Quantum Mechanical Model of Atom

In the mid of 1920's three physicists; de Broglie, Heisenberg and Schrodinger developed a new approach to study the atomic structure which became known as Quantum mechanical model of atom. It is applicable for the motion of all microscopic particle (e.g. electrons). Today, it is the generally accepted model of the atom

ⓐ Contribution of de Broglie.

According to de Broglie particles like electrons possess wave characteristics. particle and wave properties. He deduced the following expression to relate

$$\lambda = \frac{h}{mv}.$$

where h = plank's constant λ, m, v are wavelength, mass & velocity of particle respectively

ⓑ Contribution of Heisenberg

According to Heisenberg it is not possible to determine accurately the position and momentum of a microscopic particle like electron simultaneously. Mathematically it can be expressed as

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

where Δx = uncertainity in position

Δp = uncertainity in momentum

ⓒ Contribution of Schrodinger

According to him the electron bound to the nucleus behaves similar to a standing wave. The mathematical formalism that Schrodinger developed to describe the electron as a wave goes given below which is familiarly known as Schrodinger wave equation.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

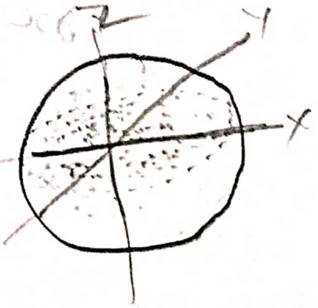
x, y, z are the space coordinates

ψ = wave function of e^-, m = mass of electron

E = Total energy of e^- V = potential energy of electron

Important features of quantum mechanical model of Atom

→ The concept of wave function (ψ) is the central idea to the quantum mechanical model of atom

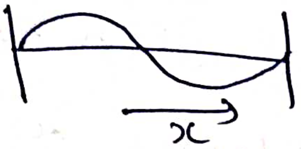


A wave function, in quantum mechanics, refers to a mathematical description of a particle's wave characteristics (momentum, time, position & spin).

By using wave function, the probability of finding an electron within the matter-wave can be explained.

Schrodinger wave Equation

The Schrodinger equation is the fundamental equation of quantum mechanics. The solutions to the Schrodinger ~~I~~ equation are called wave functions. wave function gives a complete description of any system. Solutions to time independ Schrodinger equation are called stationary state wave function because they are independent of time.



→ consider a small particle (like electron) of mass 'm'. The fundamental equation describing the behaviour of its wave motion along the 'x' direction with wavelength 'λ' is given by

$$\boxed{\psi = A\sin\frac{2\pi}{\lambda}x \longrightarrow ①}$$

where ψ = wave function and A = a constant

→ Let us do the double differentiation of equation ① with respect to 'x'

$$\frac{\partial\psi}{\partial x} = \frac{\partial}{\partial x}\left(A\sin\frac{2\pi}{\lambda}x\right)$$

$$\frac{\partial x}{\partial x} = A\frac{2\pi}{\lambda}\left(\cos\frac{2\pi}{\lambda}x\right)$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\left\{A\frac{2\pi}{\lambda}\left(\cos\frac{2\pi}{\lambda}\right)x\right\}$$

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2}A\sin\frac{2\pi}{\lambda}x$$

By using equation ① we can simplify the above one

$$\boxed{\frac{\partial^2\psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2}\psi}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 \psi}{\lambda^2} = 0 \longrightarrow ②$$

⇒ The K.E of ~~of~~ moving particle of mass 'm' and a velocity 'v' is given by

$$K.E = \frac{1}{2} m v^2 = \frac{m^2 v^2}{2m} \longrightarrow ③$$

⇒ we know the de Broglie relation;

$$\lambda = \frac{h}{mv}$$

$$mv = \frac{h}{\lambda}$$

on squaring both sides

$$m^2 v^2 = \frac{h^2}{\lambda^2} \longrightarrow ④$$

From equations ③ & ④, we can write (by substitute 4 in 3)

$$KE = \frac{h^2}{2m\lambda^2} \longrightarrow ⑤$$

If the particle moves in a field whose potential energy is V, then

$$K.E = E - V \longrightarrow ⑥$$

By substituting the, K.E ~~[illegible]~~ in ~~equation~~ equation ⑥ ~~in~~ equation ⑧

From equation ⑤ & ⑥, we can write

$$E - V = \frac{h^2}{2m\lambda^2}$$

$$\frac{1}{\lambda^2} = \frac{2m(E-V)}{h^2} \longrightarrow ⑦$$

Now from equation ② & ⑦ we can write.

$$\boxed{\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \longrightarrow ⑧}$$

This is the Schrodinger equation for one dimension.

In three dimention it becomes

$$\boxed{\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0}$$

Erwin Schrodinger developed quantum mechanics (or wave mechanics) on the basis of de-Broglies principle and Heisenberg's principle. This so called quantum-mechanical model explains the behaviour an electron in an atom in terms of Schrodinger wave equation.

x, y z are space coordinates
m = mass of the e^- h = planck's constant
E = Total energy of e^- ψ is the amplitude of wave called wave function

$\partial^2\psi/\partial x^2$ represents the second derivative of ψ w.r.t to x and so on.

Schrodinger's wave equation is a second order differential equation

Significance of ψ & ψ²

ψ is a wave function and refers to the amplitude of electron wave and itself have no physical significance.

~~However its square i.e, ψ² is measures the probability of~~

The wave function ψ may be +ve, −ve or imaginary.
In general the probability of finding e^- can be zero or +ve, but can never be −ve

ψ² is known as probability density i.e, measures the probability of finding electron of giving energy (from place to place) in a giving region around the nucleus.

i) For a one-Dimensional problem, this domain is of space between x and x+dx
ii) For a two- " " , " " is an element of area
iii) For a three-Dimesional problem, this domain region is an element of volume.

Case I: If ψ^2 is zero, then the probability of finding an electron at that point is negligable

Case II: If the wave function is imaginary, this quantity represents the probability of ψ^2, as a function of x, y & z coordinates of the system and it varies from one space region to another.

Thus the probability of finding the electrons in different region is different. This shows the agreement with uncertainity principle.

Significance of Schrodinger wave equation :-

This quantum mechanical model of atom is updates to Bohr Mod

∴ Electrons are not in circular orbits around nucleus and ~~e's~~ actually are in 3-D region around the nucleus.

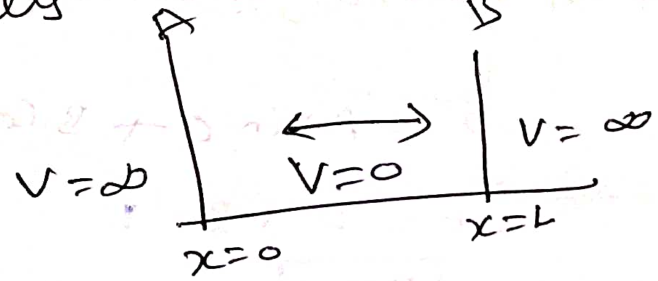
This quantum mechanical model decribes location of e's in atoms by decribing principle energy level, energy sublevel, orbital (in each sublevel) and spin

particle in one Dimensional Box

Consider a particle with mass 'm' that is free to move back and forth along one-demension between values $x=0$ and $x=L$.

We will assume that the potential energy V of the particle is Zero within the region $x=0$ to $x=L$, and outside this region the potential energy V is taken to be infinity.

~~Thus the particle is trapped~~ in a one-~~dimensional~~ box with impenetrable walls.



⇒ The Schrodinger equation in one-dimension is given by

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad —①$$

Inside the box

Inside the box $V=0$, and substitute the value of V in equation ①, we get..

$$\frac{\partial^2\psi}{\partial x^2} \cancel{=} \frac{8\pi^2 m}{h^2}(E-0)\psi = 0$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}E\psi = 0$$

$$\left(\text{Take } K^2 = \frac{8\pi^2 mE}{h^2}\right)$$

$$\frac{\partial^2\psi}{\partial x^2} + K^2\psi = 0 \quad —②$$

where K^2 is a constant.

for a particle inside a potential well in x direc

The general solution of equation ② is given by,

$$\psi(x) = A \sin Kx + B \cos Kx \quad ③$$

where A & B are constants.

$(D^2 + k^2)\psi = 0$ or

$f(D)\psi = 0$ →

A Eq $f(m) = 0$

$m^2 + k^2 = 0$

$m^2 = -k^2$

$m = \pm ik$

$C.F = A \cos kx + B \sin kx.$

For calculation of A, B, let us apply the boundary conditions

Condition - ① $\psi(x) = 0$ at $x = 0$

boundary condition - ② $\psi(x) = 0$ at $x = L$

By applying first boundary condition in equation ③, we get

$$0 = A \sin 0 + B \cos 0$$

$$0 = 0 + B$$

$$\boxed{B = 0}$$

By applying 2nd boundary condition and value B in equation ③; we get

$$0 = A \sin KL + 0$$

$$A \sin KL = 0 \rightarrow \left(\text{it means } \begin{matrix} A = 0 \\ \sin KL = 0 \end{matrix}\right)$$

→ But at the same time A, B can't be zero, So $A \neq 0$

$$\therefore \sin KL = 0$$

(general solution)

$$KL = n\pi \quad \text{with } n = 1, 2 \ldots$$

where 'n' is called as quantum number, which is a +ve Integer

$$K = \frac{n\pi}{L}$$

on squaring both sides

$$K^2 = \frac{n^2\pi^2}{L^2} \quad ④$$

on comparing Eq ③ & ④

$$\frac{n^2\pi^2}{L^2} = \frac{8\pi^2 mE}{h^2}$$

$$\boxed{E = \frac{n^2 h^2}{8mL^2}}$$

we can replace E with E_n, becaus there are many energy levels based on the value of quantum number n.

$$\boxed{E_n = \frac{n^2 h^2}{8mL^2}}$$

~~So the energy of the particle is said to be quantized.~~

Energy

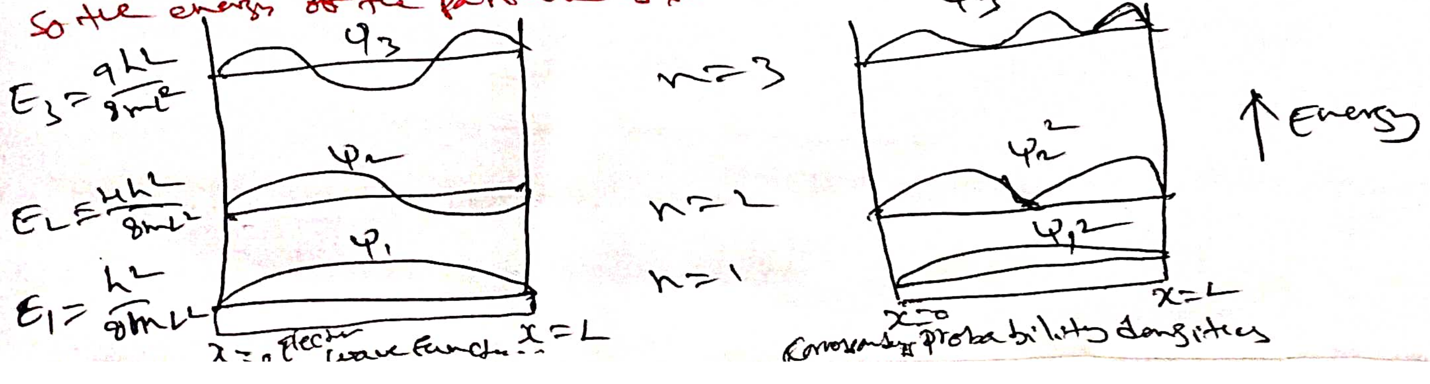
$$n = 1 \Rightarrow E_1 = \frac{h^2}{8mL^2}$$

$$n = 2 \Rightarrow E_2 = \frac{4h^2}{8mL^2}$$

$$n = 3 \Rightarrow E_3 = \frac{9h^2}{8mL^2}$$

From the above equations it is clear that particles in the box ~~wave functions~~ are having discrete energy values, these values are called Eigen values of energy E_1, E_2, E_3 etc.

So the energy of the particle is said to be quantized.



Electron wave functions

Corresponding probability densities

Ground, first, second excited states of one e^- in potential we

ecular Orbital Theory - bonding in homo & hetero nuclear diatomic molecules

Hund and Mulliken developed this theory to explain ~~the formation~~ i) chemical bond ii) relative bond strength iii) magnetic behaviour of molecules.

Postulates of MO Theory :

1) The atomic orbitals (AOs) overlap to form a new orbitals known as molecular orbitals (MOs). As a result, the AOs lose their individual identity..

2) The no. of MOs formed is equal to the no. of AOs ~~in the~~ involved in their formation.

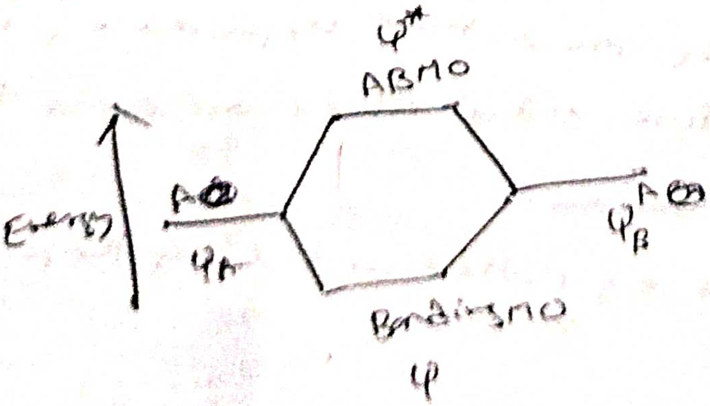
3) Only those AOs are combined to form MOs which have same/comparable energy and orientations.

For example, 1s can combine with 1s not with 2s as they have energy gap.

Further, if x is the molecular axis, i.e, p_x oriented in line of s-orbital but p_y, p_z are perpendicular then the possible combination may takes place between s-p_x, but not between s-p_y, s-p_z atomic orbitals.

4) Two types of MOs are formed, they are bonding molecular orbital (BMO), Antibonding molecular orbital (ABMO).

5) According to MOT the formation of BMO & ABMO can be explain based on Linear Combination of atomic orbitals (LCAO) method.



6) BMO has lower energy than the corresponding AOs and ABMO has higher energy than the corresponding AOs.

7) Axial overlap of A.orbitals yields σ bond formation and side-by-side overlap of A.orbitals yields π bond formation.

8) The BMOs are represented by σ, π, δ, φ etc. and ABMO are represented by σ^*, π^*, δ^* & φ^* etc..

9) It is important to note that the energies of MO's is less than the sum of energies of two AO's, consequently the resulting molecules is more stable.

10) Similar to atomic orbitals, the filling of electrons in the molecular orbitals also follows the Aufbau principle, Hund's rule and pauli's exclusion principle.

11) <u>Bond order and stability</u>

It is the no of covalent bonds btw two atoms in a molecule and is equal to half the difference btw the no. of e's in BMOs and the no. of e's in ABMOs.

Mathematically it can be written as

$$\text{Bond order} = \frac{\text{No. of e's in BMOs} - \text{No. of e's in ABMO}}{2} = \frac{N_b - N_a}{2}$$

The stability of a molecule is determined by its bond order.

(i) Bond order is inversely proportional to bond length.

ii) Bond dissociation energy is directly proportional to bond order.

12) <u>Magnetic Chatter</u> :

If a molecule contains one or more unpaired e's in its MOs it is paramagnetic in nature and if all e's are paired then it exhibits diamagnetic behaviour.

(Greater the no. of unpaired e's in the MOs higher is the paramagnetic character).

Order of MO's energy levels : (The order of energy levels of the MOs can be determined experimentally from spectroscopic studies):

⇒ If no. of e^-s in the molecule are more than 14, then the order of MO's energy levels are

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \underline{\pi 2p_y = \pi 2p_z} < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2p_x$$

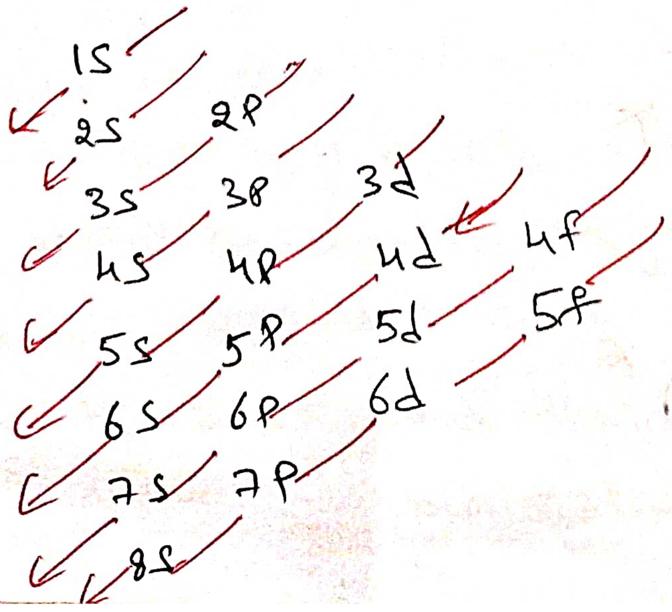
⇒ If no. of e^-s in the molecular are ~~both~~ 14 or less than 14, then the order of MOs energy levels are

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \underline{\pi 2p_y = \pi 2p_z < \sigma 2p_x} < \pi^* 2p_y = \pi^* 2p$$
$$< \sigma^* 2p_x$$

Aufbau principle : Electrons fill the lowest energy orbitals first, before they occupy orbitals with higher energy.

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s$$

$\xrightarrow{\hspace{3cm}}$ Increasing energy.

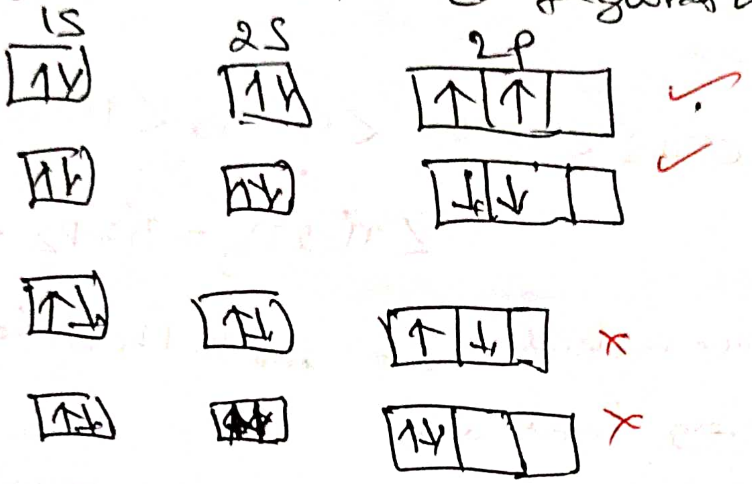


Hunds Rule

Hunds Rule of maximum multiplicity.

⇒ Pairing of electrons in the degenarate M.O does not o
until each of them has one electron each

Ex: Carbon electron configuration $1s^2 2s^2 2p^2$



Pauli exclusion principle

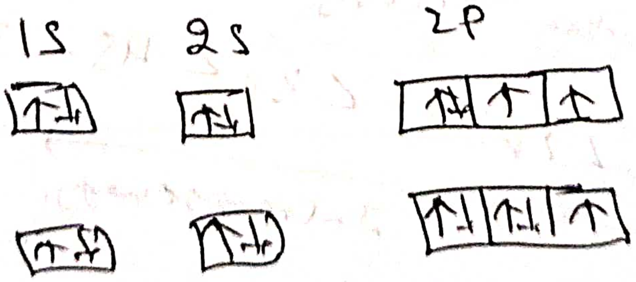
maximum number of electrons in a M.O is two and they must have opposite spins.

(or)

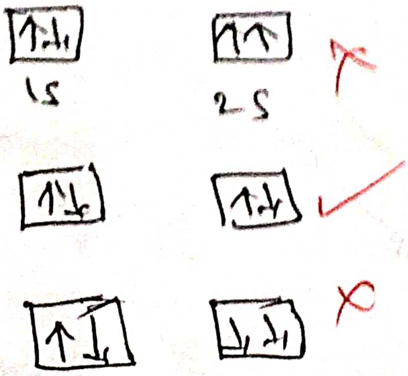
No two electrons in the same orbital can have all the quantu numbers identical.

Ex. Oxygen

Flourine



Ex.



Linear Combination of Atomic orbitals (LCAO)

To explain the LCAO approach, let us consider two atom A & B having the wave function ψ_A & ψ_B.

According to the LCAO approach, MOs are formed by the linear combination of atomic orbitals. The combination can take place by addition (constructive interaction) or substraction (destructive interaction) of the wave functions of atomic orbitals. These two types of combinations gives two categories molecular orbitals.

→ Bonding Molecular orbitals (BMOs).

These are obtained by the addition of wave functions of atoms and may be represented as

$$\psi(MO) = \psi_A + \psi_B$$

The BMO has energy lower than the energy of the atomic orbitals from which it is formed and this difference of energy is termed as the stabilisation energy

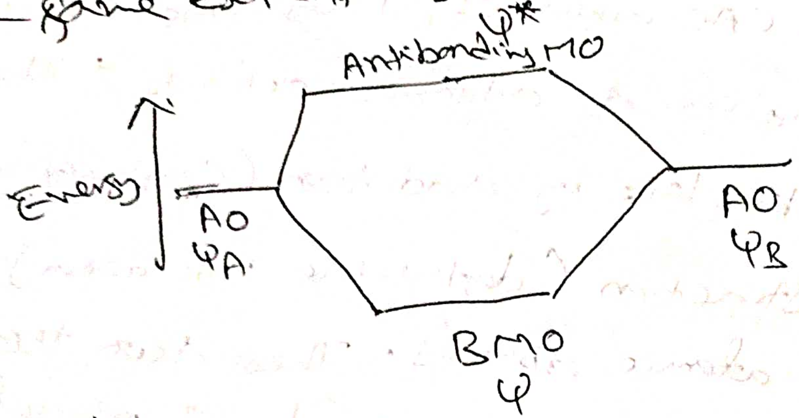
→ Anti bonding molecular orbitals (ABMOs)

These are obtained by the substraction of wave functions of atoms and may be represented as

$$\psi^*(MO) = \psi_A - \psi_B$$

An asterisk (*) represents the ABMO. The ABMO has energy higher than that of the energy of the AOs from which it is formed and ~~the~~ the difference of energy is termed as the destabilization energy.

It is important to note that the BMO is stabil
the same extent as the ABMO is destabilized.



probability density (ψ²)

The probability in BMO and ABMO is given by the square of wave function (ψ^2).

For BMO

$$\psi = \psi_A + \psi_B$$

$$\psi^2 = (\psi_A + \psi_B)^2$$

$$\psi^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

Thus, ψ^2 is greater than $\psi_A^2 + \psi_B^2$ (sum of the probability densities of individual atoms) by an amount equal to $2\psi_A + \psi_B$. Therefore, the probability of finding electrons in BMO is greater than in either of the A-O ψ_A^2 and ψ_B^2.

For ABMO:

$$\psi^* = \psi_A - \psi_B$$

$$\psi^{*2} = (\psi_A - \psi_B)^2$$

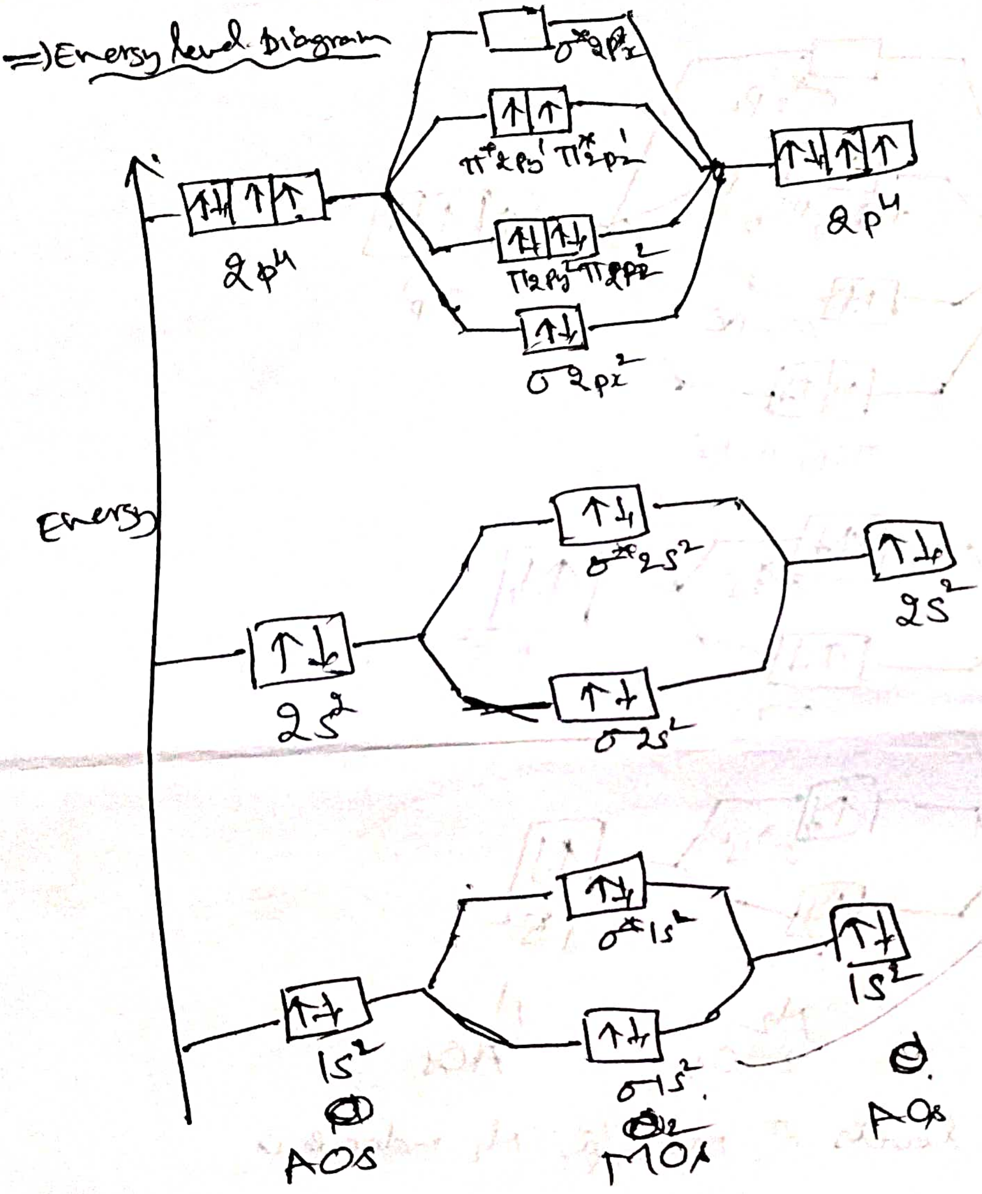
$$\psi^{*2} = \psi_2^A + \psi_B^2 - 2\psi_A\psi_B$$

Thus ψ^{*2} is less than $\psi_A^2 + \psi_B^2$ by an amount equal to $2\psi_A + \psi_B$. Therefore, the probability of finding the electrons in ABMO is less than in either of the atomic orbitals (ψ_A^2 or ψ_B^2).

nergy level diagram of O_2

→ An oxygen atom has 8 e^- with electronic configuration $1s^2 2s^2 2p^4$. Thus O_2 molecule contains 16 electrons.

⇒ Energy level Diagram



→ The order of energy levels of MO's for O_2 molecule is

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2 < \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^1 = \pi^* 2p_z^1$$

→ Bondorder $= \frac{N_b - N_a}{2} = \frac{10-6}{2} = 2$

Thus, there are two bonds (double bond) in the O_2 molecule.

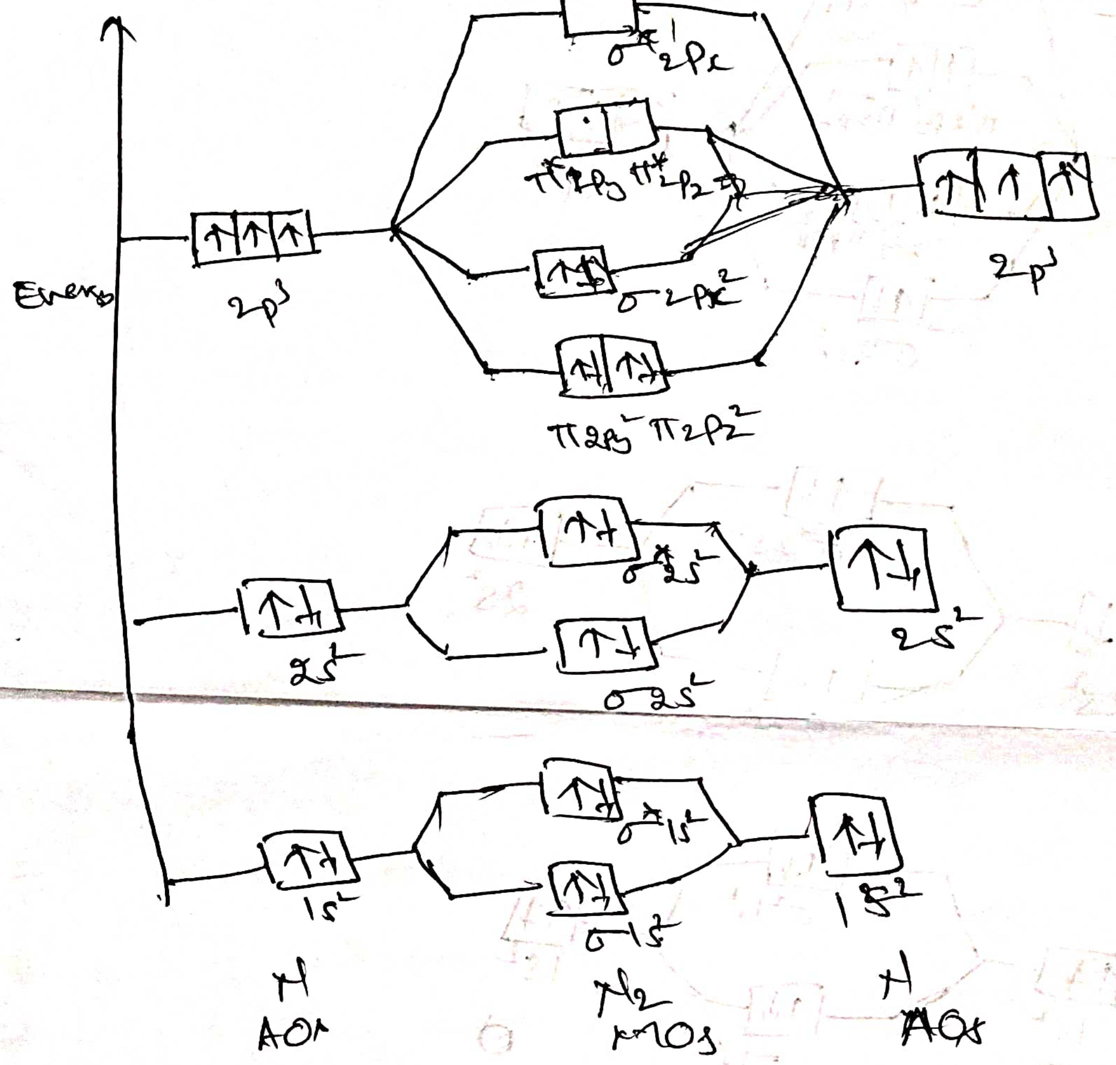
→ It has two unpaired electrons in $\pi^* 2p_y$ and $\pi^* 2p_z$ orbitals, which makes the molecule paramagnetic.

Energy level Diagram for N_2

→ ~~A~~ one nitrogen atom has 7 e⁻'s with electronic configuration $1s^2 2s$

and thus N_2 molecule has 14 electrons

Energy level Diagram



→ The order of energy levels of MOs for N_2 molecule is

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_y^2 = \pi 2p_z^2 < \sigma 2p_x^2$.

→ Bond order $= \frac{N_b - N_a}{2} = \frac{10-4}{2} = 3$

. Thus, there are three bonds (trible bonds) in N_2 molecule.

→ since all the electrons in BMOs & ABMOs are paired, N_2 molecule is diamagnetic in nature.

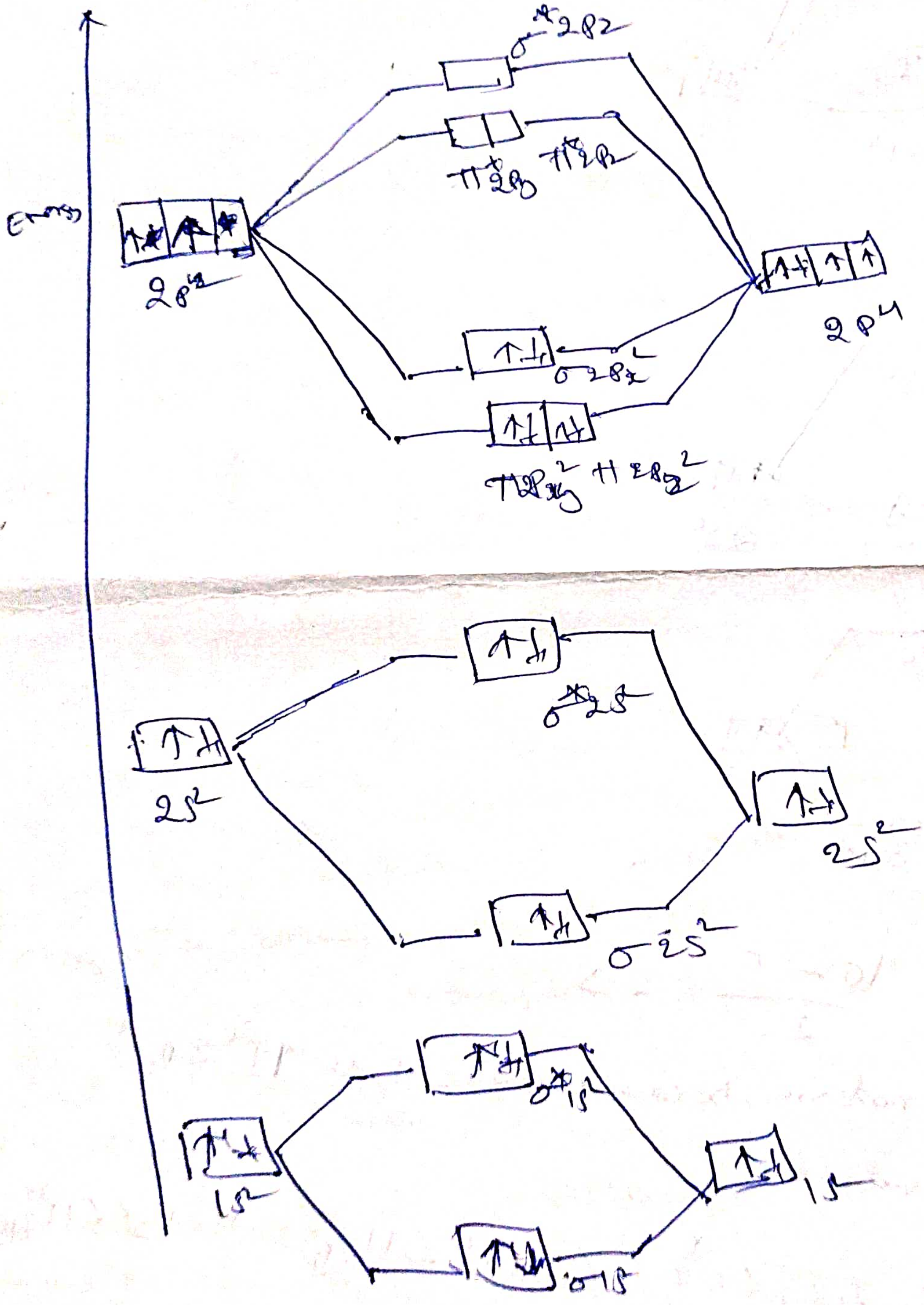
nergy level Diagram for CO

The electronic configuration of C atom is $1s^2 2s^2 2p^2$

" " " O atom is $1s^2 2s^2 2p^4$.

∴ thus CO molecule has totally 14 electrons.

→ Energy level Diagram

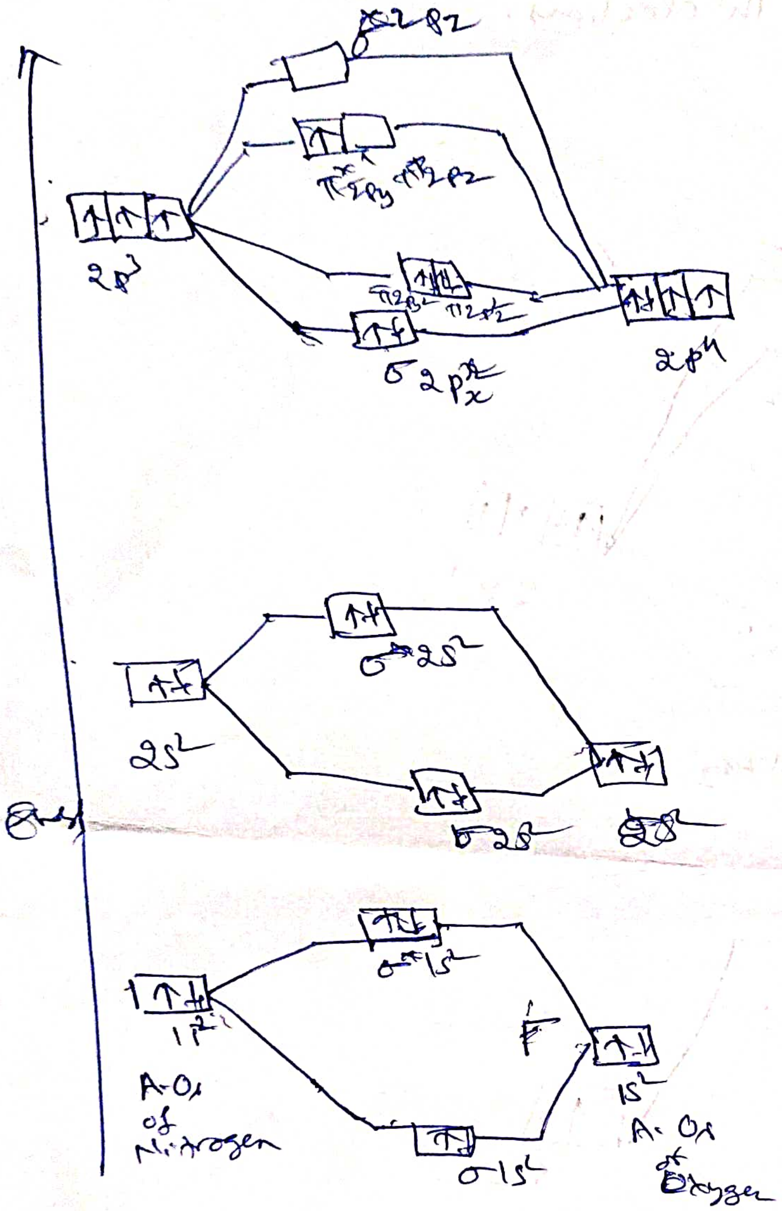


Bond order = $\frac{10-4}{2}$ = 3

Diagmagnetic

Energy level diagram for NO

* The E.C of N is $1s^2 2s^2 2p^3$
O is $1s^2 2s^2 2p^4$.



$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

paramagnetic in nature, because unpaired e^- in $\pi^* 2p_y^1$

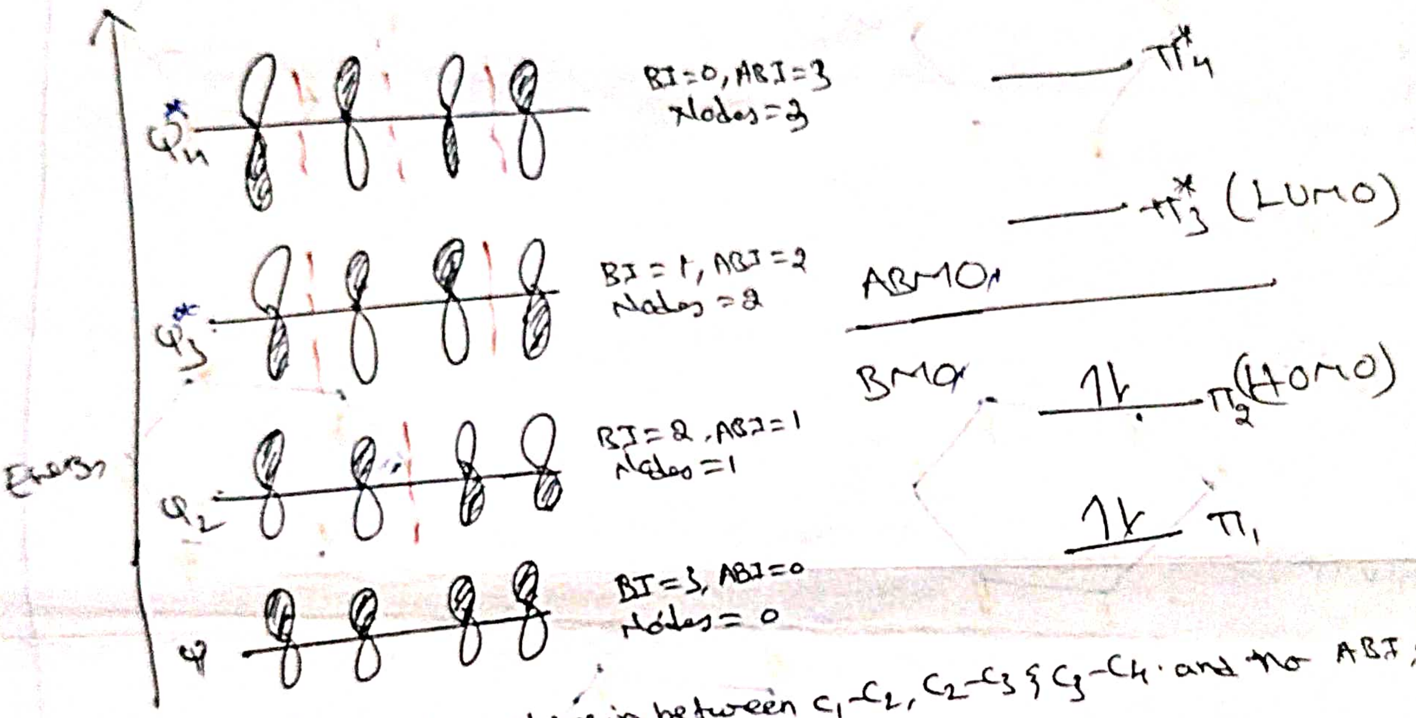
order of Energy level

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2 < \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^1$

i- molecular Orbitals of Butadiene

$H_2C=\underset{H}{C}-\underset{H}{C}=CH_2$

1,3 - Butadiene consists of ~~two~~ conjugated double bonds. It has four sp^2 hybridized carbon atoms. Each carbon atoms contributes a 'p' atomic orbital which is not involved in hybridization. These unhybridized orbitals are combined to form four molecular orbitals in four different ways. They are ψ_1, ψ_2, ψ_3 and ψ_4 ($\pi_1, \pi_2, \pi_3^*, \pi_4^*$)



→ ψ_1 has 3 bonding interactions in between C_1-C_2, C_2-C_3 & C_3-C_4. and no ABI, as well as not nodes.

→ ψ_2 has 2 bonding interactions in between C_1-C_2 & C_3-C_4 and and ABI in between C_2-C_3, No. of nodes is also one. It is ~~known as~~ the HOMO.

→ ψ_3 has only one bonding interactions in between C_2-C_3 and two ABI in btw C_1-C_2 & C_3-C_4. and the no. of nodes here is 2. It is the LUMO.

→ ψ_4 has three ABI in btw C_1-C_2, C_2-C_3 & C_3-C_4. and no of nodes here is 3.

⇒ With this information it is clear ~~that~~ ~~that~~ of the four orbitals, the MOs ψ_1 & ψ_2 are BMOs, the MOs ψ_3 & ψ_4 are A.B.M.Os.

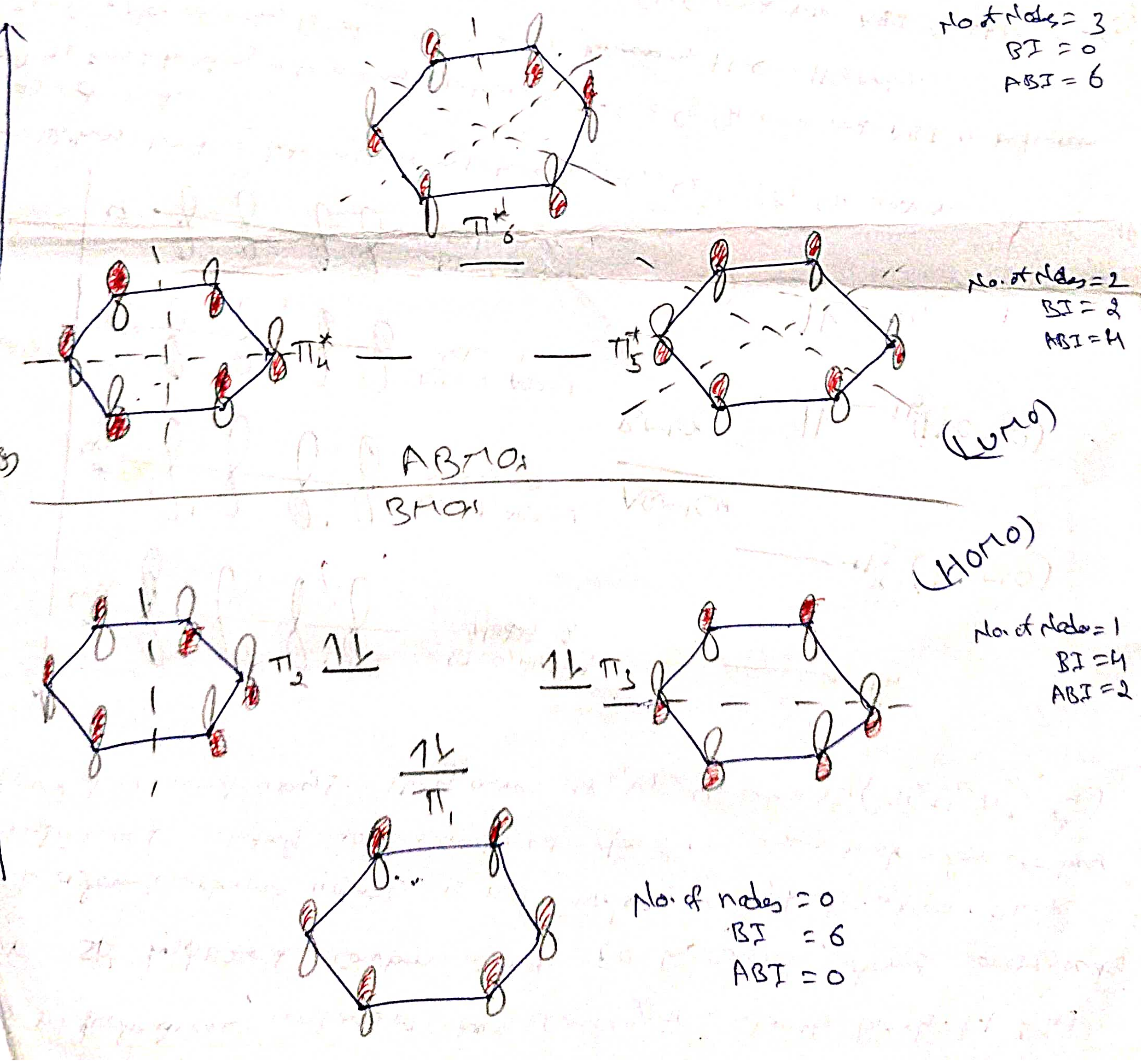
→ The energy in M.Os increases with rise in the no of nodes.

π- molecular orbitals of Benzene

→ The structure of benzene consists of 3 conjugated double bonds. It has 6 sp^2 hybridized carbon atoms. → Each carbon atom contains one unhybridized 'p' atomic orbital which contains one electron. → These six atomic orbitals overlaps partially to give six π- molecular orbitals. → The six MOs are designated as $\pi_1, \pi_2, \pi_3, \pi_4^*, \pi_5^*, \pi_6^*$ → Of these six MOs π_1, π_2 & π_3 are B.MOs, whereas $\pi_4^*, \pi_5^*, \pi_6^*$ are ABMOs

* The order of energy levels are $\pi_1 < \pi_2 = \pi_3 < \pi_4^* = \pi_5^* < \pi_6$

→ π_2 & π_3 are the HOMOs & π_4^* & π_5^* are the LUMOs



MODERN ENGINEERING MATERIALS

SEMICONDUCTORS

Semiconductors are materials which have a conductivity between conductors and insulators. These materials possess properties of both conductors and insulators. Semiconductors can be pure elements such as silicon and Germanium or compounds such as Germanium arsenide and Silicon arsenide.

IMPORTANCE OF SEMICONDUCTORS

- They are highly portable due to their small size
- They require less input power
- Semiconductor devices are shockproof
- They have a longer lifespan
- They are noise-free while operating

BAND STRUCTURE IN SEMICONDUCTORS

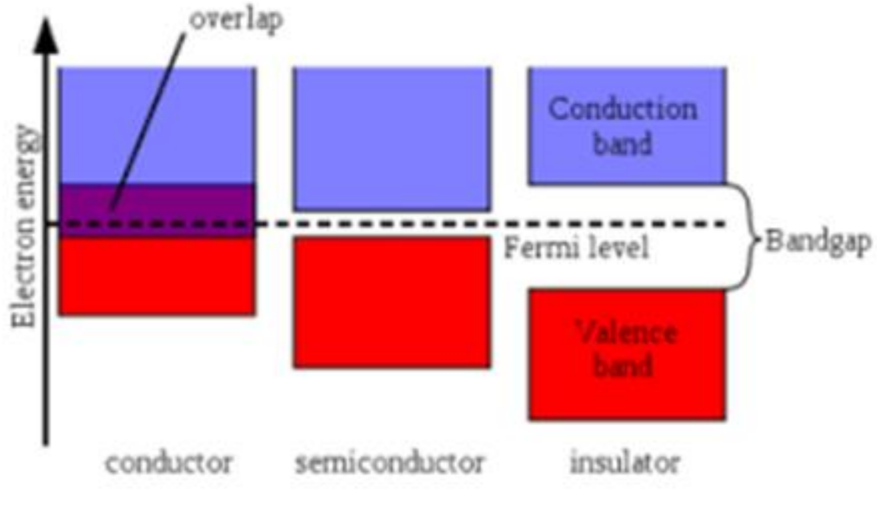
In an isolated atom, the electrons in each orbit possess definite energy. In solids, the atoms are very close each other. Due to this, the electrons in the outermost orbit of one atom experience an attractive force from the nucleus of neighboring atom. So, the electron does not possess same amount of energy, instead it exhibits different energy levels. **The set of these different energy levels of the electrons** (sharp and tightly packed energy levels) **are known as ENERGY BANDS.** The important energy bands are valency band, conduction band and forbidden band.

The electrons in the outermost orbit of an atom are called valence electron. **The energy band which is formed by the set of energy levels of the valence electrons is called 'VALENCE BAND**'. It is the highest occupied energy band.

In some materials like metals, the valence electrons are loosely bound to the nucleus. At ordinary temperatures also, some of these valance electrons come out of the orbits and become free electrons. These free electrons are called conduction electrons as these are responsible for conduction of current in a conductor. **The energy band which is formed by the set of energy levels of the free electrons is called '<u>CONDUCTION BAND</u>'**. It is the lowest, unoccupied energy level and is generally empty, that includes the energy levels of positive (holes) or negative (free electrons) charge carriers. It has conducting electrons resulting in the flow of current. The conduction band in semiconductors accepts the electrons from the valence band.

The **energy gap which is present between valence band and conduction band is called '<u>FORBIDDEN BAND' or 'FORBIDDEN GAP</u>'**. In the forbidden gap region, there is no electrons are permitted to stay. So, it is an energy band that exists with no energy. Usually, electrons are passed through this path to approach the conduction band.

The highest energy level that an electron can occupy at the absolute zero temperature is known as the **'<u>Fermi Level</u>'**. The Fermi level lies between the valence band and conduction band because at absolute zero temperature, the electrons are all in the lowest energy state.



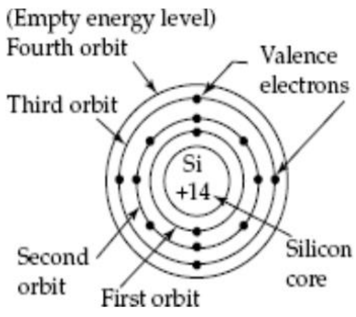
<u>Fig:</u> Energy Band Diagram for Conductors, Semiconductors and Insulators.

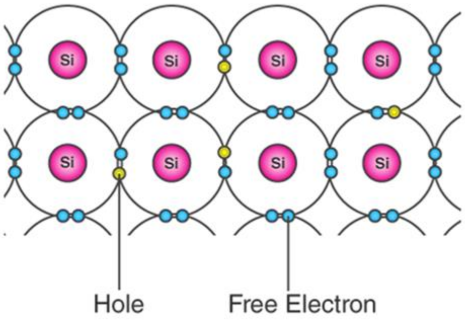
In order to transfer an electron from valence band to the conduction band, some amount of energy is to be supplied to the atom, which is equal to the forbidden energy gap in the form of light or heat. The energy associated with the forbidden band is measured in electron volt (eV).

Materials can be classified as conductors, semiconductors and insulators depending on the size of forbidden gap. The energy gap is large for insulators and small for semiconductors. In case of conductors, valence band overlaps the conduction band and there is no energy gap. **Insulators**, are the substances which do not allow the flow of electric current through them (**Ex:** Plastic, Diamond, Rubber etc.). **Conductors** are the substances which easily allow the flow of electric current through them (**Ex:** Copper, Silver, Gold, Aluminum etc.). **Semiconductors** are the substances whose electrical conductivity lies in between conductors and insulators (**Ex:** Silicon, Germanium, Gallium arsenide, Silicon arsenide etc.).

HOLES AND ELECTRONS are the types of charge carriers accountable for the flow of current in semiconductors. **Holes are the positively charged electric charge carrier, whereas electrons are the negatively charged particles.** Both electrons and holes are equal in magnitude but opposite in polarity. **In a semiconductor, the mobility of electrons is higher than that of the holes.** It is mainly because of their different band structures and scattering mechanisms.

The **bond model** of electrons in silicon of valency 4 is shown below. Here, when one of the free electrons (**blue dots**) leaves the lattice position, it creates a hole (**yellow dots**). This hole thus created takes the opposite charge of the electron and can be imagined as positive charge carriers moving in the lattice.

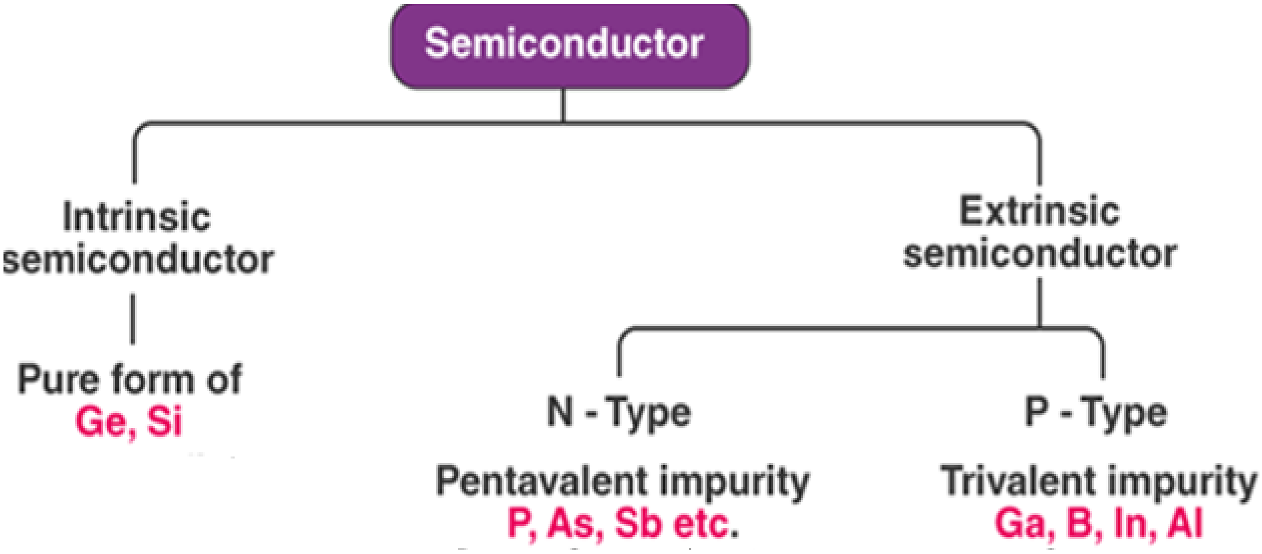


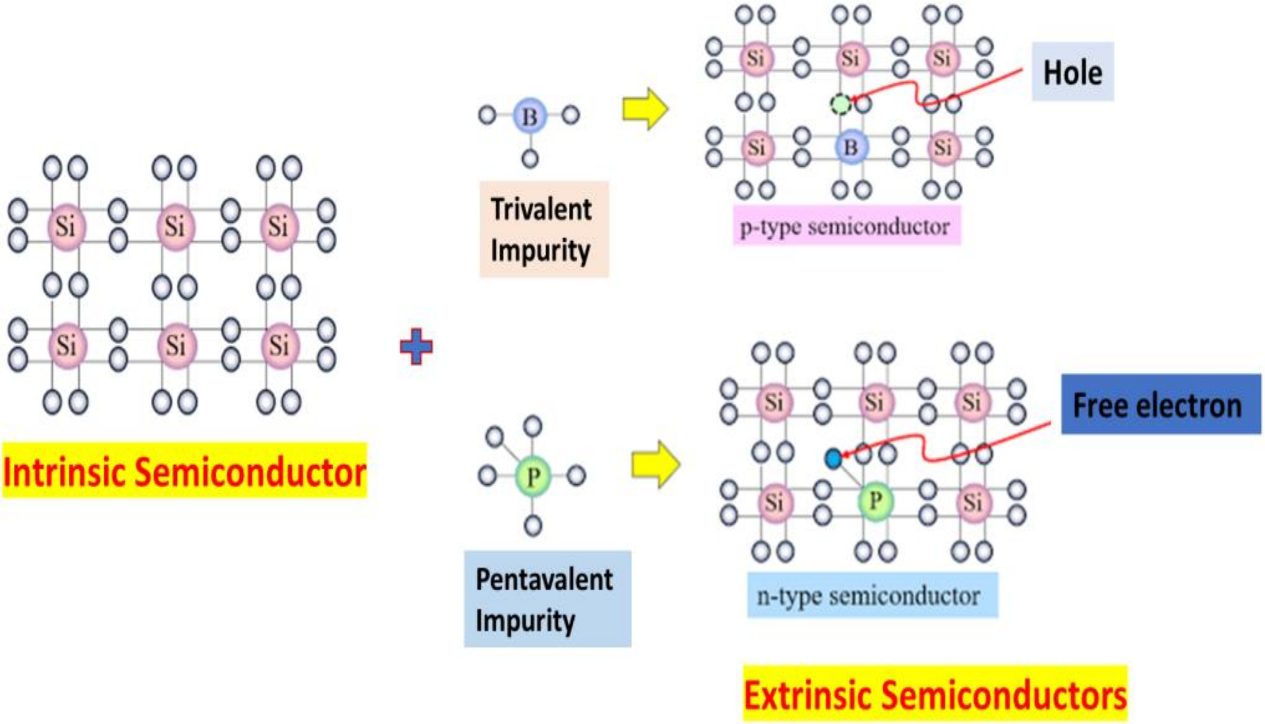


SOME IMPORTANT PROPERTIES OF SEMICONDUCTORS

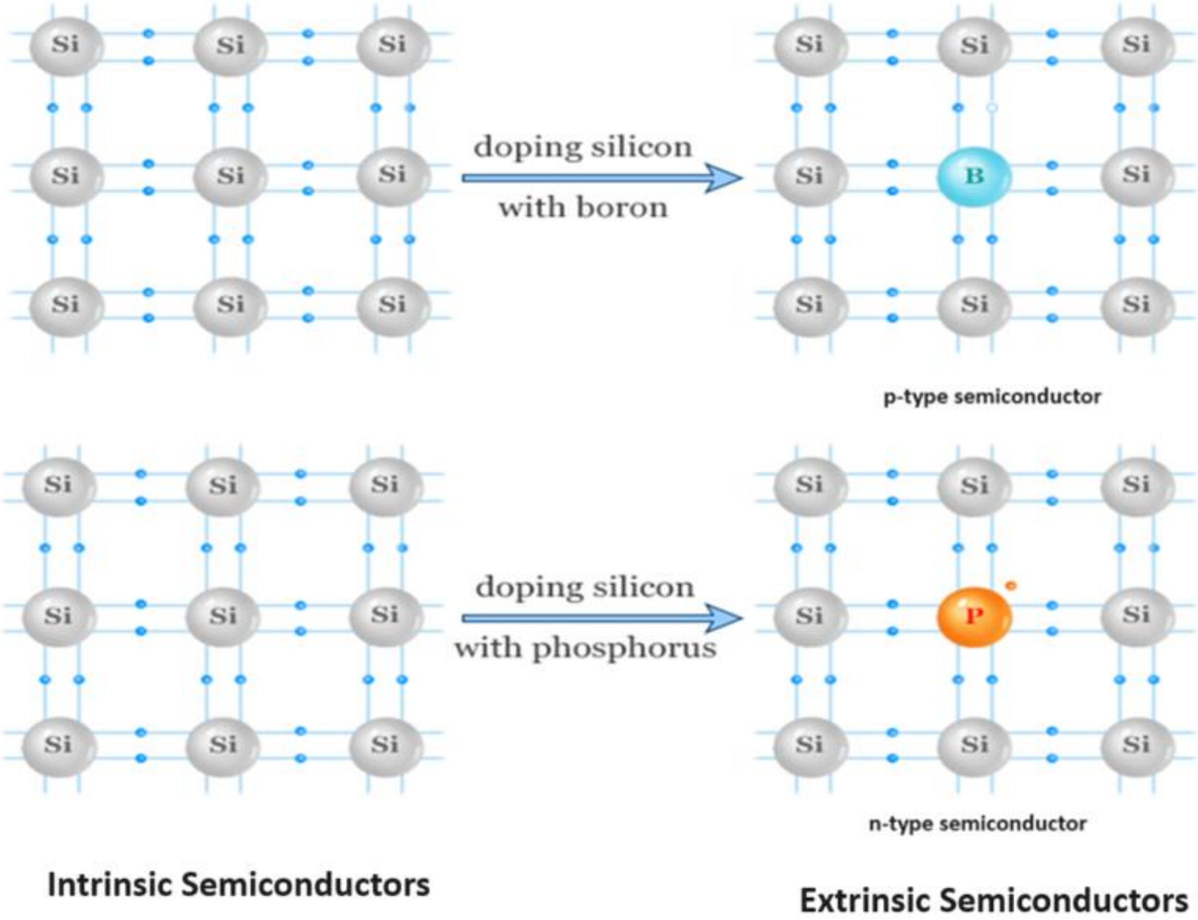
1. Semiconductors act like insulators at zero Kelvin. On increasing the temperature, they work as conductors.
2. The current flow is due to electrons and holes.
3. Due to their exceptional electrical properties, semiconductors can be modified by doping to make semiconductor devices suitable for energy conversion, switches and amplifiers.
4. Lesser power losses.
5. Semiconductors are smaller in size and possess less weight.
6. Their resistivity is higher than conductors but lesser than insulators.
7. The resistance of semiconductor materials decreases with an increase in temperature and vice-versa.

TYPES OF SEMICONDUCTORS




Si
B
P
Hole
Free electron
Trivalent Impurity
Pentavalent Impurity
p-type semiconductor
n-type semiconductor
Intrinsic Semiconductor
Extrinsic Semiconductors

(Or)


Si
B
P
doping silicon with boron
doping silicon with phosphorus
p-type semiconductor
n-type semiconductor
Intrinsic Semiconductors
Extrinsic Semiconductors

INTRINSIC SEMICONDUCTORS

An **intrinsic type of semiconductor material** is made to be very pure chemically. It is made up of only a single type of element. Germanium (Ge) and silicon (Si) are the most common types of intrinsic semiconductor elements. They have four valence electrons (tetravalent). They are bound to the atom by a covalent bond at absolute zero temperature.

When the temperature rises due to collisions, few electrons are unbounded and become free to move through the lattice, thus creating an absence in its original position (hole). These free electrons and holes contribute to the conduction of electricity in the semiconductor. In intrinsic semiconductors, the negative (electrons) and positive (holes) charge carriers are equal in number. The thermal energy is capable of ionizing a few atoms in the lattice, and hence, their conductivity is less.

EXTRINSIC SEMICONDUCTORS

The **conductivity of semiconductors can be greatly improved by** introducing a small number of suitable replacement atoms called IMPURITIES. The process of **adding impurity atoms to the pure semiconductor is called DOPING.** Usually, only 1 atom in 10^7 is replaced by a dopant atom in the doped semiconductor. An extrinsic semiconductor can be further classified into two types:

a) n-type Semiconductor

When a pure semiconductor (Silicon or Germanium) is doped by pentavalent impurity (P, As, Sb, Bi), then four electrons out of five valence electrons bond with the four electrons of Ge or Si. The fifth electron of the dopant is set free. Thus, the impurity atom donates a free electron for conduction in the lattice and is called a "**Donar**". Since the number of free electrons increases with the addition of an impurity, the negative charge carriers increase. Hence, it is called an n-type semiconductor. As conduction is due to a large number of free electrons, the **electrons** in the n-type semiconductor **are the majority carriers**, and **holes are the minority carriers**.

b) p-type Semiconductor

When a pure semiconductor is doped with a trivalent impurity (B, Al, In, Ga), then the three valence electrons of the impurity bond with three of the four valence electrons of the semiconductor. This leaves an absence of electron (hole) in the impurity. These impurity atoms which are added here are ready to accept bonded electrons are called "**Acceptors**". With an increase in the number of impurities, holes (the positive charge carriers) are increased. Hence, it is called a p-type semiconductor. As conduction is due to a large number of holes, **the holes** in the p-type semiconductor **are majority carriers**, and **electrons are minority carriers.**

Intrinsic Semiconductor	**Extrinsic Semiconductor**
It is pure form of semiconductor Ex: Si, Ge etc.,	It is impure form of semiconductor Ex: GeAs, SiAs etc.,
The number of electrons is equal to the number of holes	The number of electrons is not equal to the number of holes
Its electrical conductivity is low	Its electrical conductivity is high
Its conductivity is depending on temperature only	Its conductivity is depending on temperature, as well as on the amount of impurity added
No impurities are present	Trivalent impurity (or) pentavalent impurity is present
The energy gap between conduction and valence band is small, when compare with extrinsic semiconductor	The energy gap between conduction and valence band is high, when compare with intrinsic semiconductor
It is not further classified	It is classified as p-type & n-type semiconductors

p-type Semiconductor	**n-type Semiconductor**
Trivalent impurity is added to get p-type semiconductor	Pentavalent impurity is added to get n-type semiconductor
The added impurity creates holes	The added impurity provides extra electrons
It is also called as acceptor atom because of the presence of additional hole	It is also called as donor atom because of the presence of additional electron
Majority carriers are holes and minority carriers are electrons	Majority carriers are electrons and minority carriers are holes
Conductivity is due to presence of holes	Conductivity is due to presence of electrons
Ex: Silicon/Germanium doped with boron	Ex: Silicon/Germanium doped with phosphorous
The acceptor energy level is close to the valence band and away from the conduction band	The donor energy level is close to the conduction band and away from the valence band
Fermi level is present closer to the valence bond	Fermi level is present closer to the conduction bond

APPLICATIONS OF SEMICONDUCTORS

Semiconductors are used in almost all electronic devices. Without them, our life would be much different. Their reliability, compactness, low cost and controlled conduction of electricity make them ideal to be used for various purposes in a wide range of components and devices.

- They are used in 3D printing machines.
- Temperature sensors are made with semiconductor devices.

- Diodes and photosensors are made up of semiconductors.
- Used in microchips and self-driving cars
- Used in calculators, solar plates, computers and other electronic devices.
- Transistors used in electrical circuits are manufactured using semiconductors.
- They are used in LEDs, OLEDs, solar cells, etc.
- The microprocessor used for controlling the operation of space vehicles, trains, robots, etc., is manufactured by semiconductor materials.
- In addition to consumer electronics, semiconductors play a central role in the operation of bank ATMs, trains, the internet, communications etc.

SUPERCONDUCTORS

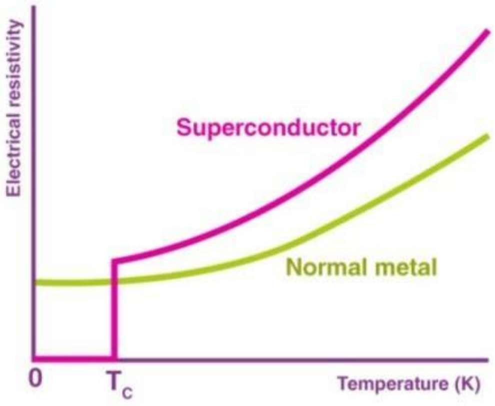
- A **superconductor** is a material that has zero electrical resistance. A superconductor is defined as a substance that offers no resistance to the electric current when it becomes colder than critical temperature.

Ex: Al, Nb, Mg-diboride, Yttrium barium copper oxide (YBCO) and iron pnictides.

- **Superconductivity** is a set of physical properties observed in certain materials, where **electrical resistance is zero and magnetic fields are expelled from the material**. Any material exhibiting these properties is a superconductor.

- Before the discovery of the superconductors, it was thought that the electrical resistance of a conductor becomes zero only at absolute zero. But it was found that in some materials electrical resistance becomes zero when cooled to very low temperatures, these materials are nothing but the superconductors. Superconductivity was discovered in 1911 by Heike Kamerlingh Onnes, who studied the resistance of solid mercury at very low temperatures. At the temperature of 4.2 K, he observed that the resistance abruptly disappears. For this discovery he got the Nobel prize in Physics at 1913.

- The below graph shows the temperature dependence of the electrical resistivity of normal metal and a superconductor.



Some of the superconducting materials along with their critical temperatures are listed below.

Superconducting Elements/Compounds	**T_C (K)**
Sn	3.72
Hg	4.15
Pb	7.19
Al	1.2
In	3.4
NbTi (Niobium Titanium)	10
Nb_3Sn (Niobium Tin)	18.1

SOME IMPORTANT PROPERTIES OF SUPERCONDUCTORS:

- Superconducting materials are generally brittle in nature. This property limits their ability to be fabricated into useful forms such as wires.
- **Infinite conductivity** – superconductors show zero resistance below 4K.
- **Critical temperature** – temperature at which electrical resistivity of the material suddenly drops of zero and the material changes from normal conductor to a super conductor is called the Transition temperature or Critical temperature (T_C).
- A superconductor exhibits perfect diamagnetism. Because of diamagnetic nature, superconducting materials strongly repel external magnets which leads to levitation effects.
- **Magnetic field Expulsion** – the material expels the magnetic fields from its interior and this is called **Meissner effect. The Meissner effect is the expulsion of a magnetic field from a superconductor during its transition to the superconducting state when it is cooled below the critical temperature**. This expulsion will repel a nearby magnet.

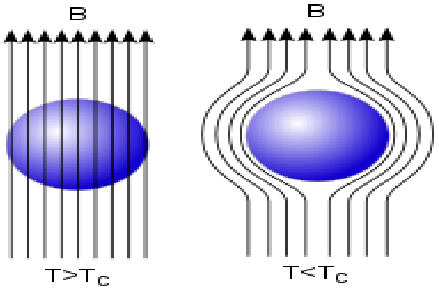


Fig: Diagram of the Meissner effect. (Magnetic field lines, represented as arrows, are excluded from a superconductor when it is below its critical temperature).

- If a sufficient strong magnetic field is applied below T_C, its superconducting property is destroyed. This strong magnetic field is the Critical magnetic field for that corresponding superconducting material. **Critical magnetic field** – it is the value of magnetic field beyond which the superconductors return to conducting state.

TYPES OF SUPERCONDUCTORS: Two types

a) Type I Superconductors (Soft Superconductors)

Type I superconductors are generally pure metals or metalloids with low critical temperatures and low critical magnetic fields. Type I superconductors have critical temperatures between 0.000325 K and 7.8 K. These are soft superconductors, exhibit Meissner Effect. Ex: Al, Pb, Hg

A few of the type I superconductors need tremendous amounts of pressure in order to achieve the superconductive state. One such material is sulfur, which needs a pressure of 9.3 million atmospheres and a temperature of 17 K to reach superconductivity.

b) Type II Superconductors (Hard Superconductors)

Type II superconductors are metallic compounds or alloys with higher critical temperatures and higher critical magnetic fields. They achieve a superconductive state at much higher temperatures compared to type I superconductors. These are hard superconductors and does not exhibit complete Meissner Effect. Ex: Boron doped diamond, metal alloys, complex oxide ceramics.

Reason for electrical resistance:

- When the temperature of metal drops below critical temp, the electrons in the metal form bonds known as Cooper pair (loosely bound pair of electrons with opposite spins and moving with the same speed in opposite directions). The electrons can't offer any electrical resistance when bonded like this and allowing electricity to flow through the metal smoothly.
- When the metal gets warm, electrons gain energy to break the bonds of cooper pairs and go back to offer resistance.

Applications of Superconductors:

- Superconductors are used in accelerators, generators, transportation, computing, electric motors, medical, power transmission etc.
- Used for creating powerful electromagnets for MRI scanners in the medical fields.
- Superconductors can used to perform logic and storage functions in computers. Superchips made of superconductors for computers can function 1000 times faster than currently used silicon chips.
- Power can be transmitted through superconducting cables without loss for long distances.
- Superconductors serve as gas sensors because their electrical resistivity sharply changes on contact with certain gases.
- Some superconductors functions as excellent catalysts for industrial chemical processes.
- Superconducting magnets are employed for operating frictionless, high speed levitating trains.
- Superconducting materials may be used in the manufacture of electrical generators and transformers in exceptionally small sizes having efficiency of 99.99 %.

SUPERCAPACITORS

A **supercapacitor,** also called an **ultracapacitor,** is a high-capacity capacitor, with a capacitance value much higher than solid-state capacitors but with lower voltage limits. It typically **stores 10 to 100 times more energy per unit volume or mass than electrolytic capacitors**, can **accept and deliver charge much faster than batteries**, and **tolerates many more charge and discharge cycles than rechargeable batteries**.

How supercapacitors are different form capacitors:

The material used to construct supercapacitors differ from the conventional capacitors.

- A **capacitor** is an electronic device that stores electrical energy in an electric field by accumulating electric charges on two closely spaced surfaces that are insulated from each other.

- A conventional capacitor consists of two conducting electrodes separated by an insulating material. The conductive plates of the capacitor are good conductors of electricity so they easily allow electric current through them. On the other hand, insulating material is poor conductor of electricity so it does not allow electric current through it. When a voltage is applied to the capacitor, opposite charges build on the surface of electrodes.
- In conventional capacitors, the capacitance (charge storage) is directly proportional to the surface area of each electrode or plate and inversely proportional to the distance between the electrodes. In simple words, the capacitor with large surface area electrodes and very thin dielectric achieves a larger capacitance (stores large amount of electric charge) whereas the capacitors with small surface area electrodes and very thick dielectric achieve a smaller capacitance (stores small amount of electric charge). This is how the conventional capacitors store electric charge.

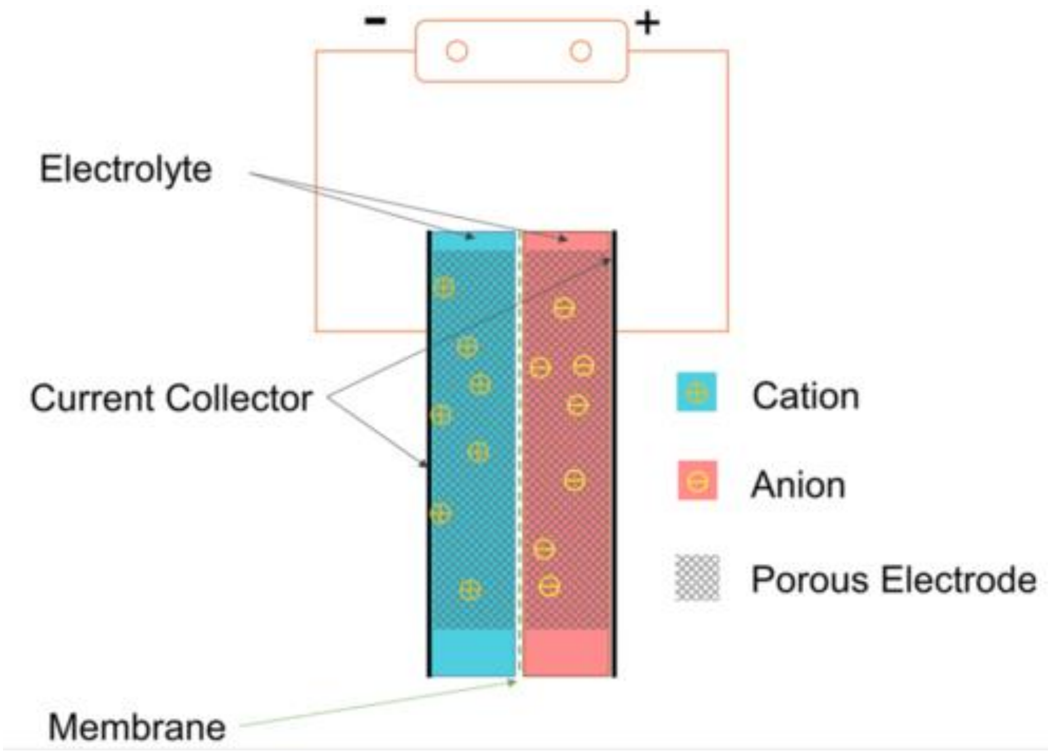


Fig: Schematic illustration of a supercapacitor

- The supercapacitors also work just like the conventional capacitors. **However, the supercapacitors differ from the conventional capacitors in two ways**: the **supercapacitors have large surface area electrodes and very thin dielectric (separation distance between electrodes is very small) compared to the conventional capacitors. This makes it possible to achieve larger capacitance (larger charge store) than the conventional capacitors**.

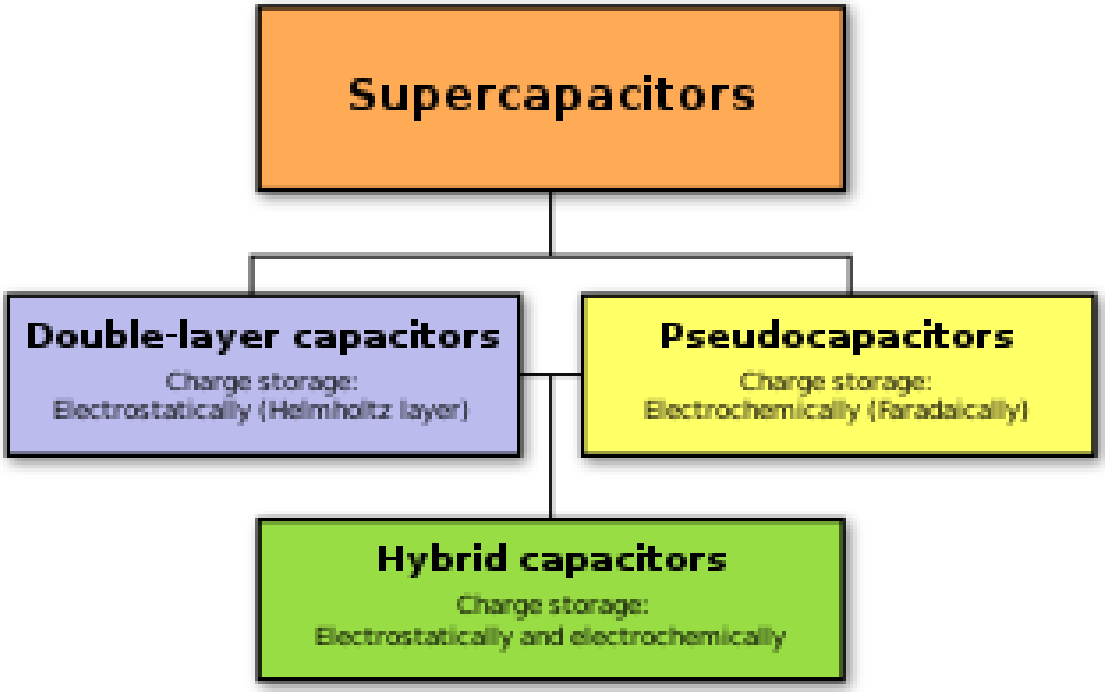
- **The supercapacitors store large amount of charge as batteries store and deliversenergy or charge very quickly as conventional capacitors deliver**.

- On the other hand, the capacitors deliver the energy (charge) very quickly (discharge very quickly) but the main drawback of capacitors is they can't store large amount of charge as batteries store.

- **These two drawbacks (large charge storage and delivering charge quickly) can beovercome by using supercapacitors.**

TYPES OF SUPERCAPACITORS

Supercapacitors are mainly classified into three types:



- **Electrostatic double-layer capacitors (EDLCs)** use carbon electrodes or derivatives and the electrostatic-capacitance is achieved by a Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte.
- **Electrochemical pseudocapacitors (ECSCs)** use metal oxide or conducting polymer electrodes and the electrochemical-capacitance is achieved by Faradaic electron charge-transfer with redox reactions, interactions or electrosorptions.
- **Hybrid capacitors** are lithium-ion capacitors which make use of electrodes with differing characteristics, one exhibiting electrostatic capacitance and other exhibiting electrochemical capacitance.

ADVANTAGES OF SUPER CAPACITORS:

- Stores large amount of charge compared to the conventional capacitors (High capacitance).
- Delivers energy or charge very quickly (high power density)
- Long lifetime
- Low cost
- Supercapacitors do not explode like batteries even if it is overcharged.

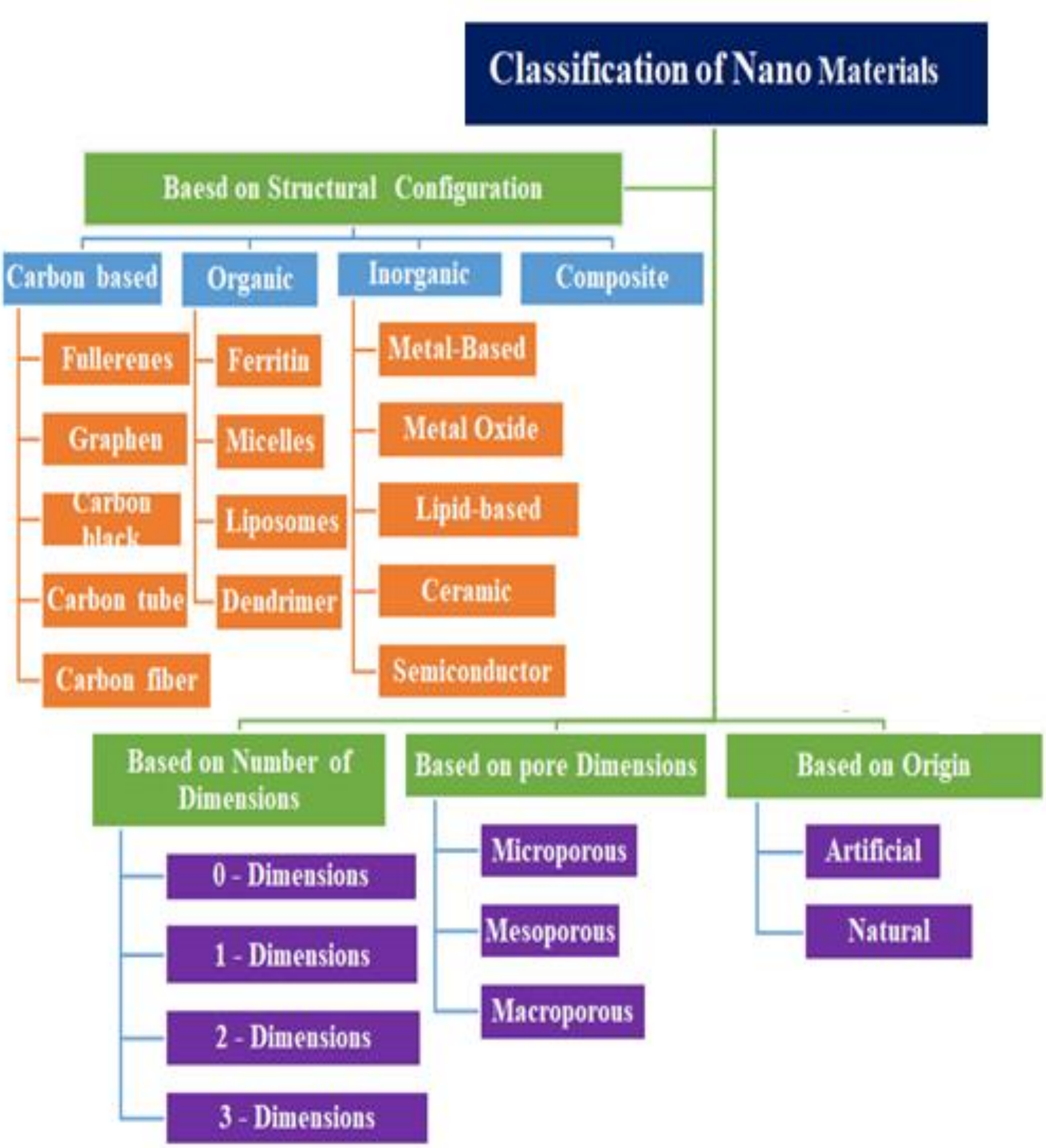
APPLICATIONS OF SUPERCAPACITORS

Supercapacitors are used where a large amount of power is required for a relatively short time.

- Supercapacitors are used in electronic devices such as laptop computers, portable media players, hand held devices, and photovoltaic systems to stabilize the power supply.
- For making cordless tools like electric screwdrivers.
- Supercapacitors provide backup or emergency shutdown power such as micro controllers, RAM and PC cords.
- Used in Flash light and Solar power applications
- Supercapacitors are used as temporary energy storage devices for energy harvesting systems.
- Supercapacitors are used in defibrillators (an instrument that controls irregular heart beatby supplying electric current to the chest wall).
- Also used in the fields of aviation. Military, railways, cranes, forklifts and in hybrid electric vehicles.

NANOMATERIALS

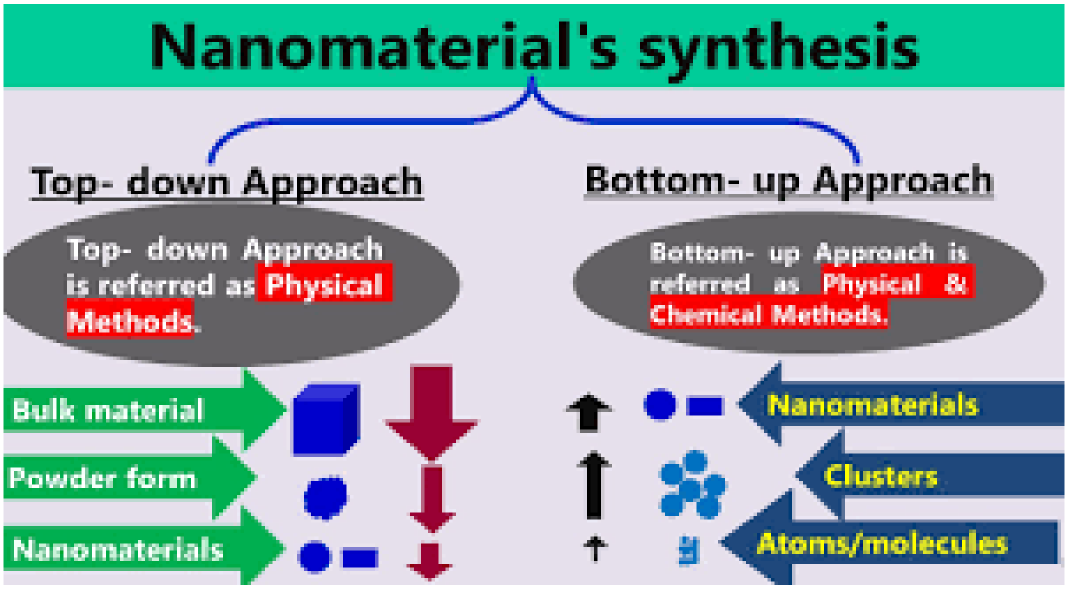
The materials with dimensions in the range of 1 nm to 100 nm are known as **nanomaterials**. One billionth of a meter (1/100,00,00,000) is called **nanometer (nm)**. Study of materials and their properties at the length of few nano scales is called **nano science**. The technique involved in the preparation, characterization and use of the properties of nanomaterials in different applications are collectively known as **nanotechnology**.

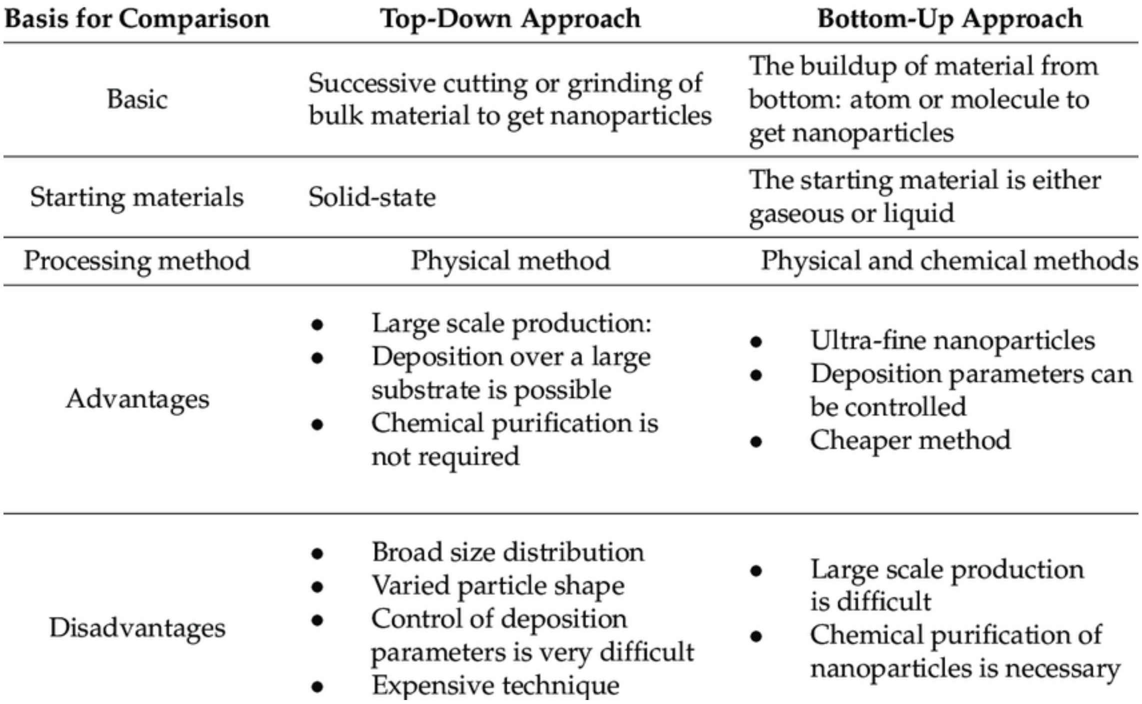


General methods of preparation:

Top-Down approach: In the top-down approach (fabricating), nano materials are constructed from larger entities without atomic level control.

Bottom-up approach: In the bottom-up approach (synthesizing), nano materials or devices are built from molecular components which assemble themselves chemically by principles of molecular recognition.





Basis for Comparison	Top-Down Approach	Bottom-Up Approach
Basic	Successive cutting or grinding of bulk material to get nanoparticles	The buildup of material from bottom: atom or molecule to get nanoparticles
Starting materials	Solid-state	The starting material is either gaseous or liquid
Processing method	Physical method	Physical and chemical methods
Advantages	• Large scale production: • Deposition over a large substrate is possible • Chemical purification is not required	• Ultra-fine nanoparticles • Deposition parameters can be controlled • Cheaper method
Disadvantages	• Broad size distribution • Varied particle shape • Control of deposition parameters is very difficult • Expensive technique	• Large scale production is difficult • Chemical purification of nanoparticles is necessary

1. SOL GEL METHOD: It's a Bottom-up approach. A sol is a colloidal suspension of solid particles of ions in a solvent. A gel is a semi rigid mass that forms when the solvent from the sol begins to evaporate and the particles left begin to form a network.

2. CHEMICAL REDUCTION METHOD: Metal nano particles are prepared by this method. (Ag, Au, Pt).

Example: Preparation of Ag nanoparticles:

Metal salt solution + metal salt precursor + stabilizer + reducing agent → stand for some time → nanoparticles separate → purification → centrifugation → freeze drying → metal nanoparticles.

PROPERTIES OF NANOPARTICLES: The following are some of the important properties of nanomaterials.

1. **Properties based on size of the particle:**

- The magnetic properties increase with decrease in size of the materials.
- Melting point of the nanomaterials increases when compared with other materials.
- Solubility of nanomaterials is more than other materials due to the decreased size
- Colour of nanomaterials is size dependent. As the size of the particle decreases the colour of the material changes. Ex: bulk gold looks yellow, but 12 nm gold particle looks red.
- Transparency of nanomaterials is more due to decreased size of the particle
- Catalytic activity of the nanomaterials is more due to decrease in size (surface area will increases).

2. Properties based on composition of nanomaterials:

The composition effects of the nanomaterials influence both physical and chemical properties of nanomaterials.

- Chemical reactivity of nanomaterials is high when compared with other materials
- Reaction rates of nanomaterials is high when compared with other materials
- Colloidal properties (optical, electrical, magnetic and gel properties) of nanomaterials are high when compared with other materials.

3. Properties due to surface of nanomaterials:

- Nanomaterials exhibit good dispersibility
- Nanomaterials can be used as good conducting, semiconducting and insulating substance depending on structure of nanomaterials.
- Nanomaterials possess good catalytic activity due to increased surface area.

Applications of Nanomaterials:

Nanomaterials have a wide range of applications across various fields due to their unique properties arising from their nanoscale dimensions. Here are some notable applications:

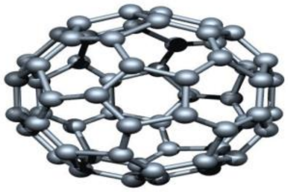
1. **Electronics:** Nanomaterials such as carbon nanotubes, graphene, and quantum dots are being used to develop smaller, faster, and more efficient electronic devices, including transistors, memory devices, and sensors.
2. **Medicine:** Nanomedicine utilizes nanomaterials for drug delivery, imaging, and therapy. Nanoparticles can deliver drugs directly to targeted cells, reducing side effects and increasing efficacy.
3. **Energy:** Nanomaterials play a crucial role in renewable energy technologies such as solar cells, fuel cells, and batteries.
4. **Catalysis:** Nanoparticles serve as highly effective catalysts used in various industrial processes, including petroleum refining, environmental remediation, and chemical synthesis.
5. **Materials Science:** Nanomaterials are used to enhance the mechanical, electrical, and thermal properties of materials.
6. **Environmental Remediation:** Nanomaterials are employed in wastewater treatment, air purification, and soil remediation processes.
7. **Food Industry:** Nanotechnology is utilized in food packaging to improve shelf life, safety, and freshness.

8. **Cosmetics:** Nanomaterials are used in cosmetics and personal care products for their ability to improve texture, appearance, and performance.

9. **Textiles:** Nano coatings and nanofibers are applied to textiles to impart stain resistance, waterproofing, antimicrobial properties, and enhanced durability.
10. **Defence and Security:** Nanotechnology contributes to the development of advanced materials, sensors, and detection systems for defence and security applications.

FULLERENE

A fullerene is an allotrope of carbon, composed entirely of carbon in the form of a hollow sphere, ellipsoid or tube. Fullerenes are similar in structure to graphite which is composed of stacked graphene sheets of linked hexagonal rings, may also contain pentagonal and heptagonal.



TYPES OF FULLERENES:

Fullerenes are a class of carbon allotropes consisting of carbon atoms arranged in closed, cage-like structures. Some common types of fullerenes are as follows

1. **Buckminsterfullerene (C60)**: This is the most well-known and studied fullerene. It consists of 60 carbon atoms arranged in a spherical structure, resembling a soccer ball.
2. **Carbon Nanotubes**: These are cylindrical fullerenes with a high aspect ratio (length-to-diameter ratio). Carbon nanotubes can be single-walled (SWCNTs), multi-walled (MWCNTs).
3. **Endohedral Fullerenes**: These are fullerenes encapsulating atoms or small molecules inside their cage structures. Endohedral fullerenes have attracted significant attention due to their unique properties and potential applications in areas such as molecular electronics, medicine, and nanotechnology. Examples include buckminsterfullerene encapsulating a metal atom like lanthanum (La@C60) or a nitrogen atom (N@C60).

4. **Fullerene Nanoparticles**: Fullerenes can also form nanoparticles with various sizes and shapes, depending on the synthesis method used. Fullerene nanoparticles have applications in drug delivery, photovoltaics, and catalysis, among others.

PROPERTIES: Fullerenes exhibit a range of interesting properties due to their unique molecular structure, which is based on carbon atoms arranged in closed, cage-like structures. Here are some key properties of fullerenes:

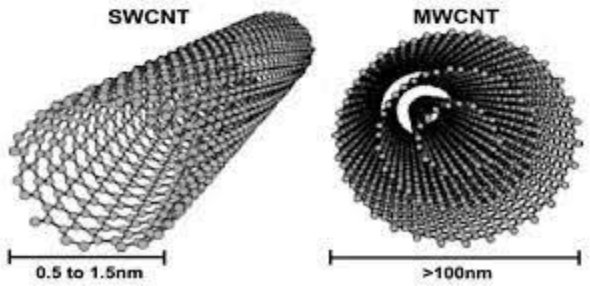
1. **Spherical Structure**: Many fullerenes, such as Buckminsterfullerene (C60), have a spherical shape resembling a soccer ball. This unique structure gives fullerenes high symmetry and stability.
2. **Hollow Interior**: Fullerenes have a hollow interior, which can encapsulate atoms or small molecules, leading to the formation of endohedral fullerenes.
3. **Carbon-Carbon Bonds**: Fullerenes are primarily composed of sp2-hybridized carbon atoms arranged in a hexagonal network. The carbon-carbon bonds in fullerenes are strong, contributing to their structural stability.
4. **Conductivity**: Some fullerenes, such as carbon nanotubes, exhibit excellent electrical conductivity along their length.
5. **Mechanical Strength**: Fullerenes possess remarkable mechanical strength and stiffness.
6. **Chemical Reactivity**: Fullerenes can undergo various chemical reactions, including addition reactions and functionalization reactions.
7. **Optical Properties**: Fullerenes exhibit interesting optical properties, including strong absorption in the ultraviolet and visible regions of the electromagnetic spectrum.
8. **Thermal Stability**: Fullerenes have high thermal stability, allowing them to withstand high temperatures without decomposing.
9. **Biocompatibility**: Some fullerenes and their derivatives exhibit biocompatibility, making them suitable for biomedical applications such as drug delivery, imaging, and therapy.

APPLICATIONS: Fullerenes have a wide range of applications across various fields due to their unique properties.

- **Nanotechnology**: Fullerenes are utilized in nanotechnology for their ability to form nanoscale structures such as nanotubes, nanowires, and nanoparticles.
- **Electronics**: Carbon nanotubes, a type of fullerene, are used in electronics for their excellent electrical conductivity, mechanical strength, and thermal properties.
- **Catalysis**: Fullerenes and their derivatives are utilized as catalysts in various chemical reactions due to their unique surface properties and high surface area. They find applications in organic synthesis, fuel cells, and environmental remediation.
- **Biomedical Applications**: Fullerenes and their derivatives show potential in biomedical applications such as drug delivery, imaging, and therapy.
- **Photovoltaics**: Fullerenes are used in organic photovoltaic devices (solar cells) as electron acceptors due to their excellent electron-accepting properties and high electron mobility.
- **Materials Science**: Fullerenes are incorporated into materials to enhance their mechanical, electrical, and thermal properties. They are used as reinforcements in composites, additives in polymers, and lubricants in coatings due to their high strength, conductivity, and lubricating properties.
- **Energy Storage**: Carbon nanotubes and other fullerene-based materials are investigated for their potential use in energy storage devices such as batteries and supercapacitors.
- **Sensors**: Fullerenes are used in the development of sensors for detecting various substances and environmental parameters.

CARBON NANOTUBES

A **Carbon nanotube** (**CNT**) is a tube made of carbon with a diameter in the nanometer range. Carbon nanotubes (CNTs) are cylindrical nanostructures composed of carbon atoms arranged in a hexagonal lattice. CNTs can be single-walled (SWCNTs), consisting of a single layer of carbon atoms rolled into a tube, or multi-walled (MWCNTs), which have multiple layers of carbon sheets rolled into concentric cylinders.



1. **Single-Walled Carbon Nanotubes (SWCNTs):** These nanotubes consist of a single layer of graphene rolled into a seamless cylinder. They exhibit remarkable electrical, thermal, and mechanical properties.
2. **Multi-Walled Carbon Nanotubes (MWCNTs):** These nanotubes comprise multiple concentric layers of graphene cylinders nested within one another. MWCNTs possess excellent mechanical strength and are often used in various applications due to their unique properties.

PREPARATION:

1. **Chemical Vapor Deposition (CVD)**: In CVD, a carbon-containing gas (such as methane or ethylene) is decomposed at high temperatures in the presence of a catalyst (usually transition metals like iron, cobalt, or nickel) to form carbon nanotubes on a substrate.

2. **Arc Discharge**: In arc discharge, a high electrical current is passed between two graphite electrodes in an inert atmosphere, causing vaporization of the graphite and formation of carbon vapor. The carbon vapor then condenses into carbon nanotubes on cooler surfaces in the reactor.

3. **Laser Ablation**: Laser ablation involves irradiating a graphite with a high-power laser beam in an inert atmosphere. The laser vaporizes the graphite, leading to the formation of a carbon plasma, which then condenses into carbon nanotubes on a substrate.

PROPERTIES: Some of the key properties of carbon nanotubes include:

1. **Exceptional Strength**: Carbon nanotubes are incredibly strong, with a tensile strength about 100 times greater than that of steel at a fraction of the weight.
2. **High Electrical Conductivity**: Depending on their structure, carbon nanotubes can exhibit either metallic or semiconducting behavior.
3. **High Thermal Conductivity**: Carbon nanotubes have excellent thermal conductivity, even surpassing that of diamond.
4. **Flexibility and Resilience**: Despite their exceptional strength, carbon nanotubes are also flexible and can bend without breaking. They can also recover their shape after deformation, making them resilient materials.
5. **Low Density**: Carbon nanotubes have a very low density, which contributes to their lightweight nature.
6. **Chemical Stability**: Carbon nanotubes are chemically stable under a wide range of conditions, including high temperatures and corrosive environments.
7. **Biocompatibility**: Some types of carbon nanotubes exhibit biocompatibility, making them suitable for use in biomedical applications such as drug delivery, tissue engineering, and biosensing.

APPLICATIONS: Some notable applications of carbon nanotubes include:

1. **Biomedical Applications**: Carbon nanotubes are explored for various biomedical applications, including drug delivery, imaging, tissue engineering, and biosensing. Functionalized CNTs can target specific cells or tissues, making them valuable in targeted drug delivery systems.
2. **Electronics and Optoelectronics**: CNTs are used utilized in displays, sensors, and photovoltaic devices due to their excellent electrical and optical properties.
3. **Composite Materials**: CNTs are incorporated into polymer matrices to produce composite materials with enhanced mechanical, electrical, and thermal properties and these nanocomposites find applications in aerospace, automotive, sports equipment, and construction industries for lightweight, high-strength materials.

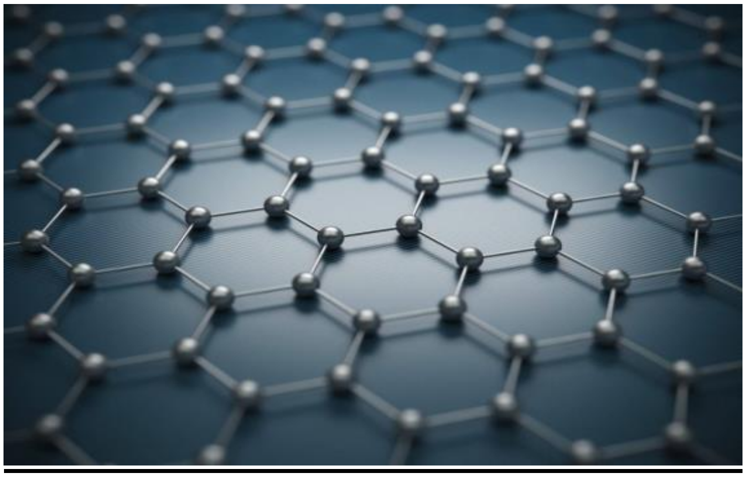
4. **Energy Storage and Conversion**: Carbon nanotubes are used in energy storage devices such as lithium-ion batteries and supercapacitors.

- **Thermal Management**: CNTs have high thermal conductivity and low density make them effective in thermal management applications, including in microelectronics and LED lighting.

5. **Environmental Remediation**: CNTs are used in environmental remediation processes for the removal of pollutants and contaminants from air, water, and soil.

GRAPHENE

Graphene is a two-dimensional material consisting of a single layer of carbon atoms arranged in a hexagonal lattice. Graphene is a material that is extracted from graphite and is made up of pure carbon, one of the most important elements in nature and which we find in daily objects like the lead of a pencil. Graphene stands out for being tough, flexible, light, and with a high resistance.



PROPERTIES: Some of the key properties of Graphene include:

1. **Exceptional Strength**: Graphene is one of the strongest materials known, with a tensile strength over 100 times greater than that of steel.
2. **High Electrical Conductivity**: Graphene exhibits extremely high electrical conductivity, even surpassing that of copper.

3. **High Thermal Conductivity**: Graphene also possesses excellent thermal conductivity, surpassing that of most other materials, including copper and diamond.
4. **Flexibility and Transparency**: Despite its strength, graphene is also flexible and transparent, allowing it to be integrated into flexible electronics, touchscreens, and optoelectronic devices.
5. **Large Surface Area**: Graphene has an exceptionally large surface area, providing ample space for chemical interactions and adsorption.
6. **Biocompatibility**: Graphene exhibits biocompatibility to a certain extent, making it suitable for biomedical applications such as drug delivery, biosensing, and tissue engineering.

APPLICATIONS:

1. **Energy Storage**: Graphene electrodes are used in high-performance lithium-ion batteries, supercapacitors, fuel cells, energy harvesting and storage devices.
2. **Materials Reinforcement**: Graphene is incorporated into polymers, ceramics, and composites to improve mechanical strength, conductivity, and thermal stability.
3. **Thermal Management**: Graphene-based thermal interface materials used for efficient heat dissipation in electronics and LED lighting.
4. **Biomedical Applications**: Graphene based nanomaterials are used in drug delivery systems and biomedical biosensors for medical diagnostics.
5. **Water Filtration and Desalination**: Graphene membranes with nanopores are used for efficient water purification, like desalination, removal of contaminants and heavy metals from water.
6. **Coatings and Barrier Films**: Graphene-based coatings are used as corrosion protection agent, anti-fouling, and gas and moisture barrier films for packaging.
7. **Environmental Monitoring and Remediation**: Graphene-based sensors are used for real-time monitoring of air and water quality.
8. **Electronics and Photonics**: Graphene-based transistors and integrated circuits are used in high-speed electronics, touch screens, OLEDs, and solar cells.

9. **Space Applications**: Lightweight and strong graphene-based materials used for spacecraft components and Radiation shielding & thermal management solutions for space exploration missions.

ELECTROCHEMISTRY & APPLICATIONS

Electrochemical cell: Electrochemical cell is a device, used to convert the chemical energy produced in a redox reaction into electrical energy.

- Electrochemical cell is also referred to as voltaic cell (or) galvanic cell.
- A galvanic cell consists of two electrodes namely anode and cathode.
- The anode is written on the left-hand side while the cathode is written on the right-hand side.
- The anode must be written by writing electrode metal first and then electrolyte. These two are separated by a vertical line (or) a semicolon.

For example Zinc is an anode then it is write as Zn/Zn^{2+} (or) $Zn;Zn^{2+}$ (or) $Zn/ZnSO_4$

- The cathode must be written by writing electrolyte first and then the electrode metal. These two are separated by a vertical line (or) a semicolon.

For example Copper is an cathode then it is write as Cu^{2+}/Cu (or) $Cu;Cu^{2+}$ (or) $Cu/CuSO_4$

- The two half cells are separated by a salt bridge, which is indicated by two vertical lines.

For example, Zinc-Copper Electrochemical cell represent as

$$\mathbf{Zn / Zn^{2+} (1M) // Cu^{2+} (1M) / Cu}$$

- The practical application of galvanic cell is Daniel cell as shown below.

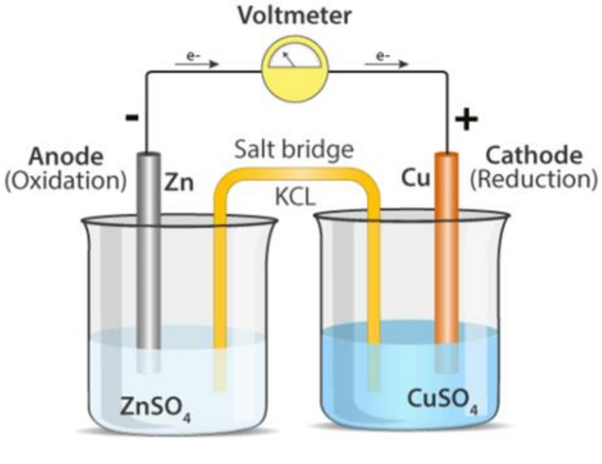


Figure: Daniel cell

Anode: Anode is the electrode at which oxidation occurs.

Cathode: Cathode is the electrode at which reduction occurs.

Oxidation/Reduction in terms of electron: Oxidation is the process of loss of electrons whereas Reduction is the process of gain electrons.

Electrode Potential: The tendency of metal electrode either to lose (or) gain electrons, when it is in contact with its own salt solution is called '**electrode potential**'.

Standard Electrode Potential: When electrode potential is measured under standard conditions namely temperature 25^0C, concentration 1 M and pressure 1 atmosphere, is known as "**Standard Electrode Potential**".

❖ **The electrode potential of an electrode is depending on**

(i) Nature of the metal
(ii) Temperature
(iii) Concentration of the electrolyte.

This can be explained in terms of Nernst equation.

Nernst equation for electrode potential

Consider the following redox reaction

$$M^{n+}\,(aq) + ne^{-} \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} M\,(s)$$

For such a redox reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are inter-related as,

$$\Delta G = RT lnK + RT\ln\frac{[Product]}{[Reactant]}$$

$$\Delta G = \Delta G^\circ + RT\ln\frac{[Product]}{[Reactant]} \quad \text{------(1)}$$

Equation (1) is known as Van’t Hoff reaction isotherm.

In a reversible reaction, the electrical energy is produced at the expense of free energy decrease i.e.

$\Delta G = -nEF$ and $\Delta G^\circ = -nE^\circ F$

Substitute ΔG & ΔG° in equation 1

$$-nEF = -nE^\circ F + RT\,ln\frac{[M]}{[M^{n+}]}$$

(Here, the concentration of metal [M] is 1 unity)

$$-nEF = -nE^\circ F + RT\,ln\frac{[1]}{[M^{n+}]} \quad \text{------(2)}$$

$$-nEF = -nE^\circ F - RT\,\ln[M^{n+}] \quad \text{------(3)}$$

Dividing the above equation (3) by - nF, then

$$E = E^\circ + \frac{RT}{nF}\ln[M^{n+}]$$

$$E = E^\circ + \frac{2.303\,RT}{nF}\log[M^{n+}] \quad \text{------ (4)}$$

This equation is known as Nernst equation for metal ion electrode potential.

When, R = 8.314 J/K/mole; F = 96500 coulombs; T = 298 K (25 °C), then the equation 4 becomes

$$E = E^\circ + \frac{0.0591}{n}\log[M^{n+}]$$

The above equation known as “Nernst equation for single electrode potential”.

From the above equations, it is clear that:

(i) If the concentration of the solution is increased, the electrode potential increases and vice versa.

(ii) If the temperature is increased, the electrode potential increases and vice versa.

Applications of Nernst equation

➢ Nernst equation is used to calculate electrode potential of unknown metal.

➢ Corrosion tendency of metal can be predicted.

EMF (or) Cell Potential of a cell:

Electromotive force (EMF) is defined as the difference of potential which causes flow of electron from one electrode of higher potential to the other electrode of lower potential.

- Mathematically Cell potential is the potential difference between two electrodes in a electrochemical cell.

$$E_{cell} = E_{cathode} - E_{anode}$$

(Or)

$$E_{cell} = E_{right} - E_{left}$$

At standard conditions, cell potential is

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

(Or)

$$E^o_{cell} = E^o_{right} - E^o_{left}$$

NUMERICAL PROBLEMS

(solved at class)

Reference Electrode

A reference electrode is a half-cell with a stable, well-defined, and reproducible electrode potential. Using reference electrodes, the potentials of another electrode can be measured.

Examples: Standard hydrogen electrode, Standard Calomel electrode, Silver-Silver Chloride electrode etc.

Reference electrodes are broadly classified into two types,

(i) Primary reference electrodes

Ex: Standard hydrogen electrode (S.H.E) is the primary reference electrode against which all other electrodes are measured. It consists of a platinum electrode in contact with hydrogen gas at 1 atm and immersed in a solution of 1 M H^+ ions. The potential of standard hydrogen electrode is taken as zero at all temperatures.

(ii) Secondary reference electrodes

Ex: Standard Calomel electrode (S.C.E) is commonly used as a secondary reference electrode. Calomel electrode contains mercury and mercury(I) chloride in a saturated potassium chloride solution. The potential value of Calomel electrode varies depending on the concentration of KCl, typically around +0.24 V in saturated KCl.

Potentiometry & Potentiometric Titrations:

Potentiometry is a technique that measures the potential difference between two electrodes to determine the concentration of a solution.

Potentiometric titration is a type of potentiometry that uses an electrochemical cell to determine the concentration of a substance in a solution.

Different types of potentiometric titration include redox titrations, acid–base titrations, precipitation titrations and complexometric titration are possible.

Basic concept of Potentiometry

Potentiometry is one of the methods of electroanalytical chemistry. It is usually employed to find the concentration of a solute in solution. In potentiometric measurements, no indicator is used, instead the electric potential is measured by the addition of the titrant to the analyte. To do this, two electrodes namely an indicator electrode and a reference electrode are used. The potential difference between the two electrodes changes as the titrant is added, and the endpoint of the titration is determined by monitoring this potential difference. The potential difference between two electrodes is measured using a high impedance voltmeter.

In the overall electrochemical cell, one half cell is formed with the indicator electrode and the ions of the analyte, which is generally an electrolyte solution. The other half-cell is formed by the reference electrode.

The overall cell potential can be calculated using the formula given below:

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}}$$

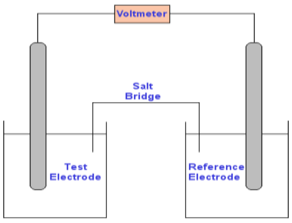
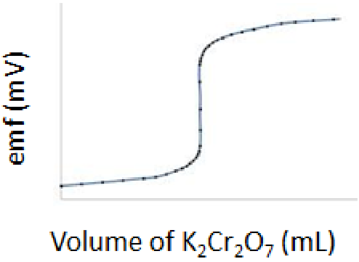


Fig: Potentiometer

The overall cell potential, E_{cell} is calculated in every interval where the titrant is measured and added to the analyte. Finally, a graph is plotted with the potential difference on the Y-axis and the volume on the X-axis as shown below.

Ex: Redox titration

A redox titration is a titration in which the analyte and titrant react through an oxidation–reduction reaction. For example, treating the ferrous solution with an oxidizing agent ($K_2Cr_2O_7$) to produce ferric ion.



Concept of Conductivity and Conductivity Cell

Conductivity is a measure of a solution's ability to conduct electricity, which is influenced by the presence of ions in the solution. It reflects how well an electric current can pass through the liquid, with higher conductivity indicating a greater concentration of charge carriers (ions).

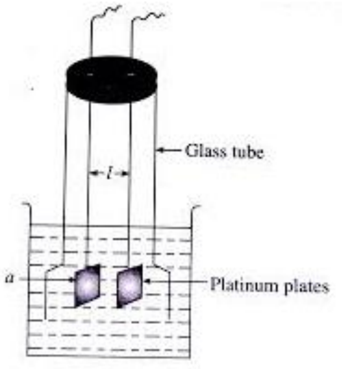
Conductivity is measured in Siemens per meter (S/m) or milliSiemens per centimeter (mS/cm) or microSiemens per centimeter (µS/cm).

Factors Affecting Conductivity:

- **Ion Concentration**: More ions in solution lead to higher conductivity.
- **Ion Mobility**: Different ions have different abilities to move through the solution. For example, H^+ ions generally have higher mobility than Na^+ ions.
- **Temperature**: Conductivity typically increases with temperature due to higher ion mobility.

Conductivity cell is a device used to measure the conductivity of a solution. Conductivity cell is also names as Conductivity sensor or Conductivity electrode.

Basically, it consists of two electrodes (platinum electrodes coated with platinum black) separated by a distance (ℓ) and area of cross section (a). The distance between the electrodes divided by their surface area is known as the cell constant. Conductivity cell is available in several designs and one of the simplest forms is shown in the following diagram.



Conductometric titrations:

Conductometric titration is a titration used to measure the amount/concentration of an analyte present in the given solution by measuring the change in the conductance as a function of volume of titrant.

In conductometric titrations, the electrolytic conductivity of the reaction mixture is continuously monitored as one reactant (titrant) is added another reactant (analyte). The equivalence point is the point at which the conductivity undergoes a sudden change.

Ex: Acid - Base Conductometric Titrations:

1. Strong Acid with a Strong Base (HCl with NaOH)

Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of H^+ by Na^+. This decrease in the conductance continues till the equivalence point. After the equivalence point, the conductance increases due to the large conductivity of OH^-.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

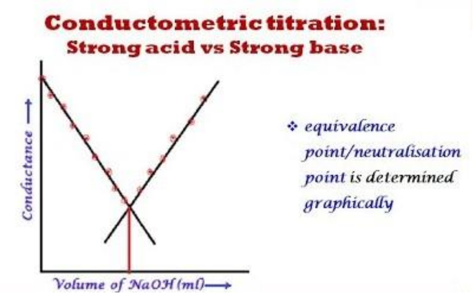


Fig: Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

2. Weak Acid with a Strong Base (CH_3COOH with NaOH)

Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases slowly up to endpoint on adding NaOH. But after the endpoint conductance increases due to the large conductivity of OH^-.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

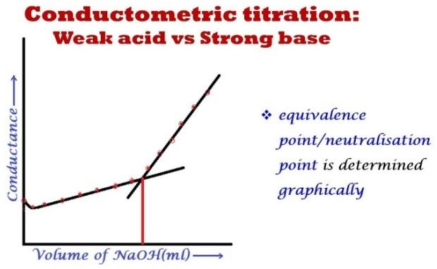


Fig: Conductometric titration of a weak acid (CH_3COOH) vs. a strong base (NaOH)

3. Strong Acid with a Weak Base (HCl with NH_4OH)

Initially the conductance is high and then it decreases due to the replacement of H^+ with NH_4^+. But after equivalence point there is very small increase in conductance because of the presence of weak base (NH_4OH), which has very low conductance.

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

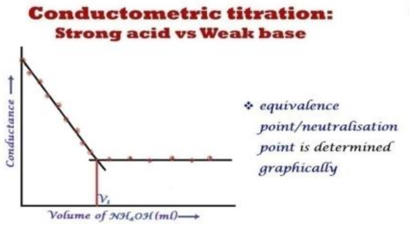


Fig: Conductometric titration of a strong acid (HCl) vs. a weak base (NH_4OH)

4. Weak Acid with a Weak Base (CH_3COOH with NH_4OH)

Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by NH_4^+ but also suppresses the dissociation of acetic acid due to common ion acetate. Further increase in conductance up to equivalence point is observed due to formation of strong salt (CH_3COONH_4). But after equivalence point there is very small increase in conductance because of the presence of weak base (NH_4OH), which has very low conductance.

$$CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$$

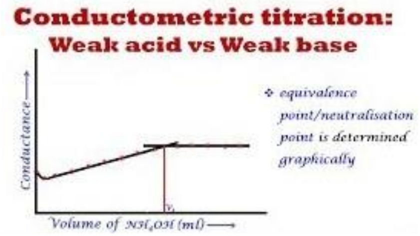


Fig: Conductometric titration of a weak acid (CH_3COOH) vs. a weak base (NH_4OH)

5. Strong Acid &Weak Acid vs Strong Base (HCl & CH_3COOH with NaOH)

When a mixture of strong acid & weak base is titrated against a strong base, the strong acid is first neutralized followed by the weak acid. The conductance of the solution decreases during the titration till whole of the strong acid is neutralized by base and then the conductance of the solution is increases due to neutralization of weak acid with the addition of base because of the formation of highly ionizable salt sodium acetate. After neutralization of weak acid, the conductance of the solution is increases very rapidly because of the presence of excess of completely ionized strong base.

$$HCl + CH_3COOH + 2\,NaOH \longrightarrow NaCl + CH_3COONa + 2H_2O$$

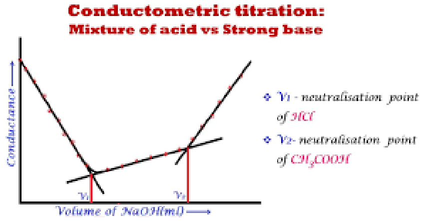


Fig: Conductometric titration of mixture of strong acid (HCl) & weak acid (CH_3COOH) vs strong base (NaOH)

SENSOR: A sensor is a device that detects and responds to some type of input from the physical environment. The input can be light, heat, motion, moisture, pressure or any number of other environmental phenomena.

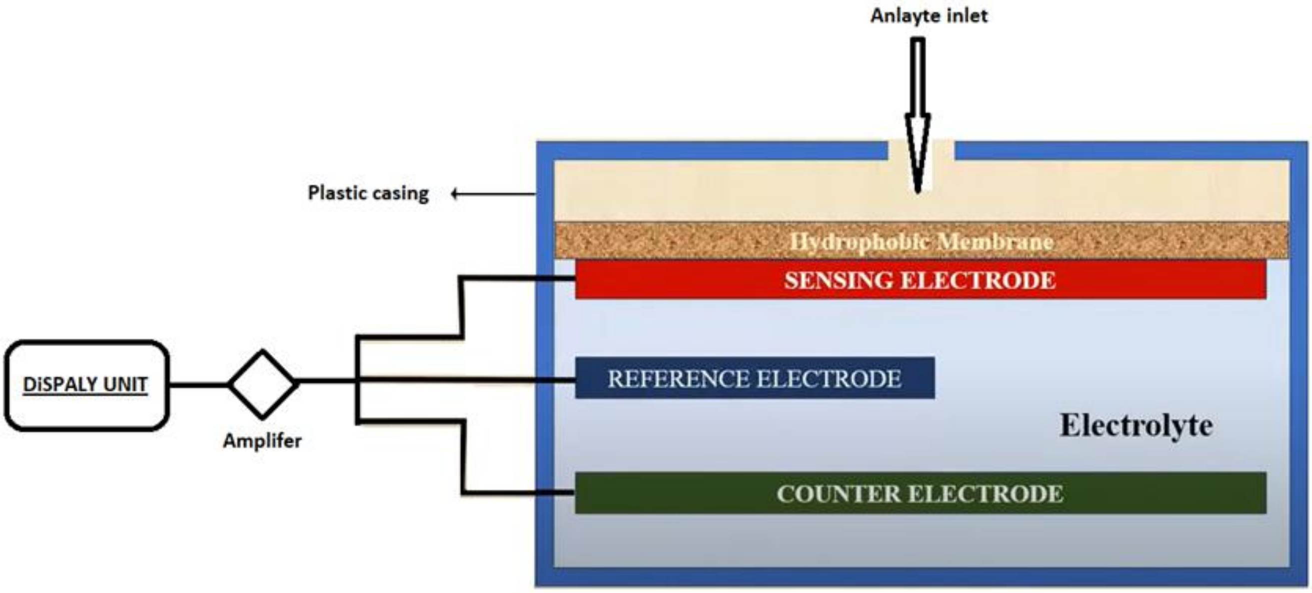
Electrochemical Sensors

Electrochemical sensors are the devices that detect and measures the concentration of an analyte by converting the effect of electrochemical reaction between analyte and electrode surface into an electrical signal. These are the devices that will converts chemical information into an electrical signal.

Construction & Working:

Electrochemical sensor device consists two/three electrodes, namely sensing electrode (working electrode), reference electrode and counter electrode. All these three electrodes were connected to the output device through an amplifier. All these electrodes are surrounded by an electrolyte in a closed plastic casing. The sensing electrode usually attached with hydrophobic membrane, which allows only a particular component of analyte. There is an inlet, where the sample to be injected.

In electrochemical sensor device, the surface of one of the electrodes used as the site of reaction, which is named as sensing electrode. This sensing electrode will interact with the analyte and undergoes either oxidation or reduction based on the nature of the electrode. At the same time at counter electrode an opposite chemical reaction occurs (i.e., if the sensing electrode is involved in oxidation, then at counter electrode reduction occurs & vice versa). So, once the analyte is interacted with the sensing electrode, there is flow of electrons takes place, then the current they produced is measure to determine the important data of an analyte such as concentration, amount etc.



<u>3 types of electrochemical sensors:</u>

a) **Potentiometric sensors** (measures the potential values).

b) **Amperomertic sensors** (measures the current flow).

c) **Conductometric sensors** (measure the conductivity).

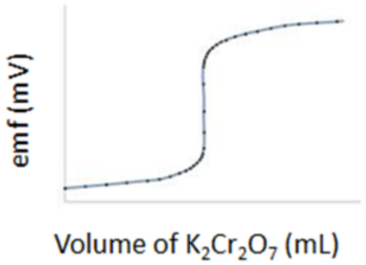
POTENTIOMETRIC SENSORS:

Potentiometric sensors are analytical devices used to measure the potential (voltage) of a solution, providing valuable information about the concentration of the analyte.

Potentiometric titrations are analytical techniques that measure the voltage (potential) changes in a solution as a titrant is added to analyte.

A potentiometric titration uses an electrode system, typically a combination of a reference electrode and an indicator electrode. The reference electrode has a stable potential, while the indicator electrode responds to the changing redox conditions in the solution. The voltage measured between the two electrodes is plotted against the volume of titrant added, creating a titration curve. In the context of redox titrations, these measurements help to determine the endpoint of a reaction involving electron transfer between oxidizing and reducing agents. Potentiometric sensors are used for the estimation of ferrous ions (Fe^{2+}) in solution, particularly when using potassium dichromate ($K_2Cr_2O_7$) in redox titrations.

$$K_2Cr_2O_7 + 6\ FeSO_4 + 7\ H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3\ Fe_2(SO_4)_3 + 7\ H_2O$$



AMPEROMETRIC SENSORS:

Amperometric sensors are electrochemical devices that measure the concentration of an analyte in solution by measures the current (amperes) produced in a redox reaction.

Amperometric titration is an analytical technique used to determine the concentration of an analyte in solution by measuring the current that develops in an electrochemical cell as a function of added titrant. In amperometric method, the current that produced is measured is actually due to the effect of the oxidation or reduction of the analyte.

Examples:

a) Amperometric Titration for Glucose estimation

In glucose estimation, the most common approach is to oxidize the glucose using an enzyme called glucose oxidase (GOx). Here, glucose is oxidized to gluconolactone, and molecular oxygen is reduced to hydrogen peroxide (H_2O_2). The produced hydrogen peroxide is then electrochemically oxidized at the working electrode. The electrons (e^-) generated in this oxidation reaction flow through the external circuit, creating an electric current that is proportional to the glucose concentration in the sample.

$$\text{Glucose} + O_2 \xrightarrow{\text{GOx}} \text{Gluconolactone} + H_2O_2$$

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

b) Amperometric Titration for Uric acid estimation

In uric acid estimation, the most common approach is to oxidize the uric acid using an enzyme called Uricase. Uricase catalyzes the oxidation of uric acid to allantoin and, hydrogen peroxide (H_2O_2). The produced hydrogen peroxide is then electrochemically oxidized at the working electrode. The electrons (e^-) generated in this oxidation reaction flow through the external circuit, creating an electric current that is proportional to the uric acid concentration in the sample.

$$\text{Uric Acid} + O_2 \xrightarrow{\text{Uricase}} \text{Allantoin} + H_2O_2$$

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

Applications: Electrochemical sensors are used

- ➢ To detect explosive gases & toxic vapours in environment.
- ➢ To monitoring oxygen levels in medical sector.
- ➢ To check the air quality.

- ➢ In food quality control, transportation, petrochemical industries.
- ➢ To detect the presence of heavy metals.
- ➢ To measure the pH of the solutions.
- ➢ In soil analysis & in agricultural applications to detect the pesticides.
- ➢ In clinical field for monitoring blood glucose levels, uric acid levels etc.

Batteries

➢ Battery is a device consisting of one or more electrochemical cells that converts stored chemical energy into electrical energy.

➢ In general battery consists of three parts; (i) negative electrode material (ii) positive electrode material (iii) electrolyte that allows ions to move between the electrodes. Terminals of electrodes allow current to flow out of the battery to perform work.

Types of battery: Depending on the method of storing energy, the batteries can be classified as;

i. Primary Battery (or) Primary Cells (or) Non-reversible battery,
ii. Secondary Battery (or) Secondary Cells (or) Reversible battery,
iii. Flow Battery (or) Fuel cells.

i. Primary battery (or) Non-reversible battery:

➢ In these cells, the electrode reactions cannot be reversed by passing an external electrical energy.

➢ In these cells, the reactions occur only once and after use the battery become dead. Therefore, they are not rechargeable. **Ex:** Zinc-air battery, Dry cell etc.

Zinc-air battery

A **zinc–air battery** is a metal–air electrochemical cell powered by the oxidation of zinc with oxygen from the air. During discharge, a mass of zinc particles forms 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 ($(Zn(OH)^{2-}{}_4)$), releasing electrons to travel to the cathode. The zincate decays into zinc oxide and water returns to the electrolyte.

Anode:

$$Zn + 4\,OH^- \longrightarrow Zn(OH)_4^{2-} + 2\,e^-$$

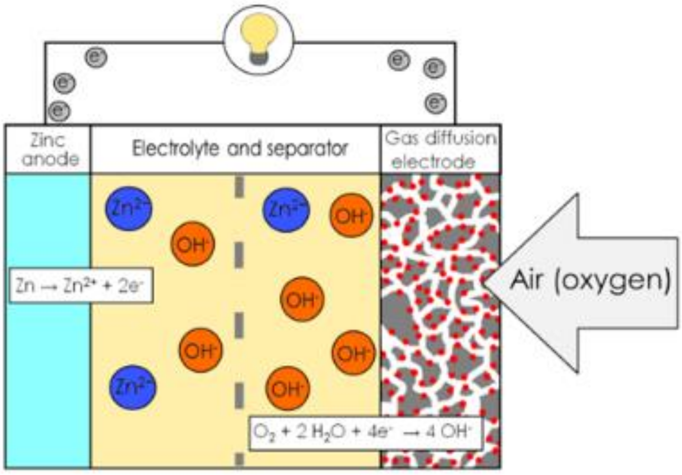
$$Zn(OH)_4^{2-} \longrightarrow ZnO + H_2O + 2\,OH^-$$

Cathode:

$$\tfrac{1}{2}O_2 + H_2O + 2\,e^- \longrightarrow 2\,OH^-$$

Overall reaction:

$$Zn + \tfrac{1}{2}O_2 \longrightarrow ZnO$$



Advantages & Disadvantages:

- ➢ These batteries consist of environmentally benign and low-cost components. They also have a long shelf life of several years when properly stored.
- ➢ The major **disadvantage** is their limited power output, which is mainly due to the inadequate performance of air electrodes.

ii. Secondary battery (or) Reversible battery:

- In these cells, the electrode reactions can be reversed by passing an external electrical energy. Therefore, they can be recharged by passing electric current and used again and again. These cells are also called storage cells (or) accumulators. **Ex:** Lithium-ion battery, Lead acid storage cell, etc.,

Lithium-ion cell:

- It is an example to advanced secondary battery. Lithium has the most negative standard reduction potential (-3.05v) of any metal, so it has a lot of appeal as an anode material.
- In Lithium-ion rechargeable cells lithium cobalt oxide ($LiCoO_2$) acts as an anode and graphite (C_6) acts as cathode. Lithium hexafluorophosphate (LiPF6) salt, dissolved in organic solvent is used as electrolyte in Lithium-ion batteries.

Charging:

- When the cell is charged, lithium ions leave from $LiCoO_2$ and travel through the electrolyte to graphite (C_6).

The reactions during charging process are

$$LiCoO_2 + C_6 \longrightarrow Li_{1-x}CoO_2 + Li_xC_6$$

Discharging:

- When the cell is discharged, lithium ions move back through the electrolyte to the Cobalt oxide, while the electrons move through external circuit from the graphite electrode to the cobalt oxide electrode.

The reactions during discharging process are

$$Li_{1-x}CoO_2 + Li_xC_6 \longrightarrow Li_{1-x+y}CoO_2 + Li_{x-y}C_6$$

- Thus, the charging and discharging cycle simply sweep Li^+ ions back and forth between two electrodes with electrons flowing through external circuit to keep the charge balance.

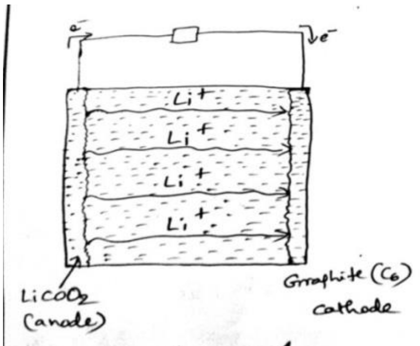


Fig : charging of Li-ion battery

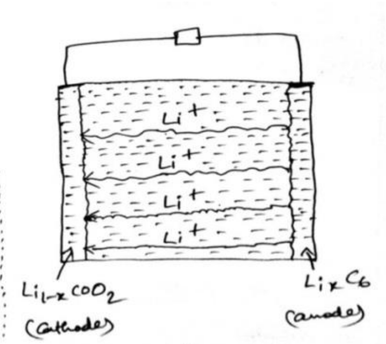


Fig : Discharging of Li-ion battery

__The popularity of the Li-ion battery is due to the advantages offered over other secondary (or) rechargeable batteries are:__

- Since Li is a light-weight metal, only 7g (1 mole) material is required to produce 1 mole of electrons.
- Since Li has the most negative E^0 value (3.0 V), it generates a higher voltage than the other type of cells.
- It has Low self-discharge rate (about 1.5% per month)
- Since all the constituents of the battery are solids there is no risk of leakage from the battery.
- Do not suffer from battery memory effect and made in a variety of sizes and shapes.

iii. Fuel cells (or) Flow battery:

- A fuel-cell is a voltaic cell, which converts the chemical energy of the fuels directly into electricity. The essential process in the fuel-cell is

$$\text{Fuel} + \text{Oxygen} \longrightarrow \text{Oxidation products} + \text{electrical energy}$$

- In a fuel cell, the reactants, products and electrolytes are continuously passing through the cell. Here chemical energy gets converted into electrical energy.

Ex: Hydrogen-Oxygen fuel cell, Polymer electrolyte membrane fuel cells, Methanol-Oxygen fuel cell etc.,

Hydrogen-Oxygen fuel cell:

- Hydrogen-Oxygen fuel cell (H_2-O_2 fuel cell) consists of an electrolytic solution such as 25% KOH solution and two inert porous electrodes contain platinum.
- Hydrogen and oxygen gases are bubbled through the anode and cathode compartments respectively, where the following reactions take place:

Reactions:

At anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

At cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

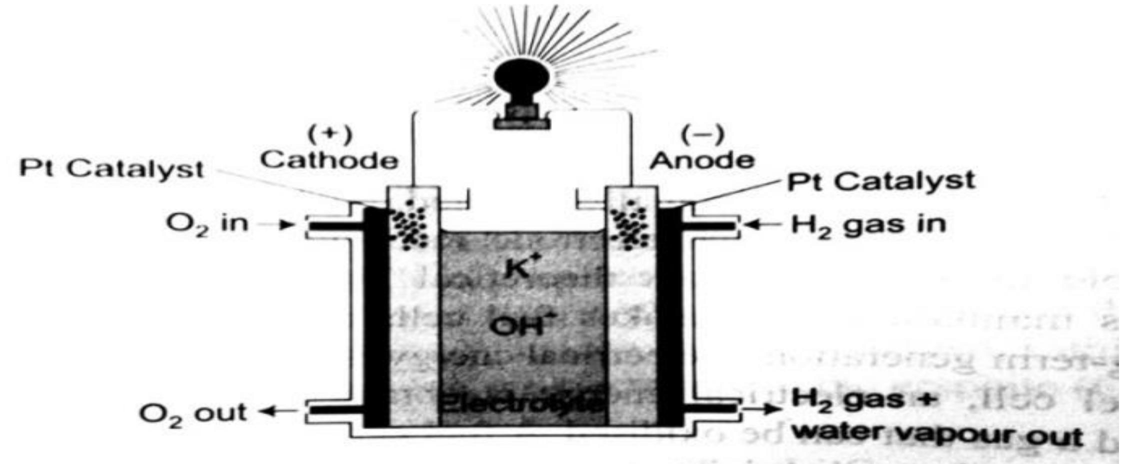


Fig. 1.10 ***Hydrogen—oxygen fuel cell***

Applications:

i. H_2-O_2 fuel cell is mainly used as auxiliary energy sources in space vehicles, sub-marines and military vehicles.

ii. Because of the light weight, these fuel cells are preferred for space crafts and produce H_2O. This H_2O is a valuable source for astronauts.

Advantages of H_2-O_2 Fuel cells:

- Fuel cells are efficient (75%) and take less time for operation.
- It is pollution free technique.
- It produces electric current directly from the reaction of a fuel and an oxidizer.

Disadvantages of H_2-O_2 fuel cells:

- Fuel cells cannot store electric energy as other cells do.
- Electrodes are expensive and short lived.
- Storage and handling of hydrogen gas is dangerous.

Polymer Electrolyte Membrane Fuel Cell (PEMFC)

Polymer electrolyte membrane (PEM) fuel cells, also called proton exchange membrane fuel cells, use a proton-conducting polymer membrane as the electrolyte & hydrogen is typically used as the fuel. A PEM fuel cell transforms the chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical energy, as opposed to the direct combustion of hydrogen & oxygen gases to produce thermal energy.

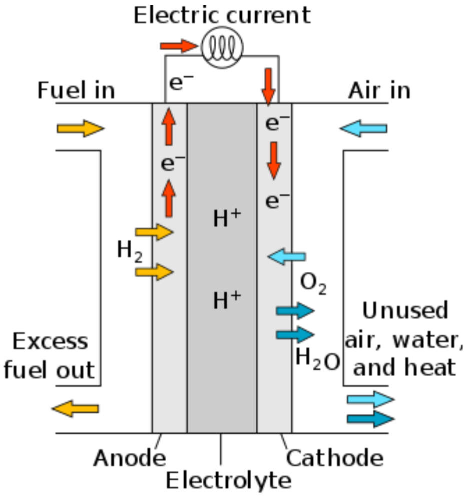
A stream of hydrogen is delivered to the anode side. At the anode side it is catalytically split into protons and electrons. This is the oxidation half-cell reaction. The newly formed protons permeate through the polymer electrolyte membrane to the cathode side. The electrons travel along an external load circuit to the cathode side, thus creating the current output of the fuel cell. Meanwhile, a stream of oxygen is delivered to the cathode side. At the cathode side oxygen molecules react with the protons permeating through the polymer electrolyte membrane and the electrons arriving through the external circuit to form water molecules. This is the reduction half-cell reaction.

Anode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Overall reaction:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$



Advantages:

- These cells operate at relatively low temperatures and can quickly vary their output to meet shifting power demands.
- High energy conversion efficiency.
- Environmentally friendly with zero emissions.

Disadvantages:

- Inability to work at high temperatures and low relative humidity.
- Rapid decay in proton conductivity.

PLOLYMER CHEMISTRY

Polymer:

- Polymer is a Greek word. In Greek terms 'poly' means "many" and "mers" means "units".
- **Definition:** "Polymers are macromolecules, which are formed by linking together of a large number of small molecules, called monomers".
- For example, polyethylene is polymer, it is formed by linking together of a large number of ethene monomer units.

$$n\,H_2C{=}CH_2 \xrightarrow{\text{polymerisation}} -\!\left(CH_2{-}CH_2\right)_n\!-$$

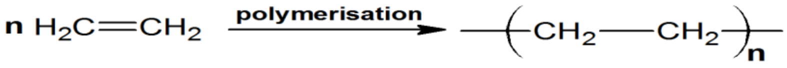
Ethylene Polyethylene

Monomer:

- Small molecules combined with each other to form big molecules. These small molecules are called 'Monomers'. (or) The repeating unit in a polymer chain is called monomer.

Degree of polymerization:

- The total number of repeating units in a polymer chain is called "Degree of polymerization".



$$n\,H_2C{=}CH_2 \xrightarrow{\text{polymerisation}} -\!\left(CH_2{-}CH_2\right)_n\!-$$

- Where 'n' is the degree of polymerization. Most of the polymers usually contain 10,000 to more than one lakh molecular mass range.

Polymerization: The Chemical process leading to the formation of a polymer is known as polymerization.

CLASSIFICATION:

Based on their availability:

a) Natural Polymers examples: Silk, Wool, Cellulose, Proteins etc.,

b) Synthetic Polymers examples: Polyethylene, Nylon, Polyester, Teflon etc.,

Based on their structural arrangement:

(i). Homo Polymers

(ii). Hetero polymers (or) Co – polymers

(i). Homo polymers:

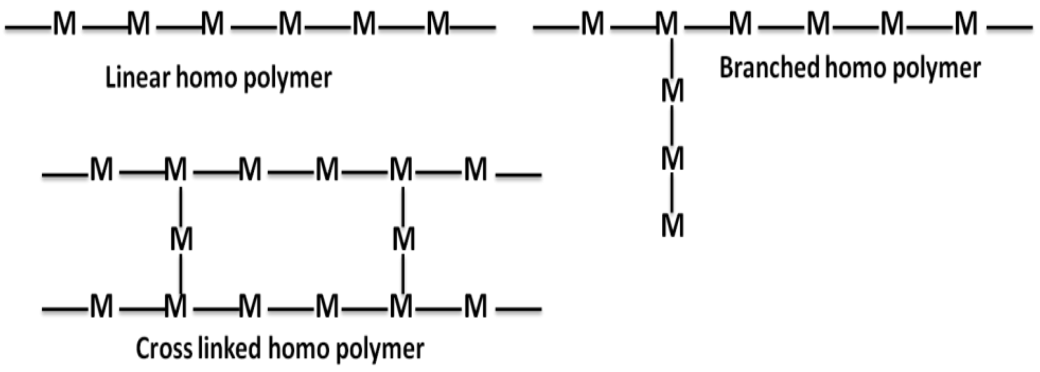
- If polymer is obtained from same kind of monomer units is known as "Homo polymers".

  Ex., PVC, PE etc.

—M—M—M—M—M—M—

- Homo polymers again subdivided into linear, branched and cross linked.

Structures of Different Homo polymers:



(ii). Hetero (or) Co polymers:

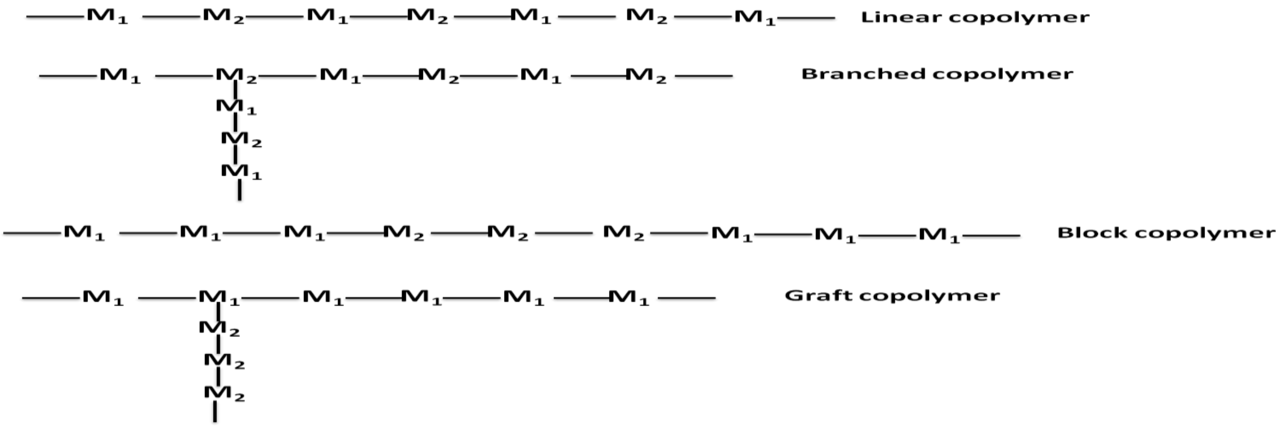
- If polymer is obtained from different kinds of monomer units, is known as “Hetero (or) Co polymer”.

  Ex., Bakelite, Buna-S etc.,

$$—M_1—M_2—M_1—M_2—M_1—M_2—$$

- Co polymers again subdivided in to Linear, Branched, Block and Graft co-polymers.

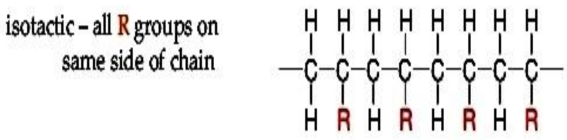
Structures of different co-polymers:



TACTICITY: “The orientation of functional groups in a polymer can takes place orderly (or) disorderly with respect to the carbon main chain, is known as Tacticity”.

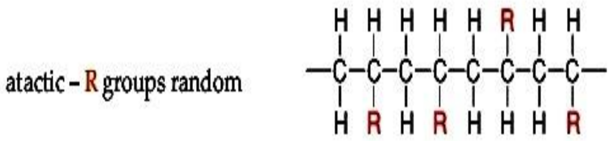
Polymer Tacticity is mainly three kinds.

1. ***Isotactic***: If the functional groups are arranged same side with respect to the carbon main chain, is known as “**Isotactic**”.



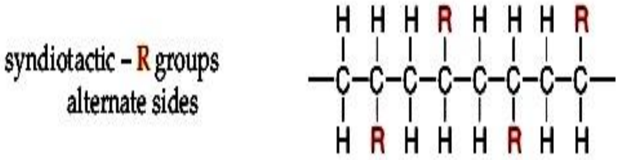
2. Atactic:

- If the functional groups are arranged randomly with respect to the carbon main chain, is known as "**Atactic**".



3. Syndiotactic:

- If the functional groups are arranged alternative fashion with respect to the carbon main chain, is known as "**Syndiotactic**".

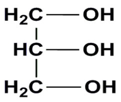


FUNCTIONALITY: The total number of bonding sites (or) reactive sites in the monomer is referred as its functionality. Minimum two sites are required to form a polymer.

For example:

$H_2C{=}CH_2$ **Functionality - 2**

$H_2N{-}(CH_2)_6{-}NH_2$ **Functionality - 2**



$H_2C{-}OH$, $HC{-}OH$, $H_2C{-}OH$ **Functionality - 3**

(i). Bifunctional Monomers (or) Linear functional Polymer: If two reactive groups are attached side by side to each other to produce bi functional polymer.

eg., ethylene, styrene, vinyl chloride, malonic acid, ethylene glycol etc.,

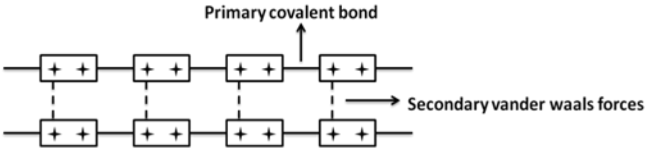


Fig: Linear functional polymer

(ii). *Mixed functional monomers (or) Branched chain functional polymer:* A Mixture of bi and tri functional monomers gives branched functional polymer.

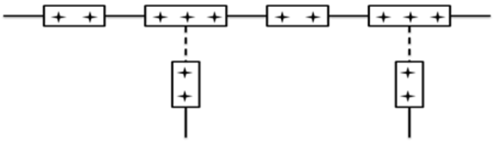


Fig: Branched chain functional polymer

(iii). ***Polyfunctional monomers (or) Cross-linked functional polymer:*** Monomers with three functional groups forms three-dimensional cross-linked network polymers called resins. In this, the moment of individual molecules is restricted.

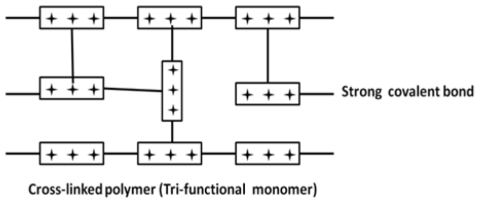


Fig: Cross-linked functional polymer

Types of Polymerization reactions:

Polymerization:

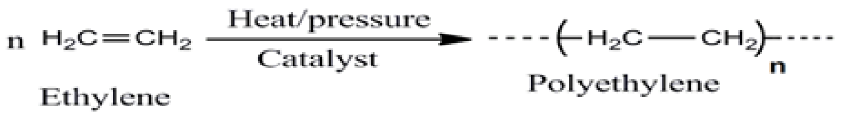
- Polymerization is a process, in which large number of monomers either same (or) different combine to give a polymer with (or) without elimination of small molecules like H_2O, HCl etc.,

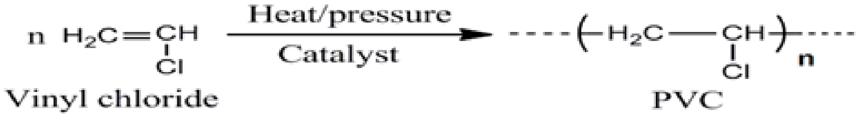
Classification of polymerization:

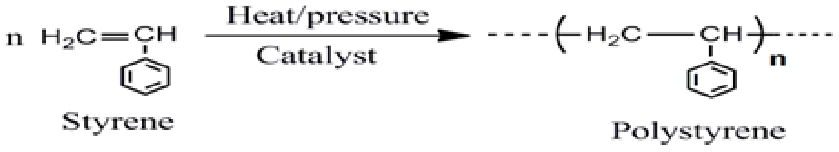
- Polymerization reactions may be carried out by any one of the following methods.
    1. Addition (or) Chain growth polymerization,
    2. Condensation (or) Step-wise polymerization,
    3. Co-polymerization.
    4. Coordination Plolymerization

1. Addition (or) Chain growth polymerization:

- Addition (or) Chain growth polymerization is a reaction, in which polymer is an exact multiple of the original monomeric molecule.
- The original monomeric molecule contains double bonds. No by-product formed.
    - The molecular weight of polymer is an integral multiple of the monomer.





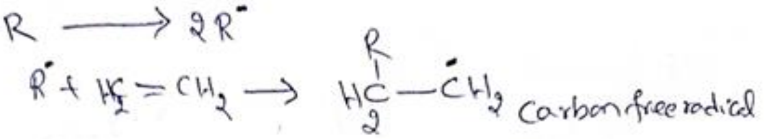


1) Mechanism of Addition polymerization

a) Free radical Mechanism

Initiation $R-R \longrightarrow 2\dot{R}$

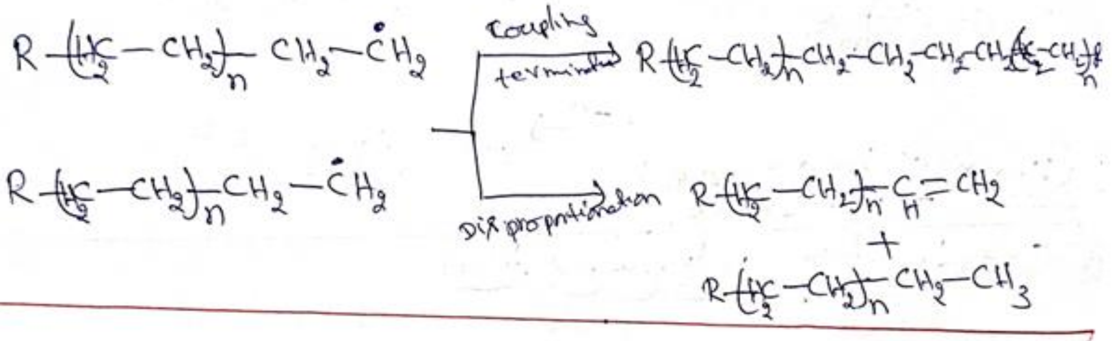
Propagation



$\dot{R} + H_2C=CH_2 \longrightarrow \overset{R}{\overset{|}{H_2C}}-\dot{C}H_2$ Carbon free radical

$R-CH_2-\dot{C}H_2 + n(H_2C=CH_2) \longrightarrow R-(H_2C-CH_2)_n-CH_2-\dot{C}H_2$

Termination

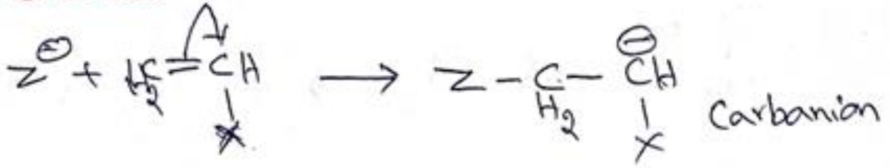


$R-(H_2C-CH_2)_n-CH_2-\dot{C}H_2 \xrightarrow[\text{termination}]{\text{Coupling}} R-(H_2C-CH_2)_n-CH_2-CH_2-CH_2-CH_2-(H_2C-CH_2)_n-R$

$R-(H_2C-CH_2)_n-CH_2-\dot{C}H_2 \xrightarrow{\text{Disproportionation}} R-(H_2C-CH_2)_n-\underset{H}{C}=CH_2 + R-(H_2C-CH_2)_n-CH_2-CH_3$

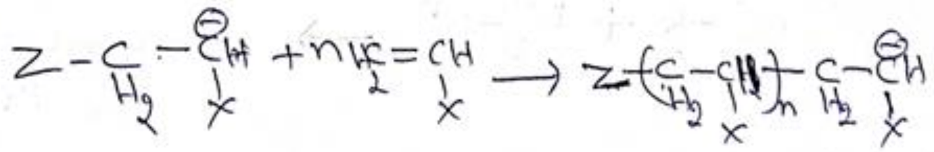
b) Anionic mechanism

Initiation



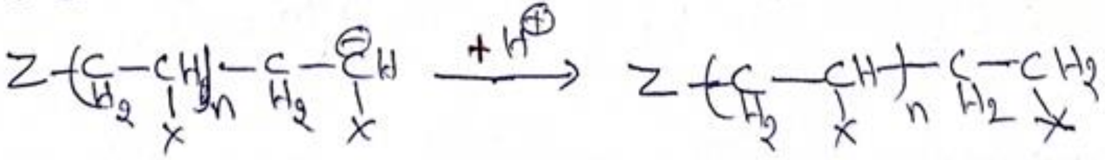
$Z^{\ominus} + H_2C=\underset{X}{\underset{|}{CH}} \longrightarrow Z-\underset{H_2}{C}-\underset{X}{\underset{|}{\overset{\ominus}{C}H}}$ Carbanion

propagation



$Z-\underset{H_2}{C}-\underset{X}{\underset{|}{\overset{\ominus}{C}H}} + n\,H_2C=\underset{X}{\underset{|}{CH}} \longrightarrow Z-(\underset{H_2}{C}-\underset{X}{\underset{|}{CH}})_n-\underset{H_2}{C}-\underset{X}{\underset{|}{\overset{\ominus}{C}H}}$

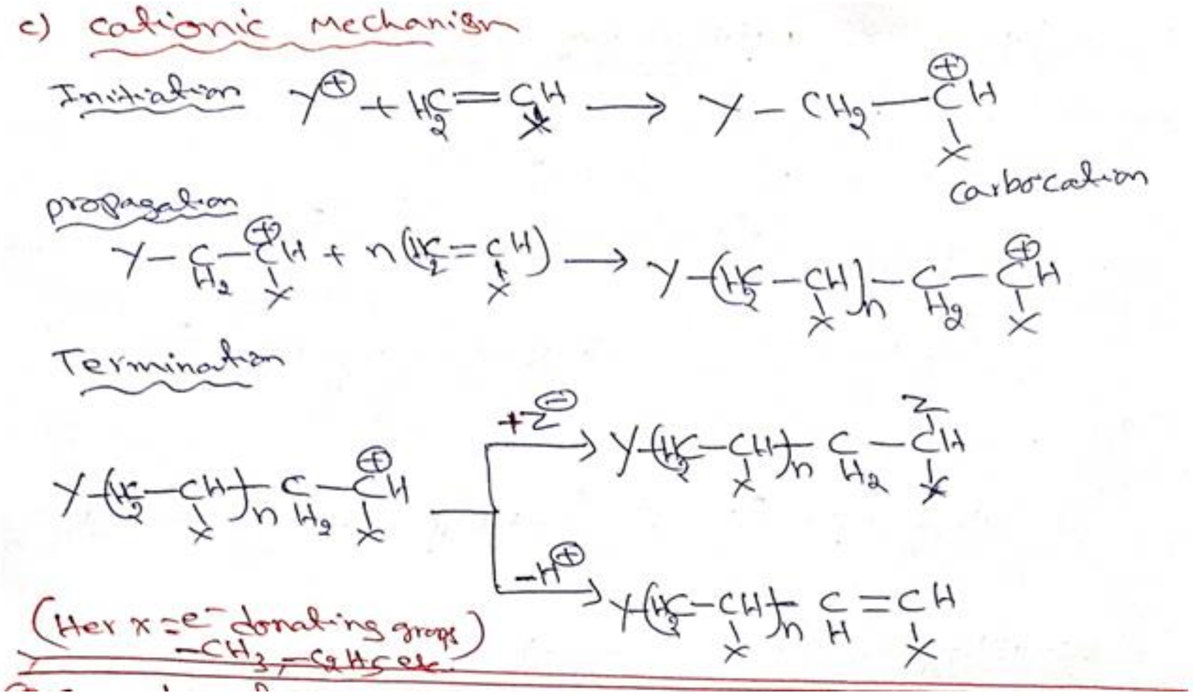
Termination



$Z-(\underset{H_2}{C}-\underset{X}{\underset{|}{CH}})_n-\underset{H_2}{C}-\underset{X}{\underset{|}{\overset{\ominus}{C}H}} \xrightarrow{+H^{\oplus}} Z-(\underset{H_2}{C}-\underset{X}{\underset{|}{CH}})_n-\underset{H_2}{C}-\underset{X}{\underset{|}{CH_2}}$

[Here X = electron withdrawing groups like −Cl, −CN etc.]

c) cationic Mechanism



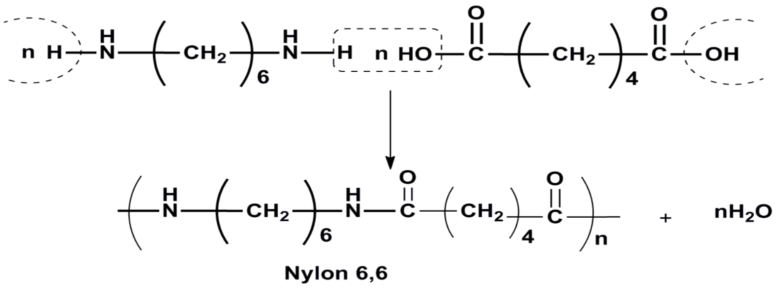
(Here x = e⁻ donating groups) $-CH_3$, $-C_6H_5$ etc.

2. **Condensation (or) Step-wise polymerization**: -

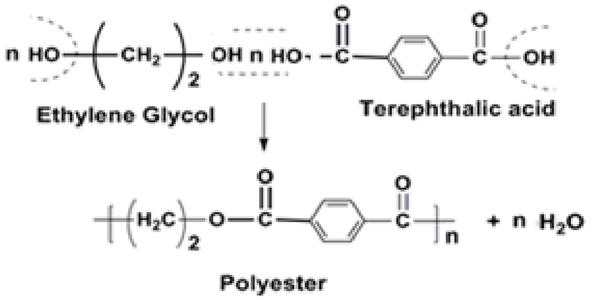
- Condensation (or) Step-wise polymerization is a reaction, in which the polymer is formed by step-wise reaction between different polar groups containing monomers.
- In which by-products like H_2O, HCl, NH_3 are eliminated.
- It forms linear (or) cross-linked polymers. Molecular weight of the polymer is not integral multiple of monomer.
- Examples of condensation polymerization are Nylon, Bakelite, and Urea– Formaldehyde resins.

Ex: Nylon 6:6

Nylon 6:6 polymer is prepared by condensation of hexamethylene di amine and adipic acid.

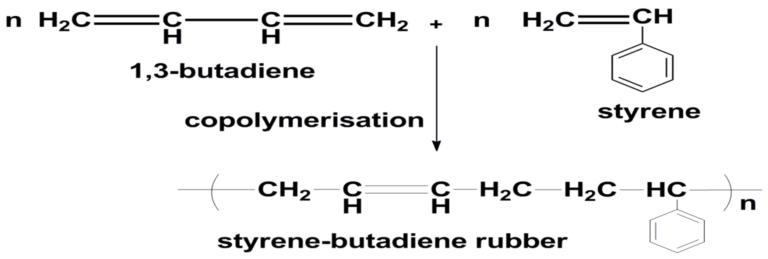


Ex: Polyester Polyester is prepared by condensation of ethylene glycol and terephthalic acid.



3. Co-polymerization:

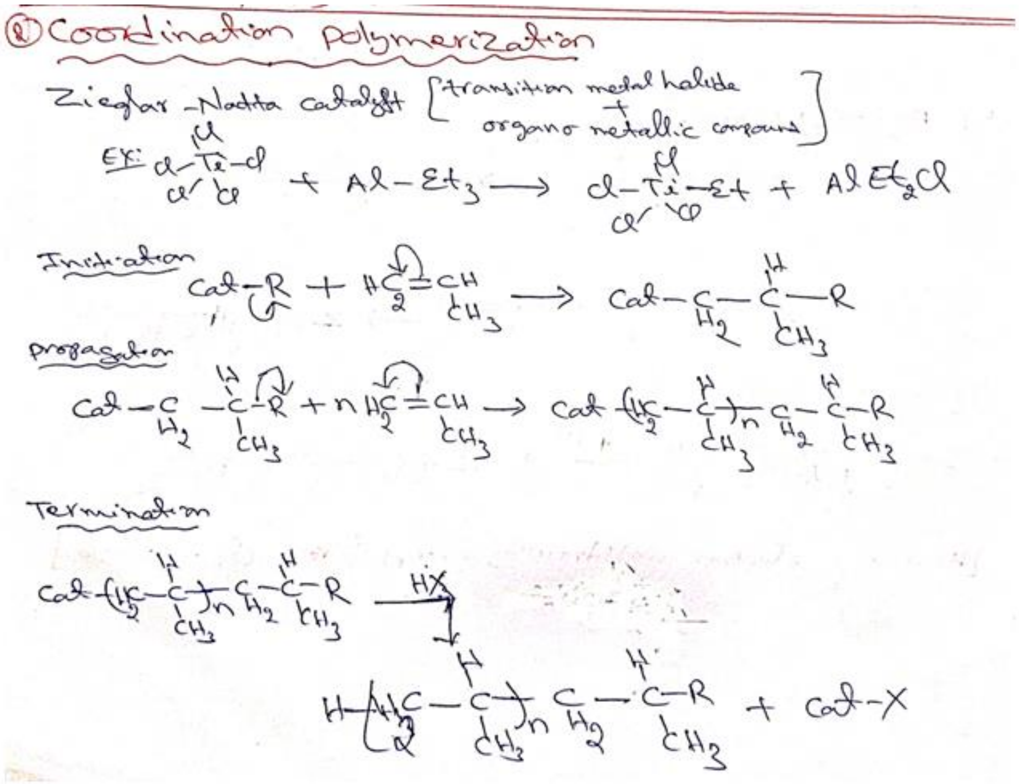
- Two (or) more different types of monomers undergo this type of polymerization.
- In this polymerization, without loss of any molecules polymer will be formed.
- The copolymers may be alternate, random, block and graft copolymers.



4) Coordination polymerization

Coordination polymerization is a type of polymerization in which monomers are polymerized through coordination with a metal catalyst.

Ziegler-Natta catalyst is the most commonly used metal catalyst used to prepare polyethylene, polypropylene etc., by coordination polymerization method. Ziegler-Natta catalyst is a combination of a transition metal halide (like $TiCl_4$, $TiCl_3$ etc.) with an organo-metallic compound (like triethyl aluminum or trimethyl aluminum). The advantages of coordination polymerization is that stereospecific polymers can be prepared by this method.



Plastics

Definition of Plastic: Plastics are high molecular weight of organic materials, which can be easily moulded into any desired shape, by the application of heat and pressure in the presence of a catalyst".

Properties of plastics (Advantages of plastics over other materials):

Plastics have mainly some properties. They are

1. Light in weight,
2. Low maintenance cost,
3. Good electrical insulation,
4. High corrosive resistance,
5. Easily moulding,
6. Good Strength and toughness etc.,

Disadvantages of plastics:

1. They have high softness,
2. They undergo embrittlement at low temperature,
3. They undergo deformation under load,
4. They undergo degradation upon exposure to heat and UV-radiation,
5. They are non-biodegradable.

Applications of plastics:

1. Making electrical goods,
2. Paints,
3. Radio and T.V parts, Water tanks etc.,

Classification of plastics:

Plastics can be classified mainly two types. They are

1. Thermoplastics,
2. Thermosetting plastics.

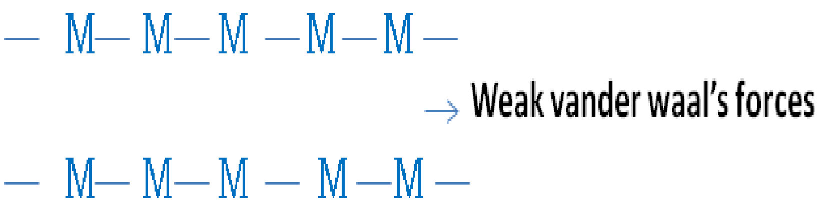


Fig: Thermoplastics

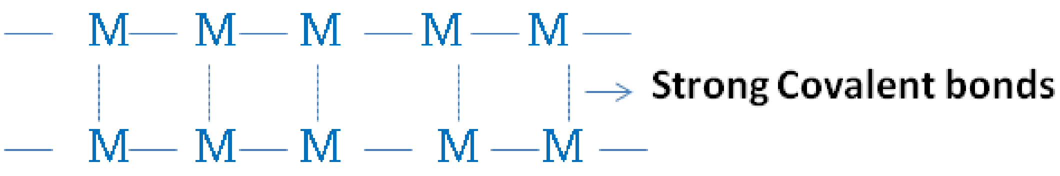


Fig: Thermosetting plastics

S. No	Thermoplastics	Thermosetting plastics
1.	They are formed by addition polymerization.	They are formed by condensation Polymerization.
2.	They consist of linear long chain polymers.	They consist of three-dimensional network structure.
3.	All the polymer chains are held together by weak Vander waal's forces.	All the polymer chains are linked by strong covalent bonds.
4.	They are soft, fusible and linear.	They are hard, non-fusible and cross-linked.
5.	They soften on heating and harden on cooling.	They do not soften on heating.
6.	They can be remoulded from wastes.	They cannot be remoulded wastes.
7.	They are soluble in organic solvents.	They are insoluble in organic solvents.
8.	Ex: Polyethylene, PVC, Poly Styrene etc.,	Ex: Bakelite, Urea-formaldehyde resin etc.,

Engineering applications and properties of PE, PTFE, PVC, Nylon and Bakelite:

(1) Teflon (or) Polytetraflouroethylene (or) PTFE:

Preparation

- Teflon is an example for Thermoplastic polymers.
- Teflon is prepared by addition polymerization of water emulsion of tetraflouoroethylene under pressure in the presence of benzoyl peroxide as catalyst.
- In First step, Tetraflouoroethylene (TFE) monomer is obtained by the following reactions.

$$\underset{\text{Chloroform}}{CHCl_3} \quad + \quad 2HF \longrightarrow \underset{\text{chlorodiflouro methane}}{CHClF_2} \quad + \quad 2HCl$$

$$2CHClF_2 \xrightarrow{\text{pyrolysis}} \underset{\text{TFE}}{F_2C{=}F_2C} \quad + \quad 2HCl$$

- In Second step, TFE undergoes polymerization and PTFE is obtained.

$$\underset{\text{TFE}}{n(F_2C{=}F_2C)} \longrightarrow \underset{\text{PTFE}}{\text{-----}(\text{--}F_2C-CF_2\text{--})_n\text{-----}}$$

Properties:

Teflon is a thermoplastic resin and has the following properties.

1. Excellent thermal stability & highly crystalline (93-98%),
2. Not soluble in any solvent,
3. Good electrical and mechanical properties.

Applications:

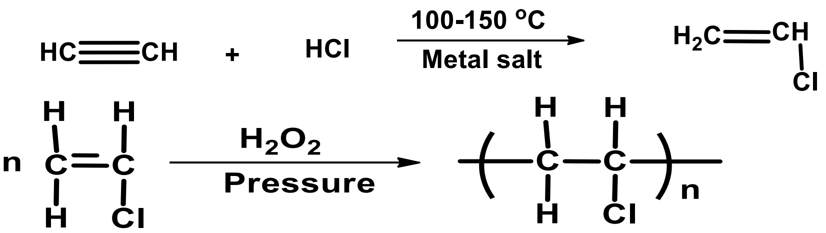
Teflon is used

1. for insulation of motors, generators, capacitors, transformers etc.,
2. for making stopcock of the burettes, non-lubricant bearings, chemical carrying pipes etc.,
3. for coating on articles like bakery trays, frying pans etc.,

(2) Polyvinyl Chloride (PVC):

Preparation:

- Polyvinyl chloride is obtained by the addition polymerization of vinyl chloride monomer units.
- Vinyl chloride is prepared by reacting acetylene with hydrogen chloride at $100-150^{0}$C in the presence of metal salt catalyst.



- PVC is prepared by heating a water emulsion of vinyl chloride in presence of benzoyl peroxide (or) hydrogen peroxide in a autoclave under pressure.

Properties:

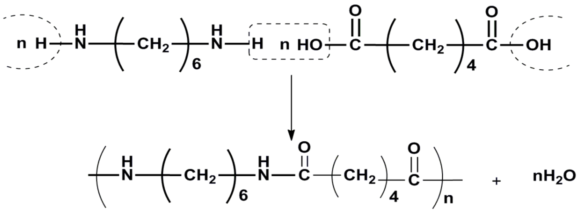
i. PVC is a colourless and odourless powder.
ii. It is non-inflammable and chemically inert.
iii. It is soluble in chlorinated hydrocarbons and ketones.
iv. It has high resistance to light, inorganic acids, alkalis and atmospheric oxygen.

Uses:

i. Plasticized PVC is used for making table cloths, raincoats, coatings for electric wire and cables, toilet articles, pipes, coupling valves etc.,
ii. Unplasticized PVC (or) rigid PVC is used for making refrigerator components, tubes, pipes.

(3) Nylon 6,6

Preparation: Nylon 6:6 is prepared by condensation polymerization of hexamethylene diamine and adipic acid.



Nylon 6,6

Properties of Nylon polymers:

1. Nylons polymers behave as plastic as well as fiber,
2. They have good mechanical properties,
3. They are insoluble in common organic solvents but soluble in formic acid and phenol,
4. They have high strength and abrasion resistance.

Uses of Nylon polymers:

1. Nylon-6,6 is used as fibre for making socks, dresses, carpets etc.,
2. Nylon polymers also used for making filaments for ropes, films, bristles of tooth brushes etc.,

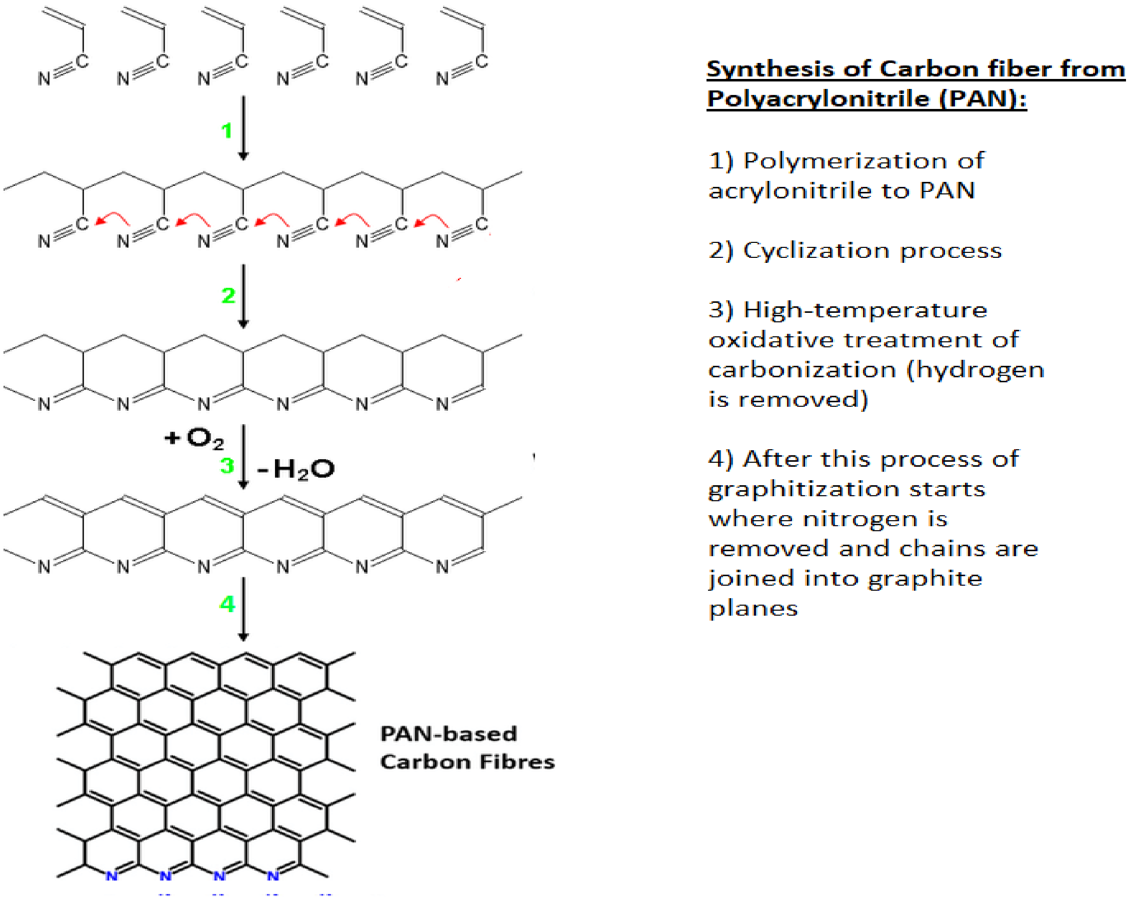
(4) CARBON FIBERS:

Carbon Fiber/carbon fibre is a polymer and is sometimes known as graphite fiber. Carbon fiber is a material consisting of thin, strong crystalline filaments of carbon, essentially carbon atoms bonded together in long chains. The fibers are extremely stiff, strong, and light, and are used in many processes to create excellent structural materials.

Properties:

- high in stiffness & high in tensile strength
- low weight to strength ratio
- high in chemical resistance
- temperature tolerant to excessive heat & low thermal expansion

Preparation: Carbon fiber is a material made from thin filaments of carbon atoms bonded together in a crystalline structure. The manufacture of carbon fiber material involves several complex steps. Most carbon fibers are produced using polyacrylonitrile (PAN) as the precursor.



Synthesis of Carbon fiber from Polyacrylonitrile (PAN):

1) Polymerization of acrylonitrile to PAN

2) Cyclization process

3) High-temperature oxidative treatment of carbonization (hydrogen is removed)

4) After this process of graphitization starts where nitrogen is removed and chains are joined into graphite planes

Applications: Carbon fiber and its reinforced composite materials are used to make racing car bodies, golf club shafts, bicycle frames, fishing rods, automobile springs, sailboat masts, aircraft parts, spacecraft parts and many other components where light weight and high strength are needed.

(5). Bakelite (or) Phenol – Formaldehyde resin:

- Bakelite is an example for thermosetting plastics. Bakelite is prepared by condensation polymerization of phenol and formaldehyde in presence of an acid (or) alkali catalyst. The reaction involves the following three steps.
- ***Properties:*** Bakelite is a hard, rigid infusible material and has excellent electrical insulating character. It is resistant to acids, salts and most organic solvents but attacked by alkali (because of presence of –OH groups).

Preparation:

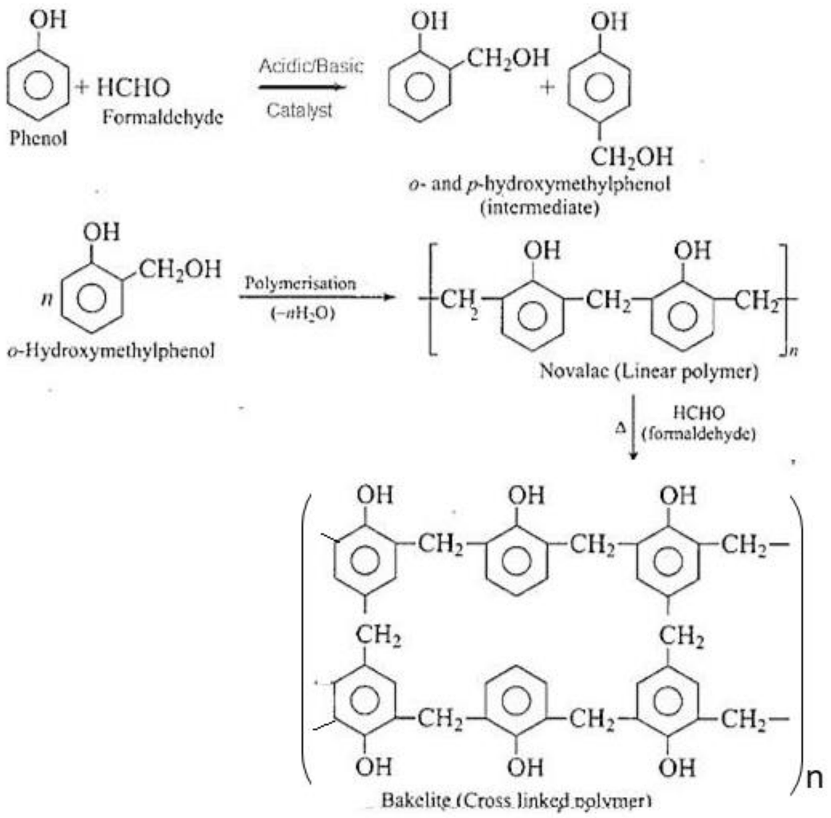
The preparation of phenol-formaldehyde resin involves two steps as follows:

1. Formation of ortho/para-(hydroxymethyl)phenol derivative

Initially the monomers combine to form ortho/para-(hydroxymethyl)phenol derivative depending upon phenol to formaldehyde ratio.

2. Formation of Novolac & Bakelite

The phenol formaldehyde derivatives react among themselves or with phenol to give a linear polymer called Novolac which upon heating to form a higher cross-linked polymer known as Bakelite.



Uses: Bakelite is used

1. For making electrical equipment like switches, plugs, holders, switch boards, heater handles etc.,
2. For making telephone parts, radio and T.V. cabinets,
3. In paints and varnishes,
4. For making bearings, propeller shafts in paper industry, rolling mills,
5. For the production of ion-exchange resins.

ELASTOMERS

Definition of rubbers (or) elastomers: Rubbers (or) elastomers are non-crystalline high polymers, having elastic properties.

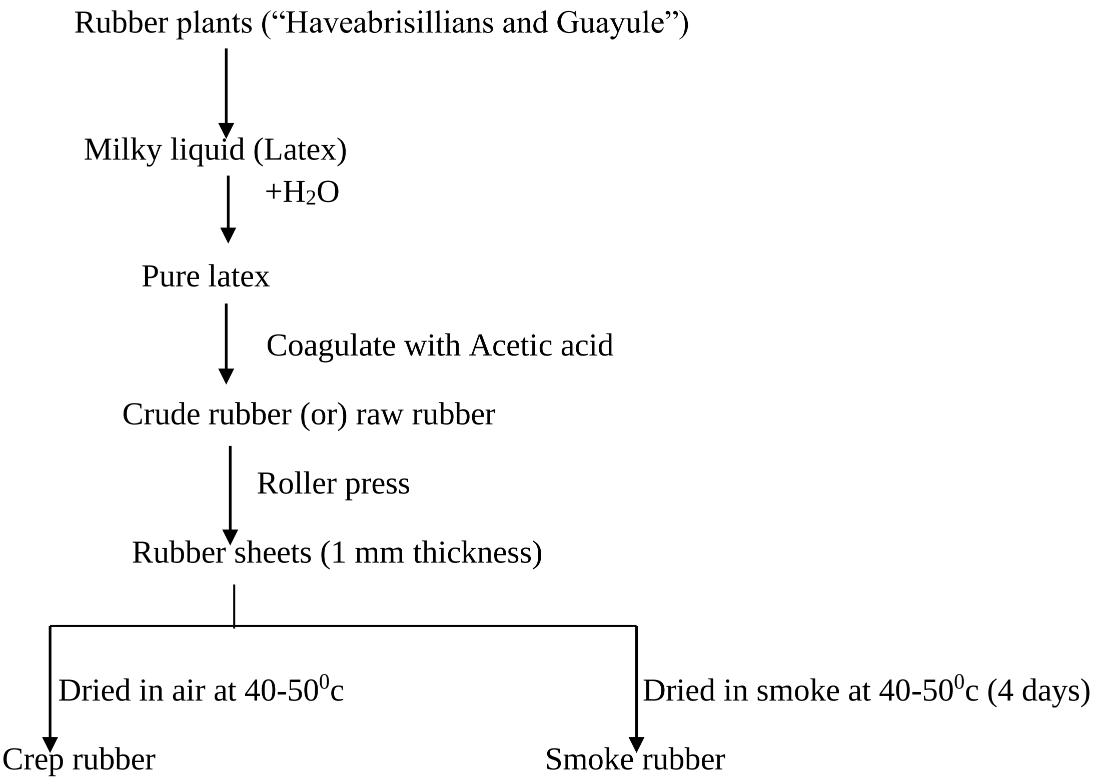
NATURAL RUBBER: n' moles of Isoprene (2-Methyl-1,3 Butadiene) monomer units undergo polymerization to produce big molecule called natural rubber.

$$n\ H_2C=\overset{CH_3}{\overset{|}{C}}-CH=CH_2 \longrightarrow \left[-H_2C-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-\right]_n$$

2-methyl-1,3 - butadiene (Isoprene)

Polyisoprene (Natural rubber)

Processing of Natural Rubber:



- Finally, smoke rubber sent to rubber factories for further processing.

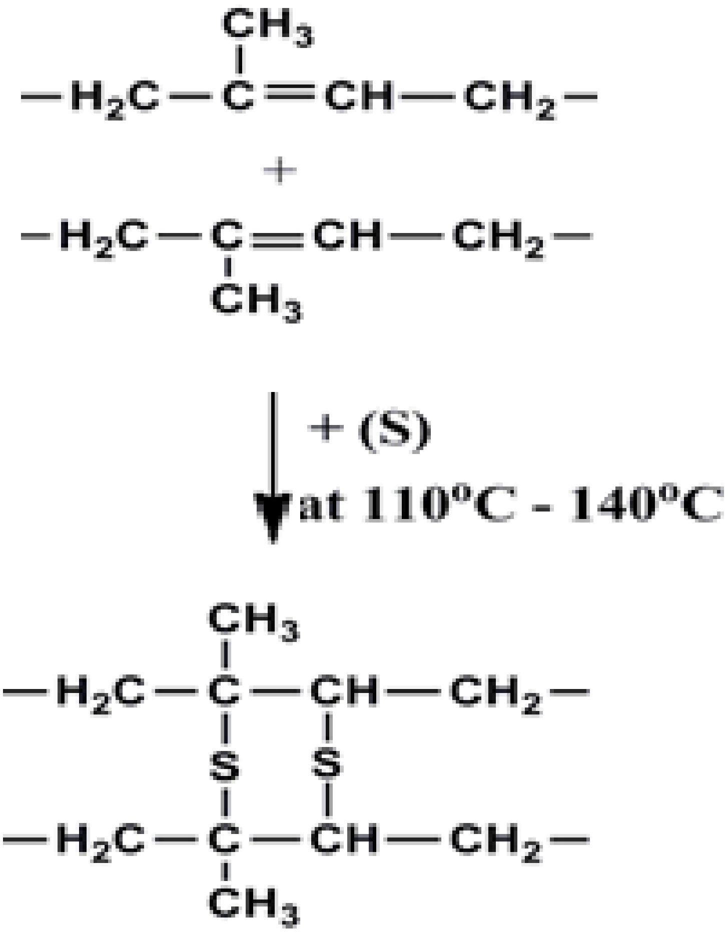
Draw backs of natural Rubber:

1. Natural rubber is plastic in nature, i.e., it becomes soft at high temperature and is too brittle at low temperatures.
2. Natural Rubber has very low tensile strength.
3. Natural rubber attacks easily by oxidizing agents,
4. Natural rubber swells considerably in organic solvents,
5. Natural rubber has large water absorption capacity,
6. Natural rubber has high elasticity,
7. Natural rubber has little durability.

All the above drawbacks of natural rubber can be rectified by the process of **vulcanization.**

Vulcanization of Natural Rubber:

- Charles Good year in 1839 discovered the vulcanization process.
- To improve the properties of natural rubber, adding sulphur to the raw rubber at 110-140^{0}c. In vulcanization process, the sulphur is chemically bonded between linear chains at the double bond and resulting the formation of three-dimensional network structures.
- The stiffness of vulcanization rubber depends on the amount of sulphur added.



Advantages of Vulcanization:

Vulcanized rubber has

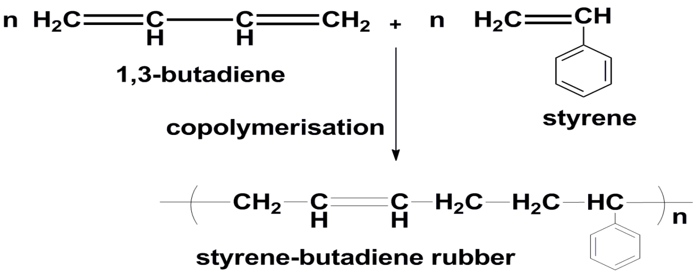
1. Useful temperature range is $40^0 – 100\ ^0C$.
2. Good tensile Strength,
3. Low water absorption capacity,
4. Higher resistance to oxidation,
5. Good durability,
6. Good resistant to swelling in organic solvents,
7. Good resistance to change in temperature.

SYNTHETIC RUBBER:

Buna –S (or) Styrene Rubber (or) GR –S Rubber:

Preparation:

- Buna – S Rubber is prepared by copolymerization of ‘n’ moles of 1,3 – butadiene and ‘n’ moles of styrene in the presence of sodium as a catalyst.



Properties:

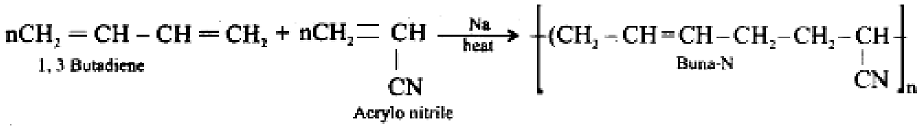
a. It possesses high abrasion resistance and high load bearing capacity
b. It easily oxidizes in presence of ozone atmosphere
c. It Swells in oils and solvents
d. It can be vulcanized in the same way as natural rubber

Applications:

Buna – S rubber is mainly used in manufacture of motor tyres, Shoe soles, Gaskets, floor tiles, adhesives, Wire and cable Insulations etc.,

Buna –N (or) Nitrile Rubber (or) GR –A Rubber:

Preparation: Buna – N Rubber is prepared by copolymerization of ‘n’ moles of 1,3 – butadiene and ‘n’ moles of styrene in the presence of sodium as a catalyst.



$$nCH_2=CH-CH=CH_2 + nCH_2=\underset{\substack{|\\ CN}}{CH} \xrightarrow[heat]{Na} \left[CH_2-CH=CH-CH_2-CH_2-\underset{\substack{|\\ CN}}{CH}\right]_n$$

Properties:

a. Because of presence of -CN group in the structure, BUNA-N possess excellent resistance to heat oils, acids and salts
b. It is a strong and tough polymer with light weight
c. It is highly resistant to atmospheric O_2, CO_2, moisture and U V light
d. It is an excellent electrical insulator
e. It can be vulcanized in the same way as natural rubber.

Applications:

a. BUNA-N is used for making conveyor belts, high altitude aircraft components and automobile parts.
b. Used for making tank linings and pipes for chemical industries.
c. It is used for making gaskets, oil resistant foams, adhesives and printing rollers

CONDUCTING POLYMERS:

- Generally, polymers like plastics, elastomers are regarded as insulators because of the presence of strong C-C covalent bond. But, under certain circumstance, polymers can be made to behave like a metal (conductor).

Reasons for the conduction in the polymer

a. Presence of unsaturated conjugated double bonds in the polymer
b. Addition (or) removal of electrons (doping) in to the polymer

Two important examples for conducting polymers are Polyaniline, Polyacetylene etc.,

Preparation of conducting polymers

Conducting polymers are mainly prepared by doping the polymers.

Doping

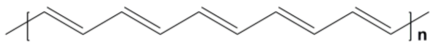
- To becoming electrically conductive, the electrons of the polymer need to be free to move.
- The polymers having conjugated double bonds has to be disturbed either by removing electron from polymer (or) inserting the electron into the polymer by oxidation (or) reduction. This process is called doping.

Types of doping

1. p-doping:
   - In p-doping, an intrinsically conducting polymer treated with Lewis acids (or) halogens, which oxidizes the polymers and creates positively charged sites on polymer back bone.
   - Due to the positive charge on the polymer backbone, they are acting as good conductors of electricity like metal. Ex., I_2, Br_2, $AlCl_3$ etc.,
2. n-doping:
   - In n-doping, an intrinsically conducting polymer treated with Lewis bases (or) alkali metals, which reduced the polymers and creates negatively charged sites on polymer back bone.
   - Due to the negative charge on the polymer backbone, they are acting as good conductors of electricity like metal. Ex., Na, K etc.,

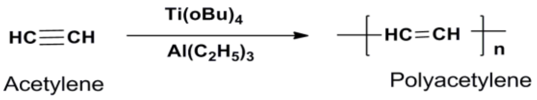
Important conducting polymers

1. Poly acetylene



Polyacetylene

Preparation: Polyacetylene is prepared by the addition polymerization of acetylene. Acetylene gas passed over the Zeigler-Natta catalyst to get polyacetylene. Polyacetylene is a infusible, insoluble and becomes brittle on expose to air.

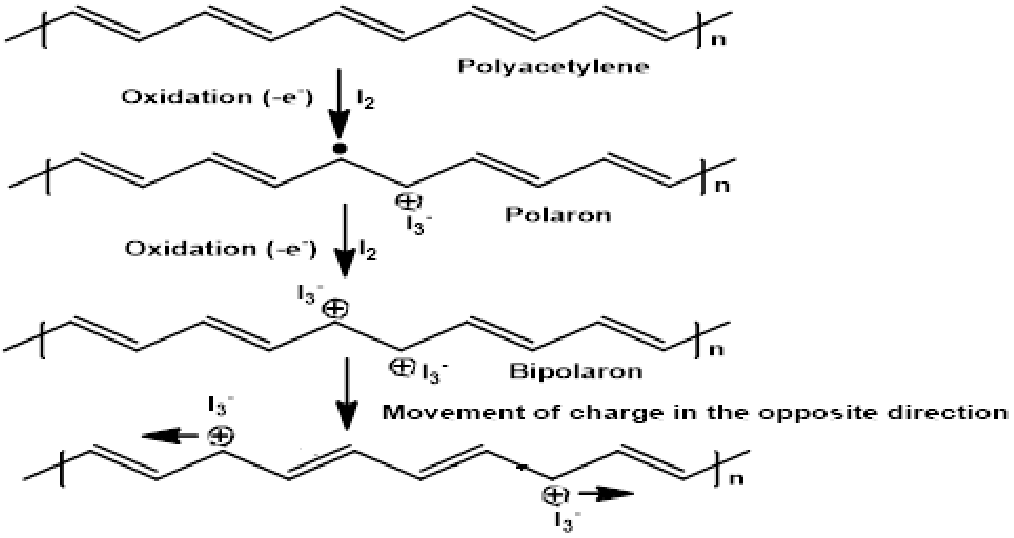


Mechanism of conduction (or) Synthesis of conducting polyacetylene:

The conductivity of polyacetylene can be improved by either p-doping or n-doping.

p-doping:

During oxidation, the Lewis acid (for example Iodine) remove electron from polyacetylene chain. Now the polyacetylene carrying the positive charge called ‘polaron’.

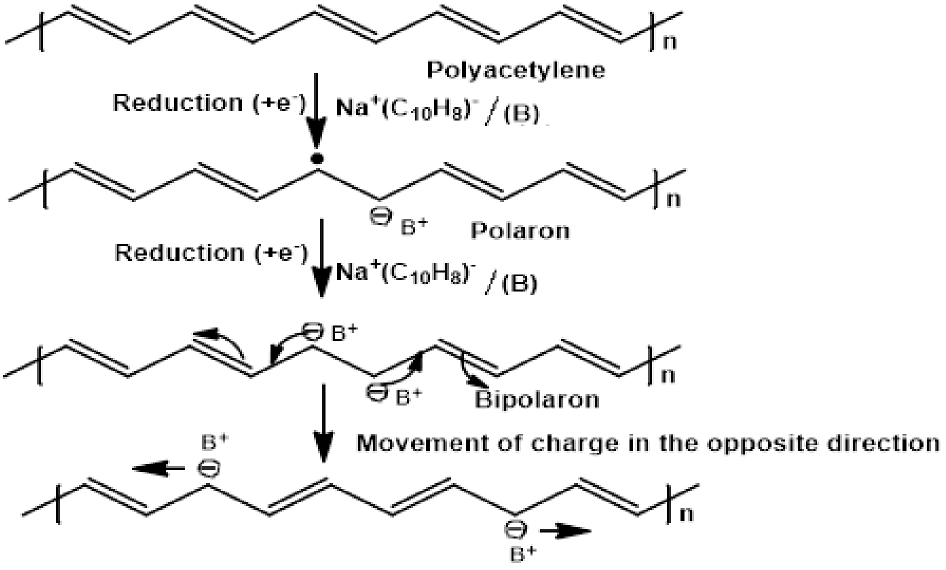


These positive charges are mobile because of delocalization and responsible for electrical conductance. Some of the common p-dopants used are I_2, Br_2, F_5, $FeCl_3$ etc.,

n-doping:

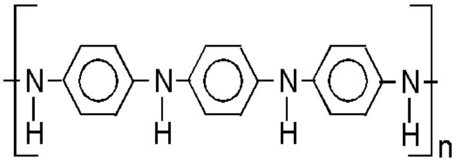
During reduction, the Lewis base (for example sodium naphthalide) donates an electron to polyacetylene chain.

Now the polyacetylene carrying the negative charge called ‘polaron’.



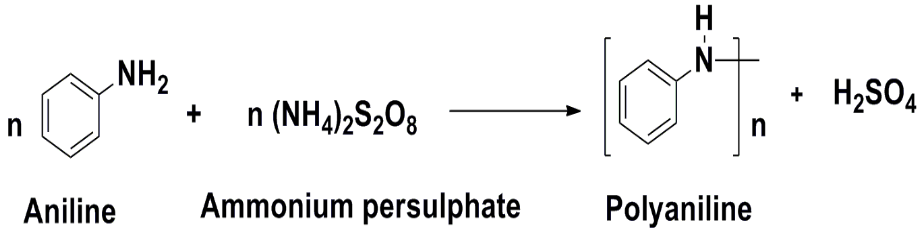
These negative charges are mobile because of delocalization and responsible for electrical conductance. Some of the common n-dopants used are Li, Na, Ca, Naphthylamine etc.,

2. Polyaniline



Preparation

- Polyaniline exists in a variety of forms that differ in chemical and physical properties. The most common green protonated emeraldine has conductivity.
- Polyaniline is a transparent and stable material. It shows green colour in conducting state. It turns to red under reducing condition and blue under oxidizing condition.
- It is prepared by the slow addition of aqueous solution of ammonium per sulphate to a solution of aniline in aqueous HCl at lower temperature (0-5^{0}C). The precipitate formed is separated by filtration, which is emeraldine salt (emeraldine hydrochloride).



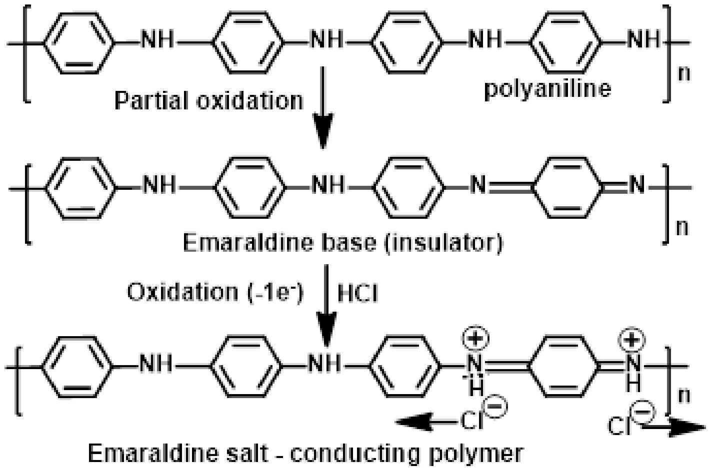
Mechanism of conduction (or) Synthesis of conducting polyaniline:

The conductivity of polyaniline can be improved by either p-doping (or) n-doping.

p-doping: It involves the following two steps.

Step 1: Step 1 involves partial oxidation of polyaniline to emaraldine base, which is non-conductive as shown in the reaction 1.

Step 2: Step 2 involves oxidation of emaraldine base using Lewis acid like HCl to **emaraldine salt**, which is a conducting polymer. During oxidation HCl removes electron from polyaniline chain and creates positive charge on the polymer back bone, which is responsible for conduction.



Application of conducting polymers:

Conducting polymers are lighter than metallic conductors. They are used in

i. Solar cells, photovoltaic devices,
ii. Telecommunication systems,
iii. Used as film membranes for gas separations,
iv. Wiring in aircrafts and aerospace components,
v. Electronic devices such as transistors and diodes,
vi. As electrode material in rechargeable batteries.
vii. Polyaniline is used in Sensors, Printed Circuit Boards, Conductive fabrics etc.,
viii. Polyaniline is used as a secondary electrode in rechargeable batteries.

BIODEGRADABLE POLYMERS

Those polymers which degrade by the enzymatic action of naturally occurring microorganisms or bacteria are called biodegradable polymers.

Biodegradable polymers are classified as 2 types:

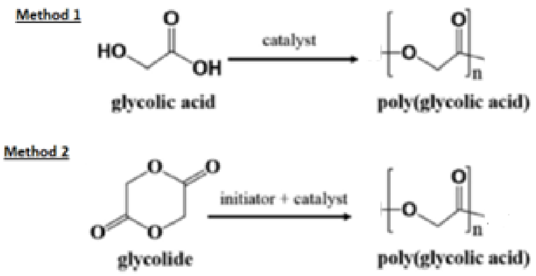
a) Naturally occurring biodegradable polymers: Strach, Cellulose, Silk, Lignin, Collagen, polylactide, polycaprolactone, Natural rubber are the examples for naturally occurring biodegradable polymers.

b) Synthetic biodegradable polymers: The polymers which are produced from chemicals or biological sources, that are biodegradable are known as synthetic biodegradable polymers.

Ex: Poly Lactic Acid (PLA), Poly Glycolic Acid (PGA), Poly Vinyl Acetate (PVA)

a) Poly Glycolic Acid (PGA)

Preparation:

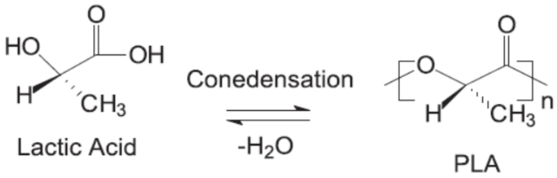


Properties: PGA is unstable to water, due to presence of the ester group linkage in its backbone. It is insoluble in almost all organic solvents. However, polyglycolide is soluble in highly fluorinated solvents like hexafluoroisopropanol (HFIP).

- **Applications:** PGA is widely used in the manufacturing of absorbable surgical sutures.
- Due to its biocompatibility and biodegradability, PGA is employed in tissue engineering applications.
- PGA is used in the development of drug delivery systems.
- PGA has been investigated for use in medical implants, such as screws and pins, as it can provide temporary support or fixation and then gradually degrade as the healing process progresses.
- PGA has been used in the production of biodegradable golf balls.
- PGA is employed in research and development as a model polymer due to its well-defined structure and predictable degradation characteristics.

b) Poly Lactic Acid (PLA)

Preparation:



Properties: PLA is Chiral compound existing as poly *l*-lactic acid. It possesses good biocompatibility, high strength.

Applications:

- PLA is commonly used for the production of food containers, cups, and films.
- PLA-based bags are used for shopping, waste disposal, and other purposes.
- PLA is employed in the production of controlled-release drug delivery systems.
- PLA is used to manufacture absorbable surgical sutures.
- PLA films can be used as mulch in agriculture, providing weed control and moisture retention while eventually breaking down into natural components.
- PLA is a popular material for 3D printing & also used in the production of textiles.
- PLA is used in the manufacturing of casings for electronic devices and components.
- PLA-based materials are used to create a variety of consumer goods, including toys, stationery, and packaging for electronics.
- PLA has been explored for use in dental implants and scaffolds.
- PLA coatings can be applied to paper and cardboard to enhance their barrier properties.
- PLA films are used in various applications, including wrapping and sealing for food products.