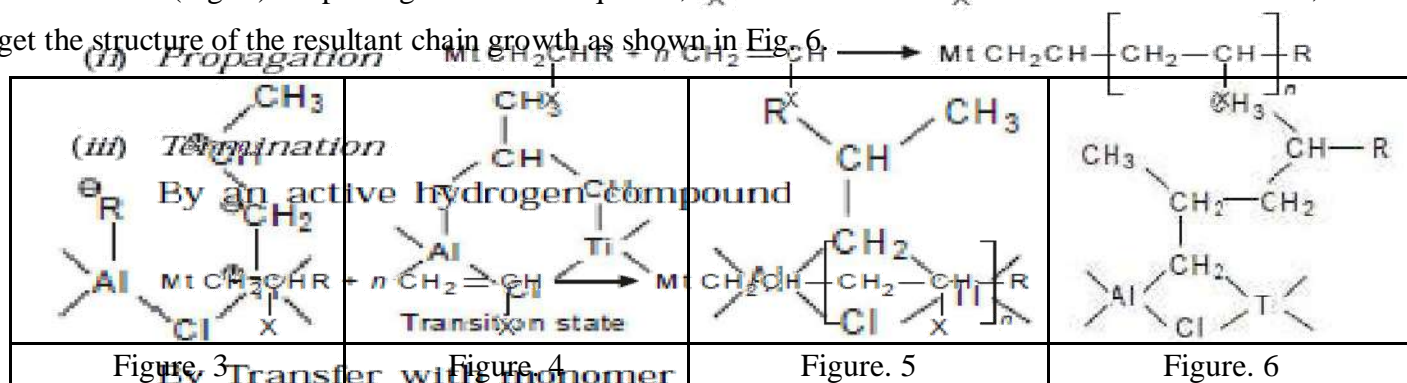
Zeigler-Nata catalysts: These are a special type of coordination catalysts, comprising two components, which are generally referred to as the catalyst and the cocatalyst. The catalyst component consists of chlorides of titanium (TiCl$_3$ and TiCl$_4$) and the cocatalysts are organometallic compound such as triethyl aluminium (Al(C$_2$H$_5$)$_3$).

Triethyl aluminium [Al(R)$_3$] act as the electron acceptor whereas the electron donor is titanium halides and the combination, therefore, readily forms coordination complexes (Fig. 1). The complex formed, now acts as the active centre. The monomer is complexed with the metal ion of the active centre in a way that the monomers attached towards the Ti— C bond (C from the alkyl group R) in the active centre, when it forms a π complex with the Ti ion(Fig. 2).

| Figure. 1 | Figure. 2 |
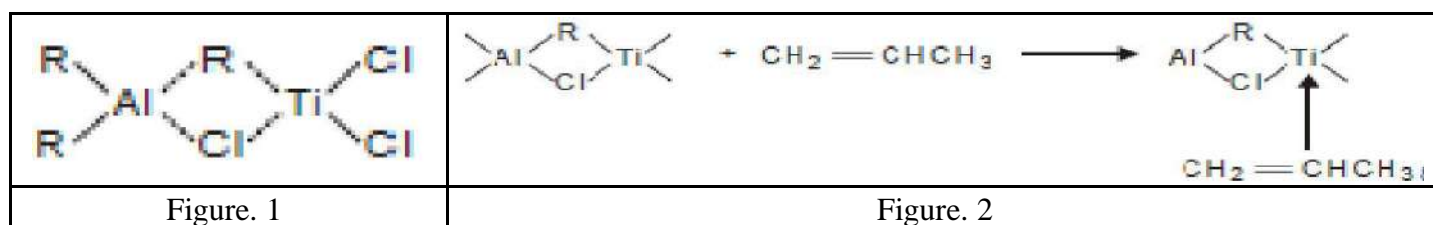
The bonds between R and Ti opens up producing an electron deficient Ti and a carbanion at R (Fig. 3). The Ti ion attracts the π electrons pair or the monomer and forms ☐ bond (Fig. 4). This transition state now gives rise to the chain growth at the metal carbon bond, regenerating the active centre (Fig. 5). Repeating the whole sequence, with the addition of second monomer molecule, we will get the structure of the resultant chain growth as shown in Fig. 6.

(i) Initiation   Mt—R + CH$_2$=CH → MtCH$_2$CHR
     active centre   X

(ii) Propagation   MtCH$_2$CHR + nCH$_2$=CH → Mt CH$_2$CH—[CH$_2$—CH]$_n$—R

(iii) Termination
By an active hydrogen compound

| Figure. 3 | Figure. 4 | Figure. 5 | Figure. 6 |

By Transfer with monomer

MtCH$_2$CH—[CH$_2$—CH]$_n$—R + CH$_2$—CH → MtCH$_2$—CH$_2$ +
   X   X   X   X

CH$_2$=CH—[CH$_2$CH]$_n$—R
    X   X

By spontaneous internal transfer

MtCH$_2$CH—[CH$_2$—CH]$_n$—R → MtH + CH$_2$=C—[CH$_2$—CH]$_n$—R
   X   X   X   X
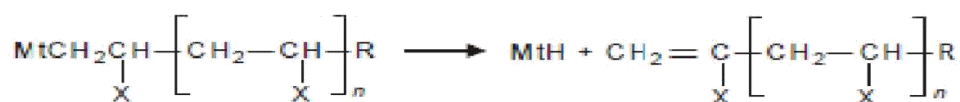
Condensation Polymerisation: This type of polymerisation generally involves a repetitive condensation reaction (two molecules join together, resulting loss of small molecules) between two bi-functional monomers. These polycondensation reactions may result in the loss of some simple molecules as water, 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 an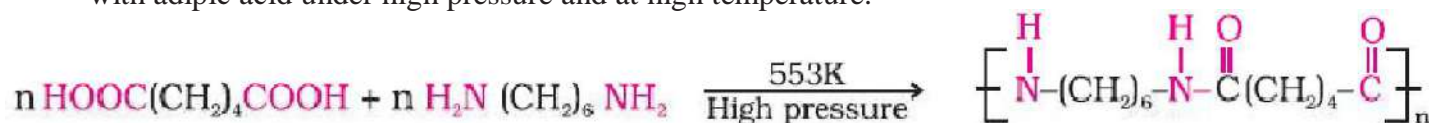d the sequence of condensation goes on. Since, each step produces a distinct functionalised species and is independent of each other; this process is also called as step growth polymerisation. The type of end polymer product resulting from a condensation polymerization is dependent on the number of functional end groups of the monomer which can react.

Monomers with only one reactive group terminate a growing chain, and thus give end products with a lower molecular weight. Linear polymers are created using monomers with two reactive end groups and monomers with more than two end groups give three dimensional polymers which are cross linked.

Polyester is created through ester linkages between monomers, which involve the functional groups carboxyl and hydroxyl (an organic acid and an alcohol monomer). The formation of polyester like terylene or dacron by the interaction of ethylene glycol and terephthalic acid is an example of this type of polymerisation.

$$n\ HOH_2C-CH_2OH\ +\ n\ HOOC-\langle\bigcirc\rangle-COOH\ \longrightarrow\ \left[OCH_2-CH_2-\overset{\overset{O}{\|}}{C}-\langle\bigcirc\rangle-\overset{\overset{O}{\|}}{C}\right]_n$$

Polyamide is created through amide linkages between monomers, which involve the functional groups carboxyl and amine (an organic acid and an amine monomer). Nylon-6 is an example which can be manufactured by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.

$$n\ HOOC(CH_2)_4COOH\ +\ n\ H_2N\ (CH_2)_6\ NH_2\ \xrightarrow[\text{High pressure}]{553K}\ \left[\overset{H}{\underset{|}{N}}-(CH_2)_6-\overset{H}{\underset{|}{N}}-\overset{\overset{O}{\|}}{C}(CH_2)_4-\overset{\overset{O}{\|}}{C}\right]_n$$

This type of polymerization normally employs two bifunctional monomers that are capable of undergoing typical organic reactions. For example, a diacid can be allowed to react with a diol in the presence of an acid catalyst to afford polyester. In this case, chain growth is initiated by the reaction of one of the diacid's carboxyl groups with one of the diol's hydroxyl groups. The free carboxyl or hydroxyl group of the resulting dimer can then react with an appropriate functional group in another

monomer or dimer. This process is repeated throughout the polymerization mixture until all of the monomers are converted to low molecular weight species, such as dimers, trimers, tetramers, etc. These molecules, which are called oligomers, can then further react with each other through their free functional groups. Polymer chains that have moderate molecular weight can he built in this manner.
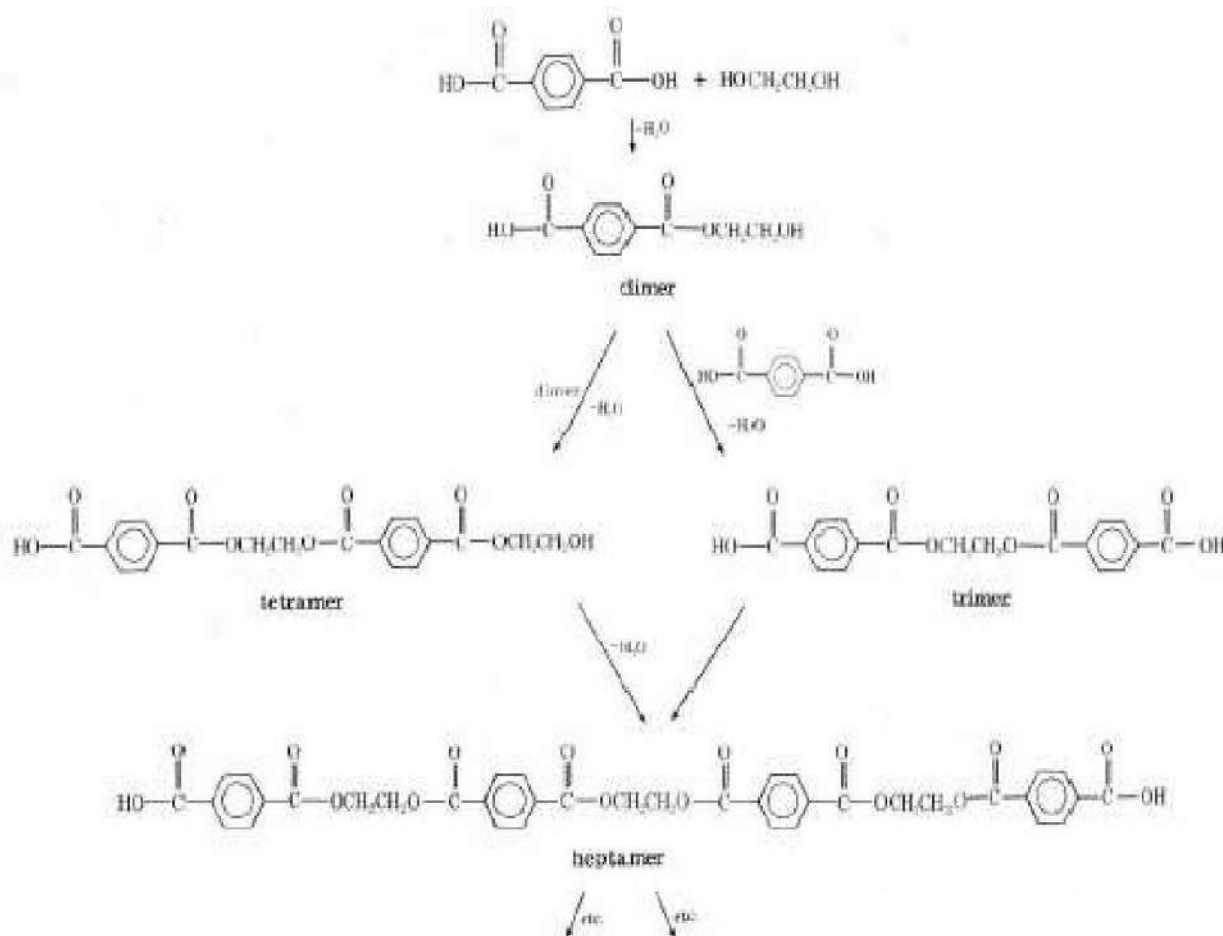
The following are several general characteristics of this type of polymerization

1) the polymer chain forms slowly, sometimes requiring several hours to several days

(2) All of the monomers are quickly converted to oligomers, thus, the concentration of growing chains is high (3) Since most of the chemical reactions employed have relatively high energies of activation, the polymerization mixture is usually heated to high temperatures (4) Step-reaction polymerizations normally afford polymers with moderate molecular weights, i.e., <100,000 (5) Branching or crosslinking does not occur unless a monomer with three or more functional groups is used.

Copolymerization: It is a polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerize and form a copolymer. The copolymer can be made not only by chain growth polymerisation but by step growth polymerisation also. It contains multiple units of each monomer used in the same polymeric chain. For example, a mixture of styrene and

1, 3 – butadiene can form a copolymer called styrene butadiene rubber (SBR).
A reaction in which a mixture of two (or) more monomers is allowed to undergo polymerisation is known as copolymerization. The polymer is known as copolymer.

$$n\ CH_2 = CH - CH = CH_2 + \underset{\text{Styrene}}{\underset{\bigcirc}{\overset{CH = CH_2}{|}}} \longrightarrow \left[CH_2 - CH = CH - CH_2 - \overset{\bigcirc}{\overset{|}{CH}} - CH_2 \right]_n$$

1, 3-Butadiene	Styrene	Butadiene - styrene copolymer
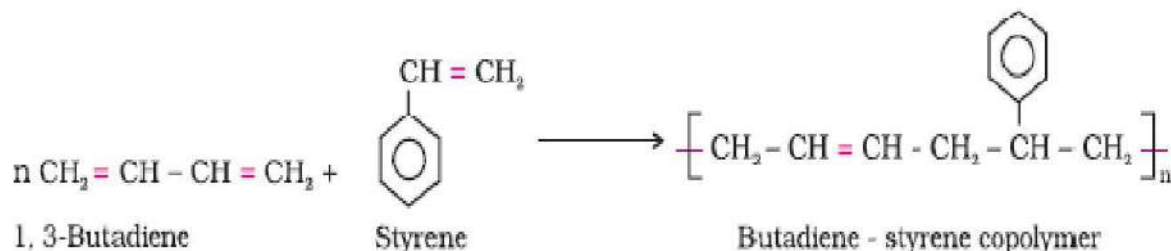
Addition polymerization	Condensation polymerization
1. No by-product is formed.	1. Generally a by-product is obtained.
2. Homo-chain polymer is obtained.	2. Hetero-chain polymer is obtained.
3. Bifunctionality is provided due to the presence of double bond in the monomer.	3. Bifunctionality is provided due to the presence of reactive functional groups present at both ends of the monomer.
4. The chain growth is at one active centre.	4. The chain growth takes place at atleast two active centres.
5. Mostly thermoplastics are formed by this process.	5. Mostly thermosetting plastics are formed.
6. The polymer product is formed immediately.	6. The polymer product is formed stepwise steadily.
7. This follows a free radical or cationic or anionic mechanism.	7. This follows the mechanism of condensation reactions such as esterification and amide formation.

Plastics(Plastomers)

Plastics are the high polymers that can be molded by the application of heat and pressure. During molding process, there is no chemical change. The plastics have linear structure.
Examples: Polythene, polyvinyl chloride, polystyrene, nylons, polyesters.

Thermoplastics

Thermo plastics are the polymers that become soft on heating and hard on cooling and the process can be   repeated for a number of times. They undergo reversible changes on heating.
Examples: Polythene (PE), polypropylene (PP), polyvinyl- chloride (PVC), polytetrafluoroethylene (PTFE or Teflon), polystyrene (PS), plexiglass, nylons, polyesters.(Polymethyl methacrylate)

Thermoplastics –1. These are formed by addition polymerisation

2. It consists of linear polymer chains with negligible cross-linking are soft and less brittle.

3. These are soluble in organic solvents.

4. soften on heating and hence are amenable for moulding into any shape in the hot

   condition on cooling, the resin becomes hard and rigid and retains the moulded shape.

5. These can be reheated and moulded into any other shape reversibly any number of times

   without any change in the chemical nature.

Thermosetting polymers or, Thermosets:

Thermosets are the polymers that undergo chemical changes and cross-linking on heating and become permanently hard, rigid and infusible. They will not soften on heating, Once they are set.
Examples: Phenol-formaldehyde resin, urea-formaldehyde resin, epoxy resins (araldite), melamine, bakelite

Thermosets (Thermosetting resins):

1. Are mostly formed by condensation polymerisation.

2. Are mostly branched polymer chains with potential to form a 3-dimensional structure.

3. become hard and rigid on heating during moulding process. are not soluble in common

   organic solvents.

4. Exhibit their characteristic properties of non-softening and non-swelling nature,

   hardness and brittleness.

5. Cannot be softened, reformed, reshaped once they are set. cannot be reclaimed from wastes.

Differences Between Thermoplastics and Thermosettingplastics

| S.No	Thermoplastics	Thermosetting plastics
1	Formed either by addition or by Condensation polymerization reactions	Formed by Condensation polymerization reactions
2	They have either linear or branched structures.	They have three dimensionalcross linked net work structures
3	Adjascent polymer chains are held together by either vanderwaals forces, or by dipole-dipole forces or by hydrogen bonds	Adjascent polymer chains are held together by strong covalent bonds called crossed-links

4	They soften on heating and stiffen on cooling	They do not soften on heating.
5	Low molecular weight thermoplastics are soluble in their suitable solvents.	They are insoluble in any solvent.
6	They can be remoulded, re-shaped and re-used.	They can be reclaimed from waste i.e., they can be recycled
7	There is no change in chemical composition and structure during moulding process.	They undergo chemical changes such as further polymerisation and cross-linking during moulding process.
8	They are soft and flexible	They are hard, rigid and infusible.
9	They can be reclaimed from waste i.e., they can be recycled.	They cannot be reclaimed from waste. They cannot be recycled.
10	They undergo reversible changes, on the application of heat.	They undergo irreversible changes on the application of heat.
11	They swell or dissolve in organic solvents.	They neither dissolve nor swell in organic solvents.
12	They are tough materials	They are brittle materials
13	The moulded articles are to be cooled to room temperature before taking out from the moulds to avoid deformation.	The moulded articles can be taken out of the moulds even when they are still hot without any deformations
14	Curing can be done by cooling.	Curing can be done by applying heat and pressure.
15	Examples: Polyethylene(PE), bakelite.	Examples: Phenol-formalde-hyde resin (PF), urea- formaldehyde resin

Moulding of Plastics

Moulding of plastics comprises of forming an article to the desired shape by application of heat and pressure to the moulding compounds in a suitable mould and hardening the material in the mould. The method of moulding depends upon the type of resins used. There are four types of moulding processes
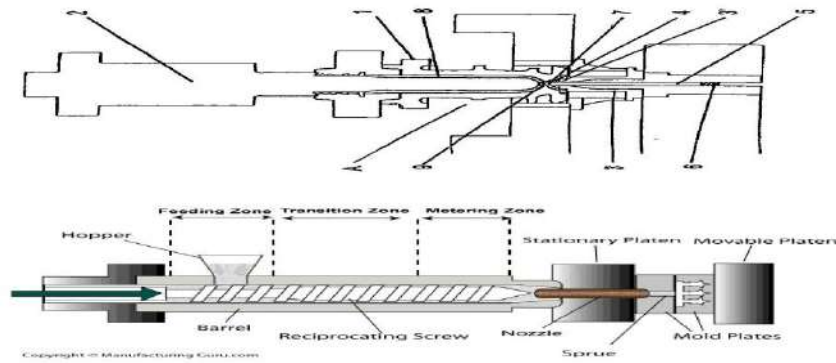
i) Compression moulding:

This method is applied to both thermoplastic and thermosetting resins. The predetermined quantity of plastic ingredients in proper properties are filled between the two half –pieces of mould which are capable of being moved relative to each other heat and pressure are then applied according to specifications. The containers filled with fluidized plastic. Two halves are closed very slowly. Finally curing is done either by heating or cooling. After curing the moulded article is taken out by opening the mould parts.

Compression Mold - OPEN

Compression Mold - CLOSED
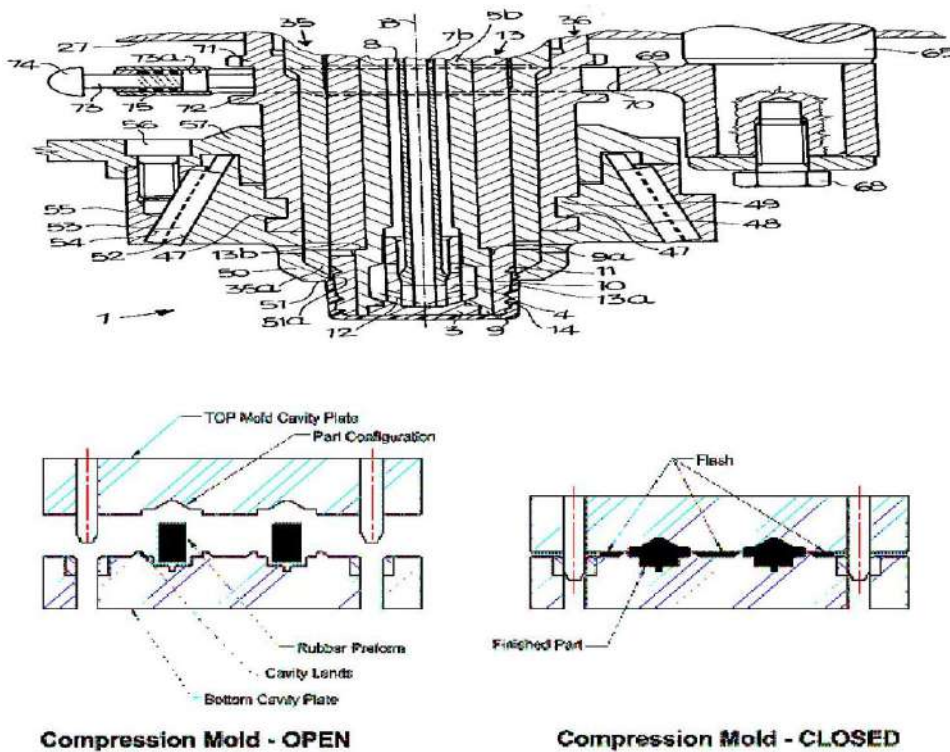
ii) Injection moulding:

In this method, the moulding plastic powder is fed into a heated cylinder from where it is injected at a controlled rate into the tightly locked mould by means of a screw arrangement or by a piston plunger. The mould is kept cold to allow the hot plastic to cure and become rigid.

When the materials have been cured sufficiently, half of the mould is opened to allow the injection of the finished article without any deformation, etc. Heating is done by oil or electricity.

Feeding Zone Transition Zone Metering Zone

Hopper   Stationary Platen Movable Platen

Barrel   Reciprocating Screw   Nozzle   Mold Plates

Sprue

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iii) Transfer moulding:

In this method, the principle is like injection moulding. The moulding powder is heated in a chamber to become plastic. Later it is injected into a mould by plunger working at high pressure through orifice. Due to this heat is developed and the plastic melts, takes the shape of the mould.

iv) Extrusion moulding:

This process is useful in the preparation of continuous wires with uniform cross section. The heated plastic is pushed into the die with the help of screw conveyor. In the die, the plastic gets cooled due to the exposure to atmosphere and by artificial air jets.

Extrusion moulding is used mainly for continuous moulding of thermoplastic materials into articles of uniform cross section like tubes, rods, strips, insulated electric cables. The thermoplastic ingredients are heated to plastic condition and then pushed by means of a screw conveyor into a die, having the required outer shape of the article to the manufactured. Here the plastic mass gets cooled, due to the atmospheric exposure (or artificially by air jets). A long conveyor carries away continuously the cooled product.

Extrusion Blow Molding (cutaway view)
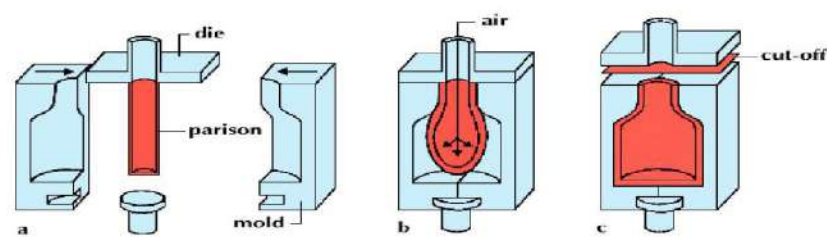
VACUUM THERMOFORMING (cutaway view)
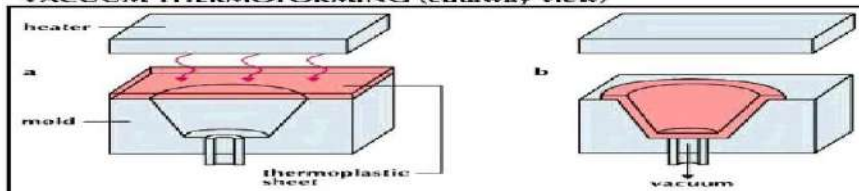
Preparation, properties and engineering applications of some plastomers

1. Bakelite:

Preparation : It is prepared by condensing phenol with formaldehyde in presence of acidic/alkaline catalyst.

The initial reaction results in the formation of O- and P- hydroxyl methyl/phenol which reacts to form linear polymer. During modeling hexamethylene tetramine is added, which converts to insoluble solid of cross-linked structure Bakalite.
Commercially these are available into two forms nova lacks & resols..

i) Nova lacks.

These are phenol formaldehyde resins obtained by condensation of phenol & formaldehyde in presence of acid as catalyst when phenol to formaldehyde ratio is greater than one
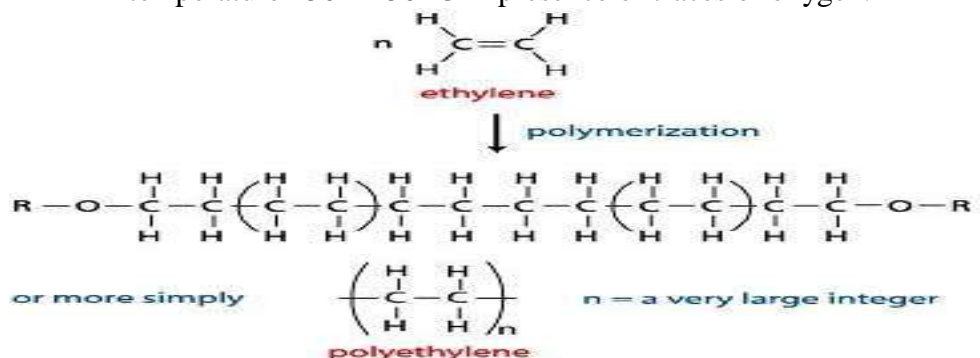
Properties.

1. Phenolic resins are hard, rigid and strong materials They have excellent heat and moisture resistance.
2. They have good chemical resitance.
3. They have good abrasion resistance.
4. They have electrical insulation characteristics
5. They are usually dark coloured.
6. Lower molecular weight grades have excellent bonding strength   and adhesive properties.

Uses: Phenol formaldehyde resins are used for

1. Domestic plugs and switches
2. Handles for cooker and saucepans.
3. Distributor heads for cars
4. Adhesives for grinding wheels and brake linings.Varnishes, electrical insulation and protective coatings.
5. The production of ion exchange resins.

Polyethylene: This can be obtained by the polymerization of ethylene at 1500 atm and a temperature 150 – 250 ^{0}C in presence of traces of oxygen.

Properties:
1. Depending upon the density, they may be LDPE and HDPE.
2. If we use free radical initiator, LDPE is the product while use of ionic catalysts results in the formation of HDPE.
3. It is a rigid, waxy white solid. Translucent.
4. It is permeable to many organic solvents.
5. It crystallizes easily.

LDPE has a density 0.91 to 0.925 g/cm^3 HDPE has a density 0.941 to 0.965 g/cm^3
HDPE is linear and has better chemical resistance.

**Uses**: 1.These are useful in the preparation of insulator parts, bottle caps, flexible bottles, pipes etc.
2.LDPE is used in making film and sheeting. Pipes made of LDPE are used for both agricultural, irrigation and domestic water line connections.
3.HDPE is used in manufacture of toys and other household articles.

PVC :
Poly Vinyl Chloride is obtained by heating a water emulsion of vinyl chloride in presence of a small amount of benzoyl peroxide or hydrogen peroxide in an auto clave under pressure.

Vinyl chloride, so needed is generally prepared by treating acetylene at 1 to 1.5 atmospheres with hydrogen chloride at 60^{0}C to 80^{0}C in the presence of metal chloride as catalyst.

$$CH = CH + HCl \text{--------}\rightarrow CH2 = CH Cl$$
Acetylene   Vinyl chloride
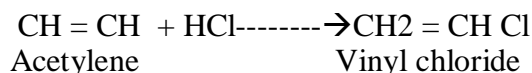
Properties:
1.It occurs as a colourless rigid mater
2. It is having high density and low softening point.
3.It is resistant to light, atmospheric oxygen, inorganic acids and alkalis.
4.It is most widely used synthetic plastic.

Uses:
1. It is mainly used as cable insulation, leather cloth, packing and toy

2. It is used for manufacturing of film, sheet and floor covering.

3. PVC pipes are used for carrying corrosive chemicals in petrochemical factories.

Vinyl Chloride

polymerization

or more simply

Poly Vinyl Chloride

$n = a$ very large integer
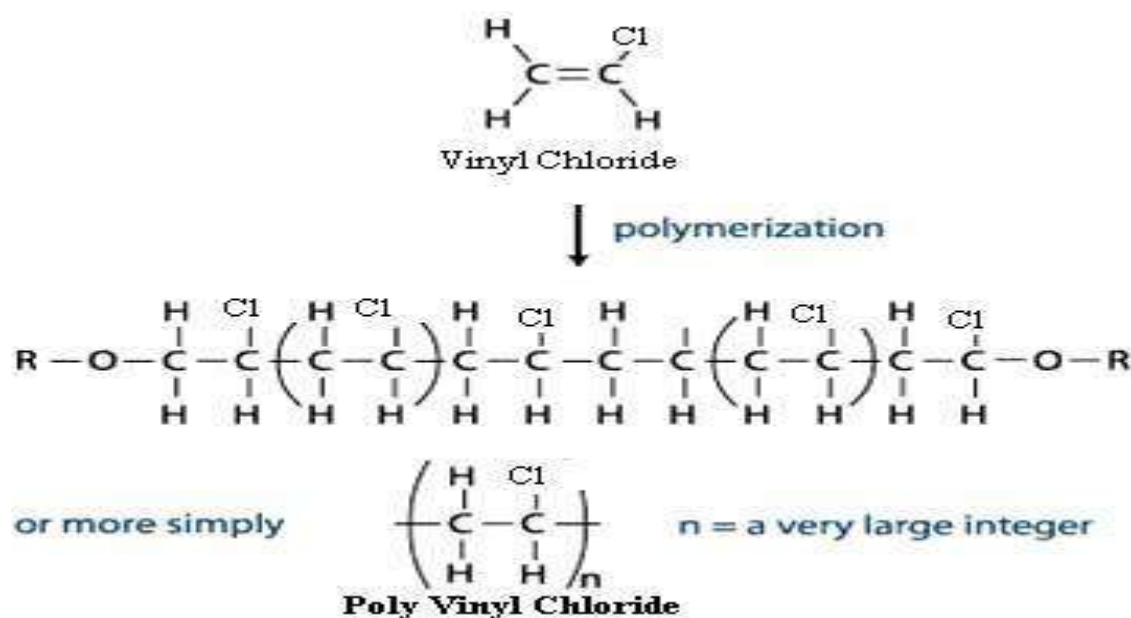
Nylon:

Synthetic fiber forming polyamides are termed as 'Nylons'.

Preparation: Nylon – 6 can be prepared by self-condensation of - amino caproic acid. Nylon-6 can be prepared by ring opening polymerisation of caprolactam.

Uses: 1. Nylon 6.6 is primarily used for fibers that find use in making socks, undergarments, carpets etc.,

2. Nylon 6.6 is also used in mechanical engineering for well known applications like gears, bearings, bushes, cans etc.,

3. Mouldings have application in medicine and pharmacy because of sterilisability.

4. Durable but costly hair combs.

5. Nylon 6.6 is also used for facketing electrical ware to provide a tough, abrasion resistant outer cover to protect the primary electrical insulation.

6. Nylon 6 is mainly used for making tyre cords.

7. Nylon 6.10 is suitable for monofilaments that are used for bristles, brushes etc.,

8. Glass reinforced Nylon plastics are used in housings and cosings of domestic

appliances, radiator parts of car and for relay coil formers.

Nylon-6,6:

It is prepared by Hexamethylene diamine and Adipic acid are polymerized in 1:1 ratio.

Properties: This is linear polymer not resistant to alkali and mineral acids.
Oxidising agents like hydrogen peroxide, potassium permanganate etc. are able
to degrade the fibres.

Uses:1.Nylon-6,6 is mainly used for moulding purposes for gear bearings and making car tyres,
used for fibres etc.
2.This is mainly used in manufacture of tyre cord. Other uses include manufacture of
carpets, rope, fibre cloth etc.

Nylon-11: Nylon – 11 can be prepared by self-condensation of w- amino undecanoic acid.

Uses: 1.Nylon 11 is used for making flexible tubing for conveying petrol

POLYESTER

Terylene is a polyester fibre made from ethylene glycol and terephthalicacid. Terephtalic acid required for the manufacture of Terylene is produced by the catalytic atmospheric oxidation of p-xylene.
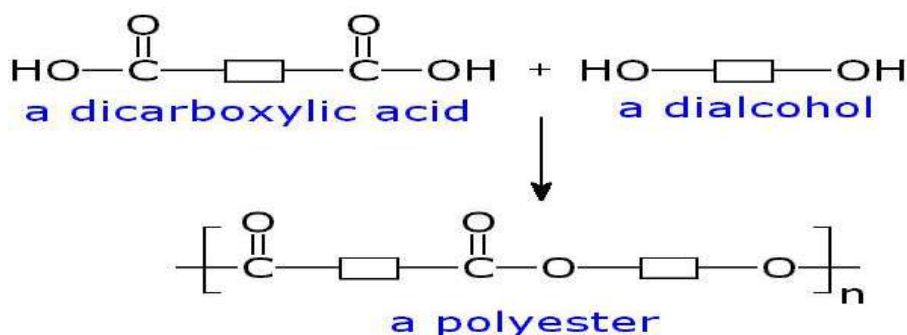
Properties: 1. This occurs as a colourless rigid substance.

              2. This is highly resistant to mineral and organic acids but is less resistant to alkalis.

              3. This is hydrophobic in nature. This has high melting point due to presence of aromatic ring.

Uses: 1.It is mostly used for making synthetic fibres.

      2. It can be blended with wool, cotton for better use and wrinkle resistance.

      3. Other application of polyethylene terephthalate film is in electrical insulation.

TEFLON OR Poly tetra fluoro ethylene:

Teflon is obtained by polymerization of water-emulsion tetrafluoroethylene, under pressure in presence of benzoyl peroxide as catalyst.

Properties: 1. Due to the presence of highly electronegative fluorine atoms and the reqular configuration of the polytetrafluoro ethylene molecule results in very strong attractive forces between the different chains.

   2. These strong attractive forces give the material extreme toughness, high softening point,

   3. exceptionally high chemical-resistance towards all chemicals, high density, waxy touch, and very low coefficient of friction,

   4. extremely good electrical and mechanical properties: It can be machined, punched and drilled.

   5. The material, however, has the disadvantage that it cannot be dissolved and cannot exist in a true Molten state.

   6. Around 350^0c, it sinters to form very viscous, opaque mass, which can be moulded into certain forms by applying high pressures.

TEFLON polymer (segment)
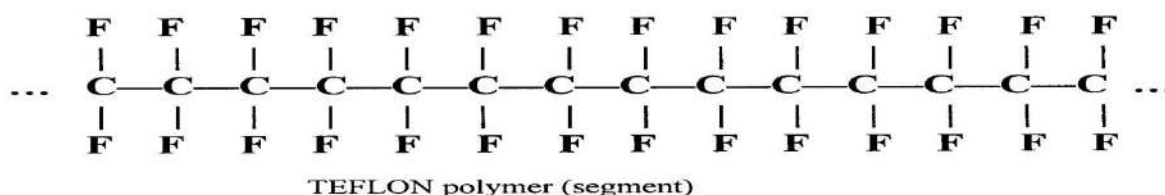
Uses: **1.** as insulating material for motors, transformers, cables, wires, fittings, etc,

2. and for making gaskets, packing, pump parts, tank linings, chemical-carrying pipes, tubing's and tanks, etc,; for coating and impregnating glass fibres, asbestos fibres and cloths; in non-lubricating bearings and non-sticking stop-cocks etc.

Natural Rubber: Rubbers also known as Elastomers, they are high polymers, which have elastic properties in excess of 300%.Natural rubbers consist of basic material latex, which is a dispersion of isoprene. During the treatment, these isoprene molecules polymerize to form, long-coiled chains of cis-polyisoprene. Natural rubber is made from the saps of a wide range of plants like Hevea brasillians and guayule.

Latex: is a milky white fluid that oozes out from the plant Hevea brasillians when a cut is made on the steam of the plant.The latex is diluted with water. Then acetic or formic acid is added [1kg of acid per 200kgs of latex] to prepare coagulum. This is processed to give wither crepe rubber or smoked rubber.

Natural rubber:

Natural rubber is found in several species of rubber trees grown in tropical countries of these Hevea brasiliensis is the most important source of natural rubber and the rubber obtained from this is known as "Hevea" rubber. Rubber is stored in the form of white fluid called 'latex' behind the bark of the rubber tree.

Natural rubber is a high polymer of isoprene (2-methyl-1,3-butadiene). It is a hydrocarbon polymer having molecular formula $(C_5H_8)_n$. Polyisopren eexists in two geometric isomers cis and transforms. Natural rubber is soft and has cis-configuration while 'Guttapercha' or, 'Ballata' has trans configuration.

Deficiencies of natural rubber:

Natural rubber as such has no practical utility value. It is because of many inherent deficiencies.

They are –

1. It is hard and brittle at low temperature and soft and sticky at high temperature.
2. It is soft and soluble in many hydrocarbon solvents and carbon disulphide (CS_2).
3. It has high water absorption power.
4. It is a sticky substance, rather difficult to handle It is readily attacked by acids and alkalies.
5. It has low tensile strength.
6. It has poor abrasion resistance.
7. It is sensitive to oxidative degradation

Vulcanization:

Vulcanization is a process of heating the raw rubber at 100 – 140ºC with sulfur for 1 – 4 hours. The sulfur combines chemically at the double bonds of different rubber molecules and provides cross-linking between the chains.

The degree of vulcanization depends on the amount of sulfur used. Tyre industry uses 3 – 5% sulfur. If the amount of sulfur is increased to 30%, a hard and rigid rubber called "ebonite" is produced.

Advantages of vulcanization:

1. The tensile strength of vulcanized rubber is very good. It is 10 times the tensile strength of raw rubber.
2. It has excellent resilience i.e., articles made from it returns to the original shape when the deforming load is removed.
3. It has better resistance to moisture, oxidation, abrasion.
4. It has much higher resistance to wear and tear compared to raw rubber.
5. It has broader useful temperature range (-40 to 100ºC) compared to raw rubber's useful temperature range (10 – 60ºC).
6. It is a better electrical insulator Ex: Ebonite
7. It is resistant to i) Organic solvents like petrol, benzene, CCl_4, ii) Fats and oils, but it swells in them.
8. It has only slight tackiness.
9. It has low elasticity. They property depends on the extent of vulcanization. Ebonite has practically no elasticity.
10. It is very easy to manipulate the vulcanized rubber to produce the desired shapes.

Vulcanization:

Vulcanization discovered by Charles Goodyear in 1839.

It consists of heating the raw rubber at 100 – 140⁰C with sulphur. The combine chemically at the double bonds of different rubber spring and provides cross-linking between the chains. This cross-linking during vulcanization brings about a stiffening of the rubber by anchoring and consequently preventing intermolecular movement of rubber springs. The amount of sulphur added determines the extent of stiffness of vulcanized rubber. For example, ordinary rubber (say for battery case) may contain as much as 30% sulphur.

Compounding of rubber:

Definition: "The process of mechanical mixing of various additives with polymers (without chemical reaction) to impart some special properties to the end product is known as compounding of plastics".

1. The additives get incorporated into the polymer to give a homogeneous mixture.
2. The functions of additives are To modify the properties of the polymer
3. To introduce new properties into the fabricated articles.
4. To assist polymer processing
5. To make the polymer products more pleasing and colourful. They should be cheap and sufficient in their functions.
6. They should be stable under processing and service conditions. They should not impart taste or odour.
7. They should be non-toxic for food grade application of final compound after processing.
8. They should not adversely affect the properties of polymer.

The principal additives used in compounding are

a) Fillers b) Plasticizers c) Lubricants d) Accelerators e) colouring agents f) Vulcanising agents

ELASTOMERS

Definition: Elastomers are high polymers that undergo very long elongation (500 – 1000%) under stress, yet regain original size fully on released of stress.
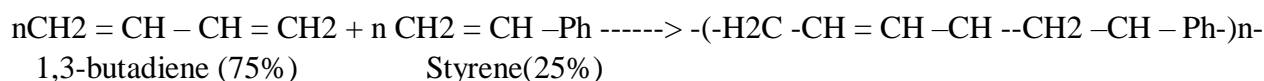
The property of elastomers is known as elasticity. This arises due to the coiled structure of elastomers.

Characteristics of Elastomers:

Elastomers have linear but highly coiled structure. Inter chain cohesive forces are negligible because these are hydrocarbons. They have high degree of elasticity. They can retract rapidly.

Buna – S or STYRENE RUBBER:

Buna-S rubber is probably the most important type of synthetic rubber, which is produced by copolymerization of butadiene (about 75% by weight) and styrene (25% by weight).

$$nCH_2 = CH – CH = CH_2 + n\ CH_2 = CH –Ph \longrightarrow -(-H_2C\ -CH = CH –CH\ --CH_2 –CH – Ph-)_n-$$

1,3-butadiene (75%)   Styrene(25%)

Properties:

1. Styrene rubber resembles natural rubber in processing characteristics as well as quality of finished products.

2. It possesses high abrasion-resistance, high load-bearing capacity and resilience.

3. However, it gets readily oxidized, especially in presence of traces of ozone present in the atmosphere.

4. Moreover, it swells in oils and solvents.

5. It can be vulcanized in the same way as natural rubber either by sulphur or sulphur monochloride (S_2Cl_2).

6. However, It requires less sulphur, but more accelerators for vulcanization.
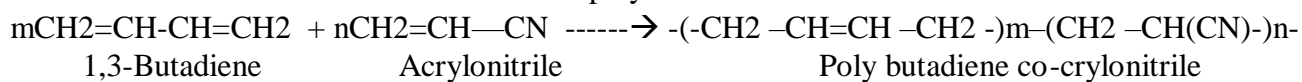
Uses:

1. Mainly used for the manufacture of motor tyres.

2. Other uses of these elastomers are floor tiles, shoe soles, gaskets, foot-wear components, wire and cable insulations, carpet backing, adhesives, tank-linings, etc.

Nitrile Rubber or GR-A or Buna – N or NBR:

Preparation: It is prepared by the copolymerization of butadiene and acrylonitrile in emulsion system.

Copolymerization

mCH2=CH-CH=CH2 + nCH2=CH—CN ------→ -(-CH2 –CH=CH –CH2 -)m–(CH2 –CH(CN)-)n-

1,3-Butadiene   Acrylonitrile   Poly butadiene co-crylonitrile

Compounding and vulcanization methods are similar to those of natural rubber.

Properties:

1. Due to the presence of cyano group, nitrile rubber is less resistance to alkalis than natural rubber;
2. Excellent resistance to oils, chemicals, aging (sun light). As the acrylonitrate percentage is increased in nitrile rubber, its resistance to acids, salts, oils, solvents etc. increases. But the low temperature resilience suffers.
3. Compared to natural rubber, nitrile rubber (vulcanized) has more heat resistance and it may be exposed to high temperatures.
4. It has good abrasion resistance, even after immersion in gasoline or oils.

USES:

1. For making Conveyor belts, Lining of tanks, Gaskets
2. Printing rollers , Oil-resistance foams
3. Automobile parts and high altitude air-craft components Hoses and adhesives.

Butyl rubber:

Preparation:

Butyl rubber is prepared by the aluminum chloride initiated cationic copolymrisation of isobutene with small amount (1-5%) of isoprene.

Properties:

1. Under normal conditions, it is amorphous but it crystallizes on stretching.
2. It is quite resistant to oxidation due to low degree of unsaturation. Due to very low unsaturation, it can be vulcanized but it cannot be hardened much.
3. It can be degraded by heat or light to sticky low-molecular weight products so stabilization is must.
4. Being non-polar, it has good electrical insulation properties.
5. Compared to natural rubber it possesses outstanding low permeability to air and other gases.
6. It does not crystallize on cooling and hence remains flexible down to -50°C
7. Because of its hydrocarbon nature, butyl rubber is soluble in hydrocarbon solvents like benzene but has excellent resistance to polar solvents like alcohol, acetone and ageing chemicals (ex: HCl, HF, HNO3, H2SO4 etc.)

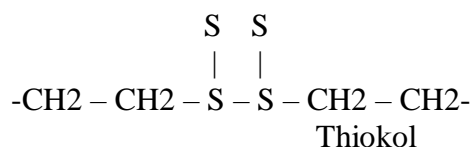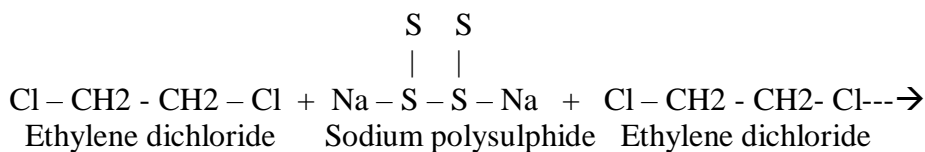## USES:

1. It is used for Insulation of high voltage wires and cables Inner tubes of

automobile tyres.
2. Conveyor belts for food and other materials.
3. Lining of tanks Hoses

Thiokol :

This also called as polysulphide rubber (or Gr-P). It can be prepared by the condensation polymerization of sodium polysulphide (Na2Sx) and ethylene dichloride.

```
                                  S   S
                                  |   |
Cl – CH2 - CH2 – Cl  +  Na – S – S – Na  +  Cl – CH2 - CH2- Cl---→
Ethylene dichloride     Sodium polysulphide   Ethylene dichloride
```

```
                         S   S
                         |   |
       -CH2 – CH2 – S – S – CH2 – CH2-
                         Thiokol
```

USES:
1. It is used for the -
2. Manufacture of oils hoses, chemically resistant tubing and engine gaskets;
3. Diaphragms and seals in contact with solvents and Printing rolls, Containers for transporting solvents and Solid propellant fuels for rockets, etc.

POLY URETHANES RUBBERS:

Polyurethane or isocyanate rubber is produced by reacting polyalcohol with di-isocyanates.

n[OH-(CH2)2-OH+O=C=N-(CH2)2-N=C=O]--→[-O-(CH2)2-O-(CO)-NH-(CH2)2-NH-(CO)-]n
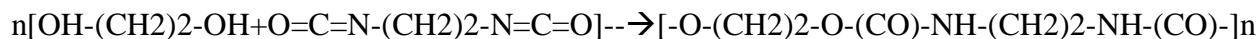
Properties:
1. Polyurethanes are highly resistant to oxidation, because of their saturated character.
2. They also show good resistance to many organic solvents, but are attacked by acids and alkalis, especially concentrated and hot.
3. The polyurethane foams are light, tought and resistant to heat, abrasion, chemicals and weathering

Uses: For surface coatings and manufacture of foams and spandex fibres.

Silicone resins:

Silicone resins contain alternate silicone-oxygen structure, which has organic radicals attached to silicon atoms. Thus, their structure is: Where R= alkyl or phenyl radical

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Preparation: reacting silicon with alkyl halide or silicon halide with Grignard reagent.

The reaction product is fractionally distilled to get different organo-silicon chlorides, which are then polymerized by carefully controlled hydrolysis.

1. Dimethyl-silicon dichloride is 'bifunctional' and can yield very long chain polymers,
2. Trimethyl silicon chloride is 'monofunctional' and hence, a 'chain-stopper'. This is, therefore, used in proportions to limit the chain-length.
3. Monomethyl silicon chlorides is 'trifunctional' and goes cross-linking to the final polymer. Its proportion used in polymerization, determines the amount of cross-linking that can be obtained.

Characteristics of silicones:

1. Depending on the proportion of various alkyl silicon halides used during their preparation, silicones may be liquids, viscous liquids, semi-solid, rubber-like and solids.
2. Because of silicon-oxygen links, they exhibit outstanding-stability at high temperatures, good water resistance, good oxidation-stability, but their chemical-resistance is generally lower than that of other plastics.
3. Their specific gravity ranges from 1.03 to 2.1.
4. Their physical properties are much less affected by variations in temperature.
5. They are non-toxic in nature.

Different types of silicones and their uses: Liquid silicones or silicone oils are relatively low molecular-weight silicones, generally of dimethyl silicones. They possess great wetting-power for metals, Low surface tension and show very small changes in viscosity with temperature.

Uses:

1. They are used as high temperature lubricants, antifoaming agents, water-repellent finishes for leather and textiles, heat transfer media, as damping and hydraulic fluids. They are also used in cosmetics and polishes.
2. Silicone greases are modified silicone oils, obtained by adding fillers like silica, carbon black, lithium soap, etc.
3. They are particularly used as lubricants in situations where very high and very low temperatures and encountered.

Conducting polymers:

Definition: A polymer that can conduct electricity is known as conducting polymer.

Classification: Conducting polymers can be classified as follows.

I) Intrinsically conducting polymers:

The polymers have extensive conjugation in the backbone which is responsible for conductance. These are of two types.

1) **Conducting polymers** having conjugated - electrons in the backbone: Such polymers contain conjugated – electrons in the back bone which increases their conductivity to a large extent

Explanation: Overlapping of conjugated -electrons over the entire backbone results in the formation of valence bands well as conduction bands that extends over the entire polymer molecule. The valence band and the conduction bands separated by a significant band gap. Thus, electrical conduction occur only after thermal or photolytic activation electrons to give them sufficient energy to jump the gap and reach into the lower levels of the conduction band.

All the three forms of polyanilines have conductivities of the order of 10 -10 Scm-1. conductivity of these polymer having conjugated -electrons in the backbone is not sufficient for their use in different applications.

Applications of Conducting Polymers:-

2. These can produce current density up to 50mA/cm^2.
3. In electrochromic displays and optical filters: ICP's can absorb visible light to give coloured products so can be useful for electrochromic displays and optical filters.
4. Thus the conducting polymers can be used as electro chromic materials i.e., the materials that change colour reversibility during the electrochemical processes of charge and discharge.
5. In wiring in aircrafts and aerospace components.
6. In telecommunication systems.
7. In electromagnetic screening materials.
8. In electronic devices such as transistors and diodes.
9. IN solar cells, drug delivery system for human body etc., In photovoltaic devices.

In non-linear optical materials.

10. In nolecular vi

res and molecular switches.

11. Membranes made up of conducting polymers can show boundary layer effects with selective permeability for ions, gases etc., Hence they are useful for ion-exchangers and controlled release of drugs

Compounding of rubber:

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8. They should be non-toxic for food grade application of final compound after processing.
9. They should not adversely affect the properties of polymer.

The principal additives used in compounding are
1) Softners and Plasticisers 2) Vulcanising Agents   3) Antioxidants 4) Accelerators
5) Fillers 6) Colouring Matter

1. **SOFTNERS AND PLASTICISERS**: These are added to give greater plasticity and flexibility to reduce the brittleness of the products eg. waxes, stearic acid and vegetable oils.

2. **VULCANISING AGENTS:** When rubber is heated with sulphur , its tensile strength,elasticity and resistance to swelling are increased.The sulphur atoms chemically bond with double bonded carbons of rubber chains and bring about excellent changes in their properties.The percentage of sulphur added variles from 0.15 to 32%. S_2Cl_2,H_2S, H_2O_2, benzoyal chloride etc., are other vulcanizing agents.

3. **ANTIOXIDANTS:** Natural rubber has tendency for oxidation. Antioxidants like phenyl naphthyl-amine and phosphites are added for preventing the oxidation of rubber.

4.**ACCELERATORS:** These shorten the time required for vulcanization and give toughness to the rubber. For eg., 2-Mercaptol and benzothiozole.

5. **FILLERS:** These are added to give rigidity and strength to the rubber. For Eg., carbon black, zinc oxide and calcium carbonate

6. **COLOURING MATTER:** These materials provide pleasing colour to the rubber product. For eg.,   Titanium oxide- White

Ferric oxide – Red

Lead chromate – Yellow

Instrumental Methods and its Applications

Introduction:-

Instrumental methods may be used to separate samples using chromatography, electrophoresis or field flow fractionation. Then qualitative and quantitative analysis can be performed, often with the same instrument and may use light interaction, heat interaction, electric fields or magnetic fields.

Spectroscopy:-

* Spectroscopy is the study of the interaction between matter and electromagnetic radiation

* Spectroscopy and spectrograph are terms used to refer to the measurement of radiation, intensity as a function of wavelength and are often used to describe experimental spectroscopic methods

Electromagnetic Radiations

The radiation which are having both electric field and magnetic field which are perpendicular to each other and are coplanar are called as "electromagnetic radiations ".

These are produced by the Oscillation of electric field and magnetic field residing on the atom
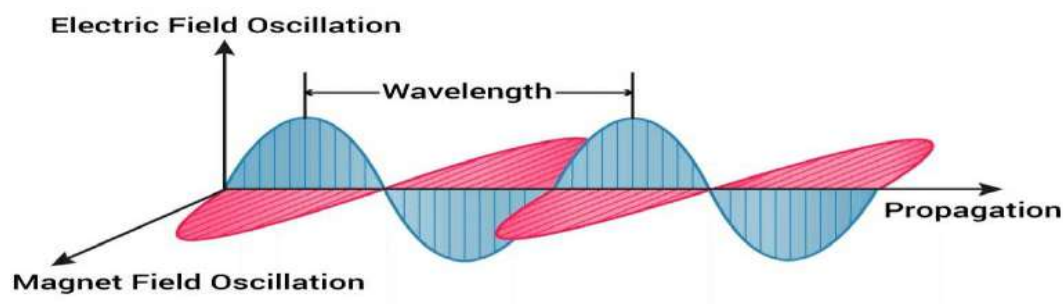
Characteristics of Electromagnetic Radiations

1. These are of characterized by their wave lengths or frequencies or wave numbers.
2. The energy carried by an electromagnetic radiation is directly proportional to its frequency.
3. The emission and absorption of radiation is quantized and each quantum of Radiation is called a photon.
4. All types of Electromagnetic radiation travel with the Same velocity and no medium is required for their propagation.
5. When visible light is passed through a prism, it is split up into seven colours. This phenomenon is called dispersion

Electromagnetic spectrum

The arrangement all types of electromagnetic radiation in order of their increasing wavelengths Or decreasing frequencies is known as electromagnetic spectrum.

Electromagnetic radiation are absorbed ,emitted or propagated in the form of Energy packets called quanta or photons.

$E=h\nu$
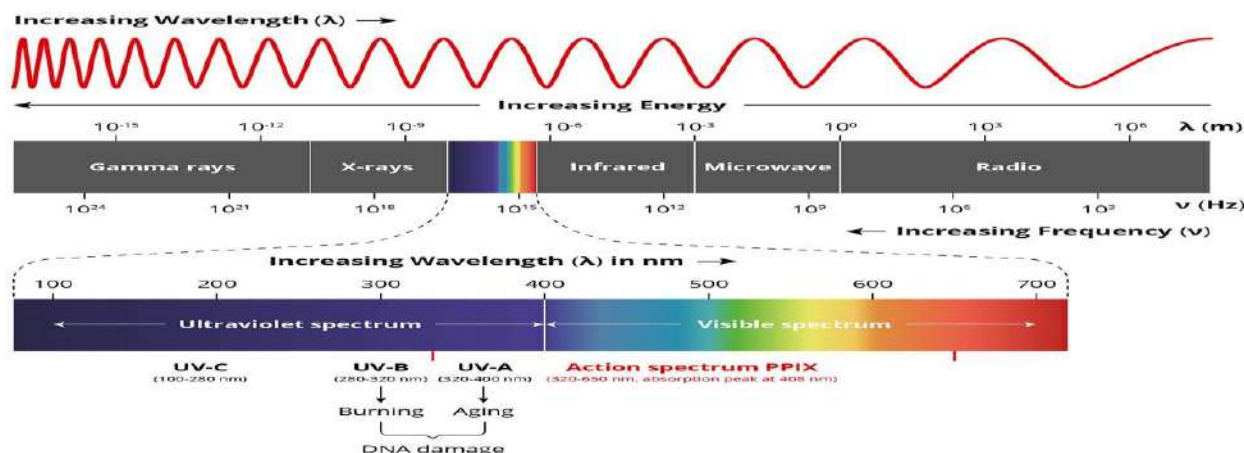
Observations of Electromagnetic Spectrum

1. Radio waves are longer wave length and less energetic

2. Cosmic waves are shorter wave length and high energetic

3. Ultra violet radiations cover the wave length range from 190-400 nm

4. Visible radiations cover the wave length range from 400-800 nm

5. IR radiations cover the wave length range from 667-4000 Cm^{-1}

6. Radio waves cover the wave length range from 60-300 MHz

Laws of light absorption

When a beam of radiation passes through a homogeneous medium the radiant energy may be partially or entirely absorbed,transmitted,reflected and scattered

$I0=Ia+It+Ir$

Where I0,Ia,It,Ir are intensity of incident light, absorbed,transmitted,reflected respectively

The process of absorption depends upon the

a) Molecular structure of the absorbing species

b) Concentration of the solution

c) Length of path of the radiation passing through the absorbing medium

The absorption of light in the visible and near UV region is governed by photo physical law known as Lamberts- Beers law

Beer's law, Lambert's law

Beer's law:

This law states that when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of absorbing solution is proportional to the intensity of incident ration as well as the concentration of the solution.

Beer-Lambert Law

$$A = \varepsilon c l$$

A = absorbance (no units).
ε = Molar extintion coefficient (M^{-1} cm^{-1}).
c = Concentration (M).
l = pathlength (cm).
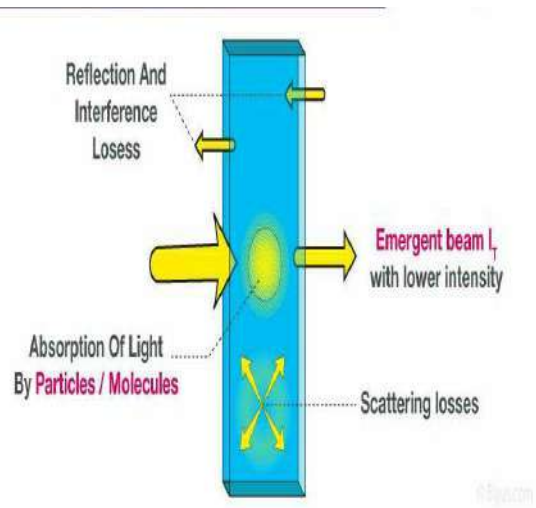
Lamberts law;

The lamberts law states that where a monochromatic light passes through a transport medium the rate of decrease in the intensity with the thickness of medium is proportional to the intensity of light, mathematically.

Mathematically it can be expressed as

$$-\frac{dI}{dx} \propto I \quad \text{--- --- --- --- --- --- (1)}$$

Where **dI** is a small decrease in intensity of light upon passing through a small distance **dx** and **I** is the intensity of the monochromatic light just before entering the medium. Equation (1) may be written as

$$-\frac{dI}{dx} = aI \quad \text{--- --- --- --- --- --- (2)}$$

Where $-\frac{dI}{dx}$ is the rate of decrease of intensity with thickness **dx** , a is called the *absorption co-efficient*. Integration of equation (2) after rearrangement gives,

$$-\ln I = ax + C \quad \text{--- --- --- --- --- --- (3)}$$

Where C is a constant of integration. At $x=0$, $I=I_o$. So, $C = -\ln I_o$. Introducing this in equation (3) we get,

$$\ln \frac{I}{I_o} = -ax \quad \text{--- --- --- --- --- --- (4)}$$

Equation (4) can also be written as,

$$I = I_o e^{-ax} \quad \text{--- --- --- --- --- --- (5)}$$

Beer- Lambert's law….

$$dI / dx \propto I \text{———————(1)}$$

Where dI is a small decrease in intensity of light upon passing through a small distance dx and I is the intensity of the monochromatic light just before entering the medium.

Equation (1) may be written as

$$-dI / dx = aI \text{———————(2)}$$

Where $-dI/dx$ is the rate of decrease of intensity with thickness dx , a is called the absorption co-efficient.

Integration of equation (2) after rearrangement gives,

$$-\ln I = ax + C \text{————-(3)}$$

At x=0, I=Io.

$$\ln I/Io = -ax \text{———————(4)}$$

Equation (4) can also be written as,

$$I = Io\, e^{-ax} \text{——————(5)}$$

Equation (5) can also be written as,

$$\log I/Io = -a/2.303\, x \text{—————(6)}$$

$$\text{or, } \log I/Io = -a`\, x \text{—————(7)}$$

Lambert's law was extended…..

$- dI /dx \propto c$ —————— (8)

The two laws may be combined to write

$- dI /dx \propto I \times c$

Or, $- dI /dx = b \times I \times c$ ————— (9)

When the concentration, c, is expressed in mol /L, b is called the molar absorption co-efficient.

As in the case of Lambert's law equation (9) may be transformed into,

$\log I/ I_o = - b /2.303 \times c \times x$ ————— (10)

$\log I/ I_o = - \in \times c \times x$ ————— (11)

The expression (equation 11) is commonly known as Beer-Lambert's law.

Colorimeter:-

A colorimeter is a light sensitive device used for measuring the transmittance and absorbance of light passing through a liquid sample. The device measures the intensity or concentration of the colour that develops upon introducing a specific reagent into a solution.

Principle;

This law states that the light absorption when passes through a medium are directly proportional to the concentration of the medium. In colorimetry, there is a ray of light with certain wavelengths is directed towards a solution.

1. It involves the quantitative estimation of colour.

2. The concentration of the coloured complex, is directly proportional to the concentration of the components

3.   The difference in colour intensity results in the difference in the absorption of light.

Polychromatic Light   Monochromatic Light

Light source   Slit   Lens   Filter   Cuvette   Photo cell   Output
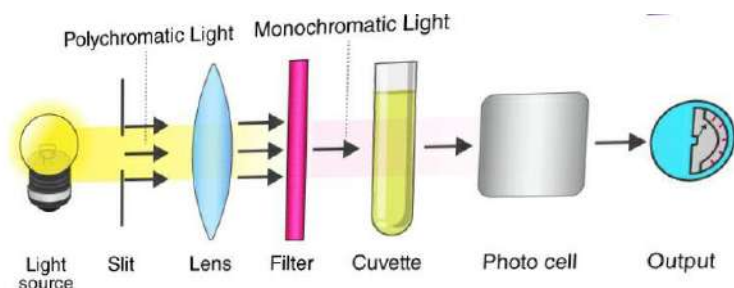
Instrumentation:-

The working principle of the colorimeter is based on Beer-Lambert's law which states that the amount of light absorbed by a colour solution is directly proportional to the concentration of the solution and the length of a light path through the solution.
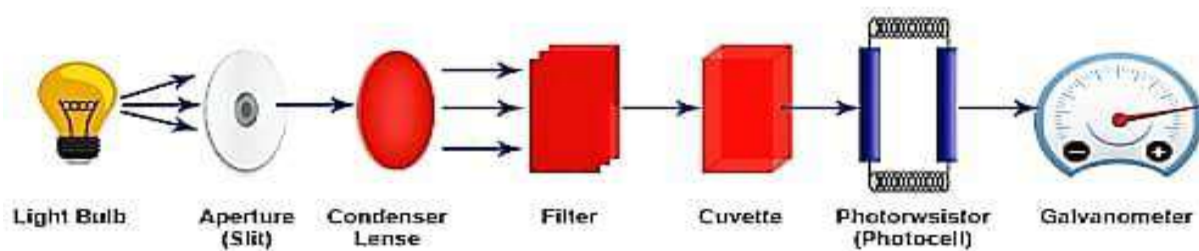
$A \propto cl$

Where,

A = Absorbance / Optical density of solution

c = Concentration of solution

l = Path length

$A = \in cl$

$\in$ = Absorption coefficient

Light Bulb   Aperture Condenser   Filter   Cuvette Photorwsistor Galvanometer
(Slit)   Lense   (Photocell)

There are 5 essential parts in a colorimeter
1. Light Source – The most common source of light used in colorimeter is a tungsten filament.
2. Monochromator – To select the particular wavelength filter or monochromators are used to split the light from the light source.
3. Sample holder – Test tube or Cuvettes are used to hold the color solutions they are made up of Glass at the visible wavelength.
4. Photo Detector System – when light falls on the detector system, an electric current is generated, this reflects the Galvanometer reading.
5. Measuring device – The current from the detector is fed to the measuring device, the Galvanometer, shows the meter reading that is directly proportional to the intensity of light.

Working of Colorimeter:-

*When the monochromatic light (light of one wavelength) reaches the cuvette some of the light is reflected, some part of the light is absorbed by the solution and the remaining part is transmitted through the solution which falls on the photodetector system. The photodetector system measures the intensity of transmitted light and converts it into the electrical signals that are sent to the galvanometer.

* The galvanometer measures the electrical signals and displays them in the digital form. That digital representation of the electrical signals is the absorbance or optical density of the solution analyzed

* If the absorption of the solution is higher than there will be more light absorbed by the solution and if the absorption of the solution is low then more lights will be transmitted through the solution which affects the galvanometer reading and corresponds to the concentration of the solute in the solution. By putting all the values in the formula given in the below section one can easily determine the concentration of the solution.

Applications of Colorimeter:-

1. The colorimeter is commonly used for the determination of the concentration of a colored compound by measuring the optical density or its absorbance.
2. It can also be used for the determination of the course of the reaction by measuring the rate of formation and disappearance of the light-absorbing compound in the range of the visible spectrum of light.
3. By colorimeter, a compound can be identified by determining the absorption spectrum in the visible region of the light spectrum
4. Analysis of blood.
5. Analysis of water.
6. Nutrients in soil.
7. Food stuff.

Atomic Absorption Spectroscopy:-

Principle:-

The technique uses basically the principle that free atoms (gas) generated in an atomizer can absorb radiation at specific frequency. Atomic-absorption spectroscopy quantifies the absorption of ground state atoms in the gaseous state
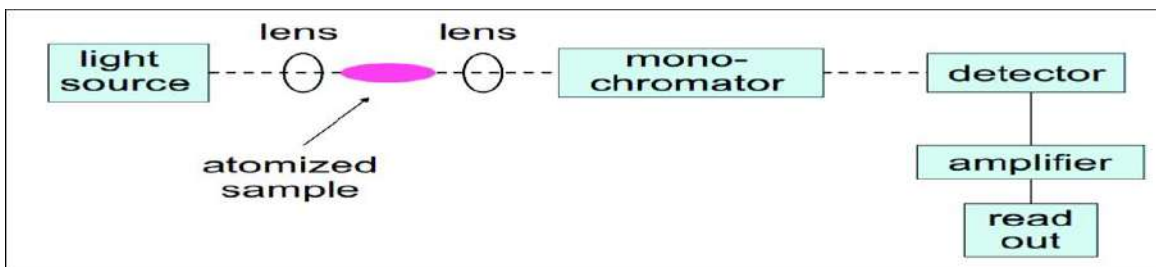
Instrumentation:-

Atomic Absorption Spectrophotometer, is used to measure the concentration of a specific element, in a given sample. In an AAS, the sample is atomized and a beam of electromagnetic radiation emitted from a light source passes through the vaporized sample. Some of the radiation

is absorbed by the atoms in the sample; the amount of light absorbed is a function of the concentration of the element of interest.

An AAS consists of five basic functional parts; a light source which is usually a Hollow Cathode Lamp, an atomizer section for atomizing the sample which could be a flame or an electrothermal or a cold vapor/hydride generation system, a monochromator for selecting the analysis wavelength for the target element, a detector for measuring the amount of light absorbed and a recorder for recording the output from the detector.

Light source: The Hollow Cathode Lamp is perhaps the most commonly used light source in an AAS. The Hollow Cathode lamp produces narrow emissions from atomic species. The Hollow Cathode Lamp consists of a cup-shaped cathode which is made from element of interest and an Anode which is usually made from tungsten and placed in a hollow tube filled with an inert gas such as Ar or Ne. Application of a high potential difference across the electrodes causes a discharge of electrons. These gaseous ions bombard the cathode and eject metal atoms from the cathode in a process called sputtering. Some sputtered atoms are in excited state and emit radiation (light) characteristic of the metal as they fall back to the ground state.

Atomizer: This consists basically of the burner for flame analysis or a graphite furnace for electrothermal analysis or cold vapor or a hydride system, the nebulizer introduces the sample as a fine mist and the spray chamber to create a good mix for both air and the fuel gas.

Monochromator: This is used to isolate a single atomic resonance line from the spectrum of lines emitted from the interaction of the sample with the resonance light from hollow cathode lamp. Essentially it is an adjustable filter that selects a specific narrow region of the spectrum for transmission to the detector and excludes all wavelengths outside this region.

Detector: It converts light coming from a monochromator into an amplified electrical signal which can be recorded. The amount of light getting to the detector is a function of the concentration of the element of interest in the sample being analyzed. The type of detector found in AAS is the photomultiplier tube – the principle of operation is the emission of electrons upon exposure to radiation.

The Recorder, which today, is usually a computer system and a suitable software, receives the analog signals from the detector and converts it to readable responses.

Applications of Atomic Absorption Spectroscopy:-

Atomic absorption spectrometry has many uses in different areas of chemistry such as clinical analysis of metals in biological fluids and tissues such as whole blood, plasma, urine, saliva, brain tissue, liver, hair, muscle tissue, Atomic absorption spectrometry can use in qualitative and quantitative analysis.
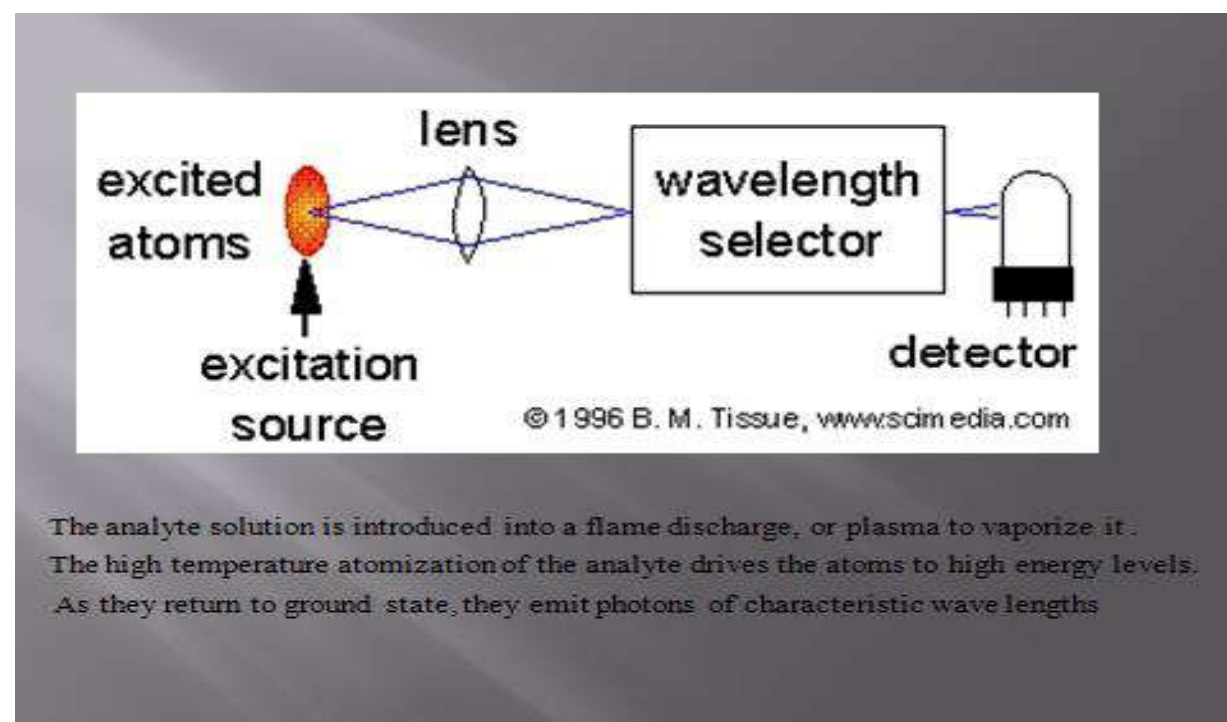
Atomic Emission Spectroscopy or Flame Emission spectroscopy

Principle:-

   A sample of a material (analyte) is brought into the flame as a gas, spray solution, or directly inserted into the flame by use of a small loop of wire, usually platinum. The heat from the flame evaporates the solvent and breaks intramolecular bonds to create free atoms. The thermal energy also excites the atoms into excited electronic states that subsequently emit light when they return to the ground electronic state. Each element emits light at a characteristic wavelength, which is dispersed by a grating or prism and detected in the spectrometer.

 Atomic emission spectroscopy (AES) is a method of chemical analysis that uses the intensity of light emitted from a flame, plasma, arc, or spark at a particular wavelength to determine the quantity of an element in a sample.

AES is an alternative to AAS. It is not as sensitive as AAS , but does have the advantage of being able to analyze multiple elements simultaneously.

lens

excited atoms

wavelength selector

detector

excitation source

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The analyte solution is introduced into a flame discharge, or plasma to vaporize it .
The high temperature atomization of the analyte drives the atoms to high energy levels.
 As they return to ground state, they emit photons of characteristic wave lengths

Instrumentation:-

As in AES spectroscopy, the sample must be converted to free atoms, usually in a high-temperature excitation source.

 Liquid samples are convert to a fine spray and carried into the excitation source by a flowing gas. Solid samples can be introduced into the source by a slurry or by laser ablation of the solid sample in a gas stream. Solids can also be directly vaporized and excited by a spark between

electrodes or by a laser pulse. The excitation source must desolvate, atomize, and excite the analyte atoms. A variety of excitation sources are listed below

Direct-current plasma (DCP) ,Flame,Inductively-coupled plasma (ICP),

Laser-induced breakdown (LIBS), Laser-induced plasma , Microwave-induced plasma (MIP),

Spark or arc

Since the atomic emission lines are very narrow, a high-resolution polychromator is needed to selectively monitor each emission line

Applications

1. In the area of material science . The electronics industry requires materials of high purity and hence there is a need to monitor trace impurity levels in materials used for electronic components

2. In clinical laboratories for measuring the major cations sodium and potassium

3. Ion selective electrodes

4. Urine analysis

5. Determination of Arsenic and selenium in drinking mineral water

Flame atomic absorption spectroscopy instrument

Distinguish between FES and AAS

AAS	FES
▪ Different hollow cathode lamps are required as source of radiation	▪ Flame serves as source for different element.
▪ Chopper is used to eliminate radiation emitted from flame.	▪ Chopper is not used.
▪ The quality of monochromator should no be of very high degree.	▪ The quality of monochromator should be of very high degree
▪ AC. Amplifier is used to amplify only AC Current.	▪ Amplifier is used to increase the output signal of detector.
▪ The absorption intensity depends upon unexcited atoms.	▪ The emission intensity depends upon excited atoms.
▪ signal is obtained due difference of energies between excited and ground state atom.	▪ Signal is obtained from wavelength emitted by atoms.
▪ High degree operator is not required	▪ High degree operator is required

Uv- spectroscopy

Ultraviolet –visible spectroscopy or ultraviolet–visible spectrophotometry (UV–Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and the full adjacent visible spectral regions. This means it uses light in the visible and adjacent ranges.

Ultraviolet-visible (UV-Vis) spectrophotometry is a technique used to measure light absorbance across the ultraviolet and visible ranges of the electromagnetic spectrum. ... A UV-Vis spectrophotometer can use this principle to quantify the analytes in a sample based on their absorption characteristics.

Principle of ultraviolet–visible absorption:-

Molecules containing bonding and non-bonding electrons (n-electrons) can absorb energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. There are four possible types of transitions ($\pi-\pi^*$, $n-\pi^*$, $\sigma-\sigma^*$, and $n-\sigma^*$), and they can be ordered as follows :$\sigma-\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi^*$.
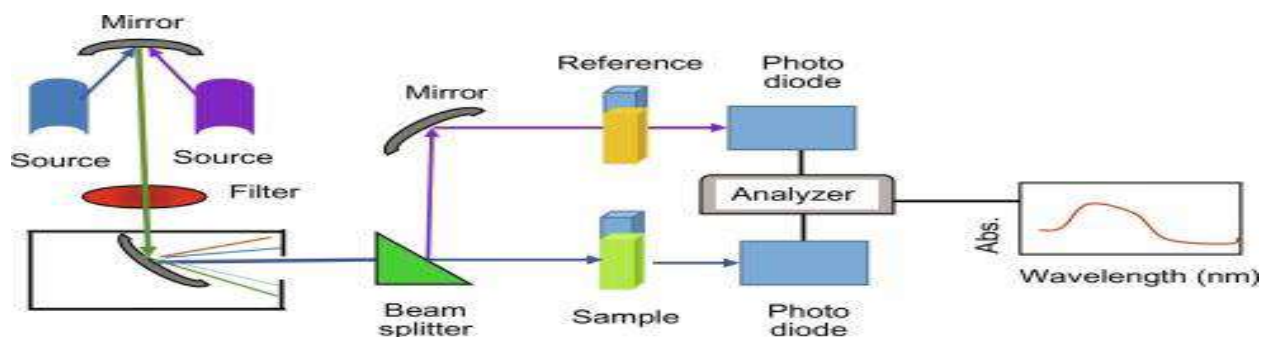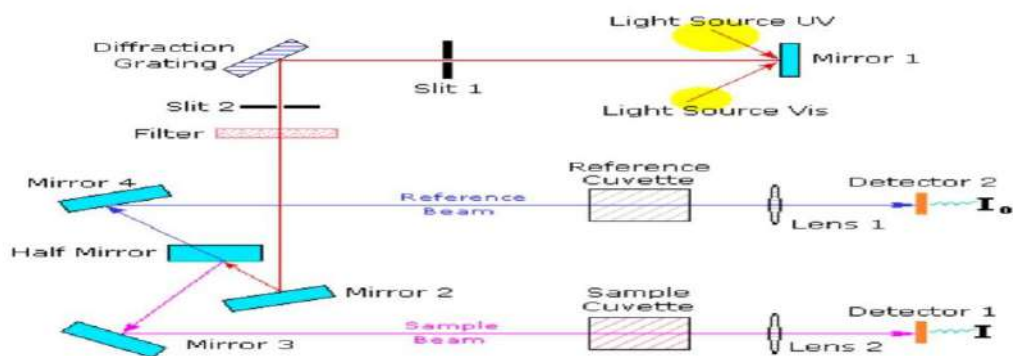
Applications of UV-Visible Spectroscopy:

➢ Detection of Impurities

➢ Structure elucidation of organic compounds

➢ Quantitative analysis

➢ Molecular weight determination

➢ Distinction between Cis & Trans isomerism

➢ Effect of Conjugation

Chromatography:-

Chromatography may be defined as method of separating a mixture of components into individual component through equilibrium distribution between two phases.
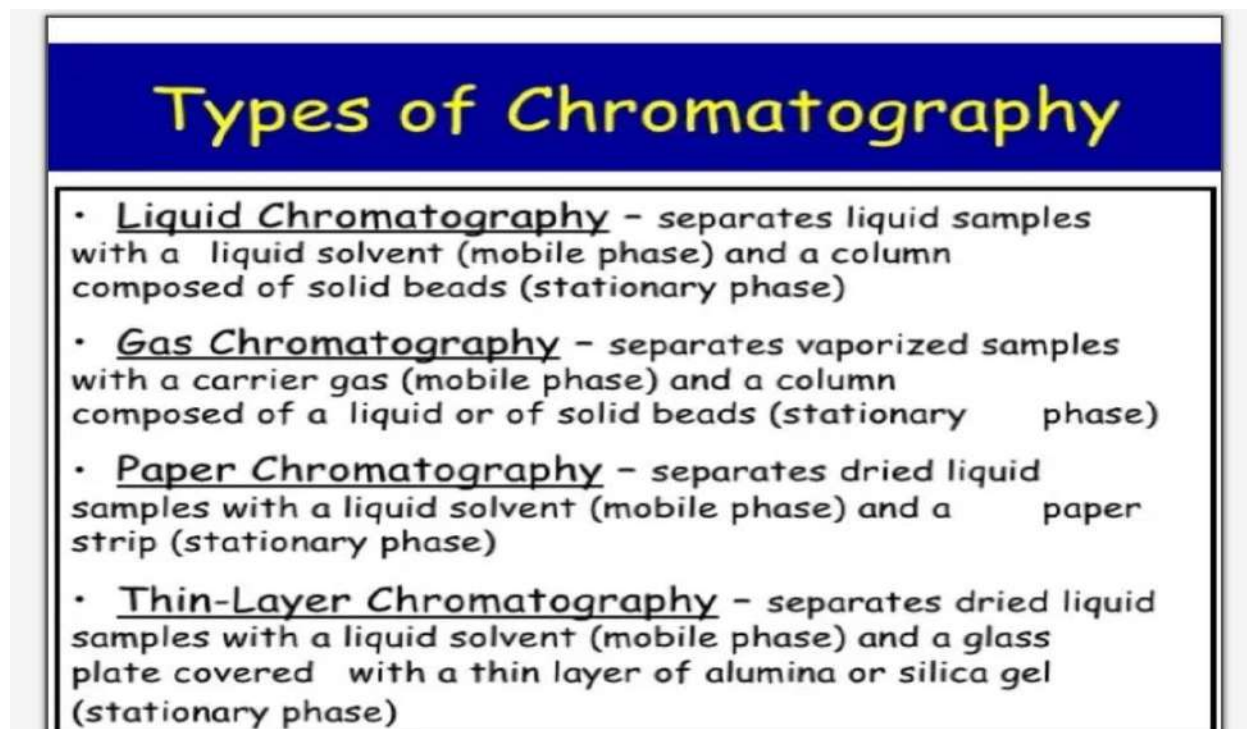... Chromatography involves a sample (or sample extract) being dissolved in a mobile phase (which may be a gas, a liquid or a supercritical fluid).

A technique Exploiting the interaction of the components of a mixture with a stationary Phase and a Mobile phase in order to Separate the components .

Components are divided different levels of absorption to the stationary phase and Solubility in the Mobile phase.

The stationary phase is a phase that is fixed in a place in a column or on a solid surface

The mobile phase is passing through the stationary phase carrying with it the sample solution

Types of Chromatography

- **Liquid Chromatography** – separates liquid samples with a liquid solvent (mobile phase) and a column composed of solid beads (stationary phase)

- **Gas Chromatography** – separates vaporized samples with a carrier gas (mobile phase) and a column composed of a liquid or of solid beads (stationary phase)

- **Paper Chromatography** – separates dried liquid samples with a liquid solvent (mobile phase) and a paper strip (stationary phase)

- **Thin-Layer Chromatography** – separates dried liquid samples with a liquid solvent (mobile phase) and a glass plate covered with a thin layer of alumina or silica gel (stationary phase)

- Types of chromatography:-

Classification

Planar chromatography………

The stationary phase is supported on a flat surface or in the pores of a paper and the mobile phase passes through the stationary phase by capillary action or under the influence of gravity

Column chromatography

The stationary phase is supported in a narrow tube through which the mobile phase is forced through a pressure

Applications:-

1. To identify and analyze samples for the presence of trace elements or chemicals.
2. Separation of compounds based on their molecular weight and element composition.
3. Detects the unknown compounds and purity of mixture.
4. In drug development.
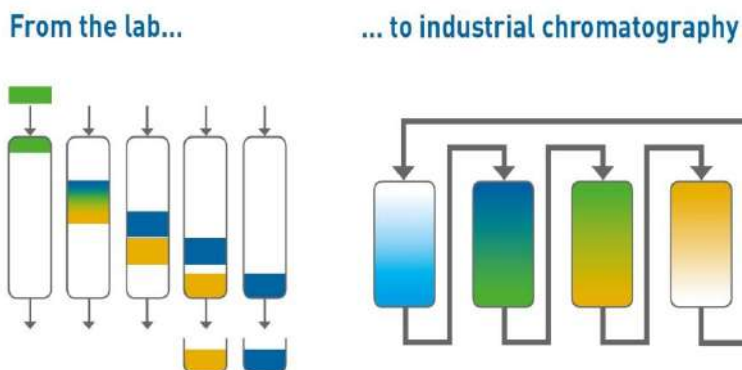
Gas chromatography…

. Gas chromatography (GC) is a common type of chromatograph used in analytical chemistry or separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined). In some situations, GC may help in identifying a compound.

Gas chromatography is also sometimes known as vapor-phase chromatography (VPC), or gas–liquid partition chromatography (GLPC)

1. Gas chromatography differs from other forms of chromatography in that the mobile phase is a gas and the components are separated as vapours.

2. It is thus used to separate and detect small molecular weight compounds in the gas phase.

3. The sample is either a gas or a liquid that is vaporized in the injection port. The mobile phase for gas chromatography is a carrier gas, typically helium because of its low molecular weight and being chemically inert.

4. The pressure is applied and the mobile phase moves the analyte through the column. The separation is accomplished using a column coated with a stationary phase.

. **Principle**

The equilibrium for gas chromatography is partitioning, and the components of the sample will partition (i.e. distribute) between the two phases: the stationary phase and the mobile phase.

Compounds that have a greater affinity for the stationary phase spend more time in the column and thus elute later and have a longer retention time (Rt) than samples that have a higher affinity for the mobile phase.

Affinity for the stationary phase is driven mainly by intermolecular interactions and the polarity of the stationary phase can be chosen to maximize interactions and thus the separation.

The separation is hence accomplished by partitioning the sample between the gas and a thin layer of a nonvolatile liquid held on a solid support.

A sample containing the solutes is injected into a heated block where it is immediately vaporized and swept as a plug of vapor by the carrier gas stream into the column inlet.

The solutes are adsorbed by the stationary phase and then desorbed by a fresh carrier gas.

Gas Chromatography
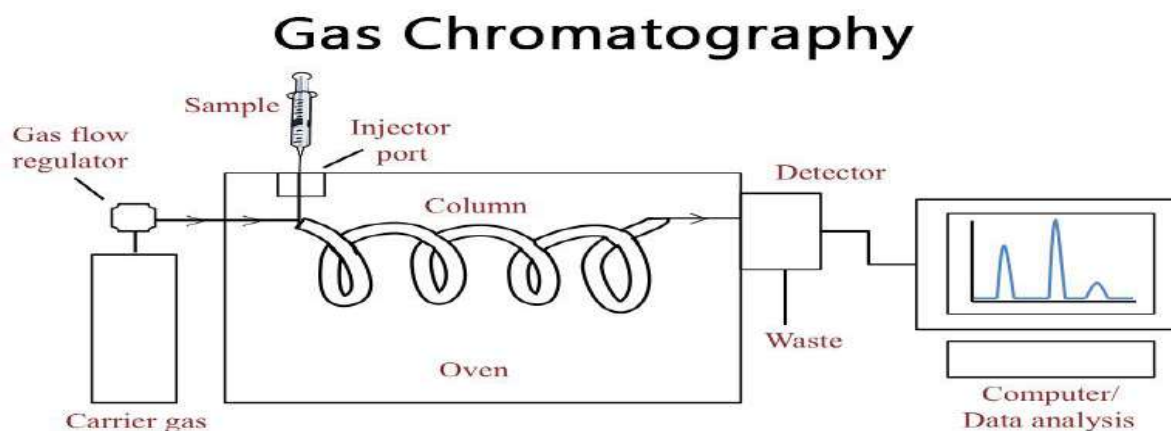
GC Basic Components
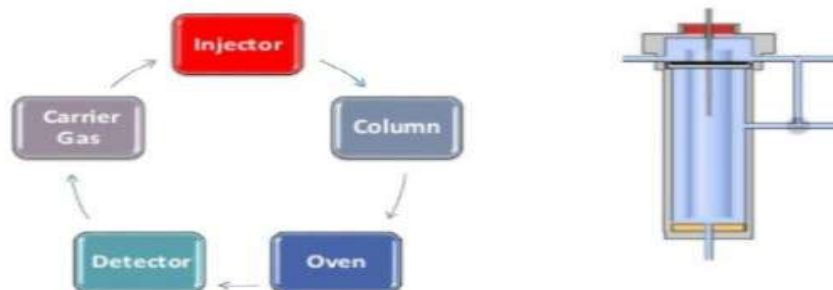
The injector can be used in one of two modes; split or splitless. In split mode sample is divided into two portions , smaller portion introduced, in splitless ode entire sample is introduced The injector contains a heated chamber containing a glass liner into which the sample is injected through the septum.

The split / splitless injector
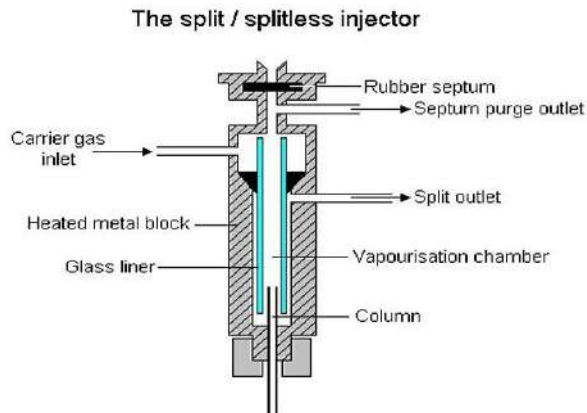
Two types of columns are used in gas chromatography: packed columns and capillary columns. Capillary columns consist of a thin, fused silica glass tube with a thin, internal liquid phase (organic silicone polymers)coating. The column is placed in a thermostatic oven

Cross section of a Fused Silica Open Tubular Column
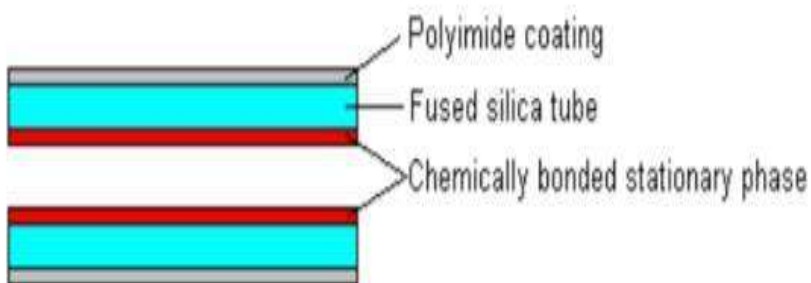
Detector

Chtomatography detector is a device used in gas chromatography (GC) or liquid chromatography (LC) to detect components of the mixture being eluted off the chromatography column.generally

selective detectors are used , as solute comes from the collumn, interact with the detector which converts that interaction into electronic signal

Oven

The oven has three functions: It keeps the column temperature constant. It allows operation at elevated temperature (faster; perhaps necessary to vaporize the sample).

carrier gas or Gas systems

Carrier gases in gas chromatography are used to move the solutes through the column. Helium, hydrogen and nitrogen are the most widely used gases. The choice of gas depends upon the choice of detector

Eg., The gases of ionization detector are hydrogen and air The liquid or gas sample is injected with the help of micro syringe into a flash vaporizer part which is in the capillary column and separated analytes Which flow through a detector and response is displayed on the computer as a

Chromatogram   The sample components are separated on the stationary phase and they will

 reach the detectors in the reverse order of their interaction strength

The chromatogram is a graph showing the detector response. It has two parameters

  1. Retention time   2. Peak area

Retention time is used for the qualitative analysis of components

Peak area is used for quantitative analysis

1. Methanol, 0.01%
2. 2-Propanol, 0.0785% (I.S.)
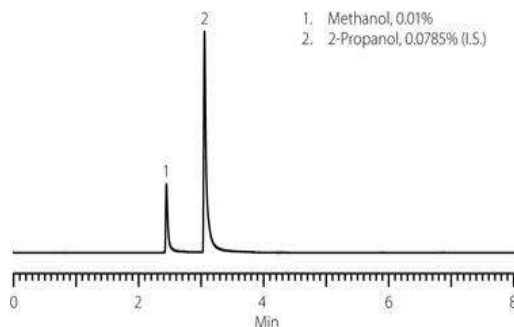
Eg.,Analysis of residual methanol in biodiesel, Chromatogram shows a standard solution of methanol with 2- propanol as the internal standard

ADVANTAGES:

High Resolution Very high sensitivity, detect down to 100 ppm.

Very good precision and accuracy.

Very good separation Time analysis is short), fast analysis is possible.

Small sample is needed-ml Good detection system Quantitative analysis

DISADVANTAGES:

Sample must be volatile

 Dirty sample choke the capillary

Applications of Gas Chromatography

Analysis of foods like carbohydrates, proteins, lipids, vitamins, steroids, drug and pesticides residues, trace elements, Pollutants like formaldehyde, carbon monoxide, benzene, DDT etc
Dairy product analysis- rancidity
Separation and identification of volatile materials, plastics, natural and synthetic polymers, paints, and microbiological samples
* Inorganic compound analysis

HPLC-High Performance Liquid Chromatography

Instrumentation:
Main components in an HPLC system include the solvent reservoir, or multiple reservoirs, a high pressure pump, a column, injector system and the detector
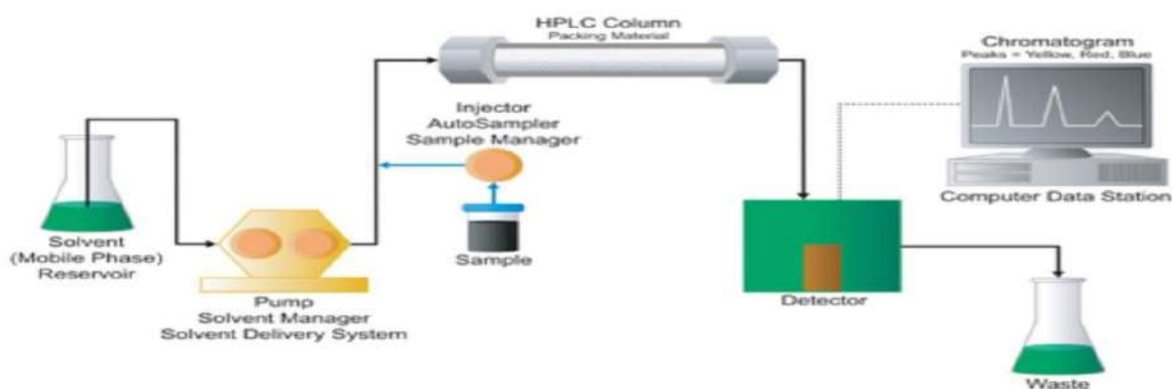
Figure E: High-Performance Liquid Chromatography [HPLC] System
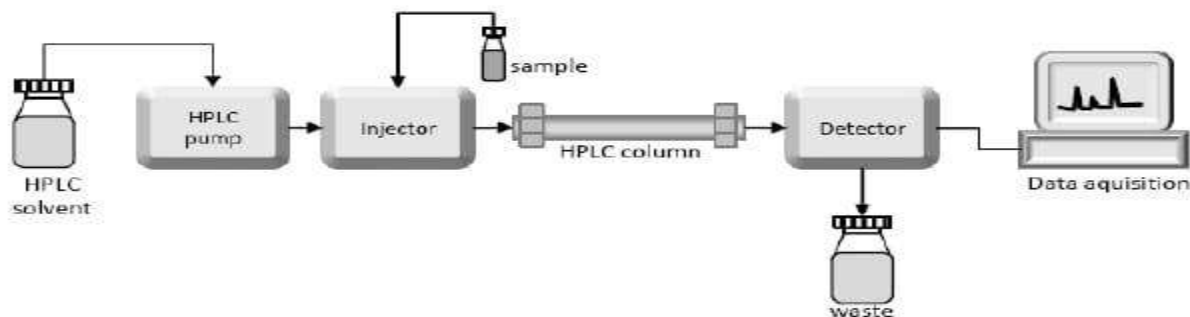
Detector

The UV, VIS, and PDA detectors are categorized as absorbance detectors. They provide good sensitivity for light absorbing compounds at ~pg level.They are easy to operate and provide good stability. UV detector is a very commonly used detector for HPLC

Solvent Reservoir

Solvent reservoir, which contains the solvent used to carry the sample through the system. The solvent should be filtered with an inlet solvent filter to remove any particles that could potentially damage the system's sensitive components.It must contain volume enough for repetitive analysis. It must be inert solvent

Pump

If one pump is used the composition of mobile phase is constant, It is called isocratic elution. If two or more pumps are used, the composition of mobile phase is variable is called gradient elution

column

Columns are the main component in HPLC because the column is responsible for the separation of the sample components. The sample passes through the column with the mobile phase and separates in its components when it comes out from the column.

Injectors:-

The most useful and widely used sampling device is the six port rheodyne valve. The sample is introduced into the sample loop using a special syringe. A clockwise rotation of the valve rotor places the sample filled loop into the mobile phase stream

Flow path of Two-Position, Six-Port Injection Valve
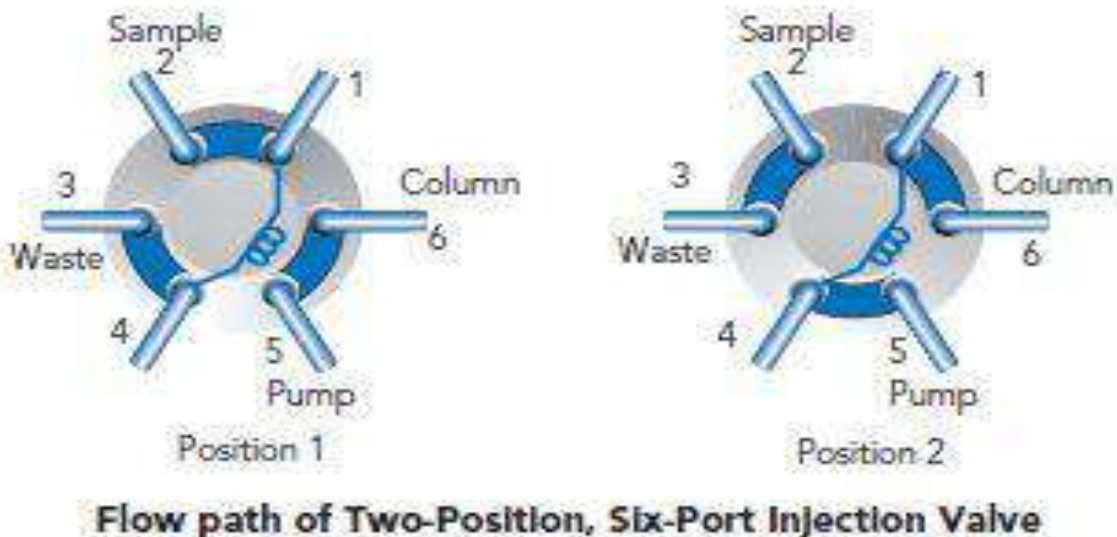
Data Collection Devices

Signals from the detector may be collected on chart recorders or electronic integrators that vary in complexity and in their ability to process, store and reprocess chromatographic data. The computer integrates the response of the detector to each component and places it into a chromatograph that is easy to read and interpret.

Applications :

1. Analysis of drugs
2. Analysis of synthetic polymers
3. Analysis of pollutants in environmental analytics
4. Determination of drugs in biological matrices
5. Isolation of valuable products
6. Product purity and quality control of industrial products and fine chemicals
7. Separation and purification of biopolymers such as enzymes or nucleic acids
8. Water purification
9. Pre-concentration of trace components
10. Ligand-exchange chromatography
11. Ion-exchange chromatography of proteins
12. High-pH anion-exchange chromatography of carbohydrates and oligosaccharides

Separation of Gaseous and liquid Mixtures Gas separation

Gas separation is a widely used technique in which the objective is the separation of one or more gases from a mixture. It is becoming crucial for several industrial processes such as the treatment of fumes from coal-fired plants, in particular, aiming for the removal of CO2 to

reduce the greenhouse effect. Growing interest is also given to other applications such as the separation and purification of commercially important gases such as H_2, CH_4 and O_2 from natural gas. The most common methods to perform gas separation are:

1. Adsorption

2. Separation with Membranes (Synthetic membranes)

3. Separation with solvent/sorbents (Absorption)

4. Separation by cryogenic distillation

1. **Adsorption**

Adsorption is the process in which atoms, ions or molecules from a substance (it could be gas, liquid or dissolved solid) adhere to a surface of the adsorbent.

It is a physical process in which only a certain kind of gas molecules are adhered to the adsorbing surface, i,e adsorbate

The adsorbate which adsorbs the one gas only to the surface and therefore the separation occurs

Eg:- Nickel metal is specific for hydrogen gas adsorption
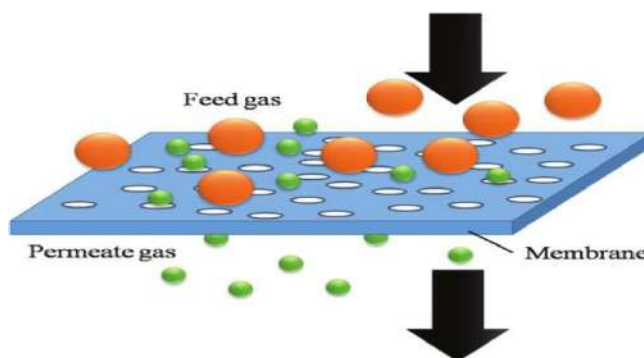
2. **Synthetic membrane**

Membranes can be used for separating gas mixtures where they act as a permeable barrier through which different compounds move across at different rates or not move at all. The membranes can be nano porous, polymer, etc. and the gas molecules penetrate according to their size, diffusivity, or solubility.

Separation of gases with membranes relies on the different affinities of one or more gases towards the membrane material, causing one gas to be permeate faster (or slower) than others. It is one of the fastest growing field for gas separation techniques, especially due the high variety

of materials which the membrane could be composed of, including Microporous Organic Polymers, Zeolites.

Eg:- A thin metal sheet of Pd allows hydrogen gas to pass through
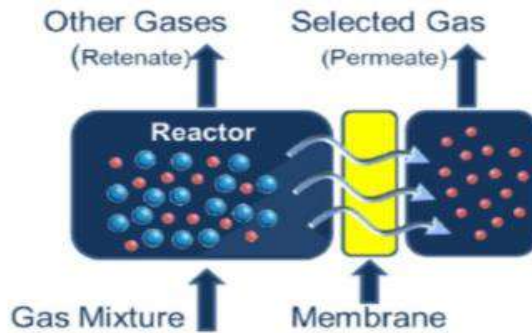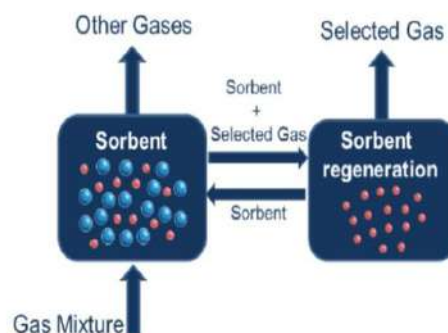

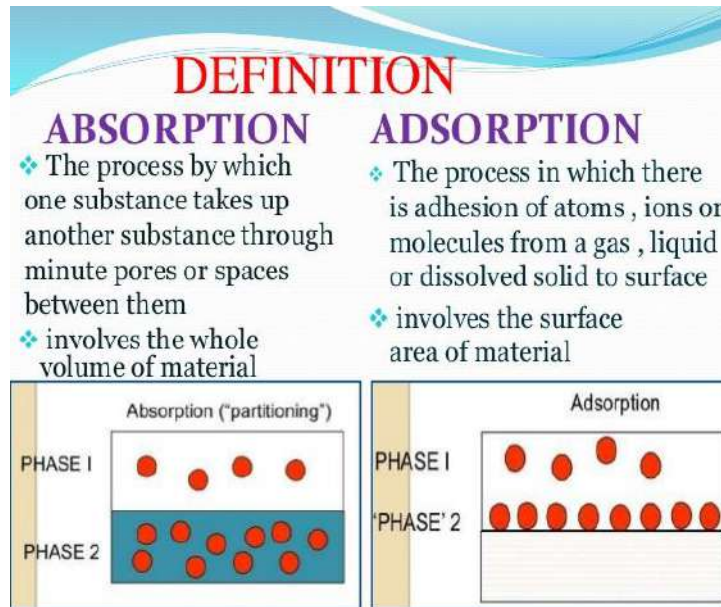Figure 3. Schematic representation of Membranes for gas separation

3. Absorption:-

Absorption is the process in which a fluid is dissolved by a liquid or a solid (absorbent). The separation with solvent/sorbents is based on the affinity of the gas towards a specific sorbent such as zeolites, alumina or activated carbon or a solvent for instance MEA (methanolamine). The separation occurs when the gas mixture comes in contact with the sorbent/solvent in a vessel which is then pressurised. The gas with the highest affinity for the adsorbent is "trapped" whereas the others pass through the system

Eg:- Liquids shall be absorbed by a solid/ Gases being absorbed by a liquid

When a mixture of gas (CO,CO2,NO,SO2) passes through a solution of NaOH , Which absorbs only CO2

DEFINITION

ABSORPTION
- The process by which one substance takes up another substance through minute pores or spaces between them
- involves the whole volume of material

ADSORPTION
- The process in which there is adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to surface
- involves the surface area of material

4. **Cryogenic Distillation**

Cryogenic distillation is very similar to other distillation systems except it is used to separate chemicals with very low boiling points (e.g. propylene/propane mixture). In the case of cryogenic distillation, a refrigeration system must be coupled with the condenser, which is at the lowest possible temperature. They could be separated by increasing decreasing the temperature and pressure of the system in which they are stored, so that they can be divided into their single components. The gas mixture is cooled down to a low temperature (typically <-50 °C). Once in the liquid form, the components of the gas can be directed in a distillation column and through a series of compression, cooling and expansion steps, they can be distributed to different channels, depending on their boiling points
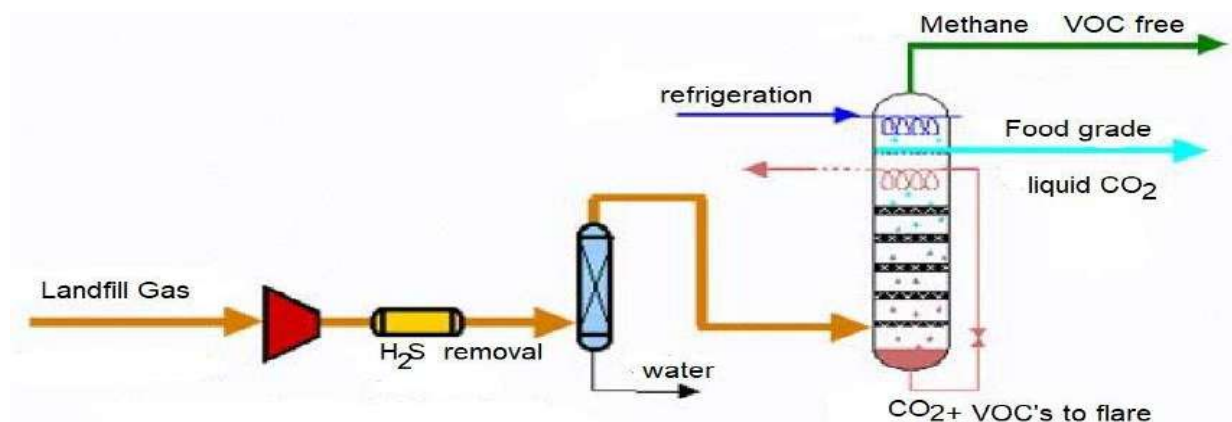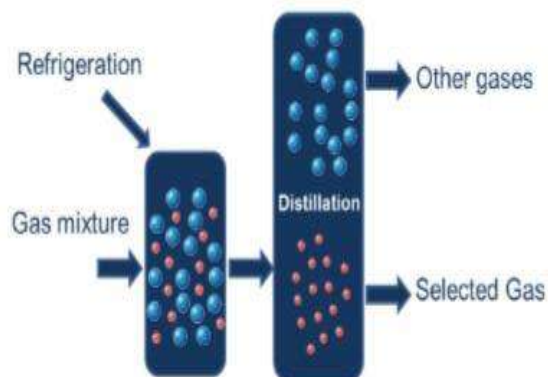
Figure 2. Schematic representation of Cryogenic distillation method

Separation of liquid mixture :-

The individual substances in a liquid mixture can be separated using different methods, depending on the type of mixture. These methods include

1. Fractional distillation

2. evaporation

3. Simple distillation

4. Chromatography.

5. Centrifugation

6. Separating funnel

1.**Fractional distillation**

Fractional distillation is the separation of a mixture into its component parts, or fractions. Chemical compounds are separated by heating them to a temperature at which one or more fractions of the mixture will vaporize. It uses distillation to fractionate.

A simple fractionating column is a tube packed with glass beads, the beads provide a surface for the vapours to cool and condense repeatedly. The vapours of the liquid with lower boiling point first pass out of the fractionating column, condense liquids are collected in the receiver flask.

Eg:- Separation of different fractions from petroleum products

FRACTIONAL DISTILLATION
CRUDE OIL
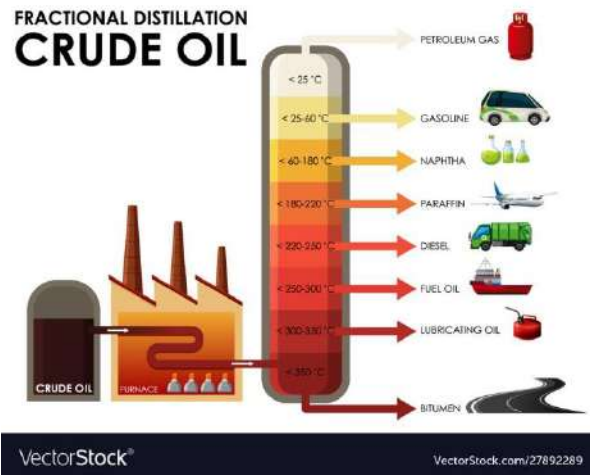
2. Evaporation

Evaporation is a technique used to separate out homogenous mixtures where there is one or more dissolved solids. This method drives off the liquid components from the solid components. The process typically involves heating the mixture until no more liquid remains, Prior to using this method, the mixture should only contain one liquid component, unless it is not important to isolate the liquid components. This is because all liquid components will evaporate over time. This method is suitable to separate a soluble solid from a liquid.
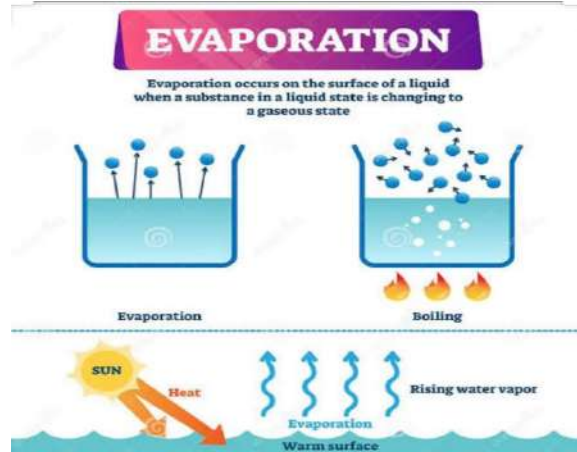
3. Simple distillation

Definition: A method of separating mixtures based on differences in their volatilities in a boiling liquid mixture. The components in a sample mixture are vaporized by the application of heat and then immediately cooled by the action of cold water in a condenser. Distillation is an effective method to separate mixtures comprised of two or more pure liquids. Distillation is a purification process where the components of a liquid mixture are vaporized and then condensed and isolated. In simple distillation, a mixture is heated and the most volatile component vaporizes at the lowest temperature. The vapor passes through a cooled tube (a condenser), where it condenses back into its liquid state. The condensate that is collected is called distillate.
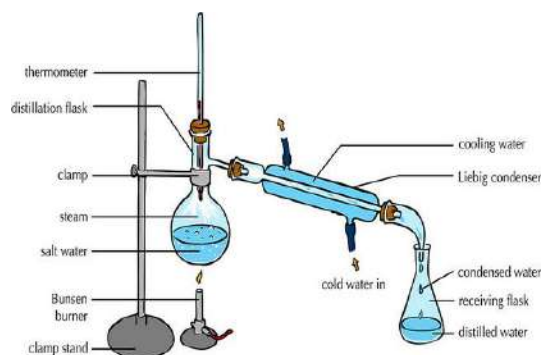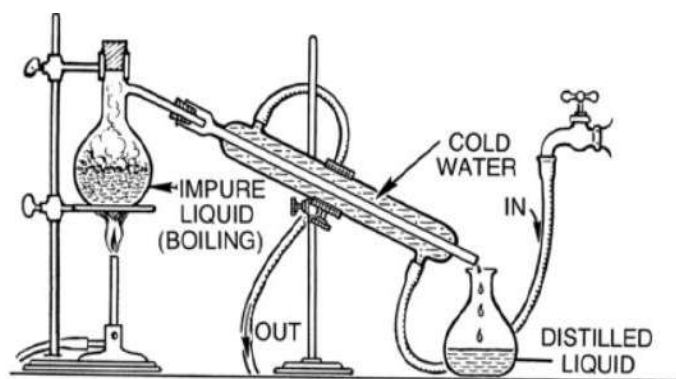
4. <u>Chromatography</u>

Chromatography is a laboratory technique for the separation of a mixture. The mixture is dissolved in a fluid called the mobile phase, which carries it through a structure holding another material called the stationary phase. The various constituents of the mixture travel at different speeds, causing them to separate.

The various components in the mixture travel at different speeds, causing them to separate

Paper chromatogrphy is one of the important chromatographic techniques, where in paper is used as the stationary phase and a liquid solvent as the mobile phase. The sample is placed in the form of spot on the paper and the paper is carefully dipped into a solvent containing in the chamber . The solvent rises up the paper due to capillary action and the components of the mixture rise up at different rates and thus are seperated from one another

Eg:- To separate drugs from blood, To separate pigments from natural colours
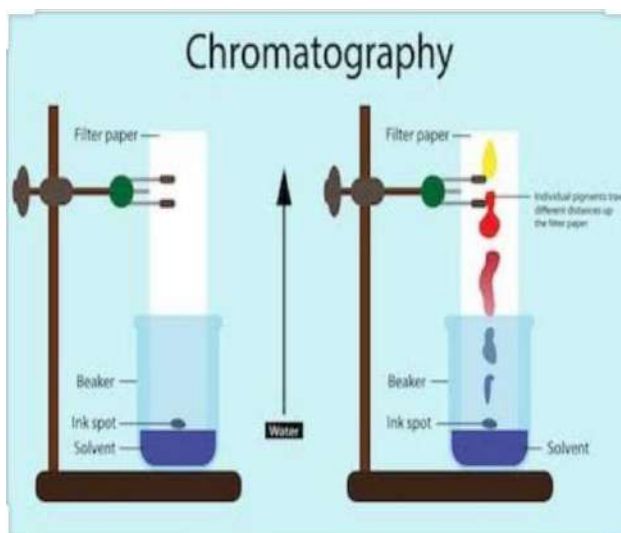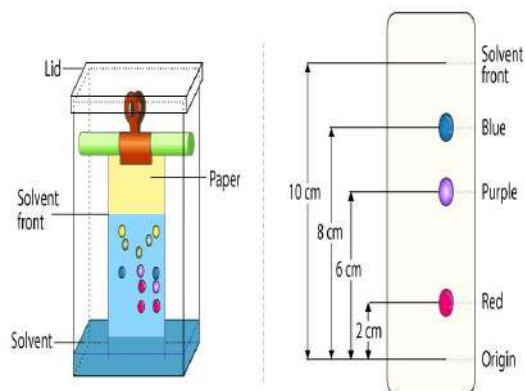
5. Centrifugation

Centrifugation is the separation process of insoluble materials from a liquid where normal filtration does not work to isolate.

Centrifugation that relies on the action of centrifugal force to separate particles in a solid–liquid mixture into two distinct phases consisting of the sediment and centrifugate (also called supernatant liquid).

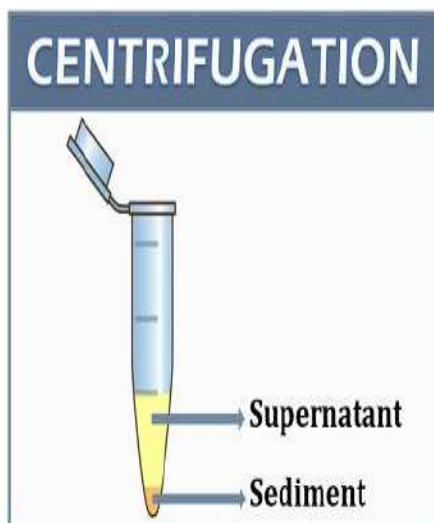In normal filtration , the solid particles in a liquid are very fine and can easily passes through filter paper

The principle is that the denser particles are forced to the bottom and lighter particles stay at the top

The apparatus called centrifuge consists of a centrifuge tube holder called rotor. The rotor holds balanced centrifugal tubes of equal amount of the solid-liquid mixture. On rapid rotation of the rotor rotate horizontally the denser insoluble particles separate from the liquid

Eg:- Used in diagnostic laboratories for blood and urine tests

Used in dairies and home to separate butter from cream

Separation of fine particles in the qualitative analysis of inorganic compounds

6. Separating funnel

A separatory funnel, also known as a separation funnel, is a piece of laboratory glassware used in liquid-liquid extractions to separate (partition) the components of a mixture into two immiscible solvent phases of different densities.

It is used for the separation of components of a mixture between two immiscible liquid phases. The separation is based on the differences in the densities of the liquids
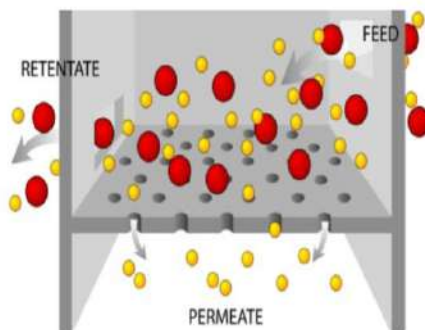
Applications: 1. To separate a mixture of oil and water

2. To separate organic and aqueous components fro the mixture
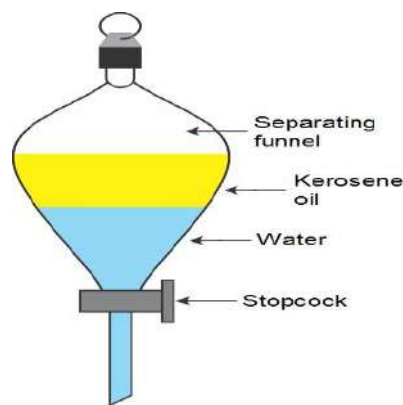
7. Filtration

Filtration is a separation method used to separate out pure substances in mixtures comprised of particles some of which are large enough in size to be captured with a porous material. Particle size can vary considerably, given the type of mixture. For instance, stream water is a mixture that contains naturally occurring biological organisms like bacteria, viruses, and protozoan's. Some water filters can filter out bacteria, the length of which is on the order of 1 micron. Other mixtures, like soil, have relatively large particle sizes, which can be filtered through something like a coffee filter.

Water Technology: Introduction, sources of water, types of impurities in water, hardness of water- temporary and permanent hardness, units of hardness, disadvantages of hard water. Estimation of hardness by EDTA method, boiler troubles.
Softening methods: Internal treatment, external treatment; zeolite process, ion exchange process, desalination of brackish water - reverse osmosis.

Introduction:

Water is nature's most wonderful, abundant and useful compound. Without food, human can survivefor a number of days, but water is such an essential that without it one cannot survive. Water is not only essential for the lives of animals and plants, but also occupies a unique position in industries.Probably, it's most important use as an engineering material is in the steam generation. Water is also used as coolant in power and chemical plants.

Water is widely distributed in nature. It has been estimated that about 75% matter on the earth's surface consists of water. Besides visible water on earth, there is large amount of water under earth to an average depth of over three kilometres. The air consists 12 to 15% of volume of water vapour. Water is found in living things. The body of human being consists of about 60% of water. Plants, fruits and vegetables contain 90 to 95% of water.

Sources of water:

(A) Surface water (B) Underground water

Surface water:

1. Rain water:

It is the purest form of naturel water, since it is obtained as a result of evaporation from the surface water. However, during the journey downwards, through the atmosphere, it dissolves a considerable amount of gases like CO_2, SO_2, NO_2, etc. and suspended solid particles.

2. River water:

In general, the greater the greater the contact that water has with the soil, or the more soluble the minerals of the soils with which it has come in contact, the greater is the amount of dissolved impurities in river water. River water thus contains dissolved minerals of the soil such as chlorides, sulphates, bicarbonates of calcium, magnesium and iron. River water also contains the organic matter, derived from the decomposition of plants, and small particles of sand and rock in suspension. Thus,river water contains considerable amounts of dissolved as well as suspended impurities.

3. Lake water:

It has a more constant composition. It, usually, contains much lesser amounts of dissolved minerals than even well water, but quality of organic matter present in it is quite high.

4. Sea water:

It is the most impure form of natural water. It contains, on an average, about 3.5% of dissolved salts, out of which about 2.6% is sodium chloride. Other salts present are sulphate of sodium; bicarbonates of potassium, magnesium and calcium etc.

Surface water, generally, contains suspended matter, which often contains the disease producing bacteria. Hence, such water is not considered to be safe for human consumption.

Underground water:

A part of the rain water, which reaches the surface of the earth, percolates into the earth. As this water journeys downwards, it comes in contact with a number of mineral salts present in the soil and dissolves some of them. Water continues it's downwards journey, till it meet a hard rock, when it retreads upwards and it may even come out in the form of *spring or well*. In general, it is clear in appearance due to the filtering action of the soil, but contains more of the dissolved salts. Thus, water from these sources contains more hardness. Usually, underground water is of high organic purity.

Types of impurities in water:

Natural water is, usually contaminated three types of impurities.

1. Physical impurities. 2. Chemical impurities. 3. Biological impurities.

Physical impurities:

(a) **Colour:** Colour in water is usually caused by *metallic substances* like salts of iron, manganese, peat, industrial effluents. Usually, yellowish tinge indicates the presence of chromium and appreciable amount of organic matter. Yellowish red colour indicates the presence of iron; while red-brown colour indicate the presence of peaty matter.

(b) **Turbidity:** It is due to the colloidal, extremely fine suspension such as clay, slit, finely divided matter etc. Turbidity expresses the optical properties of water, which scatter light rather than to transmit in straight lines. Turbidity in water can be eliminated by sedimentation, followed by coagulation, filtration, etc.

(c) **Taste:**
- Bitter taste can be due to the presence of iron, aluminium, manganese sulphate or excess of lime.
- Soapy taste can be due to the presence of large amount of sodium bicarbonate.
- Brackish taste is due to the presence of unusual amount of salts.
- Palatable taste is due to the presence of dissolved gases like CO_2. (d) Odour: The causes of odour in polluted rivers are;
- Presence of inorganic and organic compounds of N, S and P and the putrefaction of proteins and other organic materials present in sewage;
- Industrial effluents containing organic substances such as alcohols, aldehydes, phenols etc.flowing into the water bodies.

Chemical impurities:

(a) Acidity:

Surface water and ground water attain acidity from industrial wastes like acid, mine, drainage,pickling liquors, etc. Usually, acidity is caused by the presence of free CO_2, mineral acids (H_2SO_4) and weakly dissociated acids. Mineral acids are released when iron and aluminium salts hydrolyse.

(b) Gases:
- All natural waters contain dissolved atmosphere CO_2. It solubility depends upon temperature,pressure and dissolved mineral content of water.
- Concentration of dissolved atmosphere O_2 in water depends on temperature, pressure and salt content in water. Dissolved O_2 in industrial water is nuisance, since it induces corrosion reactions. On the other hand, dissolved O_2 in water is essential to the life of aquatic organisms such as fishes.

- Dissolved NH3 in water arises from the decomposition of nitrogenous organic matter. Polluted water and sewage contains nitrogen in the form of nitrogenous organic compouds and urea, which are partially converted into NH3.

(c) Mineral matter:

It has origin from rocks and industrial effluents. These include Ca2+, Mg2+, Na+, K+, Fe2+, CO_3^{-2}, Mn2+,HCO^{-3} , Cl-, SO $\square$ 24, etc. However, from industrial point of view, alkalinity and hardness are important.
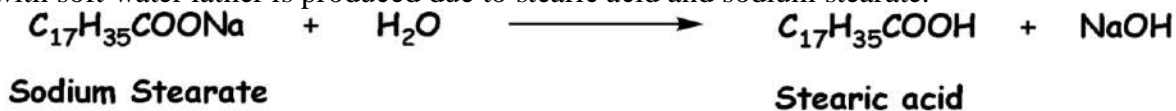
Biological impurities:

These are algae, pathogenic bacteria, fungi, viruses, pathogens, parasite worms etc. The source of these contamination is discharge of domestic and sewage wastes, excreta, etc. Micro-organisms are, usually, abundant in surface water, but their count is often quite low or even nil in deep-well waters. The common type of micro-organisms from the point of treatment are algae, fungi and bacteria, which often form slime, thereby causing fouling as well as corrosion. The slime so-formed clogs the spray nozzles and screens of the circulating pumps in air-conditioning and other industrial plants. The growth of micro-organisms takes place at temperature in between 20 to 350C.In order to control the micro-organisms, chemical treatment like chlorination is done.
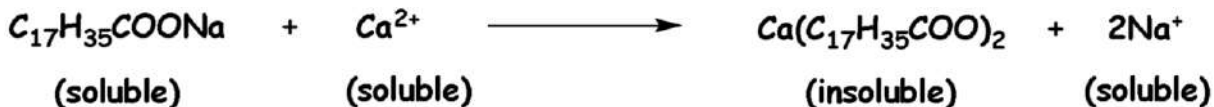
Hardness of water:

The water which does not produce lather with soap is called hard water. Thus, hardness in water is the characteristic, which "*prevents the lathering of soap*". On the other hand, the water which produce lather easily on shaking with soap solution, is called soft water.

The hardness of water is caused by the presence of dissolved salts such as bicarbonates, sulphates, chlorides and nitrates of divalent metal ions like calcium and magnesium. Soap is sodium or potassium salt of higher fatty acids like stearic, oleic and palmetic acids. When soap is mixed with soft water lather is produced due to stearic acid and sodium stearate.

$$C_{17}H_{35}COONa + H_2O \longrightarrow C_{17}H_{35}COOH + NaOH$$

Sodium Stearate $\qquad\qquad$ Stearic acid

$$C_{17}H_{35}COONa + C_{17}H_{35}COOH \longrightarrow \text{Lather formation}$$

When soap comes in contact with hard water, sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is white precipitate.

$$C_{17}H_{35}COONa + Ca^{2+} \longrightarrow Ca(C_{17}H_{35}COO)_2 + 2Na^+$$

(soluble) $\qquad$ (soluble) $\qquad\qquad$ (insoluble) $\qquad$ (soluble)

The different types of water are commercially classified on the basis of degree of hardness as follows;

| Hardness	Name of water
0-70 mg/L	Soft water
70-150 mg/L	Moderate hard water
150-300 mg/L	Hard water
>300	Very hard water

Types of Hardness:
The hardness of water is two types;
1. Temporary hardness. 2. Permanent hardness.

1. *Temporary hardness* or Carbonate hardness:
This hardness is caused by two dissolved bicarbonate salts Ca(HCO3)2 and Mg(HCO3)2. The hardness is called temporary because, it can be removed easily by boiling. During boiling, bicarbonates are decomposed to yield insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$
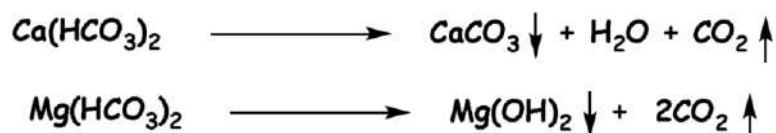
2. *Permanent hardness* or non-carbonate hardness:
This hardness is due to the dissolved chlorides, sulphates and nitrates of calcium and magnesium. These salts are CaCl2, MgCl2, CaSO4, MgSO4, Ca(NO3)2, Mg(NO3)2. It cannot be removed easily by boiling. Hence, it is called permanent hardness. Only chemical treatment can remove this hardness.

        Total Hardness = Temporary hardness + Permanent hardness

Expression of hardness:
Hardness of water is expressed in terms of calcium carbonate equivalents. The weights of different salts causing hardness are converted to weights equivalent to that of CaCO3.
If a sample of water contains two or more than two salts, their quantities are converted in equivalent to CaCO3 as mentioned above and then the sum will give the total hardness. CaCO3 was selected for expression of the degree of hardness because;
1. The Molecular Weight of CaCO3 is 100, which is easy for calculation.
2. It is an insoluble salt, and all the dissolved salts of calcium are precipitated as CaCO3.

Hardness causing salt	Molecular weight
Ca(HCO3)2	162
Mg(HCO3)2	146
CaSO4	136

CaCl2	111
MgSO4	120
MgCl2	95
Ca(NO3)2	164
Mg(NO3)2	148

Thus, 120 parts by weight of MgSO4 would react with the same amount of soap as 100 parts by weight of CaCO3. Hence, weight in terms of CaCO3 would be equal to weight of MgSO4 in water multiplied by 100/120.

The method of calculating hardness will be clear from the following formula.

Hardness of hardness causing salt in terms of CaCO3

$$= \frac{\text{Amount of the hardness causing salt x 100}}{\text{Molecular weight of hardness causing salt}}$$

Units of hardness:

There are five units in which the hardness of water is expressed.

1. Parts per million. 2. Milligrams per litre. 3. Degree Clark. 4. Degree French. 5. meq per litre.

1. *Parts per million* (ppm):

    It is the parts of calcium carbonate equivalent hardness per 106 parts of water.

        i.e. 1ppm = 1 part of CaCO3 eq hardness in 106 parts of water.

2. *Milligrams per litre* (mg/L):

    It is the number of milligrams of calcium carbonate equivalent hardness present per litre of water.

    Thus,

    1 mg/L = 1 mg of CaCO3 eq hardness per1 L of water

    But 1 L water = 1 kg = 1000g = 10^6 mg

    1 mg/L   = 1 mg of CaCO3 eq per 10^6 mg of water

            = 1 part of CaCO3 eq per 106 parts of water = 1 ppm

3. *Degree Clark* (0Cl):

    It is the number of grains of CaCO3 equivalent hardness per gallon of water. (or) It is the parts CaCO3 equivalent hardness per 70,000 parts of water.

        1^0Cl = 1 grain of CaCO3 eq hardness per gallon of water

        1^0Cl = 1 part of CaCO3 eq hardness per 70,000 parts of water

4. *Degree French* (0Fr):

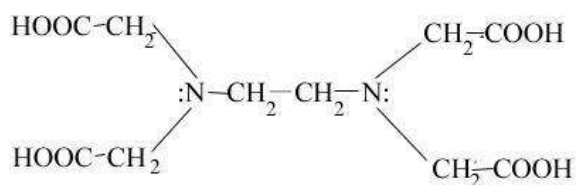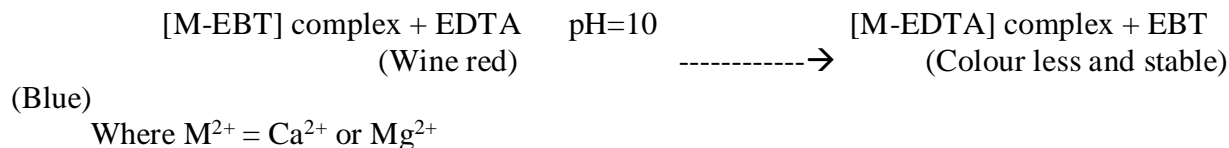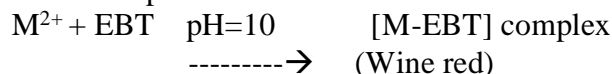   It is the parts of calcium carbonate equivalent hardness per 10^5 parts of water.

        i.e. 1^0Fr = 1 part of CaCO3 eq hardness in 10^5 parts of water.

    Relationship between various units of hardness:

1ppm = 1 mg/L = 0.1 0Fr = 0.07 0Cl = 0.02 meq/L

Estimation of hardness by EDTA method:
EDTA forms a colourless stable complex with Ca2+ and Mg2+ ions in water at pH10. Ammonia buffer is used to maintain the pH. In this method EBT (Eriochrome Black-T) is used as an indicator. Initially EBT forms an unstable complex with Ca2+ and Mg2+ ions, giving wine red colour to the solution.During the titration EDTA reacts with this complex (Ca-EBT or Mg-EBT complex), forms a stablecomplex (Ca-EDTA or Mg-EDTA) and releases the blue EBT into the solution. Hence the end point is wine red to blue colour.

$$M^{2+} + EBT \quad pH=10 \quad \text{[M-EBT] complex}$$
$$\text{---------}\rightarrow \quad \text{(Wine red)}$$

$$\text{[M-EBT] complex + EDTA} \quad pH=10 \quad\quad \text{[M-EDTA] complex + EBT}$$
$$\text{(Wine red)} \quad \text{------------}\rightarrow \quad \text{(Colour less and stable)}$$
(Blue)
        Where $M^{2+} = Ca^{2+}$ or Mg^{2+}

structure of EDTA

Various steps involved in this method are;
1. Preparation of standard hard water (1mg of CaCO3 per 1 mL of water).
2. *Standardization of EDTA solutions*:
    Pipette out 50 mL of standard hard water in a conical flask. Add 10-15 mL of buffer solution and 4 to 5 drops EBT indicator. Titrate with EDTA solution, till wine red colour changes to clear blue. Let volume used be V1 mL.
3. *Titration of unknown hard water*:
    Titrate 50 mL of water sample just as indicated above. Let the volume used be V2 mL.

4. *Titration for permanent hardness*:
        Take 250 mL of the water sample in a large beaker. Boil it, till the volume is reduced to about 50 mL. Filter, wash the precipitate with distilled water, and collect the filtrate and washings in a 250 mL measuring flask. Finally, make up the volume to 250 mL with distilled water. Then, titrate 50 mL of boiled water sample just as in step (2). Let the volume of EDTA used be V3 mL.
Calculations:
        50 mL of standard hard water = V1 mL of EDTA
        50 mg of CaCO3 = V1 mL of EDTA
        1 mL of EDTA = 50/V1 mg of CaCO3
    Now 50 mL of given hard water = V2 mL of EDTA
                        =$\underline{V_2*50}$ *X* mg of CaCO3
                                            V_1

1 L (1000mL) of given hard water
$$= 1000V2/V1 \text{ mg of CaCO3 eq}$$

Total hardness of water $= 1000V2/V1$ mg/L $= 1000V2/V1$ ppm
Now 50 mL of boiled water $= \underline{V_3*50}$ X mg of CaCO3
$$V_1$$
1 L of given hard water $= 1000V3/V1$ mg of CaCO3 eq
Permanent hardness $= 1000V3/V1$ mg/L $= 1000V3/V1$ ppm
And Temporary hardness $=$ Total hardness $-$ permanent hardness
Temporary hardness $=\underline{1000(V2\text{-}V3)}$ ppm
$$V_1$$

*Disadvantages of hard water***:**
1. In domestic use. 2. In industrial use. 3. In steam generation.
1. *In domestic use***:**
   (a) Washing:
     Hard water, when used for washing purpose, does not lather freely with
     soap. On the other hand, it produces sticky precipitates of calcium and magnesium
     This causes a wastage of lot of soap being used. Also presence of iron salts may
     cause stains on cloth.
   (b) Bathing:
     Hard water, does not lather freely with soap, but produces sticky scum on the bath-
     tub and body. Thus, the cleaning quality of soap depressed and a lot of it wasted.
   (c) Cooking:
     Due to the presence of dissolved hardness causing salts, the boiling point of water
     is elevated. Consequently, more fuel and time are required for cooking. Certain
     foods do not cook soft in hard water. Also, tea or coffee, prepared in hard water
     has an unpleasant taste and muddy-looking extract.
   (d) Drinking:
     Hard water causes bad effect on our digestive system. Moreover, the possibility of
     forming calcium oxalate crystals in urinary tracks is increased.
2. *In Industrial use***:**
(a) Textile industry: Hard water causes much of the soap to go as waste. Moreover,
   precipitates of calcium and magnesium soaps adhere to the fabrics. These fabrics,
   when died later on, do not produce exact shades of colour. Iron and manganese salts-
   containing water may cause coloured spots on fabrics, thereby spoiling their beauty.

   (b) Sugar industry: Water containing sulphates, nitrates, alkali carbonates, etc., if used in
     sugar refining, it causes difficulties in the crystallization of sugar. Moreover, the sugar
     so-produced may be deliquescent.
   (c) Concrete making:Water containing chlorides and sulphates, if used for concrete making,
     affects the hydration of cement and the final strength of the hardened concrete.
   (d) Pharmaceutical industry:Hard water, if used for preparing pharmaceutical product
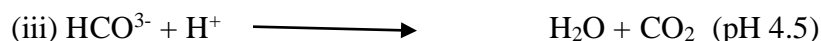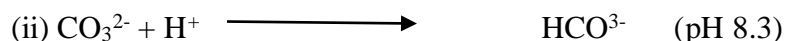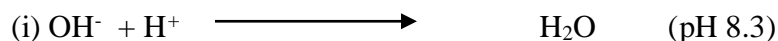   like drugs, injections and ointments etc.may produce certain undesirable products in
     them.

3. *In steam generation*:

For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as:
(i)   Scale and sludge formation (ii) corrosion (iii) priming and foaming
(iv) caustic embrittlement.

DETERMINATION OF ALKALINITY OF A WATER SAMPLE

Principle: Alkalinity of water means the total content of those substances in it which causes an increased OH^- ion concentration up on dissociation or due to hydrolysis. The alkalinity of water is attributed to the presence of (i) Caustic alkalinity (Due to OH^- and CO_3^{2-}) (ii) Temporary hardness (Due to HCO_3^{2-}) Alkalinity is a measure of ability of water to neutralize the acids Determination of alkalinity OH^-, CO_3^{2-} and HCO_3^{2-} can be estimated separately by titration against standard acid using phenolphthalein and methyl orange as indicators The determination is based on the following reactions

(i) $OH^- + H^+ \longrightarrow$ H_2O (pH 8.3)

(ii) $CO_3^{2-} + H^+ \longrightarrow$ HCO^{3-} (pH 8.3)

(iii) $HCO^{3-} + H^+ \longrightarrow$ $H_2O + CO_2$ (pH 4.5)

The titration of water sample against a standard acid up to phenolphthalein end point (P) marks the completion of reaction (i) and (ii) only. This amount of acid used thus corresponds to OH^- plus one half of the normal CO_3^{2-} present On the other hand, titration of the water sample against a standard acid to methyl orange end point (M) marks the completion of reaction (i), (ii) and (iii). Hence the total amount of acid used represents the total alkalinity.

Thus, $P = OH^- + \frac{1}{2} CO_3^{2-}$

          $M = OH^- + CO_3^{2-} + HCO^{3-}$

Procedure: **Part A: phenolphthalein alkalinity**

1. Pipette out 20 ml of water sample into a conical flask. Add 1-2 drops of Phenolphthalein indicator.
2. Rinse and fill the burette with N/10 HCl
3. Titrate the water sample in conical flask with N/10 HCl till the pink colour just disappears.
4. Note down the reading and repeat to get concordant readings.
5. Calculate phenolphthalein alkalinity by using formula given below

Phenolphthalein alkalinity=V1x $\frac{\text{normality of acid x 50 x 1000}}{20}$

Part B: Total alkalinity (Methyl orange)

1. Take 20 ml of water sample in conical flask and add methyl orange indicator to it.

2. Titrate the water sample in conical flask with N/10 HCl taken in the burette till the yellow orange colour changes to orange red.

3. Note down the reading and repeat to get concordant readings.

4. Calculate total alkalinity by using formula given below.

Total alkalinity=V2x normality of acid x 50 x 1000

DETERMINATION OF ACIDITY OF A WATER SAMPLE:

Principle: The mineral acids present in the sample which are contributing mineral acidity can be calculated by titrating with strong base NaOH at PH 4.3. The CO_2 and Bi carbonates present and contribute CO_2 Acidity in the sample can be neutralized completely by continuing the titration up to PH 8.2

Interference: Colour turbidity,iron,aluminium or Manganes and residual chlorine are Prime sources of interference,colour and turbidity can be avoided using Potentiometric titrations. Residual chlorine can be removed by adding Sodium thiosulphate iron aluminium and manganes is prevented by the addition of NaOH burette.

Procedure:

1. Take 100 ml of given sample in an Erlenmeyer flask
2. Add one drop of 0.1N $Na_2S_2O_3$ solution to remove the residual chlorine if present
3. Add 2 drops of methyl orange. The sample turns Orange
4. Proceed the titration until colour changes to yellow
5. Note down the volume of NaOH added (V1)
6. Take another conical flask containing 100 ml water sample, add 2 drops of Phenolphthalein
7. Proceed the titration until the sample turns Pink.
8. Note down the total valume of NaOH added.
Environmental Significance :
1. Acidity Interferes in the treatment of water
2.It corrodes Pipes (zinc coating of G.I pipes got dissolved)
3.Aquatic life will be affected.
4. PH is critical factor for bi-Chemical reaction.the favourable PH is 6.8 to 7.5.
5. Water contains mineral acidity more than 50 mg/l cannot be used in R.C.C works.
Application of Acidity data in Environmental Engineering Practice:-

1. The amount of CO_2 Present is an Important factor in determing whether removed by aeration or simple neutralization with lime or Sodium hydroxide will be chosen as the treatment method.

2. The size of equipment , chemical requirement storage space and cost of treatment all depend upon amount CO_2 Present.

3. CO_2 is an important consideration in estimating chemical requirements for lime or lime soda ash softening process.

4. Most industrial wastes containing mineral acidity must be eutralized be for they are subjectd to biological treatment or direct discharge into water course or sewers quantities of chemicals size of chemical feeders storage space and costs are determined from the laboratory data of acidity.

CALCULATION:

Mineral Acidity due to mineral acids $= \dfrac{V1 \times \text{normality of acid} \times 50 \times 1000}{100}$

CO_2 Acidity due to CO_2 $= \dfrac{V2 \times \text{normality of acid} \times 50 \times 1000}{100}$

Determination of the Chloride content in water

Procedure:

Transfer 100ml of water sample into a clean conical flask. Add about 1 ml of K2CrO4 indicator solution & titrate against standard (say 0.02N) AgNO3 solution until a reddish brown color persists in the white precipitate. Record the volume of AgNO3 consumed (Let 'a' cm^3). Perform a blank titration taking 100 ml of distilled water. The volume of AgNO3 consumed Let 'b' cm^3.

Calculation:
Volume of AgNO3 required for chlorine estimation $= (a-b)\ cm^3 = V$ 1000ml of
$1\ N\ AgNO3 = 35.45g/Cl^-$

$1\ ml\ of\ 1N\ AgNO3 = 0.03545g/Cl^-$
$V\ ml\ of\ 0.02\ N\ AgNO3 = 0.03545 \times V \times 0.02\ g/Cl^-$
Cl^- content in the sample $= \underline{0.03545 \times V \times 0.02}$ grams $/Cl^-100$

Cl^- content in the sample $= \underline{0.03545 \times V \times 0.02 \times 1000}$ mg$/Cl^-100$

TREATMENT OF WATER FOR DOMESTIC PURPOSE

The processes & technologies used to remove the contaminants from water & to improve its quality is recognized all over the world. The choice of which treatment to use from a great variety of available processes depends on the characteristics of the water, the type of the water quality problems to be present, & the costs of different treatments. There are different methods of water treatment the selection of which depends upon the type of source & purpose of use of water. Some of the methods are:

a) Screening
b) Plain sedimentation
c) Sedimentation by coagulation

d) Filtration
e) Disinfection

The following are different steps in treatment of water.

.REMOVAL OF SUSPENDED IMPURITIES

a) Screening : The process of removing floating matter from water is known as screening . In this process, water is passed through a screen. The floating matter is arrested by the screen and the water is free from floating matter.

b) Plain sedimentation : The process of removing big sized suspended solid particles from water is called as plain sedimentation. In this process, water is stored in big tanks for several hours. 70% of solid particles settle down due to force of gravity.

c) Sedimentation by coagulation : This is the process of removing fine suspended and colloidal impurities by adding coagulants like alum($K_2SO_4Al_2(SO_4)_3$ 24 H_2O,$FeSO_4$,$NaAlO_2$.When coagulant is added to water, floc formation takes place due to hydroxide formation which can gather tiny particles together to form bigger particles and settle down quickly.

d) Filtration: The process of passing a liquid containing suspended impurities through a suitable porous material so as to effectively removed suspended impurities and some microorganisms is called filtration. It is a mechanical process. When water flows through a filter bed, many suspended particles are unable to pass through the gaps and settle in the bed.

e) Disinfection or sterilization

The process of killing pathogenic bacteria and other microorganisms is called disinfection or sterilization. The water which is free from pathogenic bacteria and safe for drinking is called potable water. The chemicals used for killing bacteria are called disinfectants.

i) By adding bleaching powder: Water is mixed with required amount of bleaching powder, and the mixture is allowed to stand for several hours.

$$CaOCl_2 + H_2O \text{-----------} > Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \text{-----------} > HOCl + HCl$$

$$Germs + HOCl \text{-----------} > Germs \text{ are killed}$$
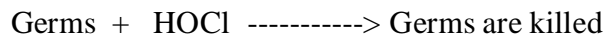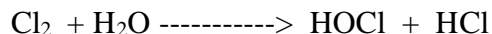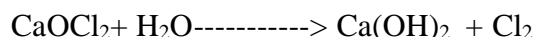
The disinfection action of bleaching powder is due to available chlorine in it. It forms hypochlorous acid which acts as a powerful germicide(disinfectant).

ii) Chlorination:

Chlorine is mixed with water in a chlorinator, which is a high tower having a number of baffle plates. Water and required quantity of concentrated chlorine solution are introduced from its top during their passage through the tower. They get thoroughly mixed and thn sterilized water is taken out from the bottom.

$$Cl_2 + H_2O \text{ -----------> } HOCl + HCl$$
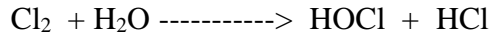
$$Germs + HOCl \text{ -----------> } Germs \text{ are killed}$$

Advantages:
1) Storage requires less space
2) Effective and economical
3) Produce no salts
4) Ideal disinfectant

Disadvantages:
1) Excess of chlorine causes unpleasant taste and odour.
2) More effective at below pH 6.5 and less effective at higher pH values.

iii) Ozonisation:

Ozone is an excellent, disinfectant which can be prepared by passing silent electric discharge through pure and dry oxygen. Ozone is highly unstable and breaks down, liberating nascent oxygen.

$$3O_2 \text{ -----------> } 2O_3$$

$$O_3 \text{ -----------> } O_2 + (O)$$
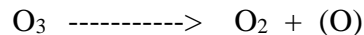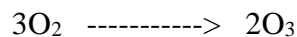
Advantages :

Removes colour , odour and taste.

Disadvantages:

The method is costly

Boiler troubles:

There are four important boiler troublers.
(1) Scale and sludge formation (2) Corrosion (3) Priming and foaming (4) Caustic embrittlement.
1. **Scale and sludge formation**:
In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively. When their concentration reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. If the precipitation takes place in the form of loose and slimy precipitate, it is called sludge
On the other hand, if the precipitated matter forms a hard adhering coating on the inner walls of the boiler, it is called *scale*.

Sludge:

It is a soft, loose and slimy precipitate formed within the boiler. Sludge can easily be scrapped off with a wire brush. It is formed at colder portions of the boiler. Sludge is formed by substances which have greater solubilities in hot water than cold water.

E.g. $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$, etc.

Disadvantages of sludge formation:
(a) Sludges are poor conductors of heat, so they tend to waste a portion of heat generated.
(b) If sludges are formed along with scales, then former gets entrapped in the latter and both get deposited as scales.
(c) Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connections.

Prevention of sludge formation:
(a) By using well softened water which is free from MgCO3, MgCl2, CaCl2, MgSO4 salts.
(b) By frequent "blow-down" operation, i.e. drawing off a portion of the concentrated water.
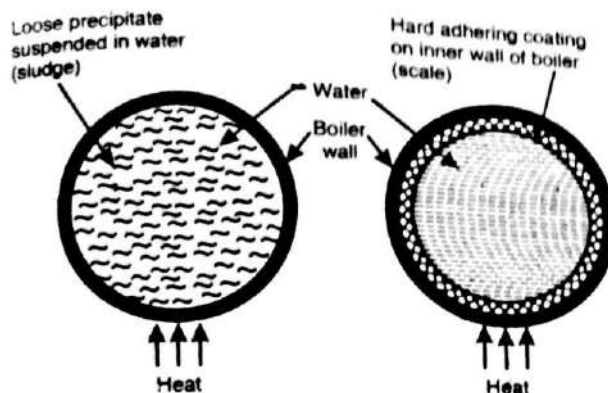

Scale:

These are hard deposits, which stick very firmly to the inner surfaces of the boiler. Scales are difficult to remove, even with the help of hammer. These are main sources of boiler troubles. Formation of scales may be due to;

(a) *Decomposition of calcium bicarbonate*:

Due to high temperature and pressure present in the boilers, the calcium bicarbonate salt decomposes in to CaCO3, which is an insoluble salt, forms scale.

$$Ca(HCO3)2 ---------\rightarrow CaCO3 + H2O + CO2$$
$$(scale)$$
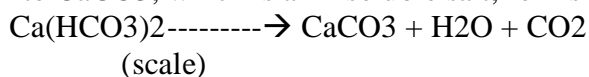
(b) *Deposition of calcium sulphate*:

The solubility of calcium sulphate in water decreases with rise of temperature. Thus, solubility of CaSO4 is 3,200 ppm at 150C and it reduces to 55 ppm at 2300C and 27 ppm at 320^0C. In other words, CaSO4 is soluble in cold water, but almost completely insoluble in super-heated water. Consequently, CaSO4 gets precipitated as hard scale on the heated portions of the boiler.

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(c) *Hydrolysis of magnesium salts*:

Dissolved magnesium salts undergo hydrolysis to form magnesium hydroxide precipitate, which forms a soft type of scale.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$
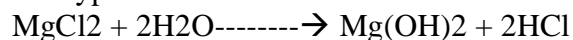
(d) *Presence of silica*:

SiO_2, even present in small quantities, deposits as calcium silicate ($CaSiO_3$) and magnesium silicate ($MgSiO_3$). These deposits stick very firmly on the inner side of the boiler surface and are very difficult to remove.

Disadvantages of scales:

(a) Wastage of fuel:Scales have a low thermal conductivity, so the rate of heat transfer from boiler to inside water gradually decreased. In order to provide a steady supply of heat to water, excessive or over-heating is done and this causes increase in fuel consumption. The wastage of fuel depends upon the thickness of scale.

Thickness of scale mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

(b) Lowering of boiler safety:

Due to scale formation, over-heating of boiler is to be done in order to maintain a constant supply of steam. This over-heating of the boiler tube makes the boiler material softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of the steam.

(c) Danger of explosion:

When thick scales crack, due to uneven expansion, the water comes suddenly in contact with overheated iron plates. This causes in formation of a large amount of steam suddenly. So sudden high pressure is developed, which even cause explosion of the boiler.

Removal of scales:

(i)   With the help of scraper or wire brush, we can remove the scales, if they are loosely adhering.

(ii)   By giving thermal shocks, we can remove the scales, if they are brittle.

(ii)   Calcium carbonate scales can be dissolved by using 5-10% HCl. Calcium sulphate scales can be dissolved by adding EDTA, with which they form soluble complexes.

(iv)   By frequent blow-down operation, if the scales are loosely adhering.
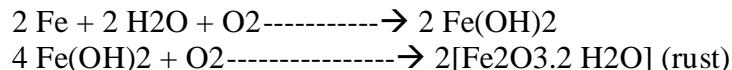
2. **Boiler corrosion**:

Boiler corrosion is "the decay of boiler material by a chemical or electro-chemical attack by its environment".

Main reasons for boiler corrosion are:

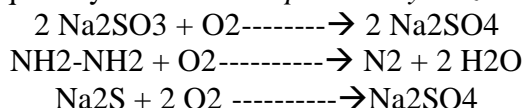(i) Dissolved oxygen. (ii) Dissolved carbon dioxide. (iii) Acids from dissolved salts.

(i) **Dissolved oxygen:**

Water usually contains about 8 ppm of dissolved oxygen at room temperature. At high temperature this D.O. can attack boiler material.
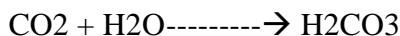
$$2 Fe + 2 H_2O + O_2 \text{-----------} \rightarrow 2 Fe(OH)_2$$
$$4 Fe(OH)_2 + O_2 \text{----------------} \rightarrow 2[Fe_2O_3.2 H_2O] \text{ (rust)}$$

Removal of dissolved oxygen:

By adding calculated quantity of *sodium sulphite* or *hydrazine* or *sodium sulphide*. Thus;

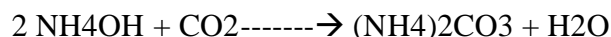$$2 Na_2SO_3 + O_2 \text{--------} \rightarrow 2 Na_2SO_4$$
$$NH_2\text{-}NH_2 + O_2 \text{----------} \rightarrow N_2 + 2 H_2O$$
$$Na_2S + 2 O_2 \text{----------} \rightarrow Na_2SO_4$$

(ii) Dissolved carbon dioxide:

$$CO_2 + H_2O \text{---------} \rightarrow H_2CO_3$$

Carbon dioxide is also released inside the boiler, if water used for steam generation contains bicarbonates.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$
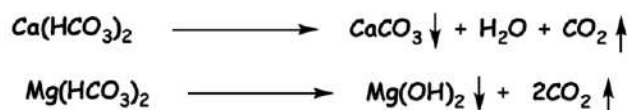
Removal of dissolved carbon dioxide:
By adding calculated quantity of ammonium hydroxide.
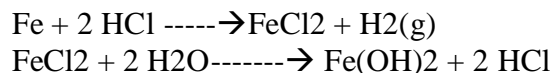
$$2 NH_4OH + CO_2 \text{-------} \rightarrow (NH_4)_2CO_3 + H_2O$$

(iii) **Acids from dissolved salts:**

Water, containing dissolved magnesium salts, liberate acids on hydrolysis.

$$MgCl_2 + 2 H_2O \text{------} \rightarrow Mg(OH)_2 + 2 HCl$$
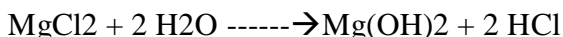
The liberated acid reacts with iron (of the boiler) in chain-like reactions, producing HCl again and again. Thus;

$$Fe + 2 HCl \text{-----} \rightarrow FeCl_2 + H_2(g)$$
$$FeCl_2 + 2 H_2O \text{-------} \rightarrow Fe(OH)_2 + 2 HCl$$

Consequently, presence of even a small amount of $MgCl_2$ will cause corrosion of iron to a large extent.

3. **Priming and foaming:**

Priming:

When a boiler is producing steam rapidly, some particles of the liquid water are carried along-with the steam. This process of 'wet steam' formation, is called *Priming*.

Priming is caused by:
(i) The presence of large amount of dissolved solids.
(ii) High steam velocities.
(iii) Sudden boiling.
(iv) Improper boiler design.
(v) Sudden increase in steam-production rate.

***Priming can be avoided by*:**
(i) Fitting mechanical steam purifiers.
(ii) Avoiding rapid change in steam rate.

(iii) Maintaining low water levels in boilers.

(iv) Efficient softening and filtration of boiler-feed water.

Foaming:

Foaming is "the production of persistent foam or bubbles in boilers, which do not break easily".Foaming is due to the presence of substances like oils, which greatly reduce the surface tension of water.

Foaming can be avoided by:

(i) Adding anti-foaming chemicals like castor oil.

(ii) Removing oil from boiler water by adding compounds like sodium aluminate.

Dis-advantages of priming and foaming:

   (i)   Dissolved salts in boiler water are carried by the wet steam to turbine blades, where they get deposited as water evaporates. This deposit reduces their efficiency.

   (ii)   Dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery.

   (iii)   Actual height of the water levels cannot be judged properly, thereby making The maintenance of boiler pressure becomes difficult.
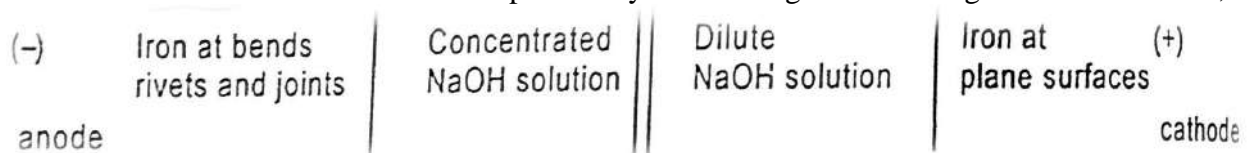
4. **Caustic embrittlement**:

Caustic embrittlement is "a type of boiler corrosion, caused by using highly alkaline water in the boiler".During softening process of water (in lime-soda process), free Na_2CO_3 is usually present in small proportion in the softened water. In high pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide. This makes the boiler water 'caustic'.

$$Na_2CO_3 + H_2O \text{ -------}\rightarrow 2NaOH + CO_2$$
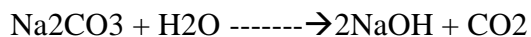
The NaOH containing water flows into the minute hair-cracks, present in the inner side of boiler, bycapillary action. Here water evaporates and the dissolved caustic soda (NaOH) concentration increases progressively. This caustic soda attacks the surrounding area, thereby corroding the iron of boiler as sodium ferrate.

This causes embrittlement (cracking) of boiler parts, particularly stressed parts (like bends, joints), causing even failure of the boiler.

Caustic embrittlement can be explained by considering the following concentration cell;

(−)	Iron at bends rivets and joints	Concentrated NaOH solution	Dilute NaOH solution	Iron at plane surfaces	(+)
anode					cathode

The iron surrounded by the dilute NaOH becomes the cathodic side; while the iron in contact with concentrated NaOH becomes anodic part, which consequently corroded.

Prevention of caustic embrittlement:

(i) By using sodium phosphate as softening reagent, instead of sodium carbonate.

(ii) By adding tannin or lignin to boiler water, which blocks the hair-cracks, thereby Preventing infiltration of caustic soda solution in cracks.

(iii) *By adding sodium sulphate to boiler water*:

Na_2SO_4 also blocks hair-cracks, thereby preventing infiltration of caustic soda solution in these cracks. It has been observed that caustic embrittlement can be prevented, if Na_2SO_4 is added to boiler water so that the ratio:

is kept as 1 : 1, 2 : 1 and 3 : 1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

Softening methods:

Water used for industrial purpose (such as fir steam generation) should be sufficiently pure. Therefore, it should be freed from hardness producing salts before put to use. *The process of removing hardnessproducing salts from water, is known as softening of water.*
In industry, main methods employed for softening of water are two types.

Softening of water	
Internal treatment	External treatment
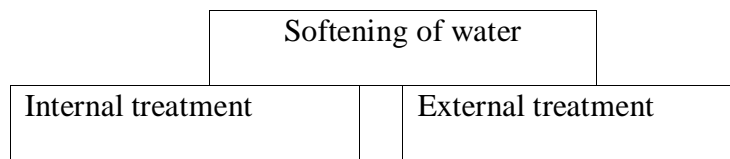
Internal treatment: (Or) Conditioning of water:
The softening of water carried out inside the boiler is called internal treatment of water. In this process the hardness causing salts are removed
1. By complexing the hardness causing soluble salt by adding appropriate reagents.
2. By precipitating the scale forming impurities in the form of sludge which can be removed by blow down operation.
3. By converting the scale forming salts into other compounds which stay in 'dissolved form' and do not cause any trouble to the boilers.
   The important internal conditioning methods are;
(a) Colloidal conditioning:
        The scale formation in low pressure boilers can be prevented by the addition of kerosene, tannin, agaragar etc. which will be get coated over the scale forming precipitates. These forms loose, non-sticky deposits (sludge) that can be removed by blow down. This type of conditioning is called colloidal conditioning.
(b) Phosphate conditioning:
        In this process, the permanent hardness causing salts in high pressure boilers will be removed by reacting with sodium phosphate. The complex formed is soft, non-adherent and easily removable.

$$3\ CaCl_2 + 2\ Na_3PO_4\ \text{------}\rightarrow Ca_3(PO_4)_2 + 6\ NaCl$$
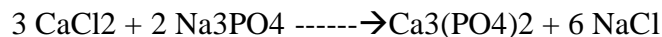
The three phosphates employed in this process are
Na3PO4 – tri-sodium phosphate (alkaline),
Na2HPO4 – disodium hydrogen phosphate (weakly alkaline) and
NaH2PO4 – sodium di-hydrogen phosphate (acidic).
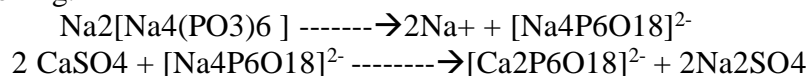
(c) Carbonate conditioning:

The hard and strong adherent scales formed due to $CaSO_4$ are avoided by the addition of sodium carbonate to boiler water and this is called carbonate condition.

$$CaSO_4 + Na_2CO_3 \xrightarrow{\hspace{1cm}} CaCO_3\downarrow + Na_2SO_4$$
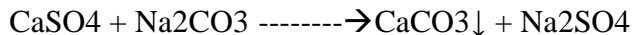
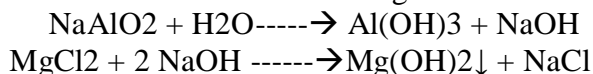The $CaSO_4$ is converted to $CaCO_3$, which is loose sludge and it can be removed by blow down.

(d) Calgon conditioning:

Sodium hexameta phosphate **$Na_2[Na_4(PO_3)_6$** or **$(NaPO_3)_6$** is called calgon. This forms solublecomplex compounds with $CaSO_4$.The treatment of boiler water with calgon is called calgon conditioning.

$$Na_2[Na_4(PO_3)_6] \xrightarrow{\hspace{1cm}} 2Na^+ + [Na_4P_6O_{18}]^{2-}$$
$$2\ CaSO_4 + [Na_4P_6O_{18}]^{2-} \xrightarrow{\hspace{1cm}} [Ca_2P_6O_{18}]^{2-} + 2Na_2SO_4$$

(e) Treatment with sodium aluminate ($NaAlO_2$):

Sodium aluminate is hydrolysed in boiler to give NaOH. The formed NaOH immediately precipitates by the reaction with some of the magnesium salts as $Mg(OH)_2$

$$NaAlO_2 + H_2O \xrightarrow{\hspace{1cm}} Al(OH)_3 + NaOH$$
$$MgCl_2 + 2\ NaOH \xrightarrow{\hspace{1cm}} Mg(OH)_2\downarrow + NaCl$$

External treatment:
The treatment given to water for the removal of hardness causing salts before it is taken into the boiler is called 'external treatment'.

External treatment
Zeolite process (Or) Permutit process:

Zeolite is hydrated sodium alumina silicate, which is capable of exchanging reversibly its sodium ions for hardness-producing ions in water. Chemical formula of sodium zeolite may be represented as;

$$Na_2O.Al_2O_3.x\ SiO_2.y\ H_2O \text{ where } x = 2 - 10 \text{ and } y = 2 - 6$$
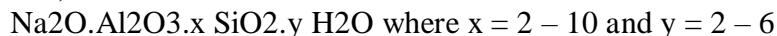
Zeolites are two types;

(i) *Natural zeolites*:

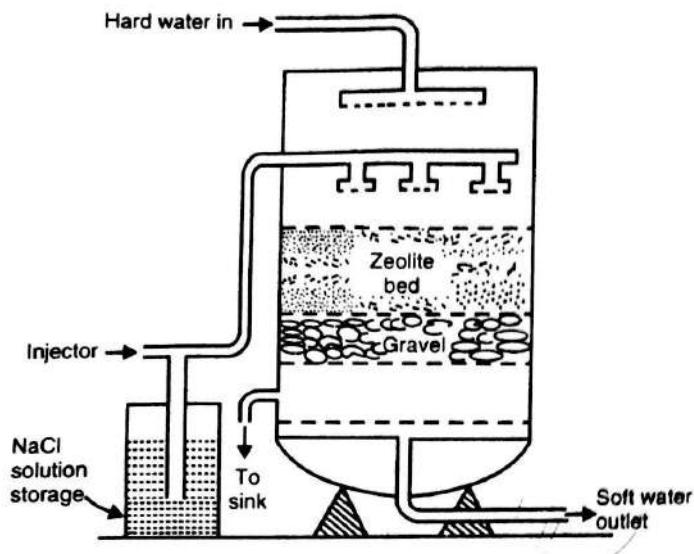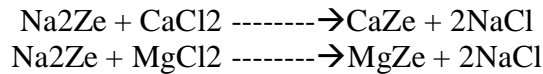These are non-porous. Eg: Natrolite $Na_2O.Al_2O_3.4\ SiO_2.2\ H_2O$

(ii) *Synthetic zeolites*:

These are porous and prepared by heating together china clay, feldspar and soda ash. Such zeolites possess higher exchange capacity per unit weight than natural zeolites.
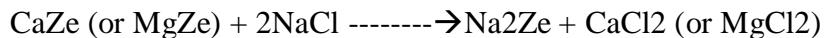
Process:

For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, kept in a cylinder. The hardness causing ions (Ca^{2+}, Mg^{2+}) are retained by the zeolite as CaZe and MgZe; while the outgoing water contains sodium salts. Reactions taking place during the softening process are;

$$Na_2Ze + Ca(HCO_3)_2 \xrightarrow{\hspace{1cm}} CaZe + 2NaHCO_3$$
$$Na_2Ze + Mg(HCO_3)_2 \xrightarrow{\hspace{1cm}} MgZe + 2NaHCO_3$$

$$Na_2Ze + CaCl_2 \longrightarrow CaZe + 2NaCl$$
$$Na_2Ze + MgCl_2 \longrightarrow MgZe + 2NaCl$$
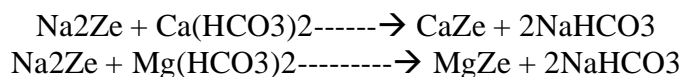
Regeneration:

After some time, the zeolite is completely converted into calcium and magnesium zeolites and it ceases to soften water, i.e. it gets exhausted. At this stage, the supply of water is stopped and the exhausted zeolite is reclaimed by treating the bed with brine solution (10% NaCl solution).

$$CaZe \text{ (or MgZe) } + 2NaCl \longrightarrow Na_2Ze + CaCl_2 \text{ (or MgCl}_2)$$

The washings (containing CaCl2 and MgCl2) are led to drain and the regenerated zeolite bed thus obtained is used again for softening purpose.

Limitations of Zeolite process:
(1) If the supplied water is turbid, the suspended matter must be removed, before the water is admitted to the zeolite bed; otherwise the turbidity will clog the pores of zeolite bed, thereby making it inactive.
(2) If water contains large quantities of coloured ions such as Mn2+ and Fe2+, they must be Removed first, because these ions produce manganese and iron zeolites, which cannot be easily regenerated.
(3) Mineral acids, if present in water, destroy the zeolite bed and, therefore, they must be neutralised with soda, before admitting the water to the zeolite softening plant.

Advantages of zeolite process:
(1) It removes the hardness almost completely, and water of about 10 ppm hardness is produced.
(2) The equipment used is compact, occupying a small space.
(3) No impurities are precipitated, so there is no danger of sludge formation in the treated water at a large scale.
(4) The process automatically adjusts itself for variation in hardness of incoming water.
(5) It requires less time for softening.

Disadvantages of zeolite process:
(1) The treated water contains more sodium salts than in lime-soda process.
(2) The method only replaces Ca2+ and Mg2+ ions by Na+ ions, but leaves all the acidic
Ions (HCO□3 and CO^{-2} 3) as such in the softened water. When such softened water
(containing NaHCO3 and Na2CO3) is used in boilers for steam generation, sodium
bicarbonate decomposes producing CO2, which causes corrosion; and sodium
carbonate undergoes hydrolysis to sodium hydroxide, which causes caustic
embrittlement.
(3) High turbidity water cannot be treated efficiently by this method, because fine
impurities get deposited on the zeolite bed, thereby creating problem for its working.

Ion exchange process (or) de-ionisation (or) de-mineralization process:
         Ion exchange resins are insoluble, cross-linked, long chain organic polymers with a micro
porous structure, and the 'functional groups' attached to the chains are responsible for the ion-
exchange properties. Resins containing acidic functional groups (-COOH, -SO3H) are capable of
exchanging their H+ ions with other cations, which comes in their contact. Resins containing
basic functional groups (amino groups) are capable of exchanging their anions with other anions,
which comes in their contact. Thus, ion-exchange resins may be classified as follows;

(i) Cation exchange resins (**RH**+):
These are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation,
become capable to exchange their hydrogen ions with the cations in their
water.
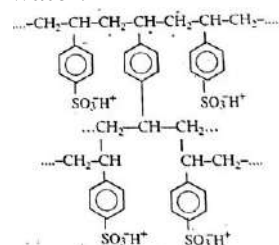

(ii) Anion exchange resins (**R'OH-**):
These are styrene-divinyl benzene or amineformaldehyde copolymers, which contain amino or
quarternary ammonium or quarternary phosphonium or tertiary sulphonium groups as an integral
part of resin matrix. These, after treatment with dil. NaOH
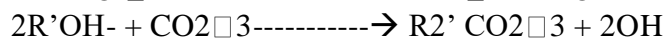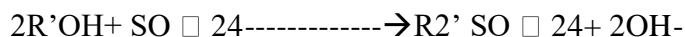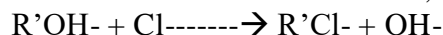solution, become capable to exchange their OHanions with anions in water.

$$\overset{\ulcorner}{\underset{CH_2NMe_2^+OH^-}{}} \qquad \overset{\ulcorner}{\underset{CH_2NMe_2^+OH^-}{}}$$
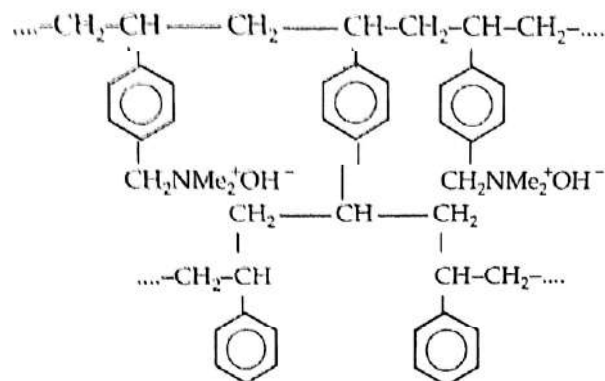
Process:

The hard water is passed first through cation exchange column, which removes the cations like Ca^{2+} and Mg^{2+} etc from it, and equivalent amount of H^+ ions are released from the column to water. Thus;

$$2RH^+ + Ca^{2+} \text{-------}\rightarrow R_2Ca^{2+} + 2H^+$$
$$2RH^+ + Mg^{2+} \text{------}\rightarrow R_2Mg^{2+} + 2H^+$$
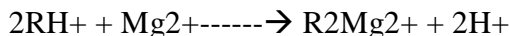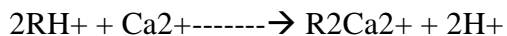
After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-}, Cl^-, CO_3^{2-} etc. present in the water and equivalent amount of OH ions are replaced from this column to water. Thus;

$$R'OH^- + Cl^- \text{-------}\rightarrow R'Cl^- + OH^-$$
$$2R'OH^+ SO_4^{2-} \text{-------------}\rightarrow R_2' SO_4^{2-} + 2OH^-$$
$$2R'OH^- + CO_3^{2-} \text{-----------}\rightarrow R_2' CO_3^{2-} + 2OH$$

   H^+ and OH^- ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecule.

$$H^+ + OH^- \text{-------}\rightarrow H_2O$$
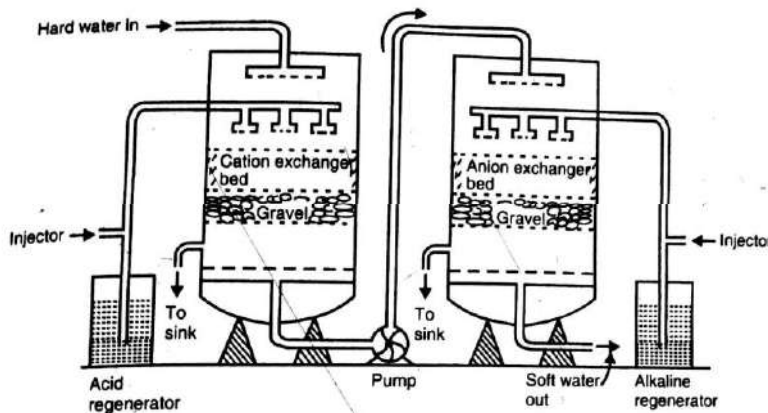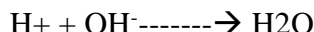
Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water is known as deionised or demineralised water.
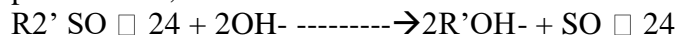
Regeneration:

When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, they are then said to be exhausted.

The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or dil. H_2SO_4. The regeneration can be represented as;

$$R_2Ca^{2+} + 2H^+ \text{--------}\rightarrow 2RH^+ + Ca^{2+}$$
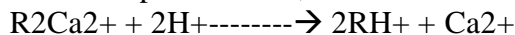
The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as;

$$R_2' SO_4^{2-} + 2OH^- \text{---------}\rightarrow 2R'OH^- + SO_4^{2-}$$

The regenerated ion exchange resins are then used again.

Advantages of ion-exchange process:

1. The process can be used to soften highly acidic or alkaline waters.

2. It produces water of very low hardness (about 2 ppm). So it is very good for treating
   Water used in high – pressure boilers.
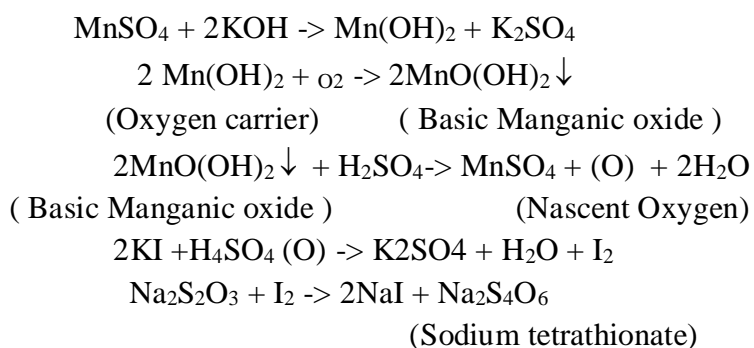
Disadvantages:
1. The equipment is costly and more expensive chemicals are needed.
2. If water contains turbidity, then the output of the process is reduced. The turbidity must
   Be below 10 ppm. If it is more, it has to be removed first by coagulation and filtration.

## ESTIMATION OF DISSOLVED OXYGEN:

The amount of oxygen present in the water in dissolved state is called dissolved oxygen

PRINCIPLE:

Dissolved oxygen can be determined by iodometric titrations. The dissolved oxygen present in water oxidizes KI liberating an equivalent amount of Iodine, which is titrated against standard hypo solution using starch as an indicator. An oxygen carrier like manganese hydroxide must be used to bring about the reaction between KI and dissolved oxygen because molecular oxygen in water is not capable of reacting with KI.

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$$

$$2\ Mn(OH)_2 + {}_{O2} \rightarrow 2MnO(OH)_2 \downarrow$$

(Oxygen carrier)   (Basic Manganic oxide)

$$2MnO(OH)_2 \downarrow\ + H_2SO_4 \rightarrow MnSO_4 + (O)\ + 2H_2O$$

(Basic Manganic oxide)   (Nascent Oxygen)

$$2KI + H_4SO_4\ (O) \rightarrow K2SO4 + H_2O + I_2$$

$$Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

(Sodium tetrathionate)

The nitrates present in water interfere with the estimation of dissolved oxygen of water, since these ions liberate iodine KI . Sodium azide is added to water which reacts with nitrate to decompose it as follows. $$2NaN_3 + H_2SO_4\ \rightarrow 2HN_3 + Na_2SO_4$$

(Sod. Azide)

$$HNO_2 + HN_3\ \rightarrow\ N2O \uparrow + N_2 + H_2O$$
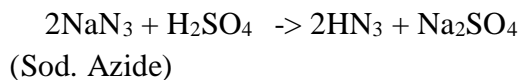
PROCEDURE:

STEP:I PREPARATION OF STANDARD POTASSIUM DICHROMATE:

- ➢ Weigh out accurately the given pure crystalline sample of potassium   dichromate and transfer into 100 ml standard (volumetric) flask provided with a funnel.
- ➢ Dissolve the dichromate in a small quantity of distilled water, and make up to the mark.
- ➢ The contents in the flask are shaken well for uniform concentration. Calculate the normality of potassium dichromate.

STEP:II STANDARDIZATION OF SODIUM THIOSULPHATE:

- Rinse the burette and fill it up with hypo solution without any air bubbles. Note the burette reading.
- Take about 20 ml of 10%KI solution in a clean conical flask and add 2 grams of sodium bicarbonate followed by 5 ml of concentrate HCl gently rotate the flask for mixing the liquids.
- Rinse the pipette with a little of potassium dichromate solution and then transfer 20 ml of the same to the conical flask. Shake it well, stopper it, and keep it in dark place for 5 minutes.
- Titrate the liberate iodine by running down hypo from the burette with constant stirring. When the solution attains a pale yellow colour add 2 ml of freshly prepared starch solution.
- The colour changes to blue. Continue the titration drop-wise till the colour changes from blue to light green indicating the end point. Repeat the titration for concurrent values.

STEP: III ESTIMATION OF DISSOLVED OXYGEN:

- Collect water sample in 300 ml capacity of BOD bottle and add 2 ml of manganese sulphate solution.
- To this add 2 ml of alkali-iodine–azide solution.
- Stopper the BOD bottle immediately.
- Appearance of brown precipitate indicates the presence of dissolved oxygen.
- Mixed well by inverting the bottle 2-3 times and allow the brown precipitate settle down.
- Add 2 ml of Conc H2SO4 to dissolve the precipitate
- Take 20 ml of the above solution in to a clean conical flask.
- Titrate the liberated iodine with standard hypo solution present in burette.
- Add 1 ml of starch solution when the color of the solution becomes blue color.
- Note the volume of the Hypo solution(v ml) repeat the titration till concurrent readings are obtained.
- Calculate the amount of dissolved oxygen present in water sample by using the formulae given below
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Dissolved oxygen in the given sample   = V x Conc. of HypoX8X1000/20 PPM

Desalination of brackish water:

The process of removing common salt (sodium chloride) from water, is known as *desalination.* The water containing dissolved salts with a peculiar salty (or brackish) taste, is called *brackish water.*Sea water, containing on an average about 3.5% salts, comes under this category. Brackish water is totally unfit for drinking purpose.
Commonly used methods for the desalination of brackish water are;
1. Electro dialysis (out of syllabus). 2. Reverse osmosis.

Reverse osmosis:
When two solutions of unequal concentrations are separated by a semipermeable membrane, flow of solvent takes place from dilute to concentrated sides, due to osmosis.
If, however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverses, i.e. solvent is forced to move from concentrated side to diluted side across the membrane. This is the principle of *reverse osmosis*. Thus, in reverse osmosis

method, pure solvent is separated from its contaminates, rather than removing contaminates from water. This membrane filtration is sometimes also called **superfiltration** or **hyper-filtration**.

Advantages:

1. This process removes, ionic as well as non-ionic, colloidal and high molecular weight organic matter.
2. It removes colloidal silica, which is not removed by demineralization process.
3. The life time of membrane is quite high, about 2 years.
4. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.
5. Due to low cost, simplicity and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water.
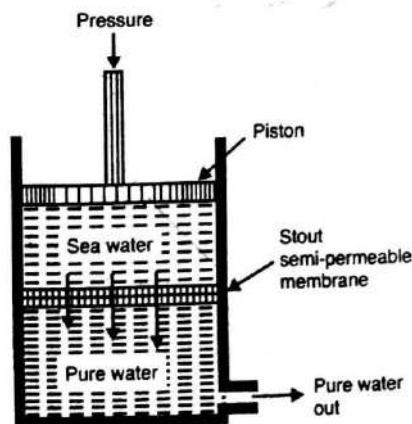
Electrodialysis.

Principle: Passage of an electric current through a solution of salt results in migration of cations towards the cathode & anions towards the anode. The use of semi permeable cation or anion exchange membrane in an electrolytic vessel permits the passage of only cations or anions respectively in the solution. An electrodialyzer consists of a chamber carrying a series of compartments fitted with closely spaced alternate cation (C) & anion (A) exchange semi permeable membranes between the electrodes. An electrodialyzer unit will have 200 to 1000 compartments. The feed water is taken in the dialyzer & the electrodes are connected to a source of an electric current.
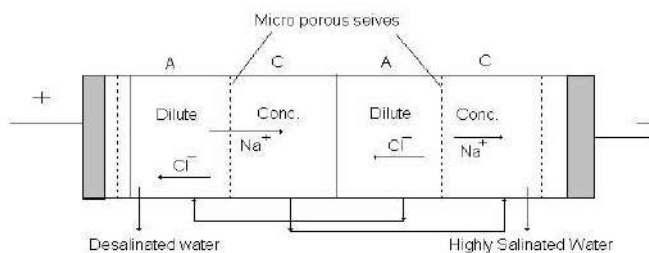
The anions pass through the anion permeable membrane towards the anode. However, these ions do not pass through the next membrane which is permeable only to cations. Similarly the cations moving in the other direction will pass through the cation exchange membrane but not the next. These anions & cations collect in the alternate chambers; the water in these is enriched with salt while that in the other compartments is desalinated. Micro porous sieves provided near the electrodes prevent the reentry of any deposit, which might have been formed on the electrodes, into the feed water. The enriched & desalinated waters are withdrawn separately. The former is rejected & the desalinated water is recycled to further reduce the salt content.