UNIT-1

Q.1 What are the main postulates of MOT.

Ans: 1. Atomic orbitals of comparable energy and proper symmetry combine together to form molecular orbitals.

2. The movement of electrons in a molecular orbital is influenced by all the nuclei of combining atoms. (Molecular orbital is poly centric in nature)

3. The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals (AO's) combine together two molecular orbitals (MO's) are formed. One molecular orbital possess higher energy than corresponding atomic orbitals and is called anti bonding molecular orbital (ABMO) and the other has lower energy and is called bonding molecular orbitals (BMO).

4. In molecules electrons are present in molecular orbitals. The electron filling is in accordance with **Pauli's exclusion principle**, **Aufbau principle** and **Hund's rule**.

Q 2. Draw the MO diagram of O_2 calculate the bond order and predict the magnetic behaviour.

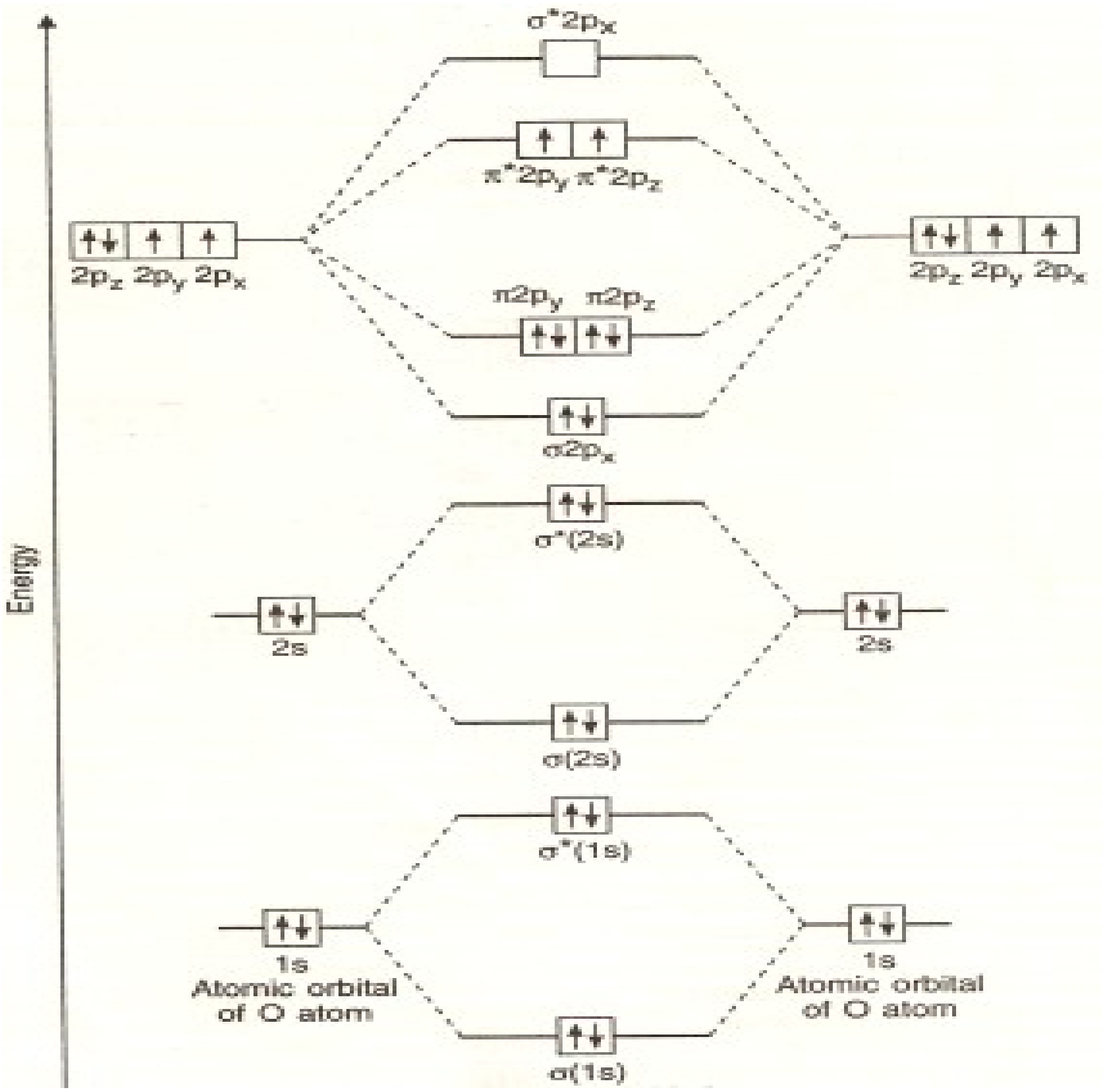
Ans:

Oxygen molecule, O_2 : Each oxygen atom has 2+6=8 electrons. Thus O2 molecule contains a total of 16 electrons. These are arranged as

$$\sigma 1s^2, \sigma{*}1s^2, \sigma 2s^2, \sigma{*}2s^2, \sigma 2p_x^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi{*}2p_y^1 \\ \pi{*}2p_z^1 \end{cases}$$

The presence of unpaired electrons in $\pi{*}2p_y$ and $\pi{*}2p_z$ give rise to paramagnetism.

B.O. of O2 = ½ (8-4) = 2



Q3. Draw the MO diagram of NO calculate the bond order and predict the magnetic behaviour.

1) <u>Nitric oxide molecule, NO:</u> The nitrogen atom has 2 + 5 = 7 electrons and the oxygen atom has 2 + 6 = 8 electrons, making 15 electrons in the molecule. The order of energy levels of the various MO's are the same as for homonuclear diatomic molecules heavier than C_2.

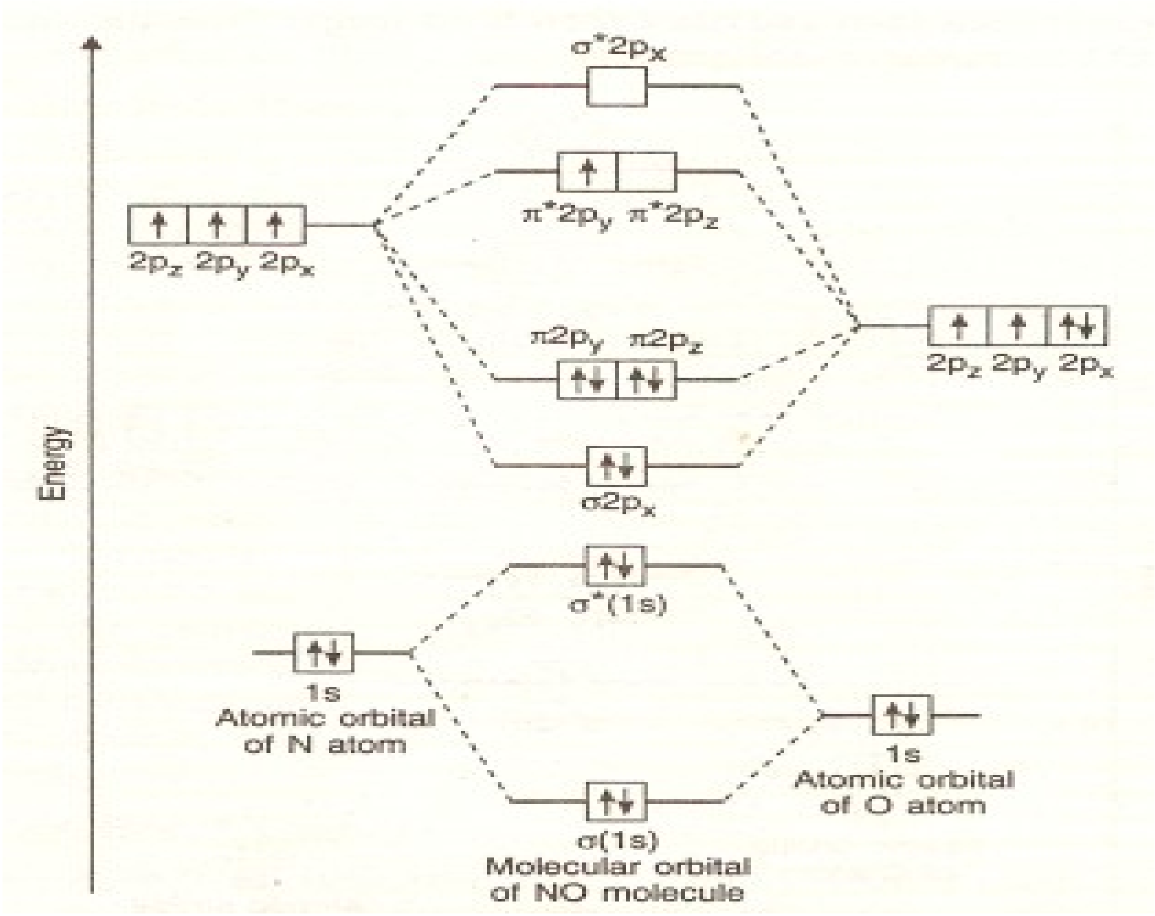
The arrangement is :

$$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_x^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi^*2p_y^1 \\ \pi^*2p_z^0 \end{cases}$$

B.O. = ½ (8 – 3)

= 2.5 Hence molecule exists.

The molecule is **paramagnetic,** since it contain an unpaired electron in π*2py or π*2pz orbital.



Q 3. Draw the MO diagram for N2 molecule.

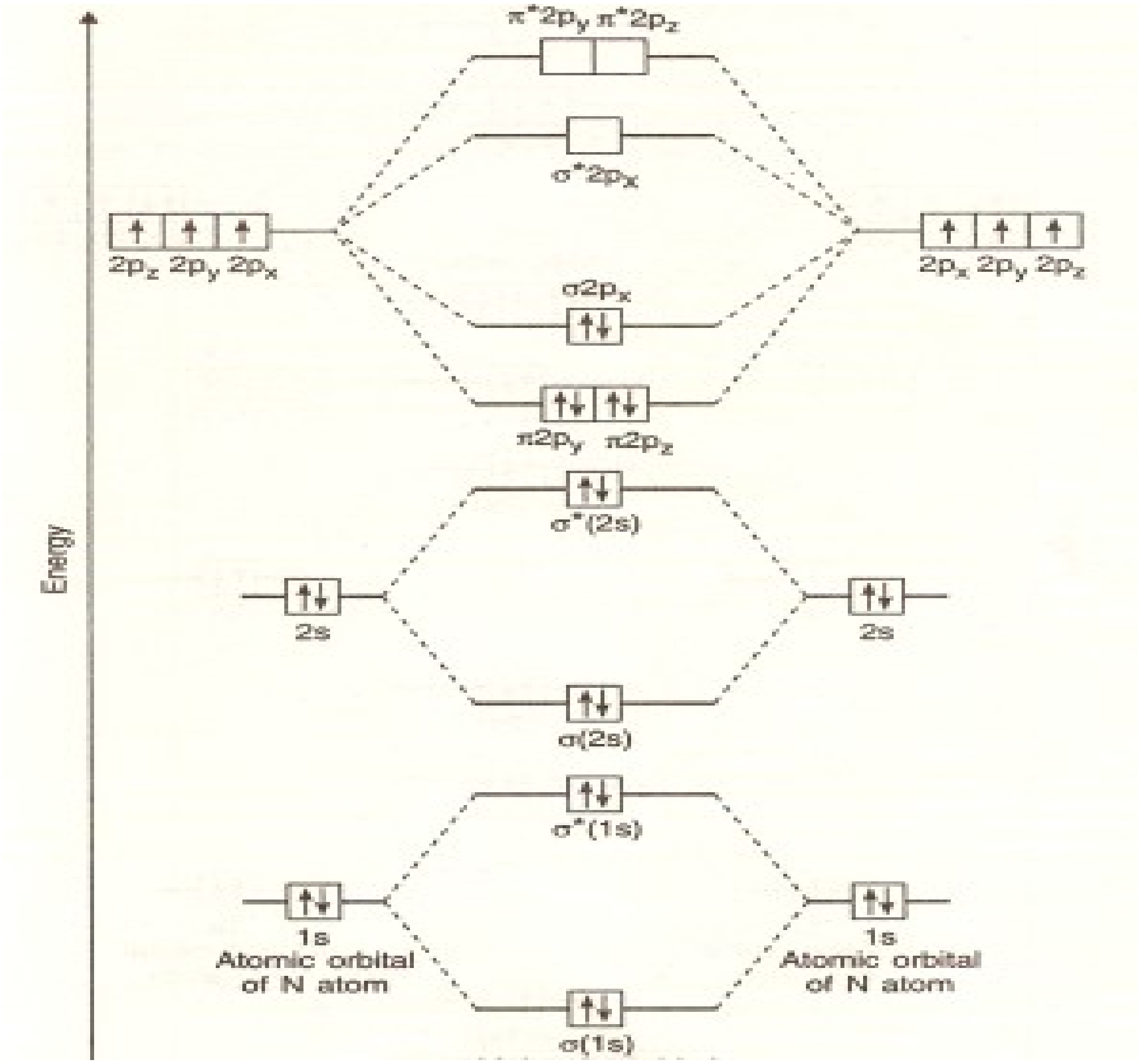
Nitrogen Molecule, N_2 : A Nitrogen atom has 2+5=7 electrons. Thus, the N_2 molecule contains 14 electrons. These are arranged as

$$\sigma 1s^2, \sigma{*}1s^2, \sigma 2s^2, \sigma{*}2s^2, \begin{cases} \pi\, 2p_y^2 \\ \pi\, 2p_z^2 \end{cases}, \sigma 2p_x^2 .$$

There are eight and two electrons in the bonding molecular orbital respectively.

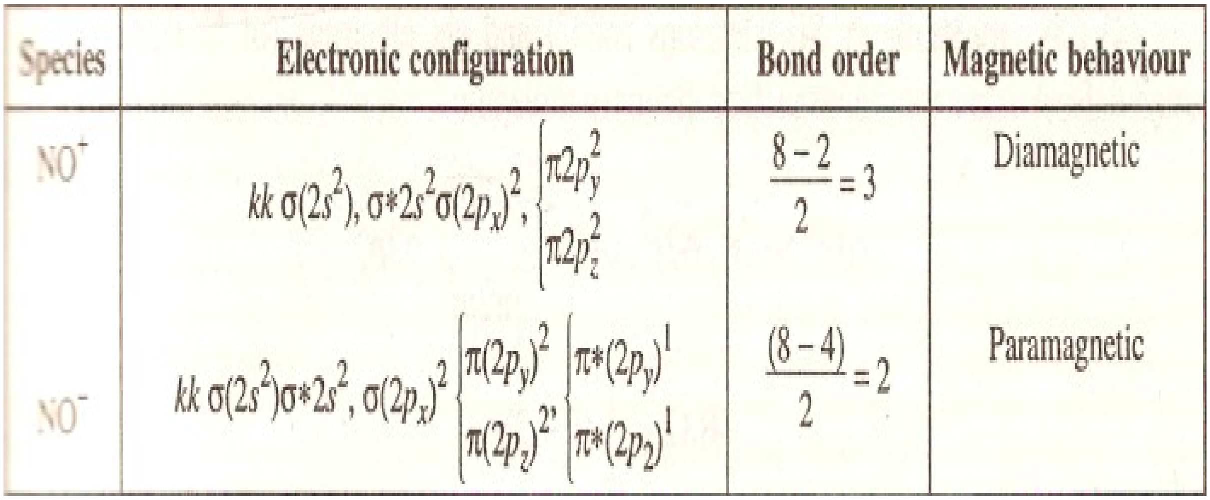
Bond order of N_2 = ½ (8-2) =3

The N2 molecule is diamagnetic as it has no unpaired electron



Q4 . Find out the bond order and magnetic behaviour of NO+ and NO-.

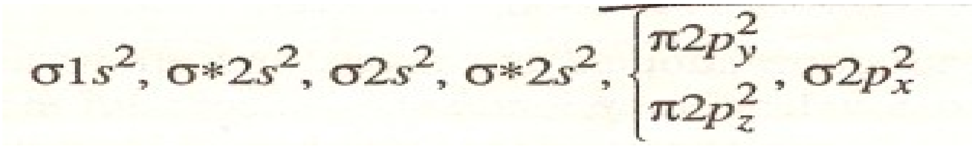
<u>Ans:</u> **<u>NO+ and NO- Ions:</u>** The electronic configuration, bond order and magnetic character of these ions are :



Species	Electronic configuration	Bond order	Magnetic behaviour
NO^+	$kk\ \sigma(2s^2), \sigma{*}2s^2\sigma(2p_x)^2, \begin{cases}\pi 2p_y^2 \\ \pi 2p_z^2\end{cases}$	$\frac{8-2}{2}=3$	Diamagnetic
NO^-	$kk\ \sigma(2s^2)\sigma{*}2s^2, \sigma(2p_x)^2 \begin{cases}\pi(2p_y)^2 \\ \pi(2p_z)^{2'}\end{cases} \begin{cases}\pi{*}(2p_y)^1 \\ \pi{*}(2p_z)^1\end{cases}$	$\frac{(8-4)}{2}=2$	Paramagnetic

Q 5. Draw the MO diagram of CO. Calculate its bond order.

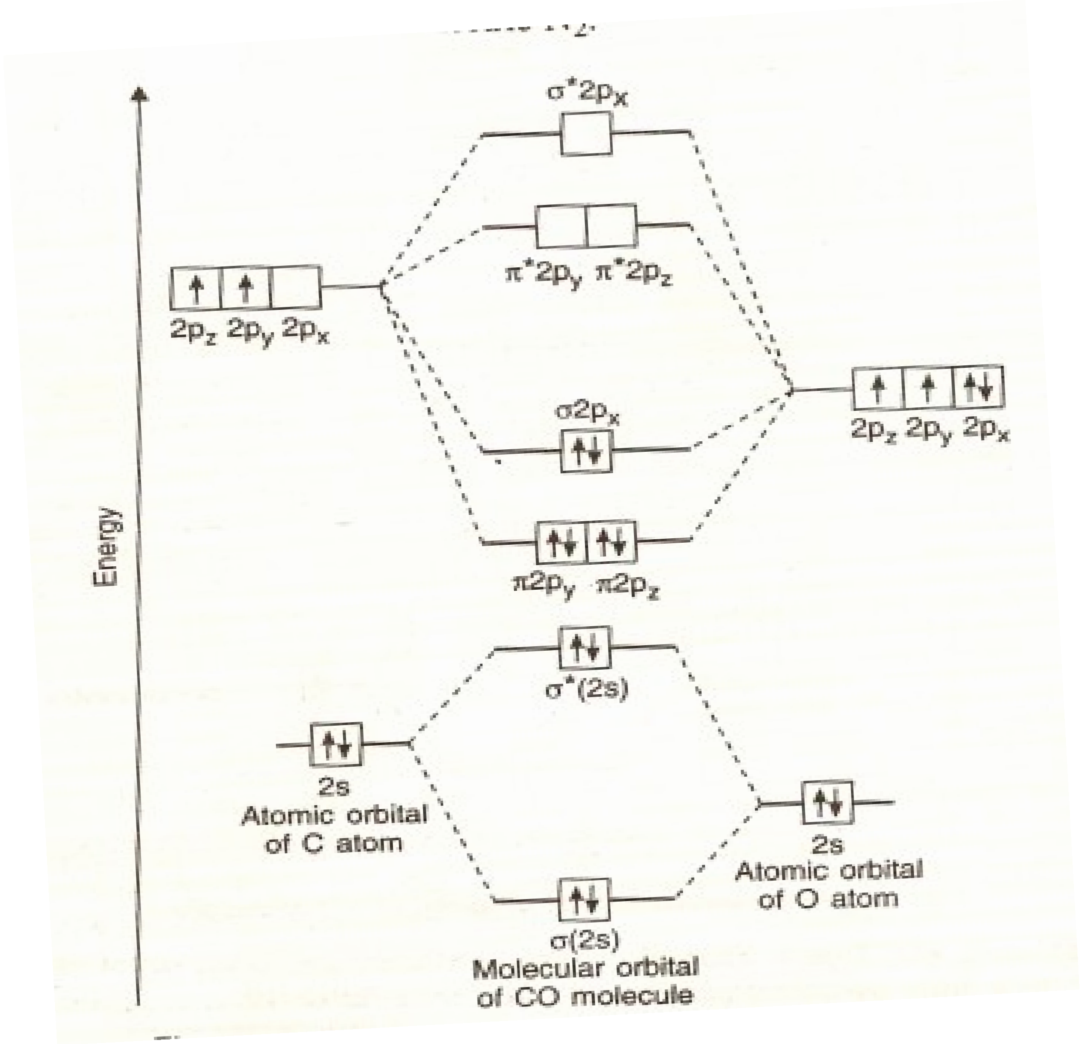
Ans: The carbon atom has 2 + 4 = 6 electrons and the O atom has 2 + 6 = 8 electrons, so the CO molecule contains 14 electrons. The order is the same as for light atoms like C



$$\sigma 1s^2, \sigma{*}2s^2, \sigma 2s^2, \sigma{*}2s^2, \begin{cases}\pi 2p_y^2 \\ \pi 2p_z^2\end{cases}, \sigma 2p_x^2$$

B.O. = ½ (8 – 2) = 3.0

Hence Molecule exists with a triple bond.



Q 6. What is metallic bond? Write down the characteristics of metals.

Ans: Definition : It may be defined as,

1. The force that binds a metal ion to a number of electrons with in its sphere of influence.
2. The attractive force which holds the atoms of two or more atoms together in a metal crystal or in an alloy.
3. A bond which is formed between electropositive elements

Characteristics of Metals :

1. They Crystallize with close packing forming bcc or fcc lattice or hexagonal close packed lattice.

2. They are good conductors of electricity and electrical conductivity decreases with temperature.
3. They are good conductors of heat.
4. They are ductile and malleable.
5. They have high densities, melting and boiling points.
6. They possess the metallic lusture.
7. They are hard and have high elasticity.
8. They form alloys with other metals easily.
9. Most metallic properties remain even when the metal is in the liquid state.

Q 7. Discuss in detail the band theory of metals.

Ans: Explanation : Molecular orbital theory extended to solids is referred as Band Theory.

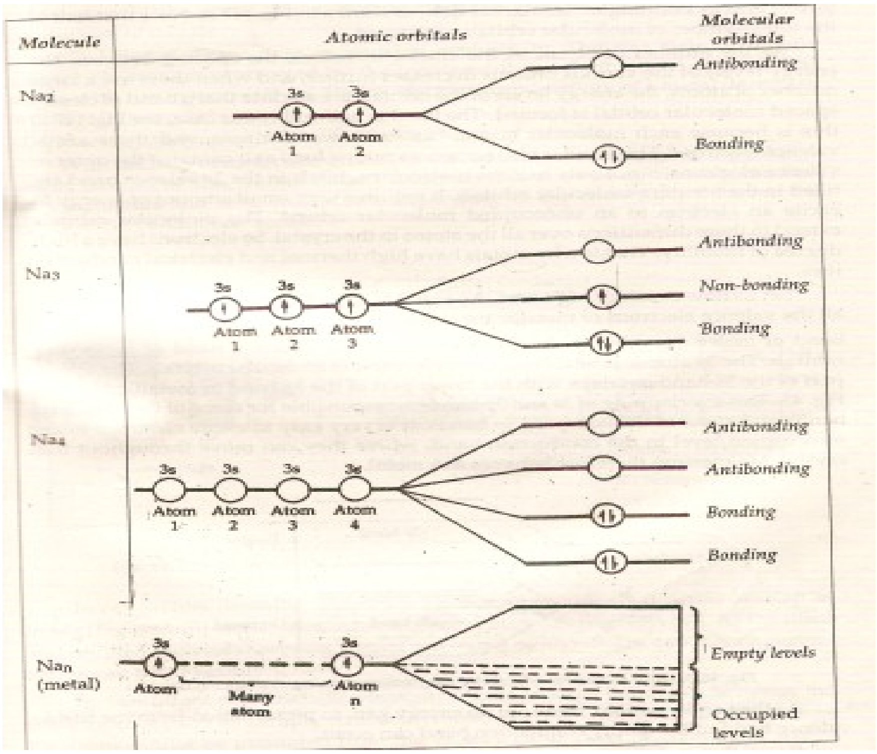
Example : Construction of a crystal of a sodium metal by adding Na atoms one at a time forming first Na_2 than Na_3, Na_4 ,Na_n respectively.

In Na_2 molecule, each Na-atom has electronic configuration [Ne] $3s^1$, with a single 3s valence electron. Two 3s-atom orbitals, one from each Na-atom, overlap to form two molecular orbitals σ (3s) and σ *(3s). There are just two valence electrons, which will occupy lower energy bonding molecular orbital σ (3s). The antibonding molecular orbital σ* (3s) is vacant.

Three Na atoms joined to form Na_3. Three 3s atomic orbitals would combine to form three molecular orbital one bonding, one nonbonding and one antibonding. The energy of the non-bonding MO is between that for the bonding and antibonding orbitals. The three valency electrons from the three sodium atoms would occupy the bonding and non-bonding molecular orbitals .

In Na_4, the four atomic orbitals would form four molecular orbitals-two bonding, and two anti-bonding. The four valence electrons would occupy the two lowest energy bonding molecular orbitals, half of the total number of molecular orbitals are vacant.

As the number of atoms in the cluster increases, the spacing between the energy levels of the various orbitals decreases further, and when there are a large number of atoms, the energy levels of the orbitals are so close that a band of closely spaced molecular orbital is formed. The band is half-full because each molecular orbital can hold two electrons, and there are N valence electrons. This band is also known as *valence band* as it contains the outer or valence electrons. The empty band is known as conduction band. Since only half the molecular orbitals in the 3s valence band are filled in the bonding molecular orbitals. It requires very small amount of energy to excite an electron to an unoccupied molecular orbital. The molecular orbitals extend in there dimensions over all the atoms in the crystal. So electrons have a high degree of mobility. That is why metals have high thermal and electrical conductivities.



Q 8. Expalin the properties of metals based on the band theory.

Ans: Explanation of Metallic Properties

(a) *Electrical conduction :* In metals, molecular orbitals extend in three dimensions over all the atoms and electrons have a high degree of mobility. In the absence of an electric field, equal number of electrons will move in all directions but in the presence of electric field, electrons readily move towards anode and hence electric current flows.

(b) *Thermal conduction:* The mobile electrons gain energy from the heated end and move to an unoccupied molecular orbital where they can travel rapidly to colder part of the metal. Thus, mobile electrons account for the high thermal conduction of metals**.**

(c) *Effect of Temperature on electrical conductivity :* The free flow of mobile valence electrons is obstructed by the increased thermal vibrations of the metal atoms with rise in temperature. Hence, electrical conductivity of a metal decreases with rise in temperature.

Q 9. With the help of Band theory, differentiate between conductors, insulators and semi-conductors?

Ans: With the help of Band theory, we can classify materials into three categories viz. conductors, insulators and semi-conductors, depending on the energy gap between the valence and conduction bands.

In conductors (metallic), either the valence and conduction bands overlap or the valence band is only partly full.

In Insulators (non-metallic elements), there is large band gap between the filled valence band and empty conduction band as in diamond. Therefore Electrons cannot qe promoted from the valence band to conduction band where they could move freely.

Semiconductors are of the types, intrinsic and extrinsic semiconductors. Intrinsic semiconductors (like Si or Ge) are having small energy gap between the filled valence band (VB) and empty conduction band (CB) sufficient to promote an electron from VB to CB. The hole left in the VB and the promoted electron in the CB both contribute towards conductivity.

Q 10. What is hybridisation?

Ans: **Definition:** The phenomenon of mixing up of atomic orbitals of similar energies and formation of equivalent number of entirely new orbitals of identical shape and energy is known as "hybridization" and the new orbitals so formed is called as "hybrid orbitals".

Important points for understanding the hybridization:

(i) The number of hybrid orbitals generated is equal to the number of pure atomic orbitals that participate in hybridization process.

(ii) Hybridization concept is not applicable to isolated atoms. It is used to explain the bonding scheme in a molecule.

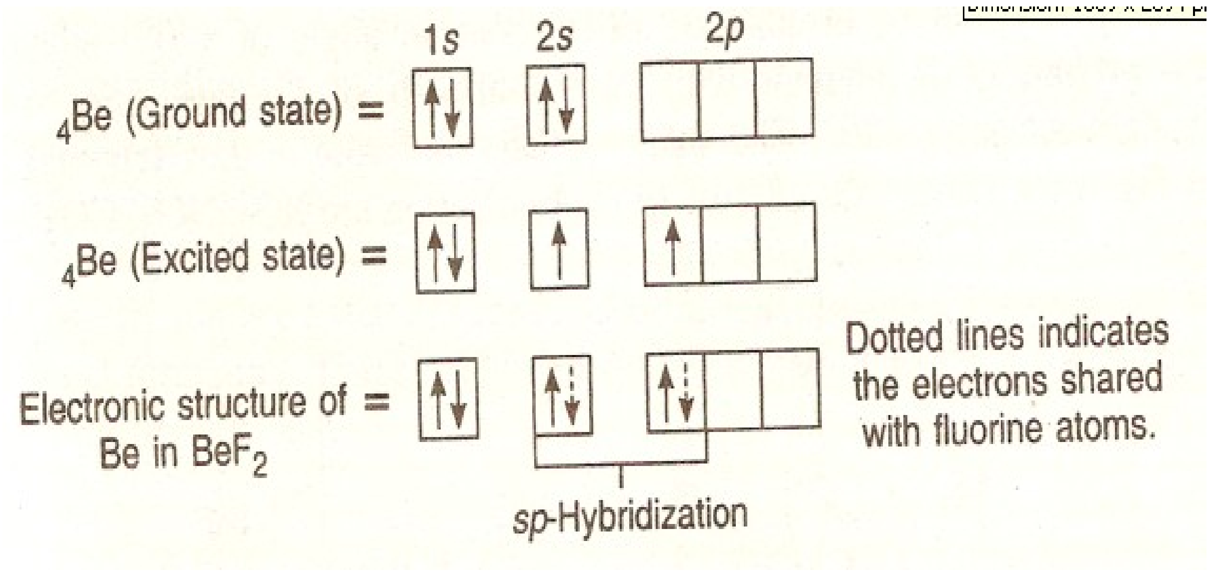
(iii) Covalent bonds is polyatomic molecules are formed by the overlap of hybrid orbitals or of hybrid orbitals with unhybridized ones.

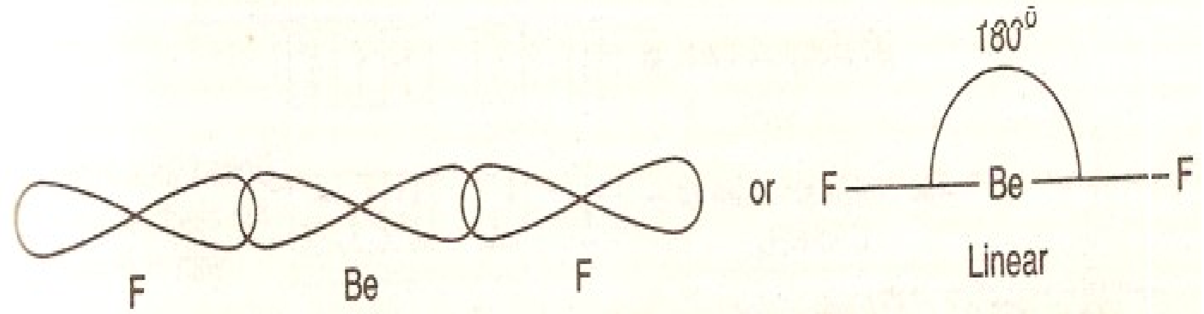
Q 11.. Discuss in detail sp, sp2 and sp3 hybridization with example.

Ans: sp-hybridization: The combination of one s and one p-orbitals to form two hybrid orbitals of equal energy is known as sp-hybridization.

Example: In BeF_2 Molecule the sp-hybridized orbitals of Be overlap with the half-filled orbitals of two fluorine atoms to give a **linear shape.**

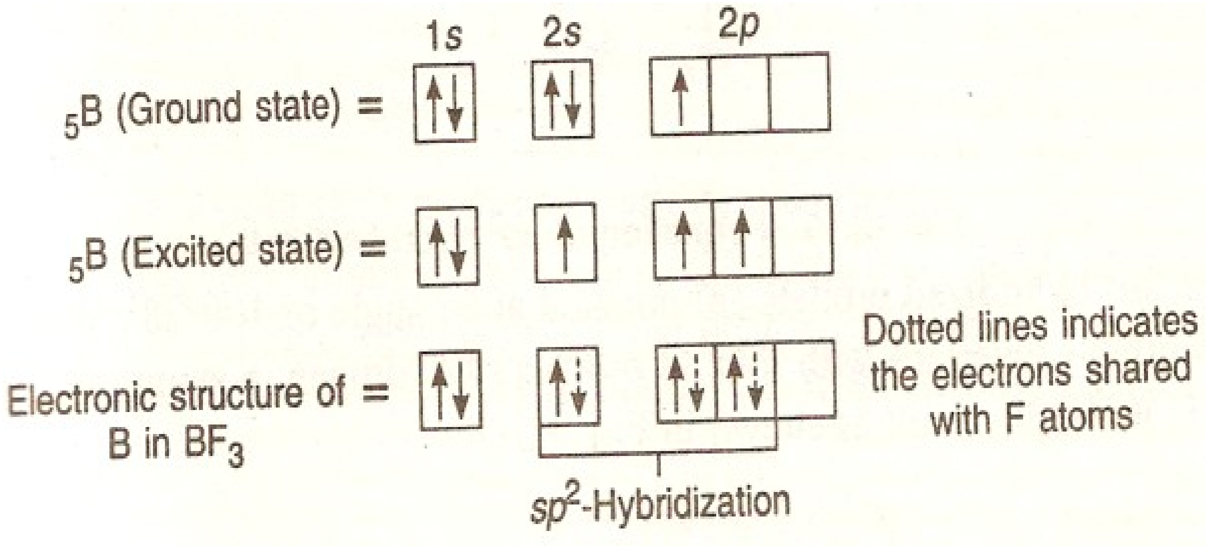
Structure of BeF_2 Molecule



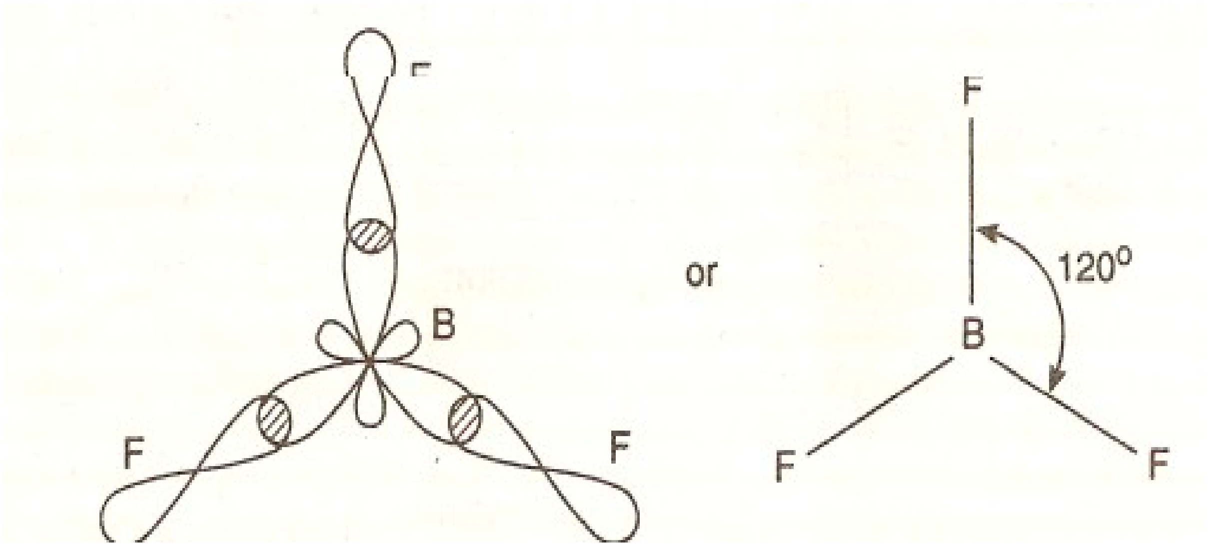


sp^2-hybridization: The combination of one s and two p-orbitals to form three hybrid orbitals of equal energy is known as sp^2-hybridization.

Example : BF_3 Molecule

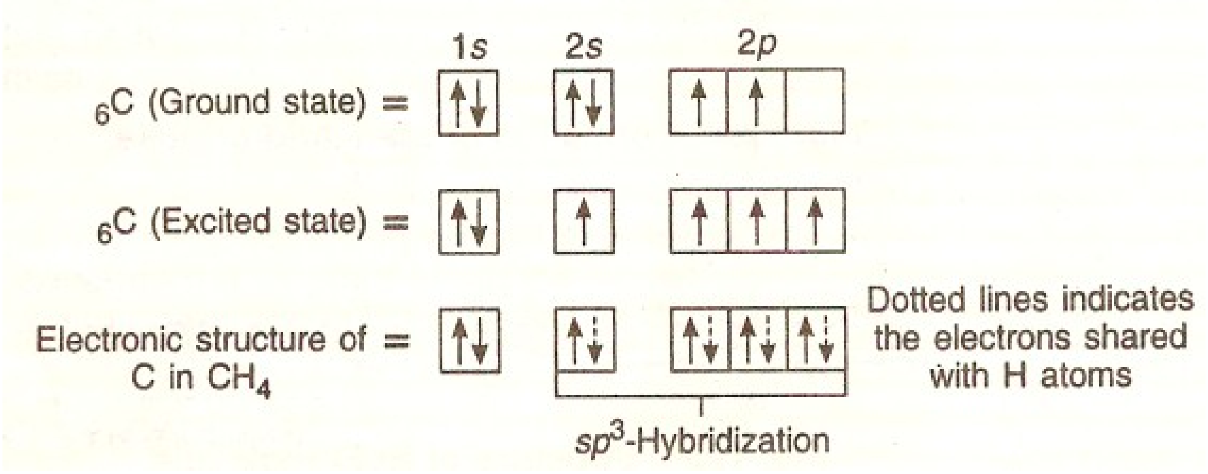


These sp2 hybridized orbitals are oriented at an angle of 120°. When three sp2 hybridized orbitals of B overlaps with three p-orbitals of fluorine, three σ -bonds are formed with bond angle 120°. The shape of BF3 molecule is thus trigonal planar

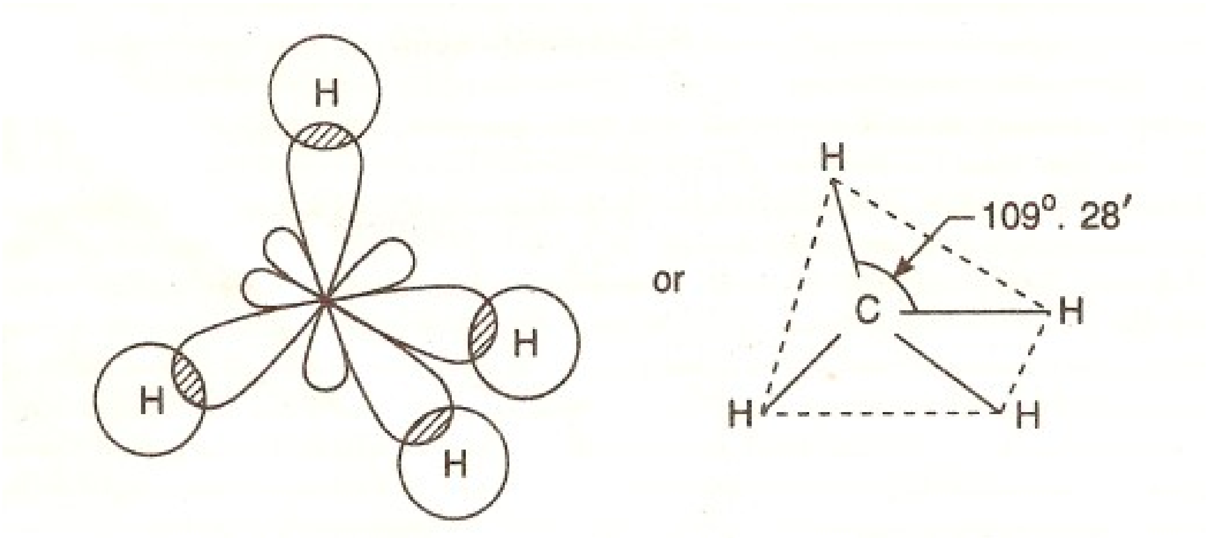


(3) sp3-hybridization: The combination of one s and three p-orbitals to form four hybrid orbitals of equal energy is known as sp3-hybridization.

Example: Methane (CH4) molecule.



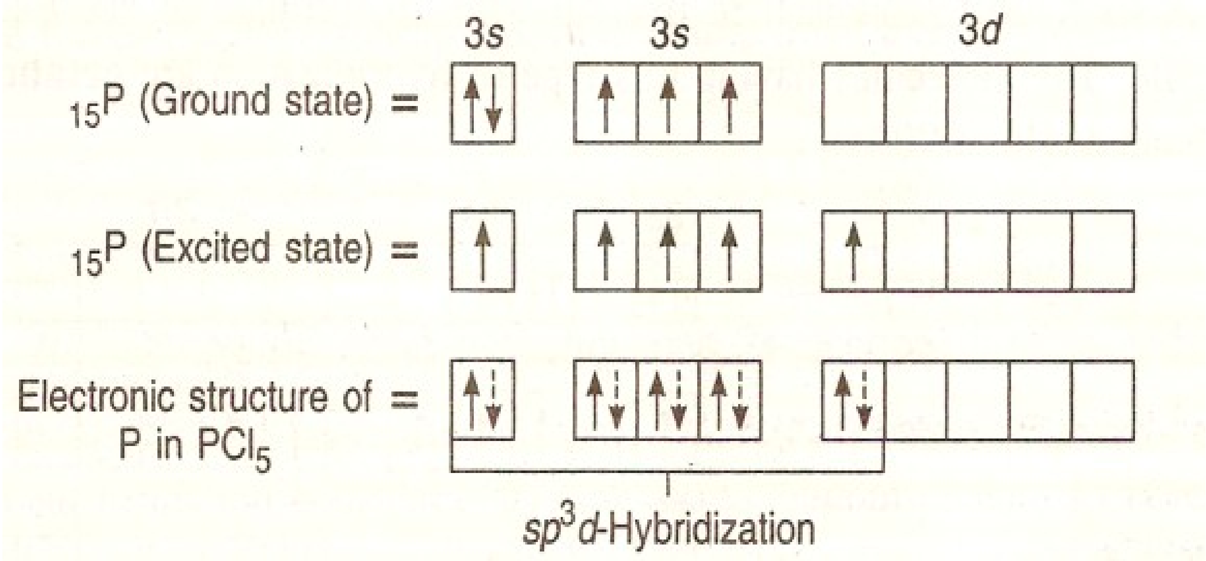
These sp3-hybridized orbitals are oriented at an angle of 109°28'. When these four sp3 hybrid orbitals overlaps with four 1s orbitals of hydrogen, a symmetrical tetrahedral shaped CH4 molecule form.



Q 11. Discuss in detail sp3d, sp3d^{2} and sp3d^{3} hybridization with example.

(4) sp3d-hybridization: The combination of one s, three *p* and one d-orbitals to form five hybrid orbitals of equal energy is known as sp3d-hybridization.

Example: PCl_5 molecule.



(5)sp^{3}d^{2}-hybridization : The combination of one s, three p and two d-orbitals to form six hybrid orbitals of equal energy is known as sp^{3}d^{2}-hybridization.

Examples : SF_6 Molecule.

Q 12. Explain amorphous and crystalline solids.

Ans: (a) CRYSTALLINE SOLIDS :

The solids in which atoms, ions or molecules are arranged in a definite pattern, constantly repeated, giving a definite geometrical shape, characteristic of substance and independent of the sources from which they have been obtained are called crystals. A crystalline solid is an aggregate of minute crystals, packed together in a well-defined order.

Properties of crystalline solids : (i) In a crystal, there is perfect and well-ordered arrangement of molecules throughout the entire body, each molecule is surrounded by a set of other molecules in a definite symmetrical way.

(ii) A crystalline solid has a sharp and definite melting point.

(iii) A crystal when melted expands only about 10% in volume or about 3% in inter-molecular spacing.

(iv) The crystals are bounded by surfaces which are planar and are arranged according to a definite plan.

(v) The crystals have a rigorous geometrical order. Thermal motions cause disorder. It is clear that if a small region of disorder is introduced into a crystal, it would cause disturbance in the long range and destroy the crystalline arrangement. This explains the reason of sharp melting point of crystalline substances.

vi) When subjected to a mechanical stress, a crystal tends to fracture along a petfectly definite direction.

(vii) The important feature of a crystal is the periodicity of arrangement along with regularity.

(viii) A crystalline substance is anisotropic, i.e., its physical properties like mechanical, electrical and optical properties are different in different directions. For example, the velocity of light passing through a crystal changes with the direction in which it is measured. Moreover, in silver iodide crystal, the coefficient of thermal expansion is positive in one direction and negative in another direction. Anisotropy offers a strong evidence for the presence of well ordered molecular arrangement in crystals.

b) AMORPHOUS SOLIDS

The solids which do not have any definite geometrical shape are called amorphous solids, e.g glass, rubber, plastic etc.

Properties of amorphous solids: (i) Amorphous solids are considered to be super-cooled liquids in which the force of attraction holding the molecules together is so great that the substance is rigid and there is no regularity of structure.

(ii) Amorphous solids do not have sharp melting points. They gradually soften on heating. Absence of sharp melting point suggests the absence of long-range order in amorphous solids.

(iii) On increasing the temperature, the viscosity of amorphous substances decreases and gradually changes into the liquid state.

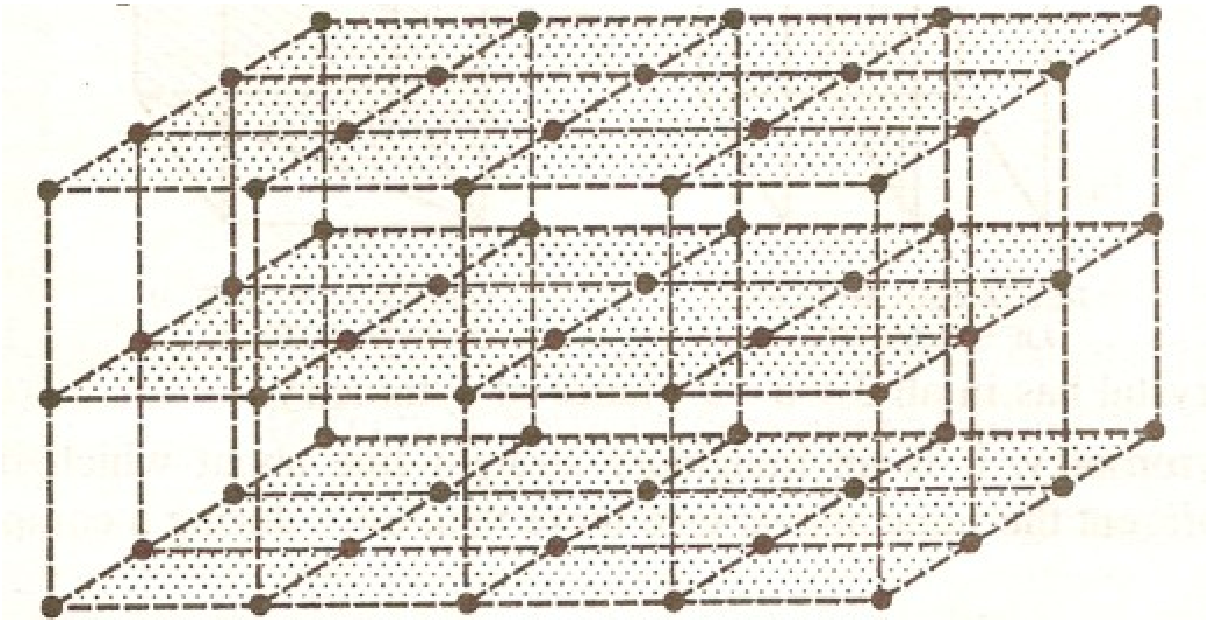
(iv) In amorphous solids, there is non-periodicity of the arrangement alongwith no regularity.

(v) Amorphous solids are isotropic, i.e., their physical properties like mechanical, thermal, electrical properties are same in all directions. In amorphous substances, the particles are randomly arranged and disordered. Due to this, all directions are equivalent and so all the propelties remain the same in all directions.

Q 13. Define space lattice

Ans: Every solid substance possesses a definite shape which is characteristic an distinctive for particular substance. In other words, a solid forms crystals. A crystal is a homogeneous portion of a solid substance made up of regular pattern, of structural units (atoms, molecules or ions) bounded by plane surfaces making definite angles with each other resulting in a definite and distinctive geometric form. The regul pattern of points which describe the three dimentional arrangement of particles in a crystal structure, is called the space lattice or crystal lattice.

A crystal can be imagined to be generated from the repetition of some basic unit of pattern. But rather than draw out the entire unit of pattern, it is much more convenient to represent the unit of pattern by a point.



Q 14. Define unit cell and explain the different types of unit cell.

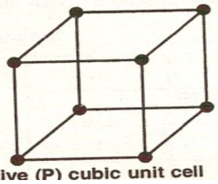
Ans: Definition: It is defined as the smallest geometrical portion of the crystal, which, when repeated in three dimensions, would generate the complete crystal. Each unit cell, in turn, must be constituted of atoms, molecules or ions, as the case may be, and arranged to give the particular geometrical configuration of the crystal.

Types of Unit cell:

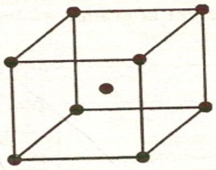
1. Simple or primitive type: It is that arrangement in which the atoms, ions or molecules are present only at the corner of the unit cell. It is labelled as P, This unit cell consists of one atom at each of the eight corners. Since each atom at the corner is shared by 8 unit cells, therefore only 1/8th of the atom is within the unit cell. Thus the number of atoms per unit cell in primitive or simple lattice is 8 x 1/8 = 1.

2. Body centered : In this arrangement in addition to the points at the corners, there is one point at the centre within the body of the unit cell. It is labelled as I. In a body centered cubic unit cell , there are eight atoms at the comers (each shared by 8 unit cells) and one at the centre (belonging to only one unit cell). Therefore, the number of atoms per unit cell is

8 x 1/8 + 1 = 2.



a) Primitive (P) cubic unit cell



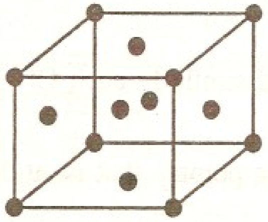
(b) Body centered (I) cubic unit cell.

3. Face-centred : When in the unit cell, besides the points at the corners there is one point present in the centre of each face, it is called face-centred arrangement. It is labelled as F. In a face centred cubic unit cell , there are eight atoms at the corners (each shared by 8 unit cells) and six at the faces (each shared by two unit cells).

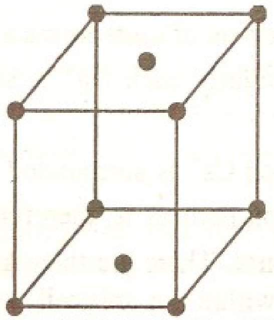
Therefore, the number of atoms per unit cell is

8 x 1/8 + 6 x 1/2 = 4.

4. End-centered : In this type there are points at the corners and at the centres of two end faces. It is labelled as C. In an end-centred orthorhombic cell (there is no end-centred cubic unit cell), there are eight atoms at the comers and two at the end faces so that the number of atoms per unit cell is 8 x 1/8 + 2 x ½ = 2.



(c) Face-centred (F) cubic unit cell.



(d) End-centred (C) orthorhomic unit cell

Q 15. Derive the expression to calculate the density of unit cell.

Ans Knowledge of the volume density and molecular weight of the constituent atoms of the cell also give information about the number of atoms or lattice per cell.

Consider a unit cell with volume *V* (in cm3) which can be calculated from the unit cell dimensions.

Let p (gm/cm2) be the density of the crystal. Then the weight of the matter in the unit cell = Volume x density =Vxp.

If n = number of atoms or molecules per unit cell.

m = atomic (molecular) weight of one atom or molecule.

Then, the weight of the matter in a unit cell $= n \times m \times 1.66 \times 10^{-24}$ gm $= n \times M$

where, 1.66×10^{-24} is the weight of an hydrogen atom in grams used in converting molecular weight in grams.

Thus

$$n \times M = V \times \rho$$

$$\rho = \frac{n \times M}{V} = \frac{n \times M}{V \times 6.023 \times 10^{23}}$$

$$\boxed{\rho = \frac{n \times M}{V \times N}}$$

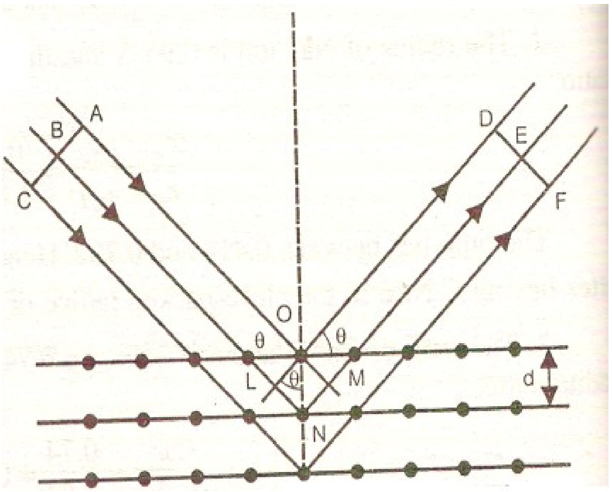
where $N = 6.023 \times 10^{23}$ is the Avogadro's number.

The volume of unit cell for different lattice is given below: Cubic $v = a^3$; Hexagonal = $abc \sin 60°$

Orthorhombic $v = abc$; Rhombohedral = $\frac{1}{2} a^3 \sin^2 \alpha / \cos \alpha/2$

Q. 16 What is Bragg's law. Derive the Bragg's equation.

Ans: W.H. Bragg pointed out that scattering of X-rays by crystal could be considered as reflection from successive planes of atoms in the crystals. However, unlike reflection ordinary light, the reflection of X-rays can take place only at certain angles which are determined by the wavelength of the X-rays and the distance between the planes in the crystal. The fundamental equation which gives a simple relation between the waveleng of the X-rays the interplanar distance in the crystal and the angle of reflection, is known as the Bragg's equation.



The horizontal lines represent parallel planes in the crystal structure separated from one another by the distance *d.* Suppose a beam of X-rays falls on the crystal at glancing angle ɵ Some of these rays will be reflected from the upper plane at the same angle ɵ while some others will be absorbed and set reflected from the successive layers.

Derivation:

Let the planes *ABC* and *DEF* be drawn perpendicular to the incident and reflected beams. The waves reflected by different layer planes will be in phase with one another only if the differencein the path lengths of the waves reflected from the successive planes is equal to an integral number of wave lengths. Drawing *OL* and *OM* perpendicular to the incident and reflect beams, it will be seen that the difference in the path lengths of the waves reflected from the first two planes is

$$\delta = LN + NM$$

This should be equal to a whole number multiple of wavelength λ

$$LN + NH = n\lambda$$

Since the triangles *OLN* and *OMN* are congruent hence *LN* = *NM*

$$2\,LN = n\lambda$$

$$\boxed{2d\sin\theta = n\lambda}$$

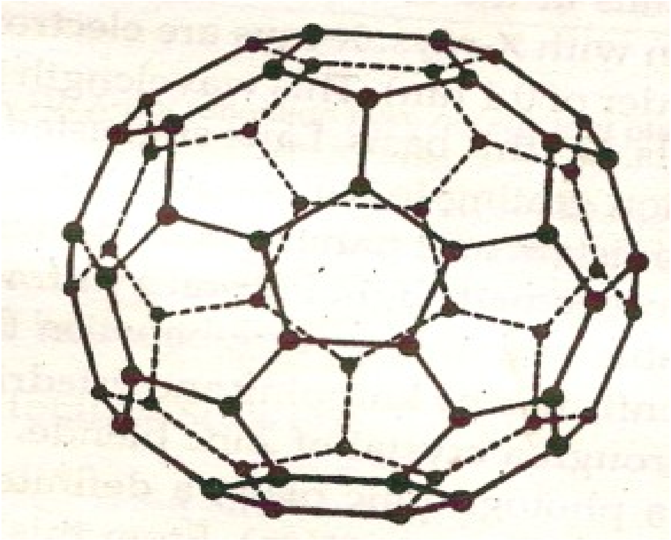
This is the Bragg's equation. This gives the condition which must be satisfied for the reflection of *X-rays* from a set of atomic planes. Knowing, *n* and *d* be can be calculated.

Q.17. Explain the structure of Fullerenes. Write down its properties and applications.

Ans: Introduction : Fullerene is an allotrope of carbon. It is a molecule of formula C_{60}. It is popularly known as Buckminster fullerene in honour of the american architect Buckminster Fuller, who designed dome structures based on hexagons & pentagons.

Preparation : Fullerenes are prepared by vaporizing a graphite rod in a helium atmosphere. Mixture of fullerenes like C_{60}, C_{70} etc., are formed which are separated by solvent extraction. Pure C_{60} is isolated from this mixture by column chromatography.

Structure : The C_{60} molecule has a truncated icosahedron structure. An icosahedron is a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. A carbon atom is present at each vertex of this structure. The molecule is aromatic and has several resonance structures. The valencies of each carbon atom are satisfied by two single and one double bond. C_{60} is also known as buckyball as it is a spherical cluster of carbon atoms arranged in series of 5and 6, membered rings to form a soccer ball shape.



Q 18: **Write down its properties and applications of Fullerenes.**

Ans: Properties of Fullerenes *:*

1. Fullerene is a black powdery material.

2. It forms deep magenta solution, when dissolved in benzene.

3. It is very tough and thermally stable.

4. It exists as a discrete molecule, unlike the other two allotropes of carbon (viz. diamond and graphite).

5. It can be compressed to lose 30% of its volume without destroying its carbon cage structure.

Applications of fullerenes :

1. It is suitable for use as a lubricant due to its spherical structure. The bucky balls would act as molecular ball bearings.

2. It can be used as a superconductor when mixed with alkali metals.

3. It can also be used as soft ferromagnet.

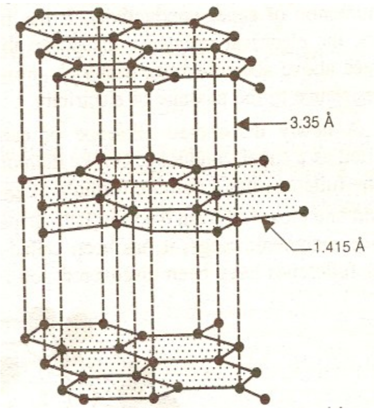
4. Other possible areas of uses are:

(i) Electronic and Microelectronic devices.

(ii) Non-linear optical devices.

Q 19 Expalin why graphite is good conductor of electricity. Discuss its structure.

Ans: Structure : Each carbon atom is covalently bonded to three others involving sp2 hybrid orbitals instead of four as in diamond. Thus, alI atoms in a single plane are linked to give flat hexagons as in benzene. The hexagons are held together in sheet like structures, parallel to one another. The C - C covalent bond distance is 1.42 A. The distance between the sheets or layers, however is comparatively large being about 3.35 A. This rules out the possibility of covalent bonding between the layers. Such crystals in which the various sheets of atoms are separated from one another by a distance larger than the maximum permissible for the formation of chemical bond are said to have layer lattices.



Graphite is a good conductor : In graphite, each carbon atom is connected only to three other carbon atoms ; while the fourth valency is unsatisfied. In other words, these delocalised electrons are free to move within the layer itself. This accounts for the fact that graphite is good conductor of electricity.

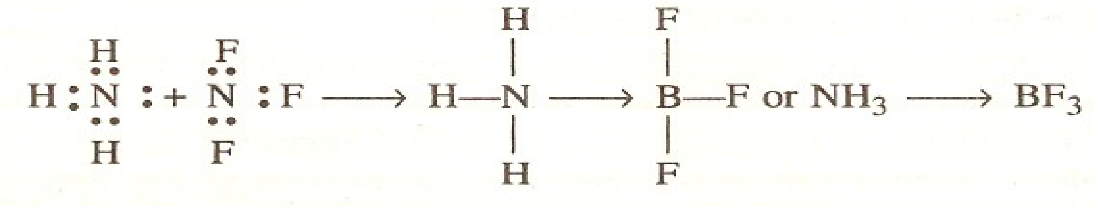
Q 20: Explain Coordinate bond with example.

COORDINATE BOND

A covalent bond results from the sharing of a pair of electrons between two atoms where each atom contributes one electron to the bond. It is also possible to have an electron. pair bond where both electrons originates from one atom and none from the other. Such bonds are called coordinate bonds Since in coordinate bonds, two electrons are shared by two atoms, they differ from normal covalent bond only in the way they are formed; and once formed they are identical to normal covalent bonds.

Covalent bonds are usually shown as straight lines joining the two atoms, and coordinate bonds as arrows indicating which atom is donating the electrons.

e.g. Combination of Ammonia and boron trifluoride : Ammonia may donate its loan pair to borontrifluoride and by this means the boron atom attains a share in eight electrons.

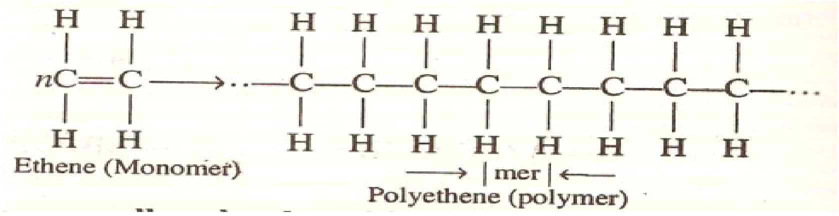


$$\mathrm{H:\overset{H}{\underset{H}{\ddot{N}}}:} + \mathrm{\overset{F}{\underset{F}{\ddot{N}}}:F} \longrightarrow \mathrm{H{-}\overset{H}{\underset{H}{N}}} \longrightarrow \mathrm{\overset{F}{\underset{F}{B}}{-}F} \text{ or } \mathrm{NH_3} \longrightarrow \mathrm{BF_3}$$

Unit 2

Q 1. Define Polymer. Give the characteristics of Polymer.

Ans: Introduction : The word "polymer" is derived from two Greek words, polys (= many) and mers (= parts or units). A polymer is a large molecule which is formed by repeated linking of small molecules called "monomers". Example: Polyethene is a polymer formedby linking together of a large number of ethene (C_2H_4) molecules.



Thus, small molecules which combine with each other to form polymer molecules, are termed monomers ; and the "repeat unit" in a polymer is called mer.

Characteristics of Polymers :

1. Polymeric molecules are very big molecules. There average molecular weights may approach 10^5 or more. That's why, they are also known as **macromolecules.**
2. Polymers are semi-crystalline materials. It means they have both amorphous and crystalline regions. In fact, polymers have regions of crystallinity, called crystallites, embedded in amor- phous regions. Crystallites provide strength and hardness and the amorphous regions provide flexibility to the polymeric material.
3. The intermolecular forces in polymers can be Vander Waals' forces, dipole-dipole attractions or hydrogen bonding. These intermolecular forces are in addition to covalent bonds which connect the repeating units into a macromolecule.
4. The chemical, electrical, optical, mechanical and thermal properties of polymers depend on (i) size and shape of polymers, and (ii) the presence or absence of characteristic intermolecular forces. These parameters not only determine the properties of the polymers, but also the performance of these materials in a given applications.
5. Polymers show time-dependent properties.
6. 6. Polymers are combustible materials.
7. 7. Polymers have low densities and they show excellent resistance to corrosion.
8. 8. Generally, polymers are thermal and electrical insulators.
9. 9. Polymeric materials are easily mouldable even into complex shapes with reproducible dimensions with a minimum of fabrication and finishing cost.

Q 2: **Classify polymers based on number of monomers.**

1. **Ans: Based on Number of Monomers : Polymers can be homopolymer or copolymer when the number of monomers are one and two respectively.**

(i) Copolymers : Molecules which are built up of at least two different kinds of monomer are known as co-polymers. Thus, a co-polymer is obtained when two or more suitable monomers are polymerised together.

The chains of co-polymer consist of repeating units derived from each monomer. Following are some common types of co-polymers :

(a) Alternating co-polymers (c) Block co-polymers

(b) Random co-polymers (d)Graft co-polymers

(a) **Alternating co-polymers:** In such Co-polymers, the different repeating units alternate in each chain. If A and B represent two different units then an alternating co-polymer will be represented as,

-ABABABAB-

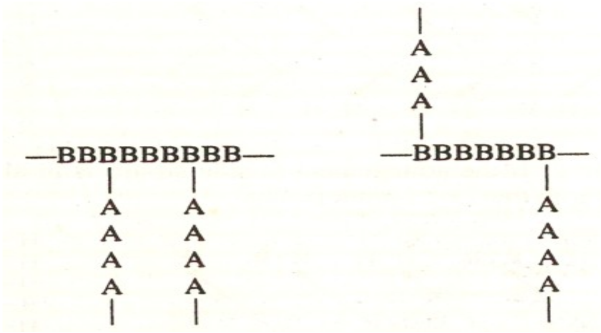
(b) Random Co-polymers: In this type of copolymers, the different repeating units are not arranged in a systematic manner but are randomly arranged, e.g.

-ABAABABBAAABA-

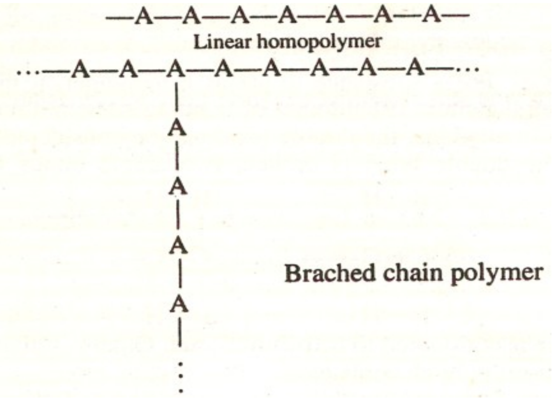
c) Block Co-polymers: In such co-polymers, block of repeating units of one type alternate with block of another type, *e.g.*

-AAAABBBBAAAABBBB-

(d) Graft Co-polymers: In such co-polymers, blocks of one repeating units are attached or grafted to a block of linear polymer, *e.g.*



(ii) Homopolymers: If the polymers consist of monomer of identical chemical structure then they are called homopolymers, *e.g.,*

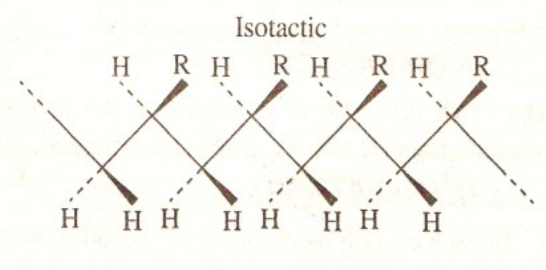


Q 3: Define Tacticity. Classify polymer based on the tacticity.

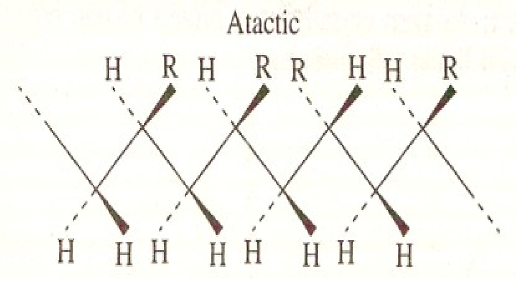
Based on Tacticity :

The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain. The difference in configuration (tacticity) do affect their physical properties. Based on tacticity they are classified as follows:

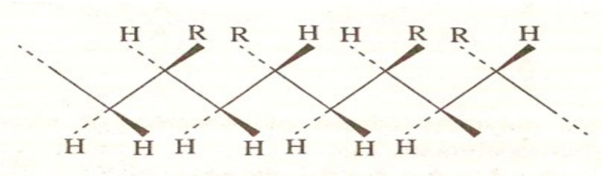
(i) Isotactic Polymer: The head-to-tail configuration, in which the functional groups are all on the same side of the chain, is called isotactic polymer, e.g.,


Isotactic

(ii) Atactic Polymer: If the arrangement of functional groups are at **random** around the main chain, it is called **atactic polymer,** *e.g.,* polypropylene.

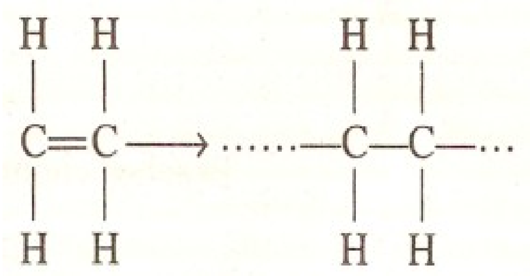

Atactic

iii) Syndiotactic: If the arrangement of side groups is in **alternating** fashion, it is called **syndiotactic polymer,** *e.g.,* gutta percha.

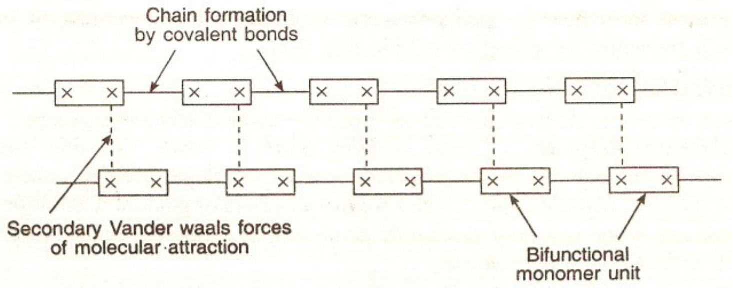


Q 4. Define Functionality and based on it classify the polymers.

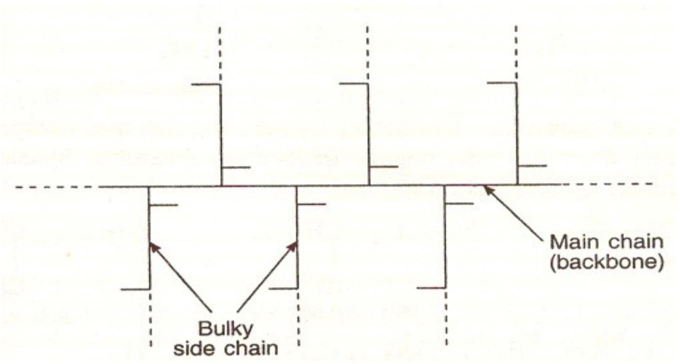
Ans: For a substance to act as a monomer, it must have at least two reactive sites or bonding sites. The number of bonding sites in a monomer, is referred to as its functionality. In ethylene, the double bond can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination.



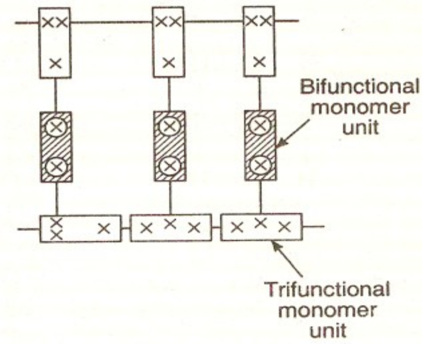
(i) Linear or Straight Chain Polymer: In case of a **bifunctional monomer,** two reactive groups attach side by side to each other forming **linear or straight chain polymer.** Linear molecules consist of monomer units linked by primary covalent bonds, but the different chains are held together by secondary vander waals forces of molecular attraction. This gives the possibility of chain movement in one direction.



(ii) Branched Chain Polymers: During the chain growth, side chains may also form, resulting in branched-chain polymers. Such a molecule is a linear, but the movement in brached-chain molecules is, generally, more restricted than that of simple straight-chain molecules. A branched-chain polymer also results, when a trifunctional monomer is mixed insmall amounts with a bifunctional monomer and polymerised.



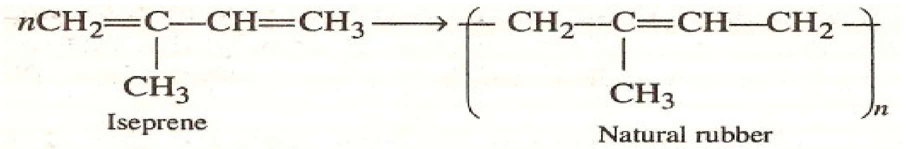
(iii) Network Polymer: In case of polyfunctional groups, monomer molecules are connected to each other by covalent bonds, resulting in the formation of a three-dimensional netwrork polymer. In such polymeric molecules the movement of individual molecules is prevented by strong cross-links.



Q 5: Differentiate between Natural and synthetic polymer.

Ans: **Natural Polymers:** These polymer occur in nature, *i.e.,* they have either vegitable or an animal origin. They include starch, cellulose, proteins, nucleic acids, natural rubbber etc. cellulose and starches are the polymers of glucose.

Natural rubber contains isoprene (2-methyl-1, 3-butadiene) repeat unit

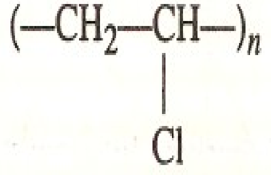


$$n\underset{\underset{\text{Iseprene}}{CH_3}}{CH_2{=}\overset{}{C}}{-}CH{=}CH_3 \longrightarrow \left(CH_2{-}\underset{\underset{\text{Natural rubber}}{CH_3}}{C}{=}CH{-}CH_2 \right)_n$$

(ii) Synthetic Polymers: Synthetic polymers are man made polymers. Most of the synthetic polymers are long-chain organic molecules containing thousands of monomer units. Most common synthetic polymers are :

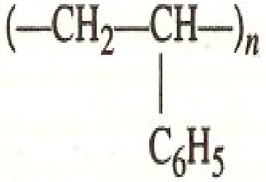
$(-CH_2-CH_2-)_n$

Polyethylene



$(-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-)_n$

Polyvinyl chloride



$(-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-)_n$

Polystyrene

Q 6. Classify the polymers Based on Molecular Forces.

(i) **Elastomers:** Held together by the weakest intermolecular forces *e.g.,* Vulcanized Rubber. Vulcanization is a process of treating natural rubber with sulphur. Rubber is vulcanized to render it nonplastic and give it greater elasticity and ductility.

(ii) **Fibres:** Strong intermolecular hydrogen bonding, *e.g.,* nylon-66.

(iii) **Thermoplastics:** Some polymers soften on heating and can be converted into any shape that they can retain on cooling. The process of heating, reshaping and retaining the same on cooling can be repeated several times. Such polymers, that soften on heating and stiffen on cooling are termed 'thermoplastics' *e.g.,* polyethylene, PVC, nylon and sealing wax.

(iv) **Thermosetting:** Some polymers undergo some chemical change on heating and convert themselves into infusible mass. They are like Yolk of egg, which on heating sets into a mass and once set cannot be reshaped. Such polymers, that become infusible and insoluble mass on heating, are called 'thermosetting' polymers *e.g.,* bakelite.

Q 7: Discuss addition polymerization with free radical mechanism.

Ans: In addition polymerization, the polymer is formed from the monomer, without the loss of any material and the product is an exact multiple of the original monomeric molecules.

Addition polymerization reactions proceed by a chain reaction mechanism consisting of three important steps,

(i) Initiation or the formation of an active centre,

(ii) Propagation or the formation of a polymer having the active centre

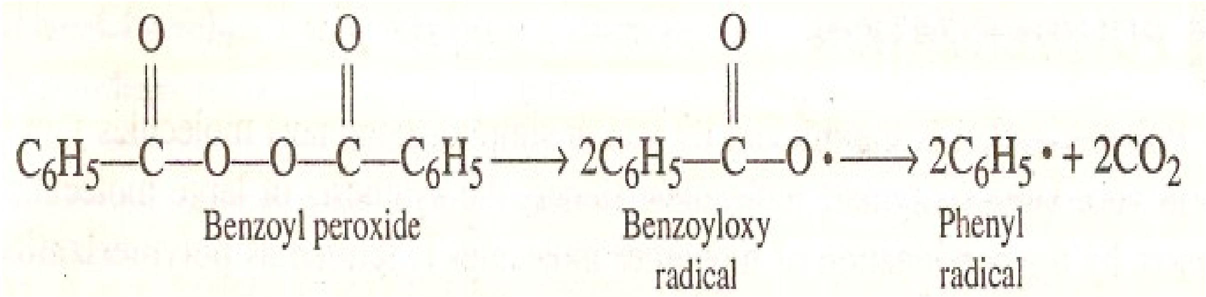
(iii) Termination or removal of the active centre.

The three different types of active centres have been found to be formed during the addition polymerization, *viz.,* free radical, carbonium ion and carbanion. So the mechanisms involving these reactive species in polymerization constitute the mechanism of addition polymerization

a) Free radical polymerization :

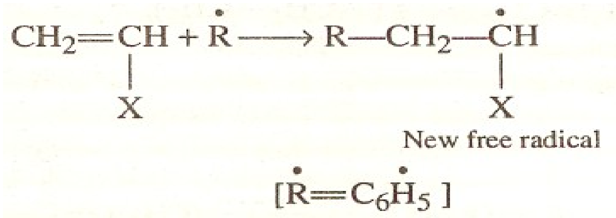
Free-radical polymerization form only linear molecules.

(i) Initiation step: It involves the formation of a free-radical from a radical initiator such as benzoyl peroxides, and other materials that can generate free radicals.



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2C_6H_5-\overset{O}{\overset{\|}{C}}-O\cdot \longrightarrow 2C_6H_5\cdot + 2CO_2$$

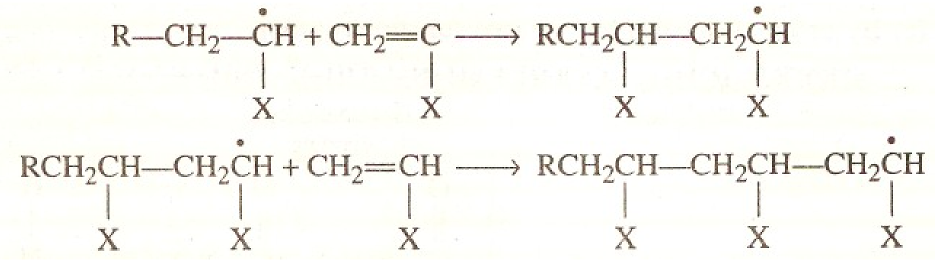
The radical so formed then adds to the monomer to form a new free radical, *e.g.,* it adds to vinyl monomer in the following way



$$CH_2=\underset{\underset{X}{|}}{CH} + \dot{R} \longrightarrow R-CH_2-\underset{\underset{X}{|}}{\dot{C}H}$$

$$[\dot{R}=C_6\dot{H}_5\,]$$

(ii) Propagation step: The new free radical now adds to another molecule of monomer to form another new free radical until a large free radical is formed .



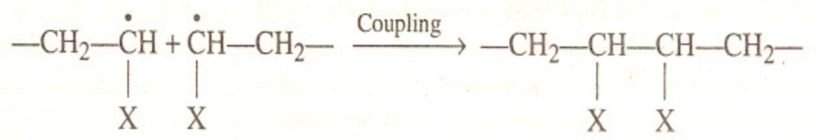
$$R-CH_2-\underset{\underset{X}{|}}{\dot{C}H} + CH_2=\underset{\underset{X}{|}}{C} \longrightarrow RCH_2\underset{\underset{X}{|}}{CH}-CH_2\underset{\underset{X}{|}}{\dot{C}H}$$

$$RCH_2\underset{\underset{X}{|}}{CH}-CH_2\underset{\underset{X}{|}}{\dot{C}H} + CH_2=\underset{\underset{X}{|}}{CH} \longrightarrow RCH_2\underset{\underset{X}{|}}{CH}-CH_2\underset{\underset{X}{|}}{CH}-CH_2\underset{\underset{X}{|}}{\dot{C}H}$$

After the first few steps the addition of a monomer unit proceeds at a constant specific rate independent of the chain length of free radical formed.

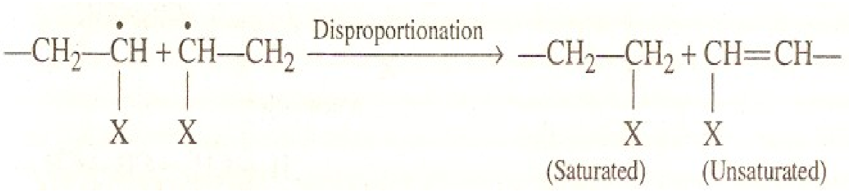
iii) Termination step: Termination of chains usually occurs by radical coupling or disproportionation reactions.

By coupling or combination, *e.g.,*



$$-CH_2-\underset{\underset{X}{|}}{\dot{C}H} + \underset{\underset{X}{|}}{\dot{C}H}-CH_2- \xrightarrow{\text{Coupling}} -CH_2-\underset{\underset{X}{|}}{CH}-\underset{\underset{X}{|}}{CH}-CH_2-$$

Disproportionation: In which a hydrogen atom of one radical centre is transferred to another radical centre. This results in the formation of two polymer molecules, **one saturated** and **other unsaturated,** *e.g.,*

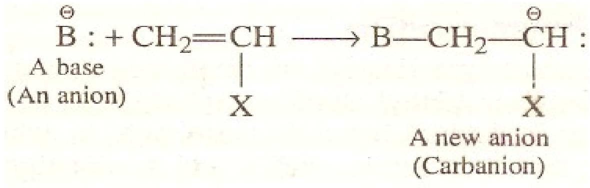


$$-CH_2-\underset{X}{\overset{\bullet}{C}H} + \underset{X}{\overset{\bullet}{C}H}-CH_2 \xrightarrow{\text{Disproportionation}} \underset{\text{(Saturated)}}{-CH_2-\underset{X}{CH_2}} + \underset{\text{(Unsaturated)}}{\underset{X}{CH}=CH-}$$

Q 8. Discuss the mechanism of Anionic polymerization.

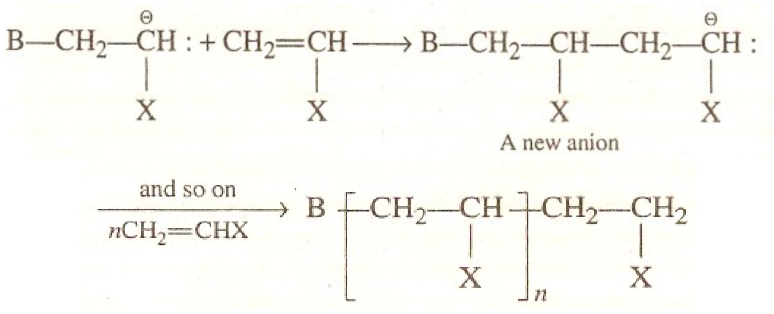
Ans **(i) Anionic Polymerization:** Anionic polymerization involves following steps:

Initiation: A number of reagents are used to bring about initiation the most important being n-butyl lithium and lithium amide.



$$\underset{\substack{\text{A base}\\\text{(An anion)}}}{\overset{\ominus}{B}:} + CH_2=\underset{X}{CH} \longrightarrow \underset{\substack{\text{A new anion}\\\text{(Carbanion)}}}{B-CH_2-\underset{X}{\overset{\ominus}{C}H}:}$$

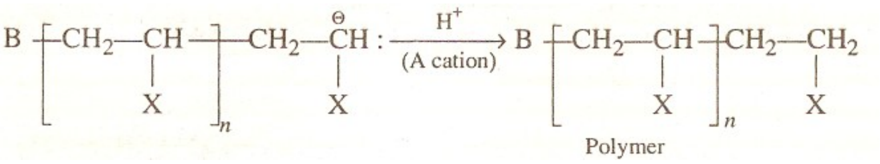
Propagation:



$$B-CH_2-\underset{X}{\overset{\ominus}{C}H}: + CH_2=\underset{X}{CH} \longrightarrow B-CH_2-\underset{\substack{X\\\text{A new anion}}}{CH}-CH_2-\underset{X}{\overset{\ominus}{C}H}:$$

$$\xrightarrow[nCH_2=CHX]{\text{and so on}} B\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{CH_2}$$

Termination: Termination occurs by a hydride transfer or by the action of reactive centres with solvent or with - nctional group of the monomer,

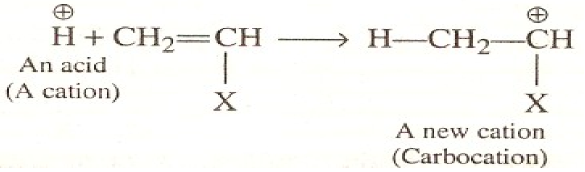


$$B\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{\overset{\ominus}{C}H}: \xrightarrow[\text{(A cation)}]{H^+} \underset{\text{Polymer}}{B\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{CH_2}}$$

Q9: Discuss the mechanism of cationic polymerization.

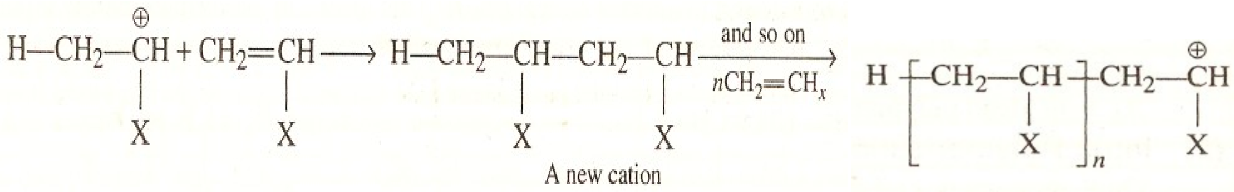
Ans: Cationic Polymerization: Cationic polymerization is initiated by acids and involves carbocationic centres. Monomers with electron-releasing substituents such as alkoxy or phenyl groups readily undergo this type of polymerization. The mechanism is as follows:

Initiation:



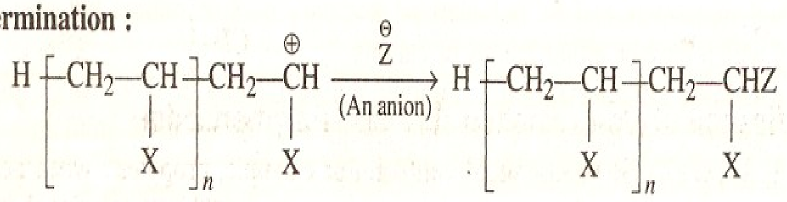
$$\underset{\text{An acid (A cation)}}{\overset{\oplus}{H}} + CH_2{=}\underset{\substack{|\\ X}}{CH} \longrightarrow \underset{\text{A new cation (Carbocation)}}{H{-}CH_2{-}\underset{\substack{|\\ X}}{\overset{\oplus}{C}H}}$$

Propagation



$$H{-}CH_2{-}\underset{\substack{|\\ X}}{\overset{\oplus}{C}H} + CH_2{=}\underset{\substack{|\\ X}}{CH} \longrightarrow \underset{\text{A new cation}}{H{-}CH_2{-}\underset{\substack{|\\ X}}{CH}{-}CH_2{-}\underset{\substack{|\\ X}}{CH}} \xrightarrow[nCH_2=CH_x]{\text{and so on}} H\left[CH_2{-}\underset{\substack{|\\ X}}{CH}\right]_n CH_2{-}\underset{\substack{|\\ X}}{\overset{\oplus}{C}H}$$

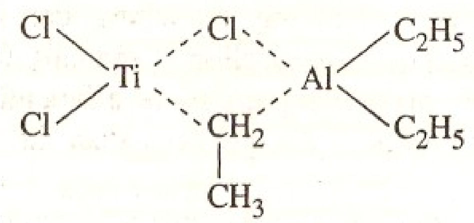
Termination :



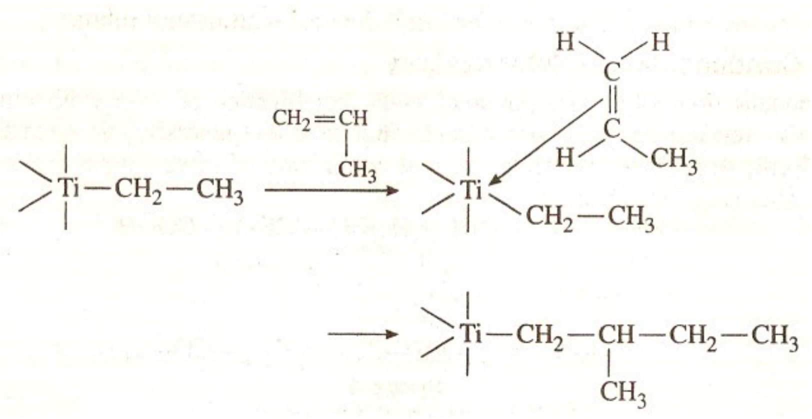
$$H\left[CH_2{-}\underset{\substack{|\\ X}}{CH}\right]_n CH_2{-}\underset{\substack{|\\ X}}{\overset{\oplus}{C}H} \xrightarrow[\text{(An anion)}]{\overset{\ominus}{Z}} H\left[CH_2{-}\underset{\substack{|\\ X}}{CH}\right]_n CH_2{-}\underset{\substack{|\\ X}}{CHZ}$$

Q 10: Disscuss the mechanism of Co-ordination polymerization.

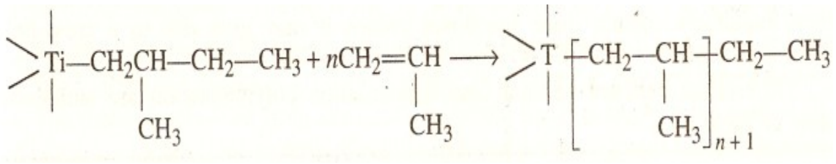
Ans: Co-ordination Polymerization : Co-ordination addition polymerization are catalysed by a catalyst known as zeiglerNatta catalysts formed between triethyl aluminium AI$(C_2H_5)_3$ and titanium halide TiCI3. A co-ordination complex is formed between these two, in which the ethyl group is co-ordinated to titanium, this is an active catalyst and its structure is as :



Initiation: In the initiation step, π-cloud of alkene overlaps with an empty orbital of titanium, then there is insertion of alkene molecules between the Ti-C bond.

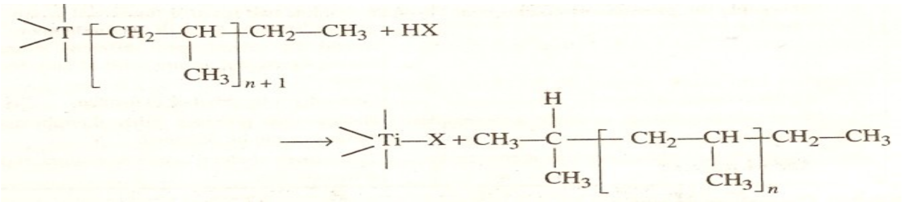


Propagation: As intermolecular rearrangement again generates a vacant site on titanium, each time one monomer molecule can be added in the same fashion.



$$>\mathrm{Ti}-CH_2\underset{CH_3}{CH}-CH_2-CH_3+nCH_2=\underset{CH_3}{CH}\longrightarrow>\mathrm{T}\left[CH_2-\underset{CH_3}{CH}\right]_{n+1}CH_2-CH_3$$

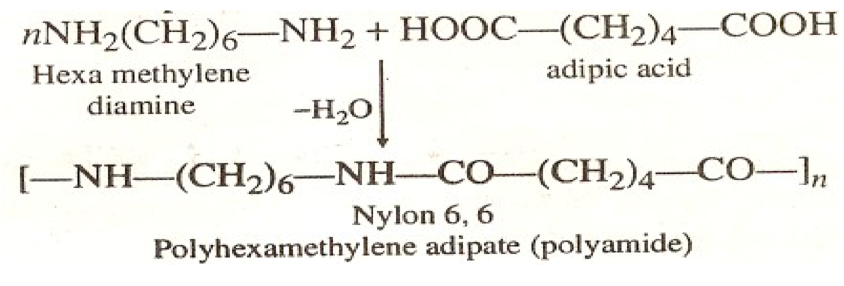
Termination: It can be done by the addition of molecules containing active hydrogen like HX.



$$>\mathrm{T}\left[CH_2-\underset{CH_3}{CH}\right]_{n+1}CH_2-CH_3+HX\longrightarrow>\mathrm{Ti}-X+CH_3-\overset{H}{\underset{CH_3}{C}}-\left[CH_2-\underset{CH_3}{CH}\right]_{n}CH_2-CH_3$$

Q 11. Discuss the condensation polymerization with at least one example.

Ans: Condensation polymerization involves the combination of several monomers to one another as a result of the migration of some mobile atom (generally hydrogen atom) from one molecule to another molecule with the elimination of some simple molecules (such as H_20, HCI etc.).

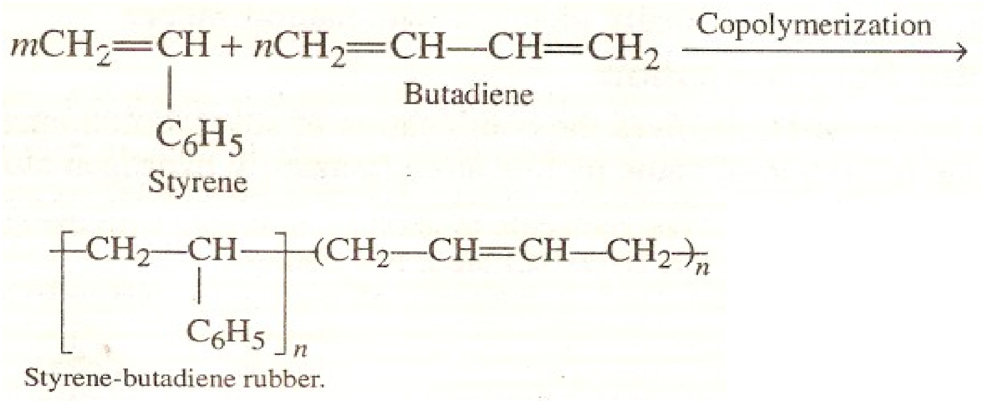


$$nNH_2(CH_2)_6-NH_2+HOOC-(CH_2)_4-COOH\xrightarrow{-H_2O}[-NH-(CH_2)_6-NH-CO-(CH_2)_4-CO-]_n$$

Nylon 6, 6
Polyhexamethylene adipate (polyamide)

Q 12. Discuss the Co -polymerization with at least one example.

Ans: **Copolymerization :** Copolymerization has been used by nature in polypeptides which may contain as many as 20 different amino acids. Copolymerization is a polymerization of two or more monomeric species together.



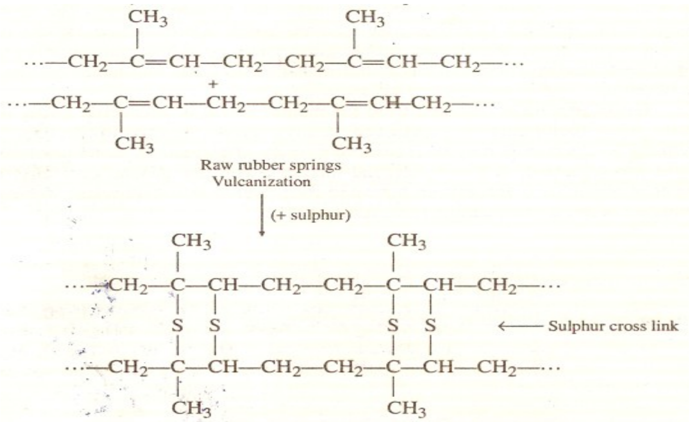
$$m\,CH_2{=}\underset{\substack{|\\ C_6H_5}}{CH} + n\,CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\text{Copolymerization}} \left[CH_2{-}\underset{\substack{|\\ C_6H_5}}{CH}\right]_n(CH_2{-}CH{=}CH{-}CH_2)_n$$

Q.13. Write note on Vulcanization of Rubber? Give its advantages also.

Ans: Vulcanization of Rubber :

Raw rubber is of little use as such because it has very undesirable properties, e.g; it possesses elasticity only over a limited range of temperature, does not resume its original shape after being extended and becomes softer, more plastic and sticky on heating and brittle on cooling. The undesirable properties may be overcome by a process known as vulcanization.

Process : The process consists in heating the raw rubber with sulphur to 100-140°C. The added sulphur combines chemically at the double bonds of different rubber springs. Vulcanization thus serves to stiffen the material by a sort of anchoring and consequently, preventing intermolecular movement of rubber springs. The extent of stiffness of vulcanized rubber depends on the amount of sulphur added. The vulcanization can also be done by hydrogen sulphide and benzoyl chlorides.



Advantages of Vulcanization Vulcanized rubber :

(1) has good tensile strength and extensibility.

(2) has excellent resilence, *i.e.,* article made from it returns to the original shape,when the deforming load is removed;

(3) has higher resistance to oxidation .

(4) has much higher resistance to wear and tear as compared to raw rubber.

(5) is better electrical insulator, although it tends to absorb small amount of water.

Ebonite (raw rubber vulcanized with about 32% rubber) is better insulator.

(6) is resistant to organic solvents (such as petrol, benzene, carbon tetrachloride), fats and oils. It swells in these liquids.

Q.No 14,15,16: Give the preparation , properties and uses of

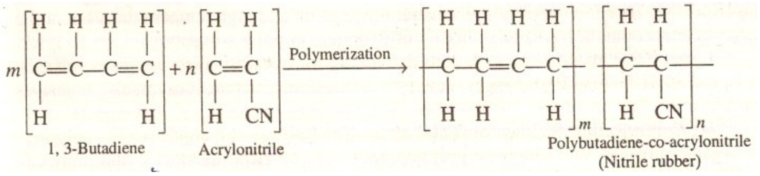
Buna-N

Buna-S

Butyl Rubber

Ans: **Buna-N**

Nitrile Rubber or Buna-N: It is a copolymer of 75% butadiene and 25% acrylonitrile (CH_2=CHCN).



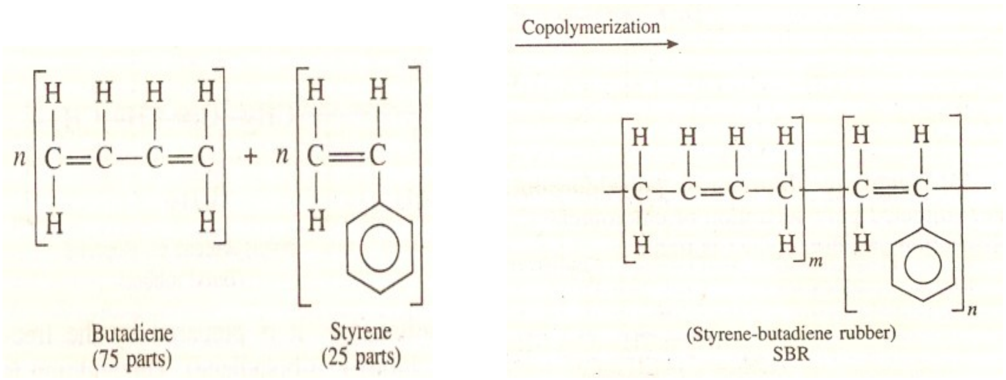
Properties:

1. It possesses excellent resistance to heat, sunlight, oils, acids and salts, but it is less resistant to alkalis than natural rubber, because of the presence of cyano groups (-CN).
2. As the proportion of acrylonitrile is increased, the resistance to acids, salts, oils, solvents, etc., increases.
3. Vulcanized-nitrile rubber is more resistant to heat and ageing than natural rubber and may be exposed to high temperatures.

Uses: For making conveyor belts, high altitude aircraft components, tank-linings, printing rollers, adhesives, oil-resistant foams and automobile parts, etc.

b) **Buna-S**

Styrene Rubber or Buna-S : Buna-S is copolymer of 75% butadiene (CH_2=CH-CH=CH_2) and 25% styrene (C_6H_5CH=CH_2). The polymerization is carried out in an emulsion system at 50°C in the presence of peroxide catalyst. The polymer consists of the repeating units of mainly 1, 4-addition product of butadiene along with a small amount of I, 2-addition product.



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

2. It possesses high load-carrying capacity.

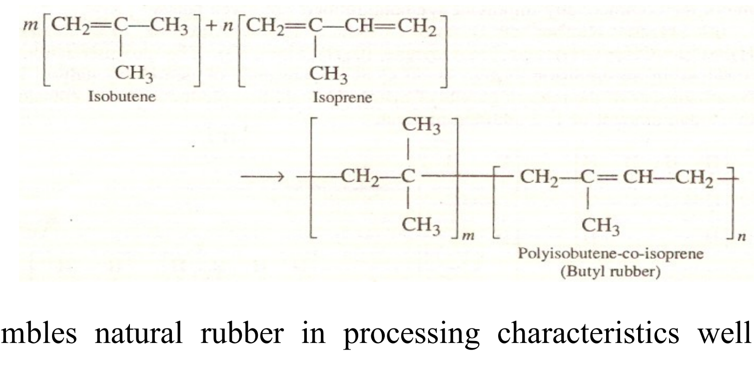
3. It gets readily oxidized, especially in presence of traces of ozone present in the atmosphere.

4. It can be vulcanized in the same way as natural rubber either by sulphur or sulphur monochloride (S_2CI_2).

Uses: 1. It is mainly used for the manufacture of motor tyres.

2. Other uses of this elastomer are floor tiles, shoe sholes, gaskets, footwear components, wire and cable insulations, adhesives etc.

Butyl Rubber: It is a copolymer of 98% isobutene (Me_2C=CH_2) and nearly 2% butadiene or isoprene (CH_2=CMe-CH=CH_2); the latter is added to introduce the necessary ethylenic linkages for vulcanization.



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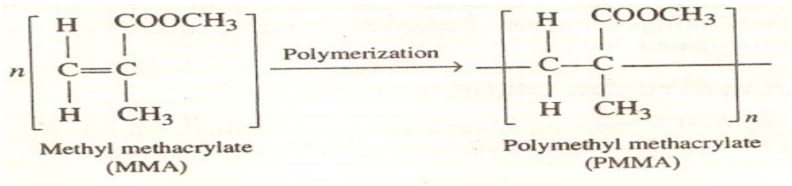
Uses: 1. It is mainly used for the manufacture of motor tyres.

2. Other uses of this elastomer are floor tiles, shoe sholes, gaskets, footwear components, wire and cable insulations, adhesives etc.

Q 17, Give the preparation, properties and uses of PMMA and polyester.

Ans: PMMA

Polymethyl Methacrylate (PMMA) or Lucite or Plexiglass : It is obtained by polymerization of methyl methacrylate (ester of methyl acrylic acid, $CH_2=C(CH_3)COOH$) in presence of acetyl peroxide or hydrogen peroxide. It is an acrylic polymer.



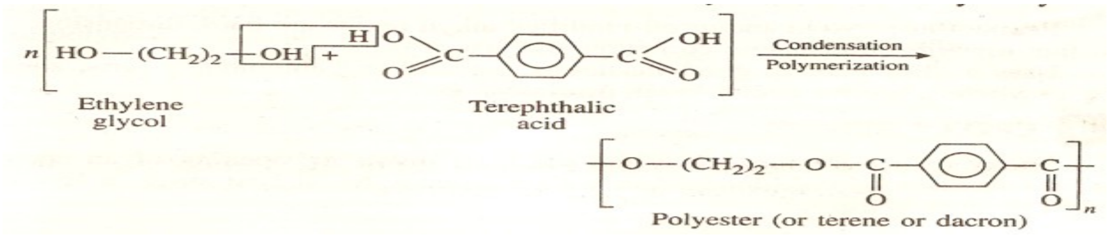
Properties:

1. Polymethyl methacrylate (PMMA) is hard, fairly rigid material with a high softening point of about 130-140°C, but it becomes rubber-like at a temperature above 65°C.
2. This relatively wide span of temperature from its rigid state to viscous consistency accounts for the outstanding shape-forming properties of polymethyl methacrylate.
3. It has high optical-transparency, high resistance to sunlight and ability of transmitting light accurately, even in curved sections.

Uses: For making lenses, aircraft light fixtares, transparent models of compljcated machines, bone splints, artificial eyes, dentares, emulsions, paints, adhesives, automotive appliances, jewellery, wind screens, T. V. Screens, guards etc.

<u>Polyester</u>

These are the condensation products of dicarboxylic acid with dihydroxy alcohols.



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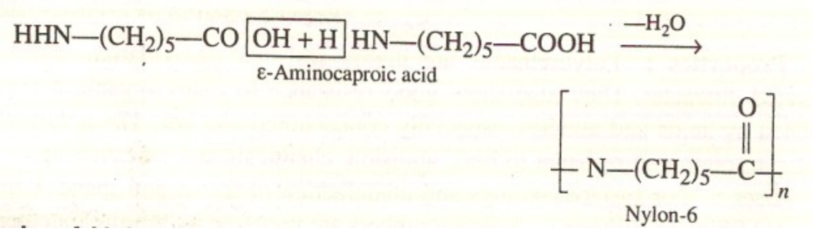
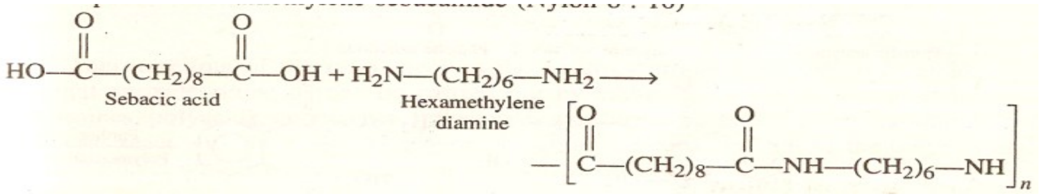
Q 18: Give preparation of Nylon 6:10, Nylon 6.

Ans: **Nylon 6 :** It is produced by the self condensation of ε-amino caproic acid.



Nylon 6:10

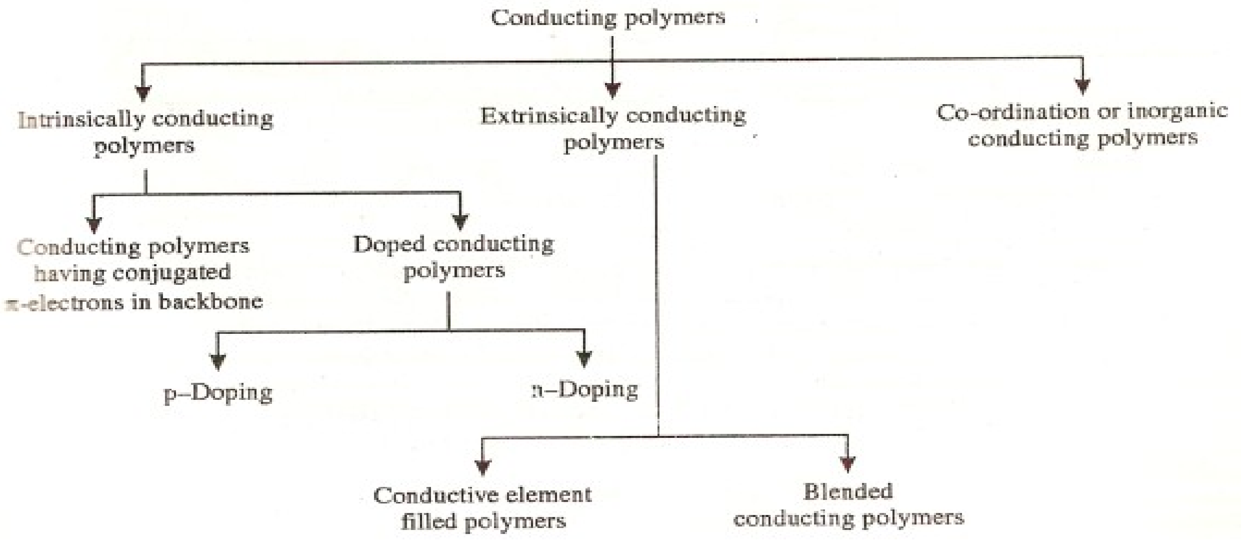
It is prepared from reaction between hexamethylene diamine and sebacic acid to produced hexamethylene sebacamide (Nylon 6 : 10).



Q.No19: Write brief note on conducting polymers?

Ans: CONDUCTING POLYMERS : Polymers which can conduct electricity are called conducting polymers. Ordinary polymers obtained by usual methods are nearly insulators. However, some specific polymers may act as conductors.

Classification: Conducting polymers may be classified as

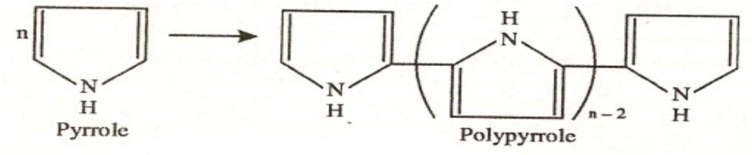


1. Intrinsically conducting polymers :

These types of polymers have a solid backbone made up of extensive conjugated system, which is responsible for conductance. They may be of two types:

(i) **Conducting polymers having conjugated π-electrons in the backbone :** These polymers essentially contain a conjugated π-electron backbone responsible for electrical charge. Under the influence of electrical field conjugated π -electrons of the polymer get excited, which can then be transported through the solid polymer. Fulther, overlapping of orbitals of conjugated π -electrons over the entire backbone results in the formation of valence bands as well as conduction bands, which extend over the complete polymer molecule. The presence of conjugated π -electrons in polymers increases its conductivity, *e.g.,*

Polypyrrole



(ii) Doped conducting polymers: The conducting polymers obtained by exposing the polymer to a charged transfer agent in either gas phase or in solution are called *doped conducting polymers.*

Doping is the process by which conductivity of the polymers may be increased by creating negative or positive charge on the polymer backbone by oxidation or reduction.

Doping may be of two types:

(A) p-Doping : It is done by oxidation process. In this process, the conducting polymer is treated with a Lewis acid.

$$\underset{\text{Polyacetylene}}{(CH)_x} + \underset{\text{Lewis acid}}{A} \rightleftharpoons \underset{p\text{-Doped polyacetylene}}{(CH)_x^+ A^-}$$

(B) n-Doping : It is done by reduction process. In this process, the conducting polymer is treated with a Lewis base.

$$(CH)_x + B \rightleftharpoons (CH)^-_x B^+$$

Polyacetylene Lewis base n-Doped polyacetylene

2. Extrinsically conducting polymers :

Those conducting polymers which owe their conductivity due to the presence of externally added ingredients in them are called *extrinsically conducting polymers.* They are of two types :

(i) Conductive element filled polymers : In this type, polymer acts as a binder to hold the conducting elements together in solid entity.

The minimum concentration of the conductive filler, which is added to let the polymer start conducting is called the *percolation threshold.*

Important characteristics of these polymers are : (a) They possess good bulk conductivity.

(b) They are cheaper.

(c) They are light in weight.

(d) They are mechanically durable and strong.

(e) They are easily processable in different forms, shapes and sizes.

(ii) Blended conducting polymers: These types of polymers are obtained by blending a conventional polymer with a conducting polymer either physically or chemically. Such polymers can be easily processed and possess better physical, chemical and mechanical properties.

3. Coordination or inorganic conducting polymers :

These polymers contain charge transfer complexes and are obtained by combining metal atoms with polydentate ligands.

Q 20: What are the advantages, Limitations and application of conducting polymer.

Ans: Advantages of intrinsically conducting polymers :

(i) Their conductivity

(ii) Their ability to store a charge.

(iii) Their ability to undergo ion exchange.

(iv) They can absorb visible light to give coloured products.

(v) They are transparent to X-rays.

Limitations of intrinsically conducting polymers:

(i) Their conductivities are poorer than metals.

(ii) Their improcessability.

(iii) Their poor mechanical strength.

(iv) They are less stable at high temperatures.

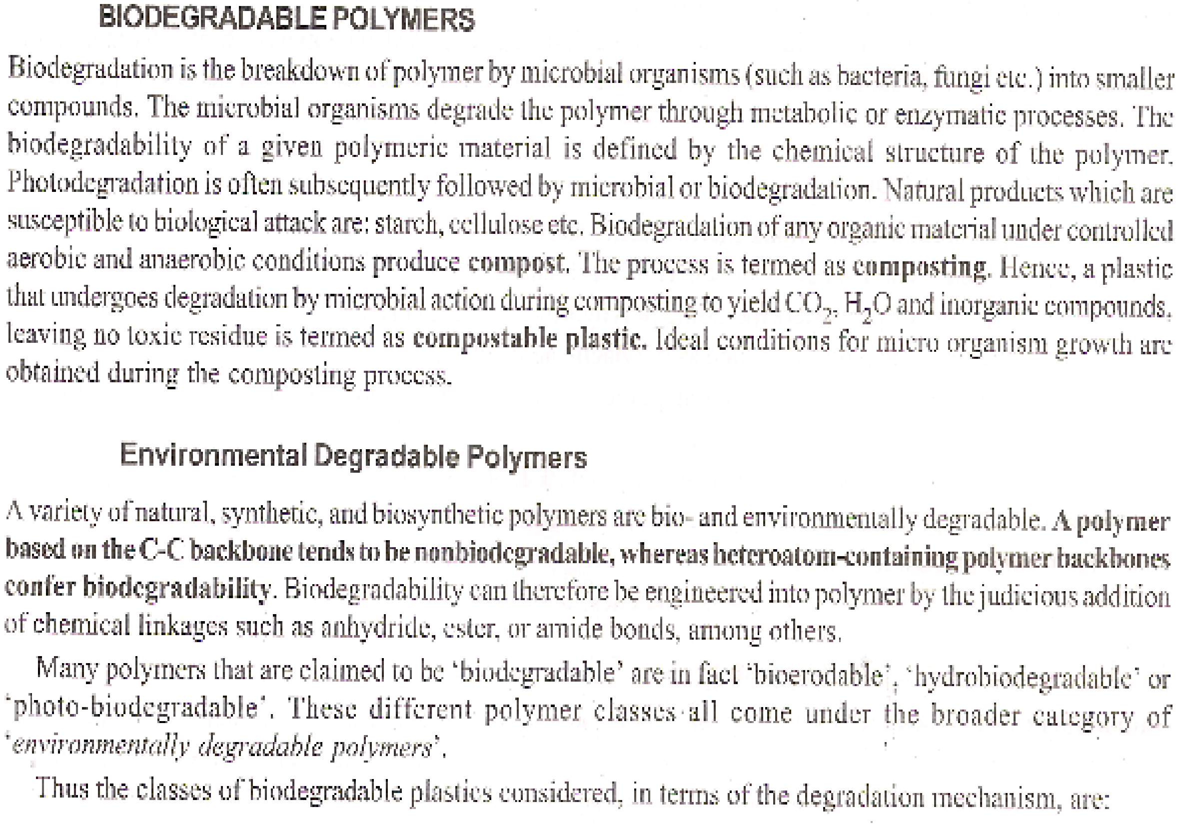
(v) On storage they lead to loss in their conductivity

Applications of conducting polymers: Conducting polymers are widely used :

1. In rechargable batteries.
2. In making analytical sensors for pH, O_2, SO_2, NH_3, glucose, etc.
3. In the preparation of ion exchangers.
4. In controlled release of drugs.
5. In optical filters.
6. In photo voltaic devices.
7. In telecommunication systems.
8. In micro-electronic devices.

9. In bio-medical applications.

Q 21: Write a note on Bio-degradable polymers.



BIODEGRADABLE POLYMERS

Biodegradation is the breakdown of polymer by microbial organisms (such as bacteria, fungi etc.) into smaller compounds. The microbial organisms degrade the polymer through metabolic or enzymatic processes. The biodegradability of a given polymeric material is defined by the chemical structure of the polymer. Photodegradation is often subsequently followed by microbial or biodegradation. Natural products which are susceptible to biological attack are: starch, cellulose etc. Biodegradation of any organic material under controlled aerobic and anaerobic conditions produce **compost**. The process is termed as **composting**. Hence, a plastic that undergoes degradation by microbial action during composting to yield CO_2, H_2O and inorganic compounds, leaving no toxic residue is termed as **compostable plastic.** Ideal conditions for micro organism growth are obtained during the composting process.

Environmental Degradable Polymers

A variety of natural, synthetic, and biosynthetic polymers are bio- and environmentally degradable. **A polymer based on the C-C backbone tends to be nonbiodegradable, whereas heteroatom-containing polymer backbones confer biodegradability**. Biodegradability can therefore be engineered into polymer by the judicious addition of chemical linkages such as anhydride, ester, or amide bonds, among others.

Many polymers that are claimed to be 'biodegradable' are in fact 'bioerodable', 'hydrobiodegradable' or 'photo-biodegradable'. These different polymer classes all come under the broader category of '*environmentally degradable polymers*'.

Thus the classes of biodegradable plastics considered, in terms of the degradation mechanism, are:

Ans:

1. Biodegradable
2. Compostable
3. Hydro-biodegradable
4. Photo-biodegradable
5. Bioerodable

Biodegradable: American society of Testing and Materials (ASTM) defines 'biodegradable' as: "*capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms, that can be measured by standardized tests, in a specified period of time, reflecting available disposal condition.*"

In simple words, biodegradation is the degradation caused by biological activity, particularly by enzyme action leading to significant changes in the material's chemical structure. In essence, biodegradable plastics should break down cleanly, in a defined time period, to simple molecules found in the environment such as carbon dioxide and water.

Compostable: Compostable plastics are a subset of biodegradable plastics. Compostable biodegradable plastics must biodegrade and disintegrate in a compost system during the composting process (typically around 12 weeks at temperatures over 50°C). The compost must meet quality criteria such as heavy metal content, ecotoxicity, and no obvious distinguishable residues caused by the breakdown of the polymers.

Hydro-biodegradable and Photo-biodegradable: Two closely linked mechanisms of degradation that are frequently confused with biodegradation are Hydro-degradation (degradation via hydrolysis) and Photo-degradation (degradation via photolysis). Since both mechanisms are often subsequently followed by microbial degradation, confusion of definition frequently occurs. Hydro-biodegradable and photo-biodegradable polymers are broken down in a **two-step** process - an initial hydrolysis or photo-degradation stage, followed by further biodegradation. Single degradation phase 'water- soluble' and 'photodegradable' polymer also exist.

Bio-erodable: Many polymers that claimed to be 'biodegradable' are in fact 'bioerodable' and degrade without the action of micro-organisms - at least initially in the first step. This is also known as abiotic disintegration, and may include process such as dissolution in water, 'oxidative embrittlement' (heat ageing) or 'photolytic embrittlement' (UV ageing).

Some Biodegradable Polymers:

- Starch based products including thermoplastic starch.
- Polyester blends and Polyvinyl alcohol (PVOH) blends.
- Naturally produced polyesters including polyhydroxybutyrate (PHB).
- Renewable resource polyesters such as polylactic acid (PLA).
- Synthetic aliphatic polyesters including polycaprolactone (PCL) and polybutylene succinate (PBS).
- Aliphatic-aromatic (AAC) copolyesters.
- Hydro-biodegradable polyester such as modified PET.
- Water soluble polymer such as polyvinyl alcohol and ethylene vinyl alcohol.
- Photo-biodegradable plastics.
- Controlled degradation additive masterbatches.

Biopolymers and Bioplastics

Biopolymers are polymers which are present in, or created by, living organisms. These include polymers from renewable resources that can be polymerized to create bioplastics.Carbohydrates and proteins, for example, are biopolymers. Many biopolymers are already being produced commercially on large scales, although they usually are not used for the production of plastics:

Q 22: Define Organo-metallic compounds and give their classification.

14.12 ORGANOMETALLICS

An organometallic compound is generally a compound which possesses a metal-carbon bond. Organometallic chemistry can be viewed as a bridge between organic and inorganic chemistry. The importance of organometallic compounds lies in the fact that these are excellent catalysts which play a major

Ans:

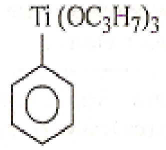
role in the production of pharmaceuticals agrichemicals, flavours and semiconductors etc. Organometallic chemistry is rapidly growing field of chemistry. The discovery of Grinard reagents in 1900 not gave versatile intermediates for a variety of organic preparations.

It may be noted that not all the compounds containing carbon and a metal atom are organometallic. The term 'organometallic' is reserved to the compounds which contain atleast one Metal-Carbon bond. An alkoxide such as $(C_3H_7O_4)$ Ti is not considered as organometallic compound because here the organic group is bonded to Ti through oxygen and not through carbon. Whereas the compound $C_6H_5Ti\ (OC_3H_7)_3$ is an organometallic compound because in this compound Ti is bonded to carbon of the organic group

$(C_6H_5 — Ti)$

$Ti — (OC_3H_7)_4$

Not an organometallic compound



Organometallic (Ti — C bond)

CLASSIFICATION

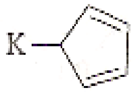
The organometallic compounds can be classified on the basis of the nature of metal-carbon bond.

(1) Ionic compounds of electropositive metals:

The organosodium and organopotassium compounds are essentially ionic organometallic compounds. In these type of compounds the bonding between the metal and the carbon is ionic. The carbon of the organic group (hydrocarbon) carry a negative charge which is strongly attracted by the positively charged metal ion by electrostatic forces of attraction.

These organometallic compounds are formed by the most electropositive metals of group IA and IIA. The formation of these compounds is favoured if the negative charge on the carbon atom is stabilized i.e it is delocalized over several carbon atoms.

Example: $K^+C_5H_5^-$ (potassium cyclopentadienyl). The negative charge is stabilized due to delocalization over the five carbon atoms of cyclopentadienyl ring.



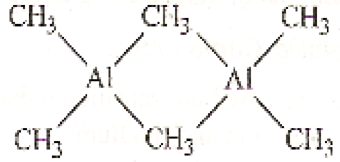
Other examples include $Na^+C_6H_5^-$, $Na^+C_4H_9^-$ etc. These compounds contain a very reactive C_5H_5 group. These compounds are referred to as metal cyclopentadienides. These organometallic compounds show behaviour typical of ionic compounds and are insoluble in organic or non-polar solvents. The reactivity of these compounds depend upon the stability of the anion. However, there are certain metal cyclopentadienides which have substantial amount of covalent character present.

(2) Covalent organometallic compounds:

These compounds have organic past bonded to the metal atom by a normal sigma covalent bond. These compounds are very common and are generally formed by Zn, Cd, Hg and representative elements of group III, IV and V. The covalent organometallic compounds are generally metal-alkyl compounds. Examples are $Pb(C_2H_5)_2$, $(C_6H_5)_2Zn$, $(CH_3)_2Cd$, C_4H_9Li etc. The polarity of the covalent bond between metal and alkyl groups depends upon the difference in electronegativity between metal atom and carbon atom.

(3) Electron deficient organometallic compounds:

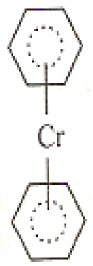
These type of compounds include the compounds having bridging alkyl groups. For example, dimeric trialkyl aluminium which have bridging alkyl groups.



Dimeric dialkyl aluminium

(4) Organometallics involving π bonds:

These constitute an important class of organometallics having metal-ligand bond between a metal and the π orbitals of organic ligands such as alkenes, benzene ring etc. Ferrocene was the first of many π complexes which came to be known as metallocenes. In these complexes the metal ion is sandwitched between two parallel carbocyclic rings became known as "sandwich" compounds. Example,

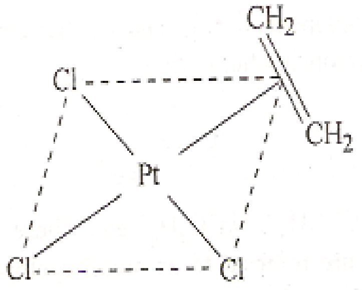


$(C_6H_5)_2$ Cr

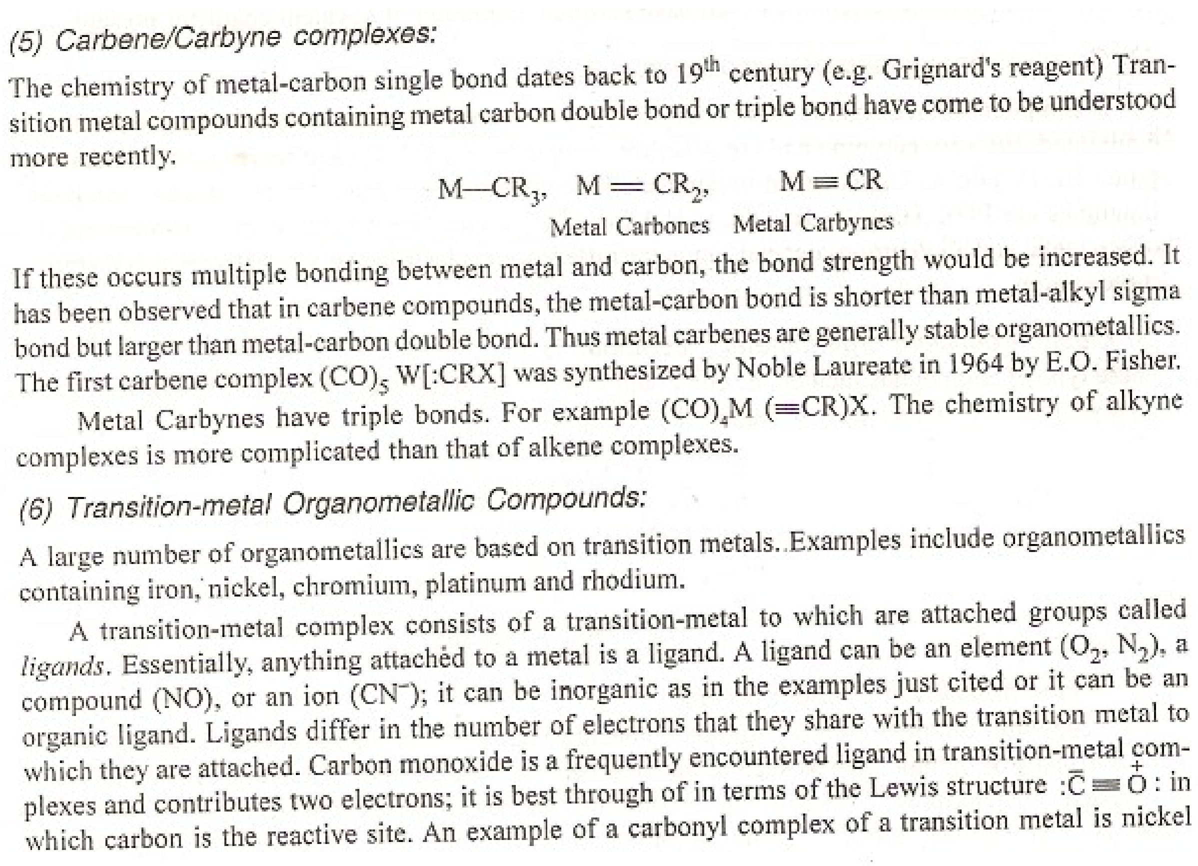
$(C_5H_5)_2$ Fe

common example of ligands forming such type of organometallic compounds are :

Complexes of alkenes are well known for transition metals like Pt(II), Pd(II), Cu(II), Ag(I), Hg(II) etc. The first compound of alkene with the metal ion was reported by Zeise (a Danish Chemist) and is known as Zeise salt. $K[PtCl_3.(C_2H_4)]$



Zeise salt
(π complex)



(5) Carbene/Carbyne complexes:

The chemistry of metal-carbon single bond dates back to 19th century (e.g. Grignard's reagent) Transition metal compounds containing metal carbon double bond or triple bond have come to be understood more recently.

$$M—CR_3, \quad M = CR_2, \quad M \equiv CR$$

Metal Carbones Metal Carbynes

If these occurs multiple bonding between metal and carbon, the bond strength would be increased. It has been observed that in carbene compounds, the metal-carbon bond is shorter than metal-alkyl sigma bond but larger than metal-carbon double bond. Thus metal carbenes are generally stable organometallics. The first carbene complex $(CO)_5$ W[:CRX] was synthesized by Noble Laureate in 1964 by E.O. Fisher.

Metal Carbynes have triple bonds. For example $(CO)_4M(\equiv CR)X$. The chemistry of alkyne complexes is more complicated than that of alkene complexes.

(6) Transition-metal Organometallic Compounds:

A large number of organometallics are based on transition metals. Examples include organometallics containing iron, nickel, chromium, platinum and rhodium.

A transition-metal complex consists of a transition-metal to which are attached groups called *ligands*. Essentially, anything attached to a metal is a ligand. A ligand can be an element (O_2, N_2), a compound (NO), or an ion (CN^-); it can be inorganic as in the examples just cited or it can be an organic ligand. Ligands differ in the number of electrons that they share with the transition metal to which they are attached. Carbon monoxide is a frequently encountered ligand in transition-metal complexes and contributes two electrons; it is best through of in terms of the Lewis structure $:\bar{C} \equiv \overset{+}{O}:$ in which carbon is the reactive site. An example of a carbonyl complex of a transition metal is nickel

Q 23: Discuss the methods for the synthesis of Organometallic Compounds.

Ans:

General Methods of Synthesis of Organometallics

(1) By reductive substitution of alkyl halides: (Preparation of metal alkyls)

The first reported organometallic compounds were prepared by the reductive substitution of alkyl halides. The following equations illustrate these reactions for the commonly used metals lithium and magnesium (R may be hydrogen or alkyl groups in any combination).

$R_3C\text{-}X + 2Li \rightarrow R_3C\text{-}Li + LiX$	An Alkyl Lithium Reagent
$R_3C\text{-}X + Mg \rightarrow R_3C\text{-}MgX$	A Grignard Reagent

The alkyl magnesium halides described in the second reaction are called *Grignard Reagents* after the French chemist, Victor Grignard, who discovered them. The solvent used in this reaction is anhydrous diethyl ether. Typical solvents are normally anhydrous diethyl ether but pentane or hexane can also be used.

The other metals react in a similar manner, but the two shown here are the most widely used.

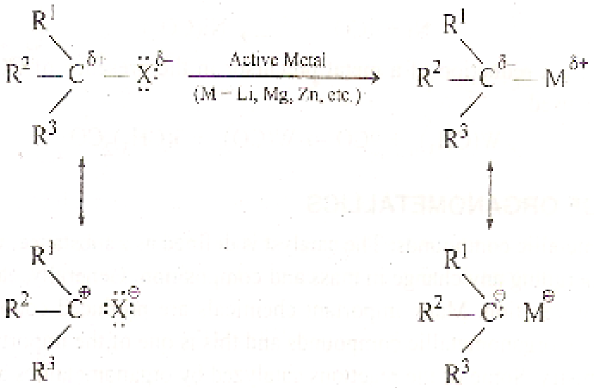
$R\text{-}X + Zn \rightarrow R\text{-}Zn\text{-}X$	An Alkyl Zinc Reagent	1849 E. Frankland
$R\text{-}X + Mg \rightarrow R\text{-}Mg\text{-}X$	A Grignard Reagent	1900 V. Grignard
$R\text{-}X + 2Li \rightarrow R\text{-}Li + LiX$	An Alkyl Lithium Reagent	1930 K. Ziegler

Reactions of organolithium and Grignard reagents reflect the nucleophilic (and basic) character of the functional carbon in these compounds

$$\text{\% Ionic Character of } H_3C - \text{Metal}$$

$$(CH_3)_2Hg < (CH_3)_2Cd < (CH_3)_2Zn < (CH_3)_2Mg < CH_3Li$$

These reactions are obviously substitution reactions, *but they cannot be classified as nucleophilic substitutions*, as were the earlier reactions of alkyl halides. Because the functional carbon atom has been reduced, the polarity of the resulting functional group is inverted (an originally electrophilic carbon becomes nucleophilic). This change, shown below, makes alkyl lithium and Grignard reagents unique and useful reactants in synthesis.



(2) Metal Exchange Reactions:

Alternative methods of preparing a wide variety of organometallic compounds generally involve an exchange reaction in which a given metal is either moved to a new location or replaced by a new metal, which may include B, Al, Ti, V, Fe, Ni, Cu, Mo, Ru, Pd, Sn, Pt, Hg & Pb. Some of these reactions are:

Type 1: $R{-}M + R'{-}H \rightleftharpoons R{-}H + R'{-}M$

Examples:

$$R-C\equiv R-C + C_2H_5MgBr \longrightarrow R-C\equiv R-MgBr + C_2H_6$$

Type 2: $R{-}M + M \rightleftharpoons R{-}M' + M$

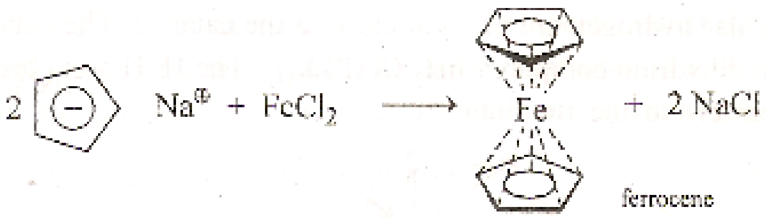
R-M is often a dialkylmercury compound.

Examples:

$$3(C_6H_5)_2Hg + 2Al \rightarrow 2(C_6H_5)_3Al + 3Hg$$

$$(C_2H_5)_2Hg + Mg \rightarrow 2(C_2H_5)_2Mg + Hg$$

Type 3: $R{-}M + M'X \rightleftharpoons R{-}M' + MX$

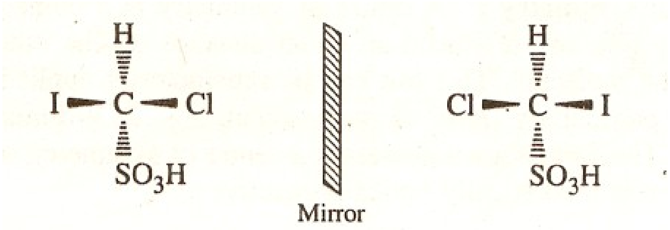


ferrocene

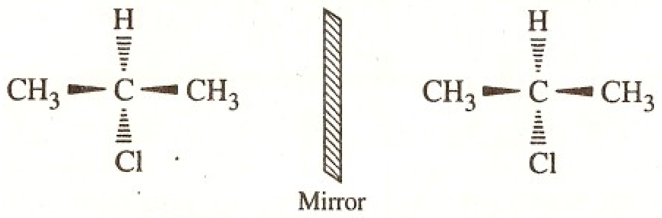
UNIT 3

Q 1. Define term chirality.

Ans: Molecules that are not superimposable on their mirror images are chiral (Greek, Cheir, 'handedness'). A hand and a glove are chiral objects whereas a ball and a cube are achiral objects. Achiral objects can be superimposed on their mirror images. There is close relationship between chirality and optical activity and quite often the scriptions optically active and chiral are interchangeably. Chirality in molecules is usuaily due to the presence of an sp3 carbon atom with 'our different groups attached to it. Such a molecule has no plane of symmetry (a plane f symmetry divides a molecule in such a way that one half is the mirror image of the ther halt) and exists as a pair of enantiomers. A chiral carbon is the one" in which all the four substituents are different. Such carbon atom is sometimes also referred to as asymmetric carbon atom.



Chloroiodomethanesulfonic acid
Not superimposable : enantiomers



Isopropyl chloride
Superimposable : not enantiomers

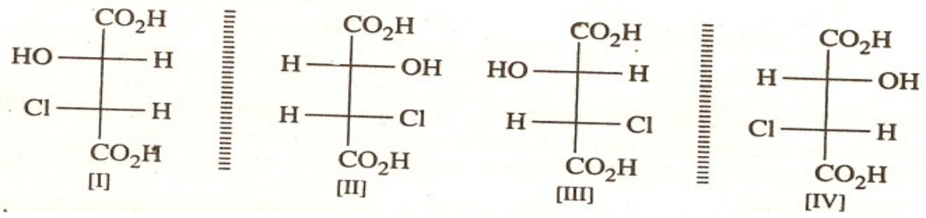
The chiral center: A carbon atom to which four different groups are attached is a chiral center. Many but not all molecules that contain a chiral center are chiral. Many but not all chiral molecules contain a chiral center. There are molecules that contain chiral centers and yet are achiral. (Such achiral molecules always contain more than one chiral center), if there is only one chiral center in a molecule. we can be certain that the molecule is chiral. There are chiral molecules that contain no chiral centers.

Q 2. What do you mean by enantiomerism?

Enantiomerism: Isomers whose structures differ only in being mirror-images of each other and they have identical physical properties except the direction of rotation of plane-polarized light. Such isomers are called enantiomers and the phenomenon is known as enantiomerism. The enantiomers react at different rates and form products in different amounts in asymmetric. environment. They have different solubilities in same chiral solvent. They act at different rates, if anyone of the reagent solvent or catalyst is chiraI. A substance composed of equimolecular amounts of a pair of enantiomers is a racemic modification.

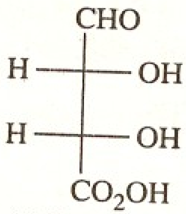
Q 3: What are diastereomers?

Ans: DIASTEREOMERS: Stereoisomers that are not mirror images of each other are called diastereomers. Compounds such as 2-chloro-3-hydroxybutanedioic acid have two dissimilar chiral carbon atoms and hence exists in four stereoisomeric forms. Stereoisomer I or II is a diastereomer of III and IV. Diastereomers are stereoisomers that are not enantiomers and they have the same configuration at one chiral centre but different configuration at the other.

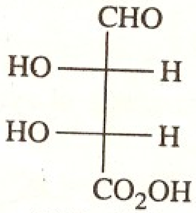


Diastereomers have different physical properties and similar but not identical chemical properties. Having different boiling points, melting points, refractive indices, solubilities, densities, molecular shape and polarity, they can be separated from each other by fractional distillation, fractional crystallization, chromatography, etc.

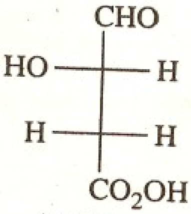
Another example of compounds with two dissimilar chiral carbon atoms are the four carbon sugars, erythrose and threose.



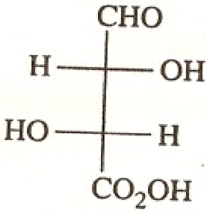
(−) Erythrose



(+) Erythrose



(−) Threose



(+) Threose

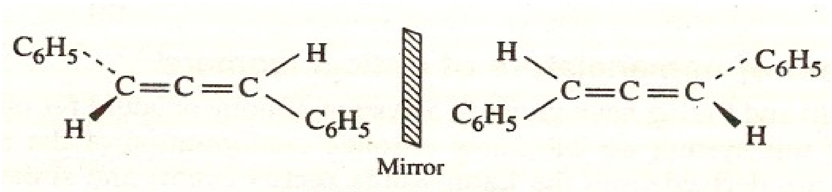
Q 4: Give examples of optical isomerism without chirality.

Ans: Generally the compounds containing an asymmetric carbon shows the optical activity. However, compounds which do not have asymmetric carbon can also shows optical activity if the molecule is dissymmetric.

Example: Allenes: Compounds in which a single carbon atom is connected to two other carbon atoms by a double bond are called allenes. Allene ($CH_2=C=CH_2$) is the simplest member of the series. In allenes the two terminal carbon atoms are sp^2 hybridized and utilize these three hybrid orbitals for forming σ bonds with two hydrogens and a carbon, while the central carbon atom is sp-hybridized and is attached to two carbons through these orbitals forming σ bonds. The central carbon atom still has two p-orbitals available for π-bonding. One of these can overlap to form a π-bond with the p-orbital of one of the methylene groups and the other will overlap in a perpendicular plane with the p-orbital of the other methylene group.

As a consequence of this special geometry of allenes, any allene with the substitution pattern abc = c = cab will exist in two enantiomeric forms.

Example: 1, 3-diphenylpropadiene exist in two enantiomeric form which are not superimposable to its mirror images and are optically active.

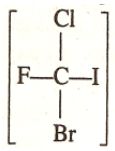


1, 3-Diphenyl propadiene .

Q **5: Discuss rules for Rand S system of nomenclature of optical isomers**

Ans: With the help of this system we can know absolute configuration of the molecule. The symbol *R and* S are derived from the Latin words rectus (right) and sinister (left). The nature of the groups is determined by the priority of the groups which depends upon the following rules :

Rule 1: If the four atoms attached to the chiral center are all different, priority depends on atomic number, with the atom of higher atomic number getting higher priority.

Thus, in bromochloro iodo methane 

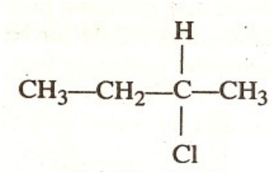
$$\left[\begin{array}{c} Cl \\ | \\ F{-}C{-}I \\ | \\ Br \end{array}\right]$$

The priority sequence of four atoms are I (Z = 53) > Br (Z = 35) > CI (Z = 17) > F (Z = 9). If two atoms are isotopes of the same element, the atom of higher mass number has the higher priority.

Example: ${}_1H^2 > {}_1H^1,\ {}_{17}Cl^{37} > {}_{17}Cl^{35}$

Rule 2: If two atoms attached to the chiral centre are the same, we compare the atoms attach to each of these first atoms.

Example, in see-butyl chloride, in which two of the atoms attached to the chiral center are themselves carbon. In CH_3 the second atoms are H, H, H; in C_2H_5 they are C, H, H.

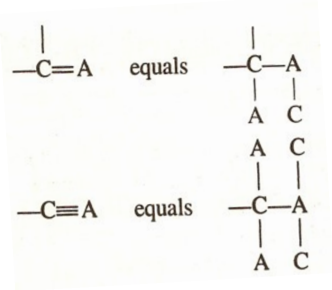


$$CH_3{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}{-}CH_3$$

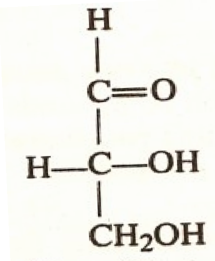
sec-butyl chloride

Since. carbon has a higher atomic number than hydrogen, C_2H_5 has the higher priority. A complete sequence of priority for see-butyl chloride is therefore CI, C_2H_5, CH_3,H.

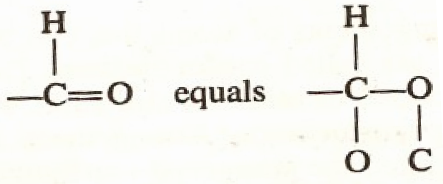
Rule 3: If there is a double or triple bond, both atoms are considered to be duplicated or triplicated. Thus,



Example : In glyceraldehyde the OH group has the highest priority of all,



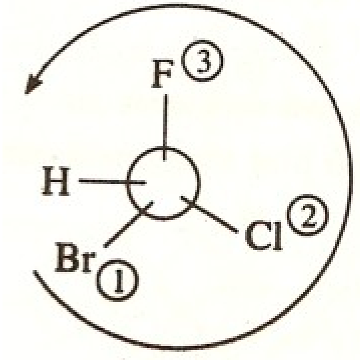
Glyceraldehyde



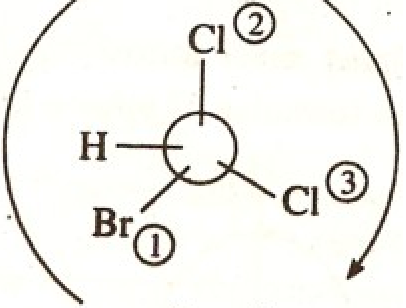
the O, O, H of -CHO takes priority over the O, H, H

of –CH_2OH. The complete sequence is then -OH, -CHO,-CH_2OH, -H

After giving priorities to four atoms or groups attached to an asymmetric centre, the molecule is now rotated so that the atom or group of lowest priority is directed away from the viewer. Now, the arrangement of remaining three atoms or groups is viewed in the decreasing order of their priorities. If the eye moves in a clockwise direction, the configuration is assigned as R (Rectus meaning 'right'). While if the eye moves in anti-clockwise direction, the configuration is assigned as S (Sinister, meaning 'left').



S-config.



R-config.

Q6: Discuss about the different types of attacking reagents.

Ans: Types of Reagents :

The attacking reagents are classified into two main groups.

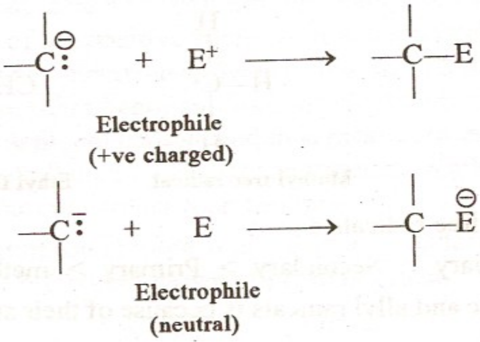
Electrophile or Electrophilic reagents

(ii) Nucleophile or Nucleophilc reagents

(i) Electrophiles or Electrophilic Reagents

A reagent which can accept an electron pair in a reaction is called an electrophile or an electrophilc species, having electron-deficient atom or centre. Electrophiles may be positive ions (including carbonium ions) or neutral molecules with electron deficient centres. E.g.

H^+, Cl^+, Br^+, I^+, NO_2^+, NH_4^+, R_3C^+, RN_2^+, $^+SO_3H$, $AlCl_3$, BF_3



$$-\overset{|}{\underset{|}{C}}\!:^{\ominus} + E^+ \longrightarrow -\overset{|}{\underset{|}{C}}-E$$

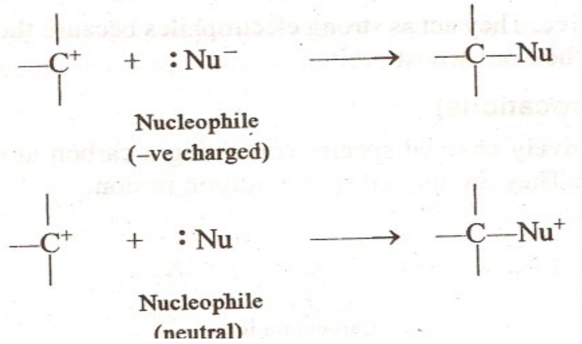
$$-\overset{|}{\underset{|}{C}}\!\overline{:} + E \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{\ominus}{E}$$

(ii) Nucleophiles :

A reagent which can donate an electron pair in a reaction is called a nucleophile. They may be negative ions (including carbanions) or neutral molecules with free electron pairs.

Example :

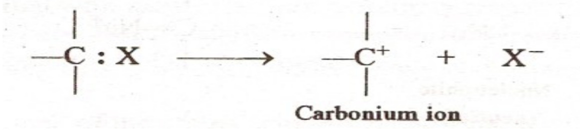
I^-, CN^-, OH^-, $R—CH_2^-$, NH_3, RNH_2, H_2O, ROH



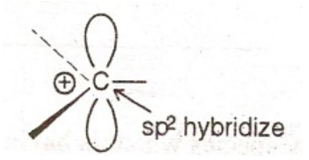
Q 7: What are carbonium ion? Discuss its structure and order of stability.

Ans: **. Carbonium ions (or Carbocations) :**

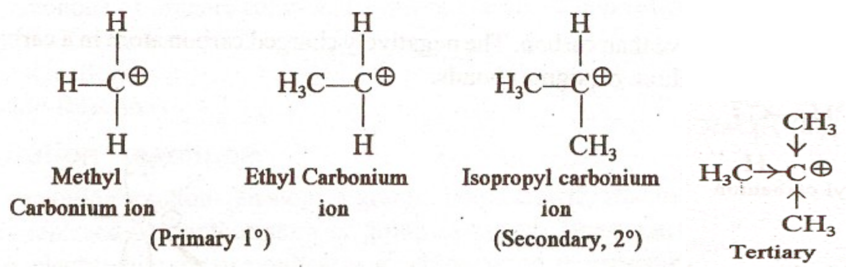
Carbonium ions are positively charged species containing a carbon atom having only six electrons in three sigma bonds. They are formed by heterolytic fission.



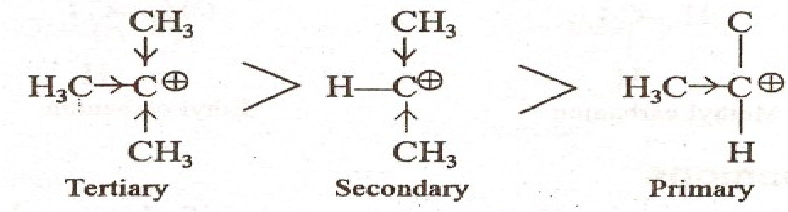
where X is more electronegative than carbon atom. The positively charge carbon atom in a carbonium ion uses sp2 hybrid orbitals to form three σ-bonds.



A vacant p-orbital extends above and below the plane of the σ-bonds. The carbon atom becomes electron-deficient by vacant p-orbital and ready to combine with any substance (nucleophile) which can donate a pair of electrons. The carbonium ions are named after the parent alkyl group and simply adding the words carbonium ion. On the basis of nature of carbon atom, carbonium ions are classified as primary, secondary or tertiary. (e.g.),



Order of stability



Q 8: Write down the mechanism for the nitration of benzene.

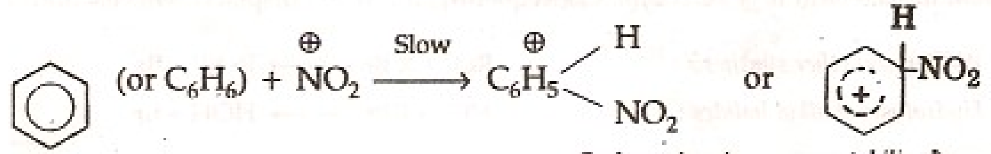
Other examples of electrophilic substitution reactions are :

(1) *Nitration of benzene with conc. HNO_3 and conc. H_2SO_4* to yield *nitribenzene.* The commonly accepted mechanism involves :

Ste I : Formation of *electrophile* (nitronium ion) from HNO_3 by strong acid, H_2SO_4.

$$\underset{\text{Nitric acid}}{HO{-}NO_2} + \underset{\text{Sulphuric acid}}{2\,H_2SO_4} \longrightarrow H_3O^+ + 2\,\overset{\ominus}{HSO_4} + \underset{\substack{\text{Nitronium ion}\\ (\textit{Electrophile})}}{\overset{\oplus}{NO_2}}$$

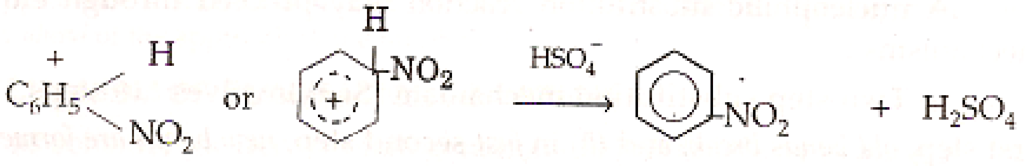
Step II : Benzene (a *nucleophile, i.e.* an electron-rich molecule) is attacked by nitronium ion forming a *carbocation*, which is *stabilized by resonance.*



Carbocation (*resonance stabilized*)

Ans:

Step III : The carbocation then *loses a proton* to yield nitrobenzene.



Nitrobenzene

Q9: Write down the mechanism for the sulphonation of benzene.

Ans:

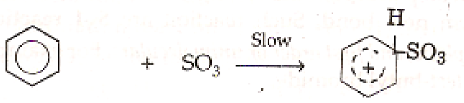
(2) *Sulphonation of benzene by conc. H_2SO_4* to yield *benzene sulphonic acid.* The commonly accepted mechanism involves :

:

Step I : Formation of *electrophile* (SO_3).

$$2\,H_2SO_4 =\!= H_3O^{\oplus} + HSO_4^{\ominus} + \underset{(\textit{Electrophile})}{SO_3}$$

Step II : Benzene (a *nucleophile, i.e.,* an electron-rich molecule) is attacked by SO_3 forming a *carbocation,* which is *resonance stabilized.*



Carbocation (*resonance stabilized*)

Step III : The carbocation then *loses a proton* to form the *anion* of benzene sulphonic acid.

Q 10: Discuss the mechanism of Unimolecular nucleophillic substitution reaction.

Ans:

MECHANISM OF NUCLEOPHILIC SUBSTITUTION REACTION

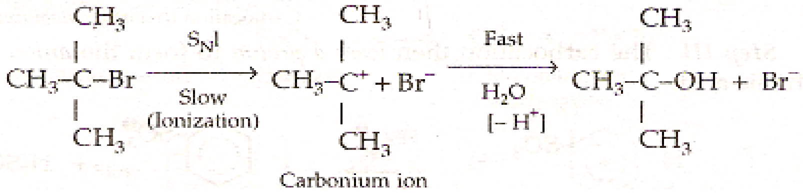
A nucleophilic substitution reaction may proceed through either of *two* mechanisms :

(*i*) **Two-step substitution mechanism (S_N1)** involves *two* steps : (*a*) In *slow* first step, *old bonds break*, and (*b*) in *fast* second step, *new bonds are formed*. Thus :

Step I : $A{-}X \xrightarrow{\text{Slow}} A^+ + X^-$

Step II : $\overline{Nu}: + A^+ \xrightarrow{\text{Fast}} Nu - A$

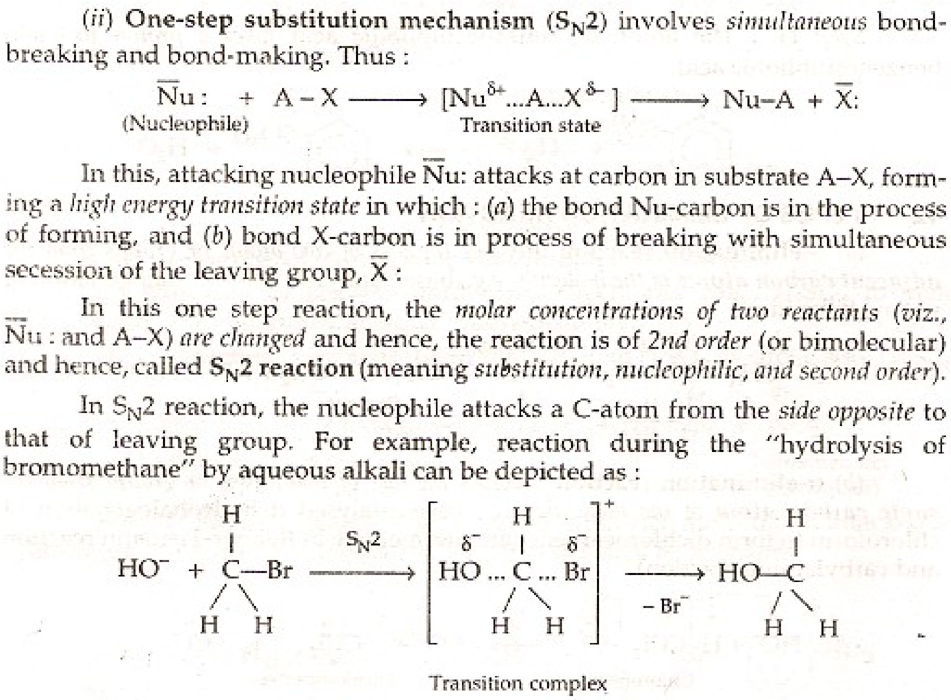
The *rate-determining step* is first step. As the first step does not involve the attacking nucleophile and *molar concentration of one reactant* (A–X) *is only changed*, so the overall reaction is of *first order*, because the time taken by the reaction depends mainly on step 1. No sooner A^+ is generated, it is attacked by the nucleophile $\overline{Nu}:$ to form new bond. Such reaction are **S_N1 reaction** (which means *substitution, nucleophilic, and first order or unimolecular*). For example, the nucleophilic substitution of *tert*-butyl bromide.



$$\underset{CH_3}{\overset{CH_3}{CH_3{-}C{-}Br}} \xrightarrow[\text{Slow (Ionization)}]{S_N1} \underbrace{\underset{CH_3}{\overset{CH_3}{CH_3{-}C^+}}}_{\text{Carbonium ion}} + Br^- \xrightarrow[H_2O\ [-H^+]]{\text{Fast}} \underset{CH_3}{\overset{CH_3}{CH_3{-}C{-}OH}} + Br^-$$

Q 11: Discuss the mechanism of Bi-molecular nucleophillic substitution reaction.

Ans:



(*ii*) **One-step substitution mechanism (S_N2)** involves *simultaneous* bond-breaking and bond-making. Thus :

$$\bar{Nu}: \; + \; A-X \longrightarrow [Nu^{\delta+}...A...X^{\delta-}] \longrightarrow Nu-A \; + \; \bar{X}:$$

(Nucleophile) Transition state

In this, attacking nucleophile $\bar{Nu}$: attacks at carbon in substrate A–X, forming a *high energy transition state* in which : (*a*) the bond Nu-carbon is in the process of forming, and (*b*) bond X-carbon is in process of breaking with simultaneous secession of the leaving group, $\bar{X}$:

In this one step reaction, the *molar concentrations of two reactants* (*viz.*, $\bar{Nu}$: and A–X) *are changed* and hence, the reaction is of *2nd order* (or bimolecular) and hence, called **S_N2 reaction** (meaning *substitution, nucleophilic, and second order*).

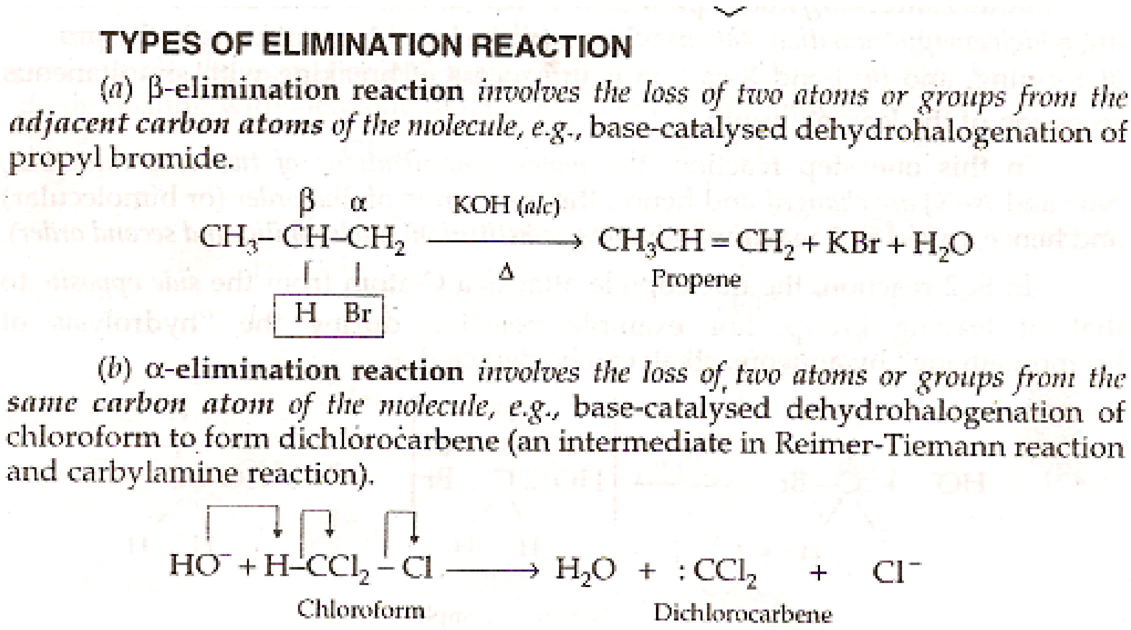
In S_N2 reaction, the nucleophile attacks a C-atom from the *side opposite* to that of leaving group. For example, reaction during the "hydrolysis of bromomethane" by aqueous alkali can be depicted as :

$$HO^- + H_3C\text{—}Br \xrightarrow{S_N2} \left[HO \overset{\delta^-}{...} CH_3 \overset{\delta^-}{...} Br\right]^+ \xrightarrow{-Br^-} HO\text{—}CH_3$$

Transition complex

Q 12: What are the different types of elimination reations?

Ans:



TYPES OF ELIMINATION REACTION

(*a*) **β-elimination reaction** *involves the loss of two atoms or groups from the* ***adjacent carbon atoms*** *of the molecule, e.g.*, base-catalysed dehydrohalogenation of propyl bromide.

$$CH_3\text{–}\underset{H}{\overset{\beta}{C}}H\text{–}\underset{Br}{\overset{\alpha}{C}}H_2 \xrightarrow[\Delta]{KOH\,(alc)} CH_3CH=CH_2 + KBr + H_2O$$

Propene

(*b*) **α-elimination reaction** *involves the loss of two atoms or groups from the* ***same carbon atom*** *of the molecule, e.g.*, base-catalysed dehydrohalogenation of chloroform to form dichlorocarbene (an intermediate in Reimer-Tiemann reaction and carbylamine reaction).

$$HO^- + H\text{–}CCl_2\text{–}Cl \longrightarrow H_2O \; + \; :CCl_2 \quad + \quad Cl^-$$

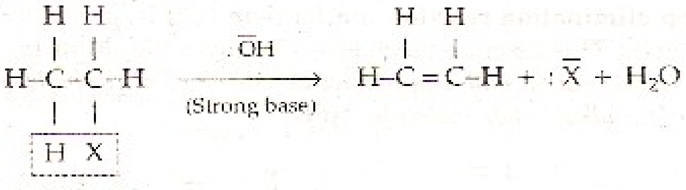
Chloroform Dichlorocarbene

Q 13: Discuss the mechanism of elimination reactions.

Ans:

MECHANISM OF ELIMINATION REACTION

Let us consider the dehydrohalogenation of alkyl halide by heating in presence of alcohol (ROH). Thus :



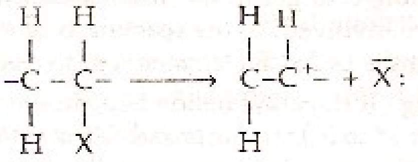
$$\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}{-}H} \xrightarrow[\text{(Strong base)}]{\bar{\mathrm{O}}\mathrm{H}} \mathrm{H{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-}H} + :\bar{\mathrm{X}} + \mathrm{H_2O}$$

Alkyl halide

Depending on the *nature of alkyl halides and other conditions*, the elimination reaction may proceed through *two* different mechanisms :

Two-steps elimination reaction mechanism (E1) involves :

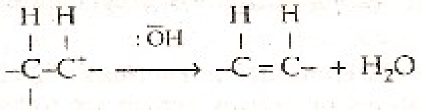
Step 1 : Heterolytic fission to yield *carbocation.*



$$\mathrm{-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}-} \longrightarrow \mathrm{\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{H}{|}}{C^{+}}-} + \bar{\mathrm{X}}:$$

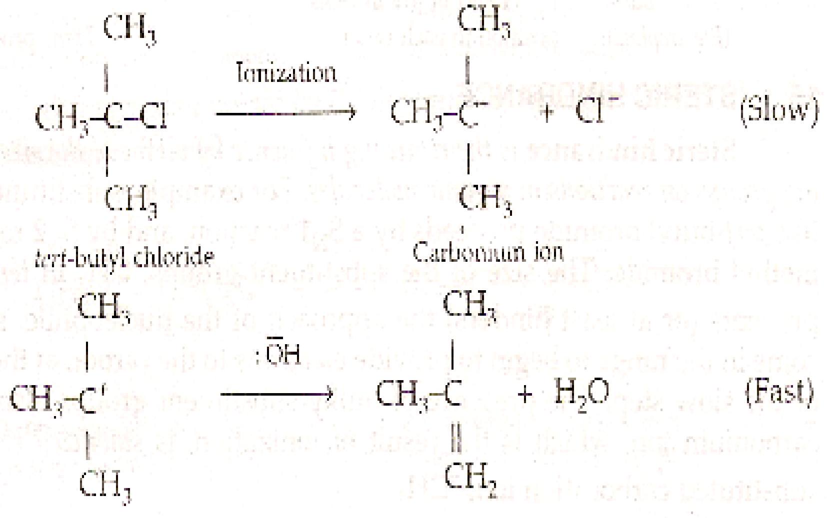
Carbocation

Step 2 : Elimination of proton from β-carbon atom to produce the alkene.



$$\mathrm{-\underset{|}{\overset{\overset{H}{|}}{C}}-\overset{\overset{H}{|}}{C^{+}}-} \xrightarrow{:\bar{\mathrm{O}}\mathrm{H}} \mathrm{-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-} + \mathrm{H_2O}$$

The first step is *slow* step and it *determines the rate*. Since this step involves *the change in molar concentration of alkyl halide only*, so the reaction is of *first order* or *unimolecular*. Hence, such a mechanism is termed E1 (*elimination, first order*). For example, the formation of 2-methylpropene (*iso*butylene) from *tert*-butyl chloride on heating with alcoholic KOH can be explained follows :



$$\mathrm{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl} \xrightarrow{\text{Ionization}} \mathrm{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^{+}}}} + \mathrm{Cl^{-}} \quad \text{(Slow)}$$

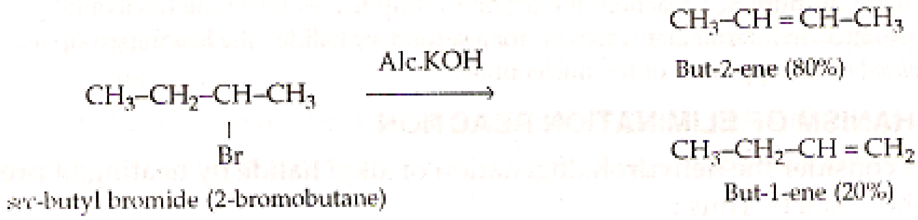
tert-butyl chloride

Carbonium ion

$$\mathrm{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^{+}}}} \xrightarrow{:\bar{\mathrm{O}}\mathrm{H}} \mathrm{CH_3-\underset{\underset{CH_2}{\|}}{\overset{\overset{CH_3}{|}}{C}}} + \mathrm{H_2O} \quad \text{(Fast)}$$

2-methylpropene

Note : Sometimes *more than one alkene* is formed. In such a case, the *main product is the maximum substituted alkene* (***Saytzeff's rule***). For example :



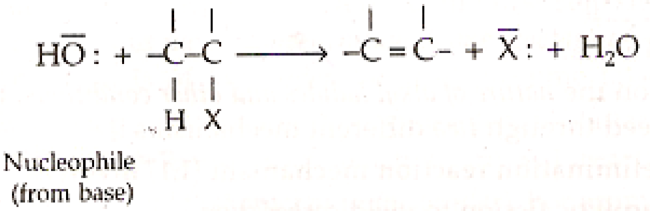
$$CH_3-CH_2-\underset{\substack{|\\ Br}}{CH}-CH_3 \xrightarrow{Alc.KOH} \begin{matrix} CH_3-CH=CH-CH_3 \\ CH_3-CH_2-CH=CH_2 \end{matrix}$$

sec-butyl bromide (2-bromobutane)

But-2-ene (80%)

But-1-ene (20%)

One-step elimination reaction mechanism (E2) is, generally, followed by *primary alkyl halides*. This reaction mechanism involves the *abstraction of a proton by base from the β-carbon atom and* **simultaneous** *release of nucleophile* ((: $\bar{X}$)) *from the α-carbon atom of the alkyl halide molecule*. Thus :



$$H\bar{O}: + -\underset{\substack{|\\ H}}{\overset{|}{C}}-\underset{\substack{|\\ X}}{\overset{|}{C}} \longrightarrow -\overset{|}{C}=\overset{|}{C}- + \bar{X}: + H_2O$$

Nucleophile (from base)

Since in this reaction, changes in the *molar concentration of two reactants* (*viz.* alkyl halide and base) are involved, so the reaction is of *second order or bimolecular*. Hence, such a mechanism is called **E2** (*elimination, second order*).

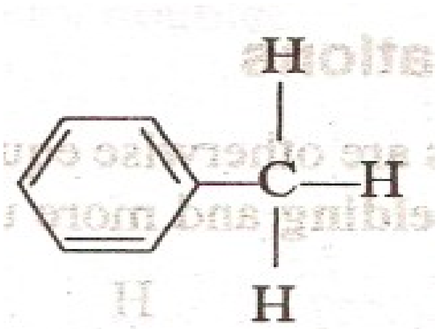
Q 14. Explain the rules governing the splitting of proton signals? Define coupling constant.

Ans: **Rules Governing the Splitting of Proton Signals**

Splitting of a proton signal is caused only by neighbouring or vicinal protons (i.e., protons on adjacent carbon atoms) provided these are non-equivalent to the absorbing proton. Thus, there would be no splitting in the spectrum of ethylene chloride $CICH_2CH_2CI$ (since adjacent carbon has equivalent protons.)

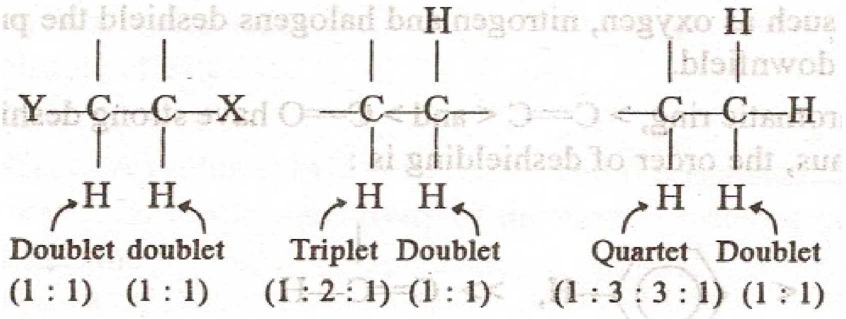
Splitting of one proton by another on the same carbon is rare because such protons are generally equivalent to each other.

The mutual splitting of protons separated by more than two carbon atoms is very uncommon. Thus, there is no splitting of signals in toluene since the nonequivalent protons are separated by more than two carbon atoms.

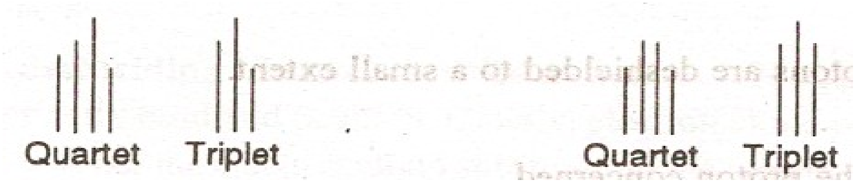


(iv) The number of peaks (N) obtained after the splitting is one more than the number of vicinal protons (n), i. e.,

N = n + 1. Thus, an NMR signal due to a proton is split into a doublet by one vicinal proton, into a triplet by two vicinal protons, into a quartet by three vicinal protons, into a quintet of four vicinal protons.



(v) All the peaks of a given multiplet are not symmetrical. The inner peaks, i. e., the peaks near the other coupled multiplets, are relatively larger than the other peaks. Thus, in case of ethyl bromide, the triplet and quartet obtained are as :



Coupling Constant : The distance between the peaks ina multiplet is referred to as coupling constant. It is represented by the symbol ‘J’ and is expressed in the unit of Hertz.

This constant is measure of the magnitude of splitting effect. Unlike the chemical shifts, the ‘J’ values are independent of the applied magnetic field but depend on the molecular structure.

Q 15: Explain the Lambert’s Beer Law.

Ans: Beer-Lambert's law

When a monochromatic light of intensity I is passed through a solution of concentration, c molar and thickness, *dx,* then intensity of transmitted light changes (due to absorption) by *dI.* Then, probability of absorption of radiation is given by

$$\frac{dI}{I} = -k\,c\,dx$$

where k is the proportionality constant. On integrating the above expression, between limits I = I0 at x = 0 and I = I at x = l, we get

$$\int_{I_0}^{I} \frac{dI}{I} = -k\,c \int_{0}^{l} dx$$

$$\ln \frac{I}{I_0} = -k\,c\,l$$

$$2.303 \log \frac{I}{I_0} = -k\,c\,l$$

$$\log \frac{I_0}{I} = \frac{k}{2.303} c\,.\,l = \epsilon\,.\,c\,.\,l = A$$

Where ϵ = k / 2.303 is called the molar absorptivity coefficient and log I0 / I = *A* is called the absorbance

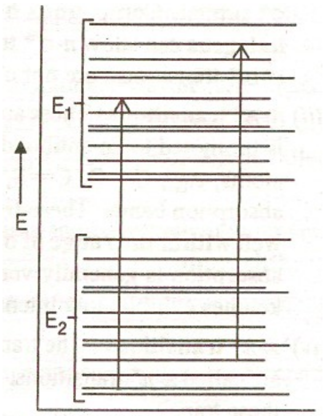
$$\boxed{A = \epsilon\,.\,c\,.\,l}$$

which is Beer-Lambert's law. Thus the absorbance *A* is directly proportional (i) to the molar concentration c as well as (ii) to the path length l.

Q 16: Explain the principle of UV-VIS spectroscopy.

Ans: **Principle :** Absorption of ultraviolet and visible light brings changes in the electronic states of molecules associated with the excitation of an electron from a lower to a higher energy level. Each electronic level in a molecule is associated with a number of vibrational sub-levels (with smaller energy separation) and each vibrational sub-level in turn is associated with a number of rotational sub-levels (with still smaller energy separation). Thus, in its transition to a higher energy level, an electron can go from any of the sub-levels (corresponding to various vibrational and rotational states) in the ground state to any of the sub-levels in the excited state . Had the electronic excitation in the molecule occurred without any accompanying changes in vibrational and rotational sub-levels, the spectrum would have consisted of sharp lines with each line representing a change in electronic state.

But due to the mixing of vibrational and rotational changes with electronic changes in the molecules, there will be a large number of possible transitions requiring only slightly different energies. This will require the absorption of a large number of wavelengths resulting in the formation of broad bands in the spectrum.



Q 17: What are the different types of electronic transitions in UV-VIS spectroscopy.

Ans: **Types of electronic transitions :**

σ- σ* transitions : The transition in which a σ-electron is excited to an antibonding σ*orbital are called σ - σ* transitions. The energy required for these transitions is very high and hence they occur at shorter wavelengths . Thus, the compounds in which all the valence shell electrons are involved in σ bond formation such as saturated hydrocarbons, do not show absorption in the ordinary ultraviolet region.

n- σ* transition : These are the excitations from a non-bonding atomic orbital to an antibonding σ* orbital. Compounds having non-bonding electrons on oxygen, nitrogen, sulphur or halogens can show n-σ* transitions. These transitions are of lower energy than σ - σ * transitions.

(iii) n-π* transition : These are the transitions in which an electron in a non-bonding atomic orbital is promoted to an antibonding π* orbital. Compounds having multiple bonds between hetero atoms, *e.g.,* C=O, C=S, N=O, show these transitions which appear as weak absorption bands. These transitions require only small amounts of energy and take place well with in the range of ordinary ultraviolet region. The intensity of absorption is very low.

(iv) **π*- π* transition :** The transitions in which a π-electron is excited to an antibonding π* orbital are called π- π* transitions. In case of simple moleculescontaining isolated unsaturated carbons, these transitions require relatively higher energy and generally take place in the far UV region.

Q18: Write note on :Chromophores, Auxochromes

Bathochromic shift, Hypsochromic shift

Hyperchromic and hypochromic shift

Ans: **Chromophore:** A structural group such as a double bond that can absorb ultraviolet radiations is called a chromophore.

Bathochromic shift: When the absorption maximum of a compound shifts to a longer wavelength due to the presence of an auxochrome, the compound is said to have undergone a bathochromic shift or red shift .

Auxochrome: An auxillary group that causes bathochromic shift in a chromophore is called an auxochrome.

. Hypsochromic shift : When the absorption maximum of a compound shifts to a shorter wavelength on certain treatment, the compound is said to have undergone a hypsochromic shift/ Blue shift .

Hyperchromic effect : It is an effect due to which the intensity of absorption of maximum increases.

Hypochromic effect : It is an effect due to which the intensity of absorption maximum decreases.

Q 18: Write down the applications of UV-VIS spectroscopy.

Ans: Applications of U.V. spectroscopy :

U.V. spectroscopy is used for characterizing aromatic compounds and conjugated olefins.

It is one of the best way for detecting impurities in organic compounds.

U.V. spectroscopy can be used to study the kinetics of chemical reactions.

Dissociation constants for weak acids and bases can be determined by U.V. spectroscopy.

Structure of chloral can be confirmed by U.V. spectroscopy.

Detection of geometrical isomers**:** UV spectroscopy can be used for detecting the geometrical isomers of a given compound. Trans isomers exhibit λ_{max} at slightly longer wavelengths and have larger extinction coefficients than the cis-isomers

Q 19: Explain the various modes of vibration in IR-spectroscopy.

Ans: **Vibrations :** A diatomic molecule has only one vibrational mode and hence it yields a rather simple system.

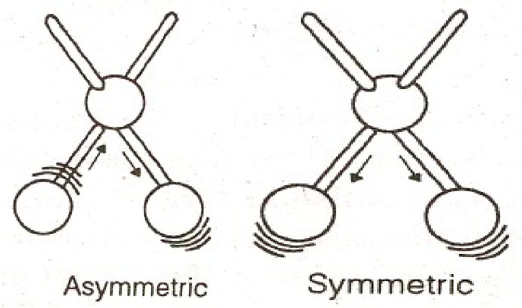
For a polyatomic molecule, several vibrational modes are possible therefore a complicated IR spectrum is obtained for it. Normal modes of vibrations are of two types:

Stretching vibrations

In this type of vibrations, the distance between two atoms increases or decreases but the atoms remain in same bond axis. Stretching vibrations are of two types; viz., **Symmetric** and **asymmetric.**

Symmetric stretching: When the stretching and compressing occurs in a symmetric way, it is called symmetric stretching.

(b) Asymmetric stretching : When one bond is compressing and the other is stretching than it is known as asymmetric stretching.



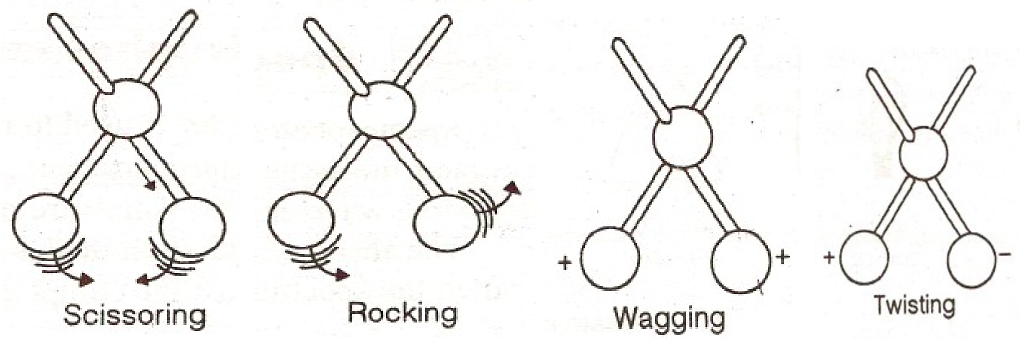
(ii) Bending or deformation vibrations : Such type of vibration may consist of a change in bond angle between bonds with a common atom. These are of four types:

Scissoring in which two atoms approach each other.

Rocking involves the movement of atoms in same direction.

Wagging in which the atoms move up and below the plane with respect to central atom.

Twisting involves the movement of one atom up and the other atom down the plane with respect to central atom.



Q 20: Discuss about the Functional group region and Finger print region in IR Spectroscopy.

Ans: **Functional group region**: The bands in this region are particularly useful in identification of the type of functional groups present in the organic molecule. This region lies in between 5000 cm^{-1} to 1300 cm^{-I}.

Finger print region: The area from 1300 cm^{-1} to 687 cm^{-1} is called the finger print region. The IR spectrum of an unknown substance is compared with spectra of possible substances. It is associated with complex vibrational and rotational energy changes and is characteristic of the molecule as a whole . No two compounds, however, closely related can have identical or superimposable bands in this region.

Q 21: Write down the Applications of IR Spectroscopy .

Ans: 1. Detection of functional groups: Since a particular functional group absorbs IR radiation of nearly same wavelength in all molecules, the presence of characteristic absorption band in that range confirms the presence of that functional group in a molecule.

Determination of molecular structure: The absorption bands in the functional group region (2.5-7μm) tell about the nature of the functional group present in the molecule while those in the finger print region (7-11μm) give substantial information about the structure of the molecule, particularly about the patterns of substitution.

. **Identity of the compounds:** Due to the appearance of a large number of absorption bands in the IR spectra of organic compounds, the probability that any two compounds will produce identical spectra is practically zero. Thus, if two samples afford identical spectra under similar conditions of measurement, they must be samples of the same substance.

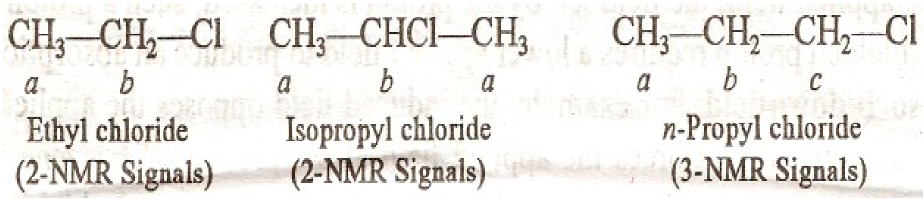
Testing the purity of a sample: It is possible to test the purity ofa given sample by comparing its IR spectrum with that of the pure sample. The spectrum of a pure sample, in general, is sharp and well defined while that of crude or impure sample is blurred, has broad and poorly resolved absorption bands and also contains many extra bands characteristic of the impurities.

5. It has been useful to study inter-molecular and intra-molecular hydrogen bonding.
6. It is useful in the determination of the shape or symmetry of a molecule.
7. It can be used in studying tautomeric equilibria, such as keto-enol.
8. It has been used to determine molecualr weight of polymers by measuring end group concentration.

Q 22: Expain the Equivalent and Non-Equivalent Protons in NMR spectroscopy.

Ans: Equivalent and Non-Equivalent Protons : The protons with the same environment *(i.e., equivalent protons)* absorb at the same applied field strength and produce only one signal while protons with different environment *(i.e., nonequivalent protons)* absorb at different applied strengths and produce different signals. Thus, the **number of signals** in the NMR spectrum tells us how many kinds of protons are present in a given molecule.

The equivalence of protons can be judged by following the method of isomer number. We imagine each hydrogen or proton in the molecule to be substituted by some other atom (say Z). If the substitution of two protons by Z is expected to furnish either the same product or two enantiomeric products (i. e., mirror images), the two protons are chemically and magnetically equivalent, otherwise not.



$\underset{a}{CH_3}-\underset{b}{CH_2}-Cl$ Ethyl chloride (2-NMR Signals)

$\underset{a}{CH_3}-\underset{b}{CHCl}-\underset{a}{CH_3}$ Isopropyl chloride (2-NMR Signals)

$\underset{a}{CH_3}-\underset{b}{CH_2}-\underset{c}{CH_2}-Cl$ *n*-Propyl chloride (3-NMR Signals)

Equivalent protons are represented by the same letter, and non-equivalent protons by different letters. In the above example n-propyl chloride gives 3-NMR signals and has 3-nonequivalent set of protons, whereas its isomer isopropyl chloride gives 2-NMR signals and has two sets of equivalent protons and one non-equivalent proton.

Q 23: What do you mean by chemical shift? Explain shielding and de-shielding.

Ans Chemical shift : The shifts in the position of NMR signals arising from the shielding or deshieldingl,by electrons are referred to as chemicals shifts.

Shielding : When a molecule is placed in a magnetic field, its electron are made to circulate and thus generate a secondary magnetic field called induced magnetic field which may either reinforce or oppose the applied magnetic field. In case the induced field opposes the applied field, the field felt by the proton is diminished; such a proton is said to be shielded. A shielded proton requires a stronger magnetic field to produce an absorption signal and thus is said to absorb upfield.

Deshielding : If the induced field reinforces the applied field, the field felt by the proton is increased; such a proton is said to be deshielded. A deshielded proton requires a lower applied field to produce an absorption signal and thus is said to absorb down field.

Q 24: Which factors Influence the Chemical Shift

Ans: Factors Influencing Chemical Shift

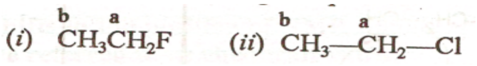
Inductive effect

van der Wall's deshielding

Hydrogen bonding

(i) Inductive effect: A proton is said to be deshielded if it is attached to an electro-negative atom or group. Greater the electro-negativity of the atom, greater is the deshielding caused to the proton.

Example :



(*i*) $\overset{b}{CH_3}\overset{a}{CH_2}F$ (*ii*) $\overset{b}{CH_3}-\overset{a}{CH_2}-Cl$

Two signals are expected for each of the two compounds. Deshielding for protons ‘a’ in compound (i) is more than that for similar protons in compound (ii). As the distance from the electronegative atom increases, the deshielding effect due to it decreases. Protons 'b' are comparatively less shielded .

ii) van der Wall's deshielding : In over crowded molecules it is possible that some proton may be occupying sterically hindered position. Clearly, electron cloud of the bulky group (hindered group) will tend to repel the electron cIoud surrounding the proton. Thus, such a proton will be deshielded and will resonate higher value of δ than expected in the absence of this effect.

Hydrogen bonding : If a hydrogen atom exhibits the property of hydrogen bonding in a compound, it will get deshielded due to the strongly electronegative atoms attached to it. As a result, absorption is shifted down- field.

Q 25: Write down the applications of NMR Spectroscopy :

Identification of substances: Like infrared spectrum, the NMR spectrum of a substance often serves as the 'fingerprint' of the substance. If the NMR spectrum of a given sample is exactly the same· as that of a Known substance, its structural identity is estabiislied.

Qualitative analysis : The NMR spectrum helps to establish the presence or absence of functional groups or other characteristic structural features of a given substance from their characteristic chemical shifts, Appearance of a signal at δ 9.5, is indicative of -CHO group in the sample.

3. Rate of reactions: The NMR spectroscopy forms a means of studying certain reactions which are too fast for measurement by ordinary techniques. One such relation is the fast exchange of protons between two molecules having protons attached to electronegative atoms with lone pair of electrons.

4. Determination of molecular structure.

5. It is used to assay phannaceutical formulations such as aspirin, Phenacitin and Caffeine.

6. It is used for the determination of fluorine content in plastics.

Q 26: Wrrite down the advantages of NMR Spectroscopy

Ans:

It is a totally non-destructive technique.

Compared to IR spectroscopy, it is much easier to study solid samples by this technique as a wide variety of solvents is available.

The NMR spectrometers used now-a-days are so improved that the spectra can be recorded as fast or even faster than IR spectra.

4. It is possible to have computer calculation of NMR spectra.

UNIT-4

Que 1 What do you mean by Hardness of Water

Hardness of water defined as which prevent the lathering of soap.

This is due to presence of in water of certain salts of Ca^{+2}, $Mg+^{2}$ and other Heavy metals dissolved in it. Soaps are Sodium or Potassium salts of higher fatty acids like Oleic acid or Palmitic acid or stearic acids. C17H35COONa Temporary Hardness is mainly caused by Bicarbonates of Calcium, Magnesium and other heavy metals.

$$2C_{17}H_{35}COONa+CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca+2NaCl$$

$$2C_{17}H_{35}COONa+MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2Mg+Na_2SO_4$$

Que 2. What do you mean by temporary and permanent hardness.

Ans: Hardness of water is mainly TWO types

1.Temporary Hardness

2. Permanent Hardness

1. **Temporary Hardness** mainly caused by the presence of dissolved Bicarbonates of Calcium, Magnesium and other Heavy metals and the carbonate of Iron.

Temporary hardness of water mainly responsible salts are…

1. Calcium bicarbonate **$Ca(HCO_3)_2$**
2. Magnesium bicarbonate **$Mg(HCO_3)_2$**

When bicarbonates are decomposed a, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel.

Temporary Hardness can be largely removed by mere Boiling of water.

Temporary Hardness is also known as….Carbonate Hardness or Alkaline Hardness

- $$Ca(HCO_3)_2 \xrightarrow{\textbf{Heat}} CaCO_3+H_2O+CO_2$$

Calcium bicarbonate

- $$Mg(HCO_3)_2 \xrightarrow{\textbf{Heat}} Mg(OH)_2+2CO_2$$

Magnesium bicarbonate

2. Permanent harness: It is due to the presence of dissolved Chlorides and sulphates of Calcium, Magnesium, Iron and other metals

Permanent hardness responsible salts are **$CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$**

Permanent Hardness cannot remove by boiling but it can be removed by the use of chemical agents.

Permanent Hardness also known as Non-Carbonate Hardness, Non-Alkaline

Que 3:What are the various unit of hardness?

Ans: a. 1Parts Per Million : Parts of CaCO3 equivalent hardness per 10^6 parts of water.

1 ppm = 1 part of CaCO 3 equivalent hardness in 10^6parts of water.

b. Milligrams per litre :- Number of milli grams of Calcium Carbonate equivalent hardness present in 1 litre of water.

1 mg / L = 1 mg of $CaCO_3$ equivalent hardness present in 1 liter of water.

1 L = 1 Kg = 1000 g = 1000 x 1000 mg = 10^6 mg.

1 mg /L= 1 mg of $CaCO_3$ eq per 10^6mg of H_2O = 1 ppm

c. Clarke's degree : (°Cl) : It is the number of grams (1/7000 lb) of CaCO 3 equivalent hardness per 70,000 parts of water.

1Clarke = 1 gram of $CaCO_3$ eq hardness per gallon of water.

= 1 part of CaCO3 of hardness per 70,000 parts of water.

d. Degree French (°Fr) : It is in the parts of CaCo3 eq hardness per 10^5 parts of water.

Relation between various units o hardness:

1 ppm = 1 mg /L = 0.1 0Fr = 0.07 0CL = 0.02 meg / L

Q4. One liter of water showed the following analysis: Mg(HCO3)2 = 0.0256 gms, Ca(HCO3)2 = 0.0156 gms, NaCl = 0.0167 gms, CaSO4 = 0.0065 gms, and MgSO4 = 0.0054 gms. Calculate temporary, permanent and total hardness.

S.No.	Constituent	Amount mg/lit	MF	Equivalent of CaCO3 (mg/l)
1.	CaSO4	6.	100/136	4.77

2.	$MgSO_4$	5.	100/120	4.5
3.	$Ca(HCO_3)_2$	15.	100/162	9.6
4.	$Mg(HCO_3)_2$	25.	100/146	17.5
5.	NaCl	16.	--	--

Temporary hardness = $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$

= 17.5 + 9.6 = 27.1 ppm

Permanent hardness = $CaSO_4$ + $MgSO_4$

= 4.77 + 4.5 = 9.27 ppm

Total Hardness = Temporary hardness + Permanent hardness = 27.1 + 9.27 = 36.37 ppm.

Q5. 2 liters of water obtained from a bore well gave thefollowing analysis for salts. $FeSO_4$=30.4mg, $CaSO_4$=13.6mg, $MgCl_2$=48mg, $Ca(HCo_3)_2$=32.4 , $mg(HCo_3)_2$=14.6mg, NaCl=11.7mg. Find the total hardness of water in ppm units, giving temporary &permanent hardness assuming the at. Mass of Fe=56, Ca=40, Mg=24, Na=22.

S.No	**Constituent**	**Amount mg/lit**	**MF**	**$CaCO_3$ equivalent**
1.	$FeSO_4$	30.4	100/152	20
2.	$CaSO_4$	13.6	100/136	10
3.	$MgCl_2$	48	100/95	50
4.	$Ca(HCO_3)_2$	32.4	100/162	20
5.	$Mg(HCO_3)_2$	14.6	100/146	10
6.	NaCl	11.7	---	--

Temporary hardness = $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$

= 10 + 20 = 30 ppm

Permanent hardness = $FeSO_4$ + $CaSO_4$ + $MgCl_2$

= 20 + 10 + 50 = 80 ppm

Total Hardness = Temporary hardness + Permanent hardness = 30 + 80 = 110 ppm

Q6. One litre of water from an underground reservoir in Tirupathi Town in Andhra Pradesh showed the following analysis for its contents: $Mg(HCO_3)_2$ = 42 mg; $Ca(HCO_3)_2$ = 146mg; $CaCl_2$ =71mg; NaOH = 40mg; $MgSO_4$ = 48 mg; organic impurities = 100 mg; Calculate temporary, permanent and total hardness. [JUNE-2011]

S.No.	Constituent	Amount mg/lit	MF	Equivalent of $CaCO_3$ (mg/l)
1.	$CaCl_2$	7	100/111	65.4
2.	$MgSO_4$	4	100/120	40
3.	$Ca(HCO_3)_2$	1	100/162	90.1
4.	$Mg(HCO_3)_2$	4	100/146	28.7
5.	NaOH	4	--	--

Temporary hardness = $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$

= 28.7 + 90.1 = 118.8 ppm

Permanent hardness = $CaCl_2$ + $MgSO_4$

= 65.4 + 40 = 105.4 ppm

Total Hardness = Temporary hardness + Permanent hardness = 118.8 + 105.4 = 124.2 ppm

Q7. One liter of water from an underground reservoir in Nalgonda Town in Andhra Pradesh the following analysis. for its contents:: $Mg(HCO_3)_2$ = 0.0146 gms; $Ca(HCO_3)_2$ = 0.0081 gms; $MgSO_4$ = 0.0012 gms; $CaSO_4$ = 0.0136 gms; NaCl = 0.0585 gms; Organic impurities = 100 mg; Calculate temporary, permanent and total hardness of this sample of water in degree French. [JAN-2012]

S.No.	Constituent	Amount mg/lit	MF	Equivalent of $CaCO_3$ (mg/l)
1.	$CaSO_4$	136	100/136	100
2.	$MgSO_4$	12	100/120	10
3.	$Ca(HCO_3)_2$	81	100/162	50
4.	$Mg(HCO_3)_2$	146	100/146	100
5.	NaCl	585	--	--

Temporary hardness = $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$

= 100 + 50 = 150 ppm

Temporary hardness = 150 X 0.1 = 15 ^{0}Fr

Permanent hardness = $CaSO_4$ + $MgSO_4$

= 100 + 10 = 110 ppm

Permanent hardness = 110 X 0.1 = 11 ^{0}Fr

Total Hardness = Temporary hardness + Permanent hardness = 150 + 110 = 260 ppm

Total hardness = 260 X 0.1 = 26 ^{0}Fr

Q.8 One liter of water sample collected from a water source has shown the following analysis. $Mg(HCO_3)_2$ = 14.6 mg, $MgSO_4$ = 12 mg, $Ca(HCO_3)_2$ = 16.2 mg, $CaCl_2$ = 22.2 mg, $MgCl_2$ = 9.5 mg and organic impurities 100 mg. Calculate temporary and permanent hardness in Degree French. [JUNE-2012]

S.No.	Constituent	Amount mg/lit	MF	Equivalent of $CaCO_3$ (mg/l)
1.	$MgCl_2$	9.	100/95	10
2.	$MgSO_4$	1	100/120	10
3.	$Ca(HCO_3)_2$	16.	100/162	10
4.	$Mg(HCO_3)_2$	14.	100/146	10

Temporary hardness = $Mg(HCO_3)_2 + Ca(HCO_3)_2$

= 10 + 10 = 20 ppm

Temporary hardness = 20 X 0.1 = 2 ^{0}Fr

Permanent hardness = $MgCl_2 + MgSO_4$

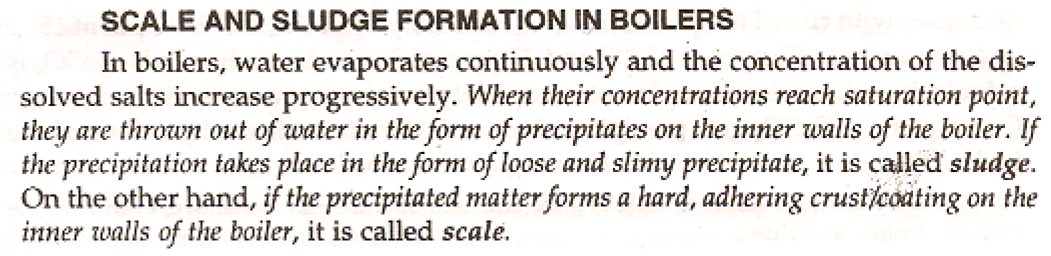
= 10 + 10 = 20 ppm

Permanent hardness = 20 X 0.1 = 2 ^{0}Fr

Total Hardness = Temporary hardness + Permanent hardness = 20 + 20 = 40 ppm

Total hardness = 40 X 0.1 = 4 ^{0}Fr

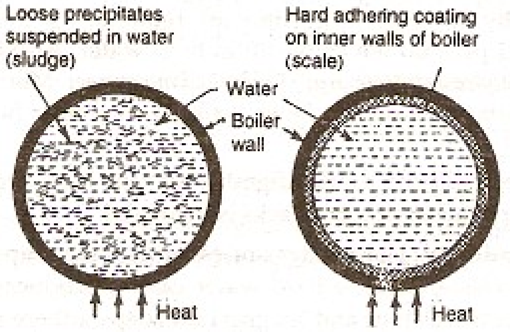
Q.no9: Write note on scale and sludge?



SCALE AND SLUDGE FORMATION IN BOILERS

In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively. *When their concentrations reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. If the precipitation takes place in the form of loose and slimy precipitate,* it is called ***sludge***. On the other hand, *if the precipitated matter forms a hard, adhering crust/coating on the inner walls of the boiler,* it is called ***scale***.

Sludge *is a soft, loose and slimy precipitate formed within the boiler.* Sludge can easily be *scrapped off with a wire brush.* It is formed at comparatively *colder portions of the boiler* and collects in areas of the system, where the *flow rate is slow or at bends. Sludges are formed by substances which , have greater solubilities in hot water than in cold water, e.g.,* $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$, *etc.*



Scale and sludge in boilers.

Hardness – < 0.2 ppm
Caustic albalinity – 0.15 – 0.45 ppm
Soda alkalinity – 0.15 – 1 ppm
Excess soda ash – 0.3 – 0.55 ppm

If excess of impurities are present in boiler feed water, they cause the following problems.

(*i*) Scale or sludge formation
(*ii*) Corrosion
(*iii*) Priming
(*iv*) Foaming
(*v*) Caustic embrittlement
(*vi*) Scale formation due to presence of silica

Que 10: **What re disadvantages and prevention of scale and sludge formation.**

Disadvantages of sludge formation : (1) Sludges are poor conductor of heat, so they tend to waste a portion of heat generated. (2) If sludges are formed along-with scales, then former gets entrapped in the latter and both get deposited as scales. (3) Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, gauge-glass connection, thereby causing even choking of the pipes.

Prevention of sludge formation : (1) By using well softened water. (2) By frequently *'blow-down operation'*, *i.e.*, drawing off a portion of the concentrated water.

Scales *are hard deposits, which stick very firmly to the inner surfaces of the boiler.* Scales are difficult to remove, even with the help of hammer and chisel. *Scales are the main source of boiler troubles.* Formation of scales may be due to :

(1) *Decomposition of calcium bicarbonate* :

$$Ca(HCO_3)_2 \longrightarrow \underset{\text{Scale}}{CaCO_3} \downarrow + H_2O + CO_2 \uparrow$$

However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low-pressure boilers. But in high-pressure boilers, $CaCO_3$ is soluble.

$$CaCO_3 + H_2O \longrightarrow Ca(OH)_2\ (\text{soluble}) + CO_2 \uparrow$$

(2) *Deposition of calcium sulphate :* The solubility of calcium sulphate in water decreases with rise of temperature. Thus, solubility of $CaSO_4$ is 3,200 ppm at 15°C and it reduces to 55 ppm at 230°C and 27 ppm at 320°C. In other words, $CaSO_4$ is soluble in cold water, but almost completely insoluble in super-heated water. Consequently, $CaSO_4$ gets precipitated as *hard scale* on the heated portions of the boiler. *This is the main cause of scales in high-pressure boilers.*

Note : Calcium sulphate scale is quite adherent and difficult to remove, even with the help of hammer and chisel.

(3) *Hydrolysis of magnesium salts* : Dissolved magnesium salts undergo hydrolysis (at prevailing high temperature inside the boiler) forming magnesium hydroxide precipitate, which forms a *soft type of scale, e.g.,*

$$MgCl_2 + 2H_2O \longrightarrow \underset{\text{Scale}}{Mg(OH)_2} \downarrow + 2HCl \uparrow$$

(4) *Presence of silica* : (SiO_2), even present in small quantities, deposits as calcium silicate ($CaSiO_3$) and / or magnesium silicate ($MgSiO_3$). These deposits stick *very firmly* on the inner side of the boiler surface and are *very difficult to remove.* One important source of silica in water is the *sand filter.*

Disadvantages of scale formation : (1) ***Wastage of fuel* :** Scales have a *low thermal conductivity*, so the rate of heat transfer from boiler to inside water is greatly decreased. In order to provide a steady supply of heat to water, *excessive or over-heating* is done and this causes *increase in fuel consumption.* The wastage of fuel depends upon the thickness and the nature of scale :

Thickness of scale (mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

(2) *Lowering of boiler safety* : Due to scale formation, *over-heating* of boiler is to be done in order to maintain a constant supply of steam. The over-heating of the boiler tube makes the boiler material *softer* and *weaker* and this causes *distortion of boiler tube* and makes the boiler *unsafe* to bear the pressure of the steam, especially in high-pressure boilers.

(3) *Decrease in efficiency* : Scales may sometimes deposit in the valves and condensers of the boiler and choke them partially. *This results in decrease in efficiency of the boiler.*

(4) *Danger of explosion* : When thick scales crack, due to uneven expansion, the water comes suddenly in contact with over-heated iron plates. This causes in formation of *a large amount of steam suddenly*. So sudden high-pressure is developed, which may even cause explosion of the boiler.

Removal of scales : (*i*) With the help of scraper or piece of wood or wire brush, if they are loosely adhering. (*ii*) By giving *thermal shocks* (*i.e.*, heating the boiler and then suddenly cooling with cold water), if they are brittle. (*iii*) By dissolving them by adding them *chemicals*, if they are adherent and hard. Thus, calcium carbonate scales can be dissolved by using 5–10% HCl. Calcium sulphate scales can be dissolved by adding EDTA (ethylene diamine tetra acetic acid), with which they form soluble complexes. (*iv*) By frequent *blow-down operation*, if the scales are loosely adhering.

Q.No11. Explain priming and foaming?

PRIMING AND FOAMING

When a boiler is steaming (i.e., producing steam) rapidly, some particles of the liquid water are carried along-with the steam. This process of 'wet steam' formation, is called **priming**. Priming is caused by : (*i*) the presence of large amount of dissolved solids ; (*ii*) high steam velocities ; (*iii*) sudden boiling ; (*iv*) improper boiler design, and (*v*) sudden increase in steam-production rate.

Foaming *is the production of persistent foam or bubbles in boilers, which do not break easily*. Foaming is due to presence of substances like *oils* (which greatly reduce the surface tension of water).

Priming and foaming, usually, occur *together*. *They are objectionable because :* (*i*) dissolved salts in boiler water are carried by the wet steam to super-heater and turbine blades, where they get deposited as water evaporates. This deposit reduces their efficiency ; (*ii*) dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery ; (*iii*) actual height of the water column cannot be judged properly, thereby making the maintenance of the boiler pressure becomes difficult.

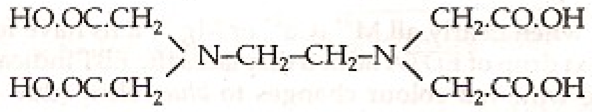
Priming can be avoided by : (*i*) fitting mechanical steam purifiers ; (*ii*) avoiding rapid change in steaming rate ; (*iii*) maintaining low water levels in boilers, and (*iv*) efficient softening and filtration of the boiler-feed water.

Foaming can be avoided by : (*i*) adding anti-foaming chemicals like castor oil, or (*ii*) removing oil from boiler water by adding compounds like sodium aluminate.

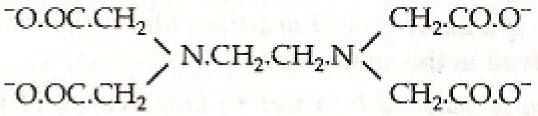
Q.No 12. Explain the estimation of hardness with EDTA method?

ESTIMATION OF HARDNESS OF WATER

EDTA method : This is a *complexometric method*. Ethylene diamine tetraacetic acid (EDTA),

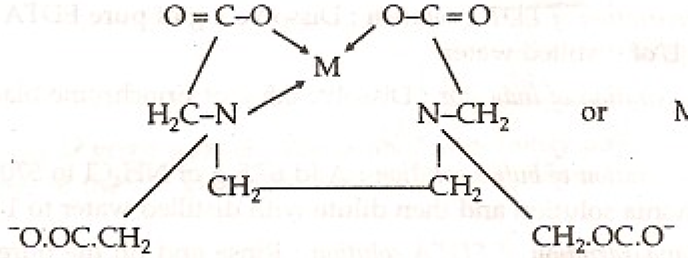


in the form of its sodium salt yields the *anion* ;



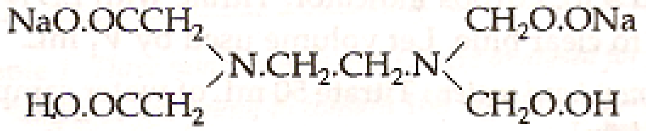
which *forms complex ions* with Ca^{2+} and Mg^{2+}.

Thus :



or MY^{2-}

where M = Ca or Mg. It may be pointed the EDTA is employed as its *disodium salt*,



(or Na_2H_2Y)

(Mol. wt. = 372.24 ; Eq. wt. = 186.14), *i.e.*, M soln. = 2 N soln.)

In order to determine the *equivalence point* (*i.e.*, just completion of metal-EDTA complex formation), indicator **eriochrome black-T** or **EBT** (an alcoholic solution of blue dye) is employed, which form *unstable wine-red complex* with Cu^{2+} and Mg^{2+} ions. However, this indicator is effective at a *pH of about 10.* When EBT is added to hard water buffered to a pH of about 10 (by employing $NH_4OH–NH_4Cl$ buffer), a *wine-red* unstable complex is formed. Thus :

$$\underset{(Ca^{2+} \text{ or } Mg^{2+} \text{ of hard water})}{M^{2+}} + \text{EBT} \xrightarrow{pH = 10} \underset{\text{Wine-red}}{[\text{M–EBT}] \text{ complex}}$$

So initially a wine-red coloured is obtained. During the course of titration against EDTA solution, EDTA combines with M^{2+} (or Ca^{2+} or Mg^{2+}) ions from *stable complex*, M-EDTA and releasing free EBT, which instantaneously combines with M^{2+} ions still present in the solution, thereby wine-red colour is retained. Thus :

$$\underset{\text{Wine-red}}{[\text{M–EBT] complex}} + \text{EDTA} \xrightarrow{\text{Titration}} [\text{M–EDTA] complex} + \underset{\text{(Blue)}}{\text{EBT}}$$

$$\underset{(Ca^{2+}\text{ or }Mg^{2+}\text{ still present})}{M^{2+}} + \underset{\text{(Blue)}}{\text{EBT}} \longrightarrow \underset{\text{Wine-red}}{[\text{M–EBT] complex}}$$

However, when nearly all M^{2+} (Ca^{2+} or Mg^{2+}) ions have formed [M-EDTA] complex, then next drop of EDTA added displaces the EBT indicator form [M-EBT] complex and the wine-red colour changes to *blue colour* (due to EBT). Thus, at equivalence point,

$$[\text{M–EBT] complex} + \text{EDTA} \longrightarrow [\text{M–EDTA] complex} + \text{EBT (blue)}$$

Thus, change of ***wine-red*** *colour to distinct* ***blue*** *marks the end-point of titration.*

Standardization of EDTA solution : Rinse and fill the burette with EDTA solution. Pipette out 50 mL of standard hard water in a conical flask. Add 10-15 mL of buffer solution and 4 to 5 drops indicator. Titrate with EDTA solution, till wine-red colour changes to clear blue. Let volume used by V_1 mL.

Titration of unknown hard water : Titrate 50 mL of water sample just in step (5). Let volume used be V_2 mL.

Titration of permanent hardness : Take 250 mL of the water sample in a large beaker. Boil it, till the volume is reduced to about 50 mL [when all the bicarbonates are decomposed to insoluble $CaCO_3 + Mg(OH)_2$]. Filter, wash the precipitate with distilled water, collecting filtrate and washings in a 250 mL measuring flask. Finally make up the volume to 250 mL with distilled water. Then, titrate 50 mL of boiled water sample just as in step (5). Let volume used by V_3 mL.

Calculations : 50 mL of standard hard water

$= V_1$ mL of EDTA

$\therefore$ 50 × 1 mg of $CaCO_3$ $= V_1$ mL of EDTA

$\therefore$ 1 mL of EDTA $= 50/V_1$ mg of $CaCO_3$ eq

Now 50 mL of given hard water $= V_2$ mL of EDTA

$$= \frac{V_2 \times 50}{V_1} \text{ mg of } CaCO_3 \text{ eq}$$

$\therefore$ 1 L (1,000 mL) of given hard water

$$= 1{,}000\, V_2/V_1 \text{ mg of } CaCO_3 \text{ eq}$$

$\therefore$ *Total* hardness of water $= 1{,}000\, V_2/V_1$ mg/L

$$= \boxed{1{,}000\, V_2/V_1 \text{ ppm}} \qquad ...(i)$$

Now 50 mL of boiled water $= V_3$ mL of EDTA

$$= \frac{V_3 \times 50}{V_1} \text{ mg of } CaCO_3 \text{ eq}$$

$\therefore$ 1,000 mL (= 1 L) of boiled water $= 1{,}000\, V_3/V_1$ mg of $CaCO_3$ eq

$\therefore$ *Permanent* hardness $= 1{,}000\, V_3/V_1$ ppm ...(*ii*)

and *temporary* hardness = [Total – Permanent] hardness

$$= 1{,}000 \left[\frac{V_2}{V_1} - \frac{V_3}{V_1}\right] \text{ ppm.}$$

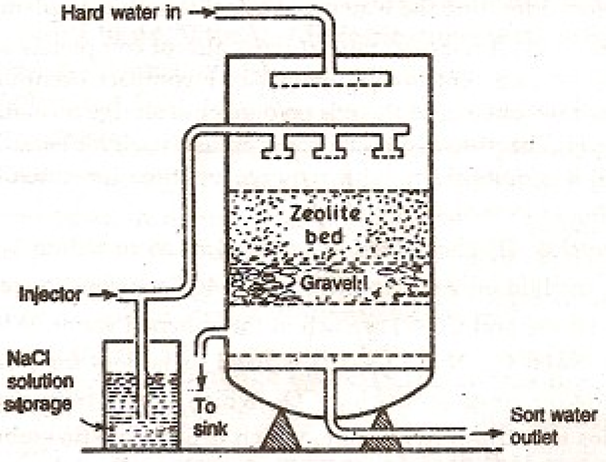
$$= \boxed{\frac{1{,}000\,(V_2 - V_3)}{V_1} \text{ ppm}} \qquad ...(iii)$$

Advantages of EDTA method : This method is definitely preferable to the other methods, because of the : (*i*) greater accuracy ; (*ii*) convenience, and, (*iii*) more rapid procedure.

Q.No13 Explain the zeolite method for softening of water?

(2) **Zeolite or permutit process :** Chemical structure of sodium zeolite may be represented as: $Na_2O.Al_2O_3.\ x\ SiO_2.\ y,H_2O$ where $x = 2 - 10$ and $y = 2 - 6$.. Zeolite is hydrated sodium alumino silicate, capable of exchanging reversibly its sodium ions for hardness-producing ions in water. Zeolites are also known as permutits. Zeolites are of two types : (*i*) ***Natural zeolites*** are *non-porous*. For example, natrolite, $Na_2O.Al_2O_3.4SiO_2.2H_2O$. (*ii*) ***Synthetic zeolites*** are porous and possess *gel structure*. They are prepared by heating together china clay, faldspar and soda ash. Such zeolites possess higher exchange capacity per unit weight than natural zeolites.

Process : For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, kept in a cylinder (see Fig.). The hardness-causing ions (Ca^{2+}, Mg^{2+}, etc.) are retained by the zeolite as CaZe and MgZe ; while the outgoing water contains sodium salts. Reactions taking place during the softening process are :



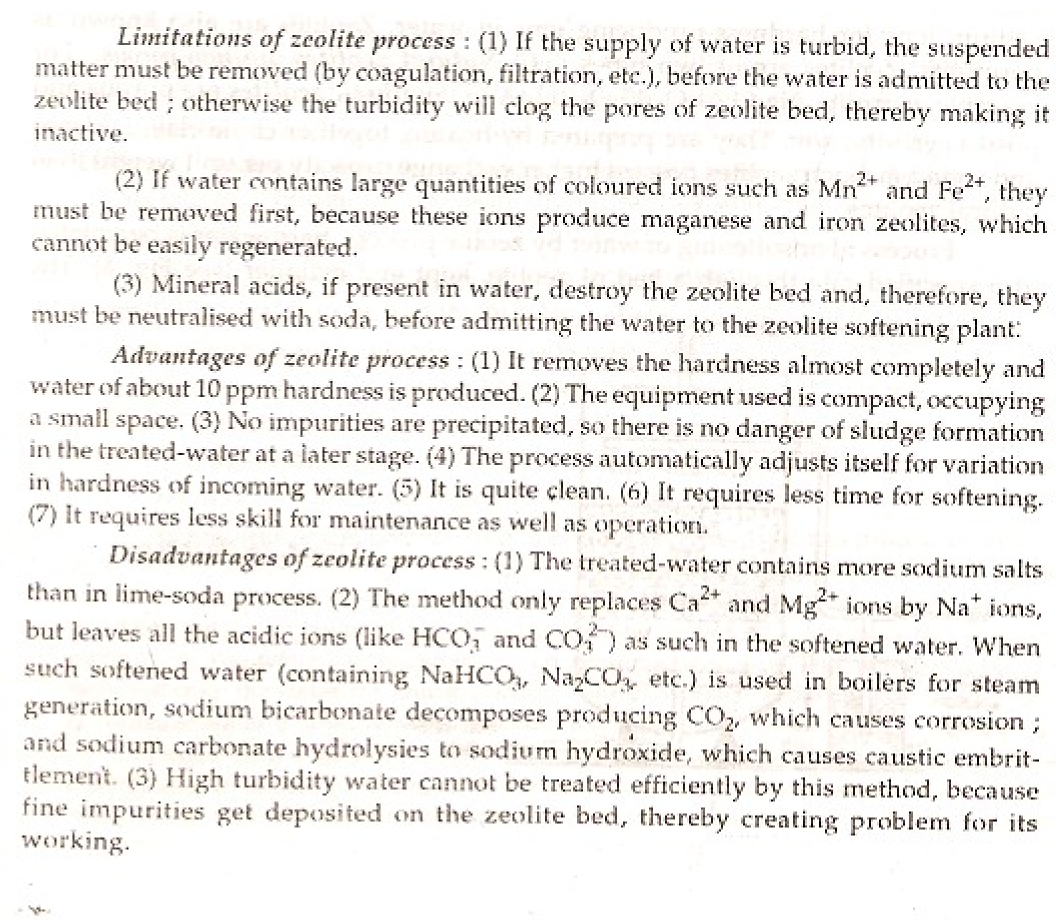
. Zeolite softener.

$$\begin{aligned}
Na_2Ze + Ca(HCO_3)_2 &\longrightarrow CaZe + 2NaHCO_3 \\
Na_2Ze + Mg(HCO_3)_2 &\longrightarrow MgZe + 2NaHCO_3 \\
Na_2Ze + CaCl_2\ (\text{or } CaSO_4) &\longrightarrow CaZe + 2NaCl\ (\text{or } Na_2SO_4) \\
\underset{\text{(Zeolite)}}{Na_2Ze} + \underset{\text{(Hardness)}}{MgCl_2\ (\text{or } MgSO_4)} &\longrightarrow MgZe + 2NaCl\ (\text{or } Na_2SO_4)
\end{aligned}$$

Regeneration : After some time, the zeolite is completely converted into calcium and magnesium zeolites and it ceases to soften water, i.e., it gets exhausted. At this stage, the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated (10%) brine (NaCl) solution.

$$\underset{\text{(Exhausted zeolite)}}{CaZe\ (\text{or } MgZe)} + \underset{\text{(Brine)}}{2NaCl} \longrightarrow \underset{\substack{\text{(Reclaimed}\\ \text{zeolite)}}}{Na_2Ze} + \underset{\text{(Washings)}}{CaCl_2\ (\text{or } MgCl_2)}$$

The washings (containing CaCl2 and MgCl2) are led to drain and the regenerated zeolite bed thus-obtained is used again for softening purpose.



Limitations of zeolite process : (1) If the supply of water is turbid, the suspended matter must be removed (by coagulation, filtration, etc.), before the water is admitted to the zeolite bed ; otherwise the turbidity will clog the pores of zeolite bed, thereby making it inactive.

(2) If water contains large quantities of coloured ions such as Mn^{2+} and Fe^{2+}, they must be removed first, because these ions produce maganese and iron zeolites, which cannot be easily regenerated.

(3) Mineral acids, if present in water, destroy the zeolite bed and, therefore, they must be neutralised with soda, before admitting the water to the zeolite softening plant.

Advantages of zeolite process : (1) It removes the hardness almost completely and water of about 10 ppm hardness is produced. (2) The equipment used is compact, occupying a small space. (3) No impurities are precipitated, so there is no danger of sludge formation in the treated-water at a later stage. (4) The process automatically adjusts itself for variation in hardness of incoming water. (5) It is quite clean. (6) It requires less time for softening. (7) It requires less skill for maintenance as well as operation.

Disadvantages of zeolite process : (1) The treated-water contains more sodium salts than in lime-soda process. (2) The method only replaces Ca^{2+} and Mg^{2+} ions by Na^+ ions, but leaves all the acidic ions (like HCO_3^- and CO_3^{2-}) as such in the softened water. When such softened water (containing $NaHCO_3$, Na_2CO_3, etc.) is used in boilers for steam generation, sodium bicarbonate decomposes producing CO_2, which causes corrosion ; and sodium carbonate hydrolysies to sodium hydroxide, which causes caustic embrittlement. (3) High turbidity water cannot be treated efficiently by this method, because fine impurities get deposited on the zeolite bed, thereby creating problem for its working.

Q 14: **What do you mean by Calgon Conditioning?**

CALGON CONDITIONING: Involves in adding calgon to boiler water. it prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.

Calgon = Sodium hexa Meta phosphate = $(NaPO_3)_6$

$Na_2 [Na_4 (PO_3)_6] ==== 2Na^+ + [Na_4P_6O_{18}]-$

$2CaSO_4 [Na_4P_6O_{18}]^{-2} \longrightarrow [Ca_2P_6O_{18}]^{-2} + 2Na_2SO_4$

Q. 15 Write a note on Lime Soda Process.

Ans: LIME-SODA PROCESS: In this method, the soluble calcium and magnesium salts in water are chemically converted in to insoluble compounds, by adding calculated amount of Lime and Soda. **$CaCO_3$** and $Mg(OH)_2$ so precipitated, these precipitates are filtered off.

Lime soda process mainly two types, they are

1. Cold Lime-soda process
2. Hot Lime-soda process.

Lime requirement for softening =

$$\frac{74}{100}\left[\begin{array}{l}\text{Temp. } Ca^{+2} + \text{Temp. } Mg^{+2} + \text{Perm.}(Mg^{+2} + Fe^{+2} + Al^{+3}) + CO_2 + H^+ \\ (\text{HCl or } H_2SO_4) + HCO_3^- \;-\; NaAlO_2 \text{ all in terms of } CaCO_3 \text{ equivalent}\end{array}\right]$$

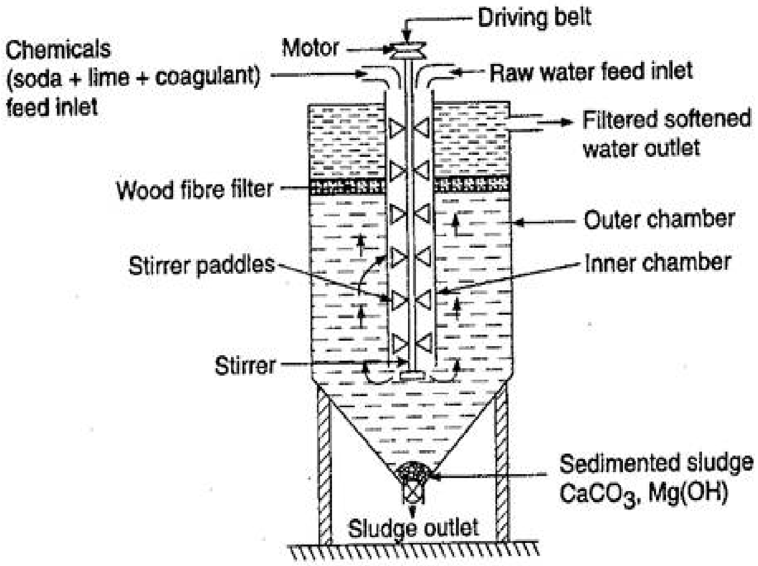
Soda requirement for softening =

$$\frac{106}{100}\left[\begin{array}{c}\text{Perm. }(Ca^{+2} + Mg^{+2} + Fe^{+2} + Al^{+3}) + H^+ (\text{HCl or } H_2SO_4) - HCO_3^- \\ \text{all in terms of } CaCO_3 \text{ equivalent}\end{array}\right]$$

Cold lime soda process: In this method, calculated quantity of chemical like lime and soda are mixed with water at Room temperature. At room temperature, the precipitates formed are finely divided, so they do not settle down easily and cannot be filtered easily.Consequently, it is essential to add small amounts of coagulants like alum, aluminum sulphate, sodium aluminate, etc. Which hydrolyze to flocculent, gelatinousprecipitate of aluminum hydroxide, and entraps fine precipitates. Use of sodium aluminate as coagulant also helps the removal of silica as well as oil,If present in water. Cold L-S process provides water, containing a residual hardness of 50 to 60 ppm.

$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3$

$Al_2(SO4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4 + 6CO_2$



METHOD: Raw water and calculated quantities of chemicals (Lime + soda + Coagulants) are fed from the top into the inner vertical circular chamber, fitted with a vertical rotating shat carrying a number of paddles. As the raw water and chemicals flow down, there is a vigorous stirring and continuous mixing, wherebysoftening of water reaches up. The softened water comes into the outer co-axial chamber, it rises upwards. The heavy sludge or precipitated floc settles down the outer chamber by the time the softened water reaches up. The softened water then passes through a filtering media this is usually made of wood fibres to ensure complete removal of sludge. Filtered soft water finally flows out continuously through the outlet at the top. Sludge settling at the bottom of the outer chamber is drawn of occasionally

HOT LIME-SODA PROCESS:

a.The reaction proceeds faster

b. The softening capacity f hot process is increased to many fold

c. The precipitate and sludge formed settle down rapidly anhence, no coagulants are needed
d. Much of the dissolved gases such as CO2 and air driven out of the water

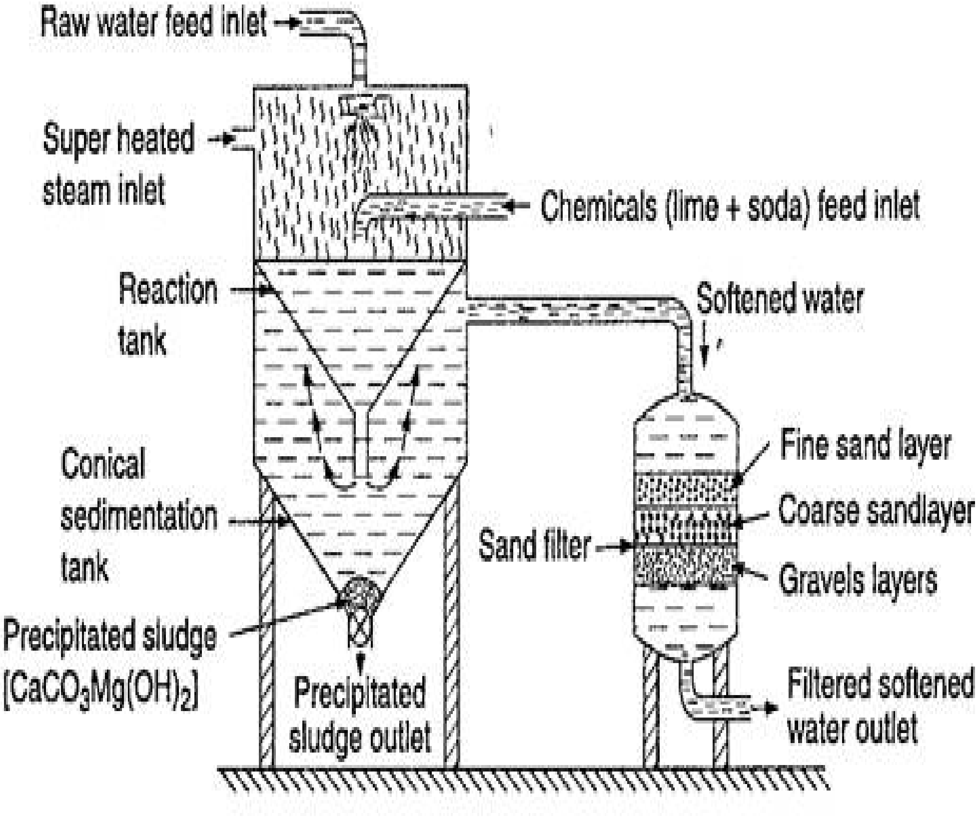
e. Viscosity of softened water is lower, so filtration of water becomes much easier. this in-turn increases the filtering capacity of filters, and

f. Hot lime-soda process produces water of comparatively lower residual hardness of 15 to

30 ppm.

Hot lime-soda plant consists essentially of three parts

1. A ‘Reaction tank’ in which raw water, chemicals and steam are thoroughly mixed.
2. A ‘Conical sedimentation vessel’ in which sludge settles down, and
3. A ‘sand filter’ which ensures completes removal of sludge from the softened water.



Q.16. What are the advantages and dis-advantages of Lime-Soda Process.

Ans: ADVANTAGES OF LIME-SODA PROCESS:

1. It is very economical

2. If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed.

3. The process increases the pH value of the treated-water; thereby corrosion of the distribution

pipes is reduced.

4. Besides the removal of harness, the quantity of minerals in the water is reduced.

5. To certain extent, iron and manganese are also removed from the water.

6. Due to alkaline nature of treated-water, amount of pathogenic bacteria in water is considerably reduced.

DIS-ADVANTAGES OF LIME-SODA PROCESS:

1. For efficient and economical softening, careful operation and skilled supervision is required.

2. Disposal of large amounts of sludge or insoluble precipitates poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city.

3. This can remove hardness only up to 15 ppm, which is not good for boilers.

Q. 17. Define ion-exchange process in detail.

Ans: Ion exchange process

Ion exchange process also known as demineralization or de-ionization process.

Ion-Exchange resins are insoluble. Cross linked long chain organic polymers with a micro porous structure, and the “functional Groups” attached to the chains are responsible for the ion-exchanging properties.

In De-ionization process all the ions present in water are eliminated by using ion-exchange resins. Basically resins with acidic functional group are capable of exchanging H+ ions with other cations. Resins with functional groups are capable of exchanging OH- ions with other anions.

Resins are classified as:

1. Cation Exchange Resins

2. Anion Exchange Resins

Cation Exchange Resins: These are mainly styrene divinyl benzene co-polymers, which on sulphonation or carboxylation. These are capable of exchanging their hydrogen ions with cations in water.

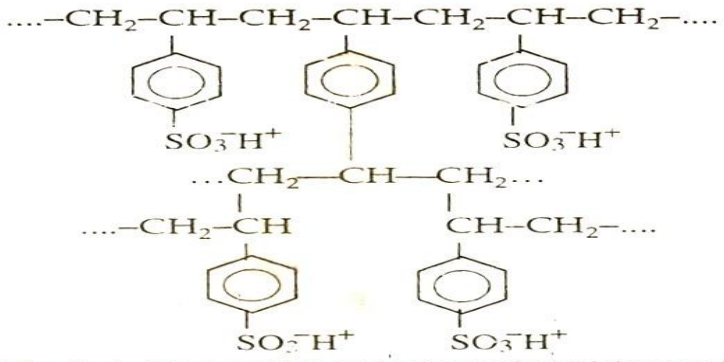
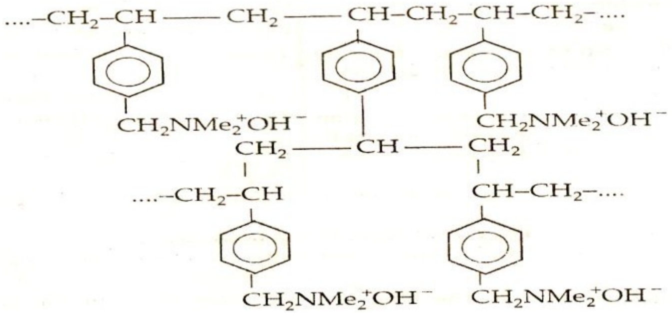


Fig. 6. Acidic or cation exchange resin (sulphonate form).

Anion Exchange Resins: Anion exchange resins are styrene-divinyl benzene or amine-formaldehyde copolymers, which contains amino, quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an internal parts of the resin matrix. These after treatment with dilute NaOH solution. Become capable of exchanging their OH- ions with anions in water.



Q.No 18: What do you mean by potable water? Give its specifications

One of the basic questions a person asks on arriving at a place is, whether the water available, is safe to drink or not. About 80% of the sickness in the world is attributed to the lack of safe drinking water. It is unfortunate that a large portion of world's population lack a safe supply of water for drinking, washing and other domestic purposes.

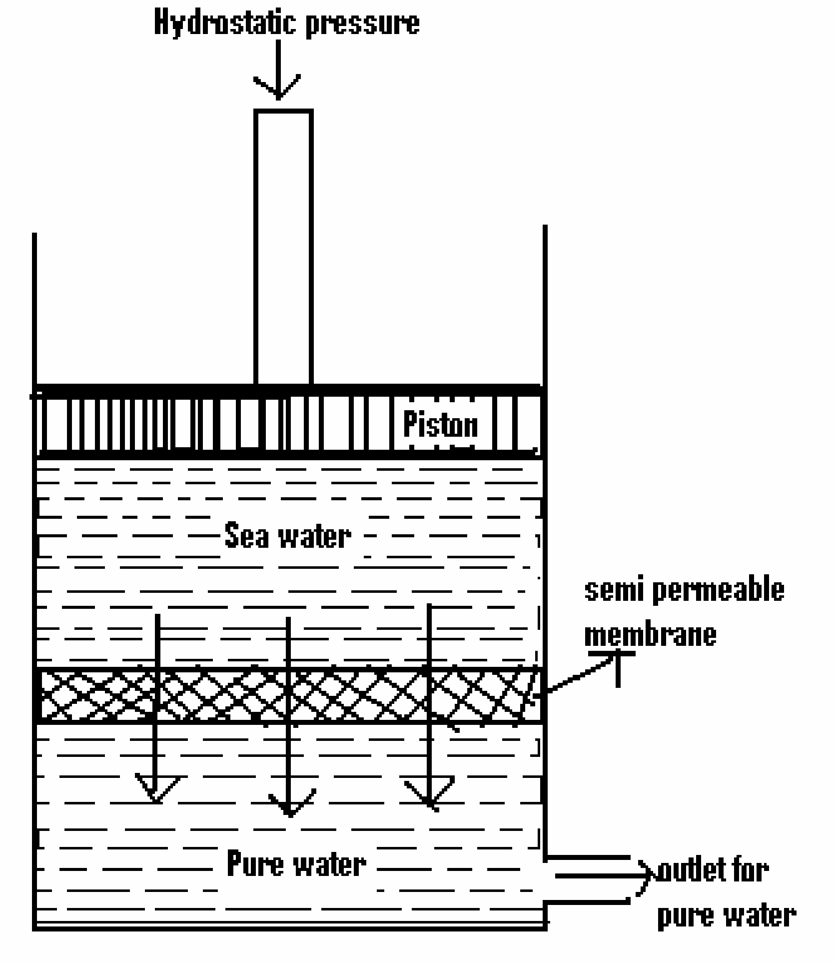
As water flows over the surface of earth it picks up a number of impurities in the form of dissolved particles of soil, garbage, pesticides and other human, animal or chemical wasters. Some of these impurities may make water more useful and potable and some of these render it harmful and unfit.

Municipalities have to supply potable water, i.e., water is safe to drink. Drinking or potable water, fit for human consumption, should satisfy the following essential requirements:

1. It should be sparking clear and odour less.
2. It should be pleasant in taste.
3. It should be perfectly cool
4. Its turbidity should not exceed 10 ppm.
5. It should be free from objectionable dissolved gases like hydrogen sulphide.
6. It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts.
7. Its alkalinity should not be high.
8. Its pH should be about 8.0
9. It should be reasonably soft.
10. Its total dissolved solids should be less than 500 ppm.
11. It should be free from disease-producing micro-organisms

Q. 19 What do you mean by reverse osmosis?

Ans: Reverse Osmosis: When two solutions of unequal concentrations are separated by a semi permeable membrane, flow of solvent takes place from dilute to concentrated sides, due to osmosis. If, however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverse, ie. Solvent is forced to move from concentrated side to dilute side across the membrane. This is the principle of reverse osmosis. Thus, in reverse osmosis (RO) methods, pure solvent is separated from its contaminants, rather than removing contaminants from the water. This membrane filtration is also called ‘super-filtration’ or ‘hyper – filtration’. Process: in Reverse osmosis process, pressure (15 to 40 kg cm-2) is applied to the sea water or impure water to force its pure water out through the semi-permeable membrane, leaving behind the dissolved solids. The principle of reverse osmosis, as applied for treating saline or sea water. The membrane consists of very thin films of cellulose acetate, affixed to either side of a perforated tube. However, mover recently superior membranes made of polymethacrylate and polyamide polymers.



Advantages:

a. Reverse osmosis possesses a distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.

b. It removes colloidal silica, which is not removed by demineralization.

c. The maintenance cost is almost entirely on the replacement of the semi permeable membrane.

d. The life time of membrane is quite high, about 2 years.

e. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.

f. Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.

Q. 20 .What are the disadvantages of using Hard water in boilers?

The following are the disadvantages of using hard water in boilers are as follows:

- Scale and sludge formation
- Caustic embrittlement.
- Priming and foaming
- Corrosion

Q. 21 Define Phase rule.

Ans: Phase Rule :

Gibbs phase rule may be stated as follows :

"In a heterogeneous system in equilibrium, the number of degrees of freedom plus the number of phases is equal to the number of components plus two".

Mathematically, $F + P = C + 2$

or $F = C - P + 2$

where

F = number of degrees of freedom

C = number of components

P = number of phases

2 = additional variables of temperature and pressure besides the concentration variables.

Q 22. Explain the phase, component and degree of freedom with example.

Phase: " The physically distinct, homogenous and mechanically separable part of a system are called phases".

Examples

(i) A gaseous mixture constitutes a single phase since gases are completely miscible. Air is a mixture of N_2, O_2, CO_2, water vapour etc. Which constitute a single phase.

(ii) Two or more liquids which are miscible with one another constitute a single phase as there is no bounding surfaces separating the different liquids. e.g., water and alcohol, benzene & chloroform constitute one phase system.

(iii) A system consisting of a liquid in equilibrium with its vapour constitute a two phase system.

Component :

The number of component of a system at equilibrium is defined as the minimum number of independently variable constituents which are required to express the composition of each phase in the system.

In a chemically reactive system, the number of components is given by

$$C = N - E$$

where C = components.

N = Number of chemical species

E = Number of independent equations relating the concentrations of the N species.

Each independent chemical equilibrium involving the constituents counts as one equation.The condition that a solution be electrically neutral also counts as one equation if ions are considered as constituents.

Degrees of Freedom :

The degree of freedom or variance of a system is defined as the minimum number of variable factors such as temperature, pressure and concentration which should be arbitrarily fixed in order to define the system completely.

Examples

(i) For a given sample of any gas PV = nRT. Any two of the three variables P, V, T define the system completely. Hence the system is bivariant or it has two degrees of freedom.

(ii) A gaseous mixture say N_2 and O_2 gases (mixed 50% each), is completely defined when three variables temperature, pressure and concentration are specified. Thus, the degrees of freedom is three or the system is trivariant.

Q 23. Discuss the Advantages and Limitations of Phase rule.

Ans: Advantages of Phase' Rule :

(i) It provides a simple method of classifying equilibrium states of systems.

(ii) The phase rule confirms that the different systems having the same number of degrees of freedom behave in same manner.

(iii) It is applicable only to macroscopic systems and not concerned with molecular structure.

(iv) It predicts the behaviour of systems with changes in the variables that govern the system in equilibrium.

(v) It predicts under given conditions whether a number of substances taken together would remain in equilibrium as such or would involve interconversion or elimination of some of them.

(vi) It takes no account of nature of the reactants or products in phase reactions.

vii) It finds extensive use in the study of many heterogenous systems. In particular it has been found

extremely useful in the extraction of metals.

Limitations:

(i) The phase rule is applicable to heterogeneous systems in equilibrium, so, it is therefore of no use for such systems which are slow in attaining the equilibrium state.

(ii) It is applicable to a single equilibrium state, so it never gives information about the other possible equilibrium in the system.

(iii) In Gibbs phase rule, various variables are temperature, pressure and composition. It does not take in account the electric and magnetic influences. For consideration of such variables, the factor 2 of the Phase rule has to be adjusted accordingly.

Q 24: Discuss in detail the phase diagram of water system (One component system).

Ans: **Phase diagrams :**

The number of phases that exist in equilibrium depends upon the conditions of temperature and pressure or temperature and composition, pressure being constant. These conditions are determined experimentally and interdependence of values of the variables can be shown graphically using appropriates coordinates. These diagrams are termed phase diagram. **A phase diagram is the sum total of the description of the behaviour of the phases under equilibrium.** It is very easy to describe the phase behaviour of a system by such diagrams and to investigate the conditions in which various phases will constitute the system.

Application of Gibbs Phase Rule to One Component System:

From the mathematical expression,

$$F = C - P + 2$$

When $C = 1$, $P = 1$

$$F = 1 - 1 + 2$$

$$= 2$$

Hence, all one component systems can be completely described graphically by stating only two variables, pressure and temperature on appropriate axis.

The Water System :

It is a one component system. Water exists in three possible phases viz. ice (solid) , water (liquid), and vapour (gas). These three single phases may form four possible equilibria.

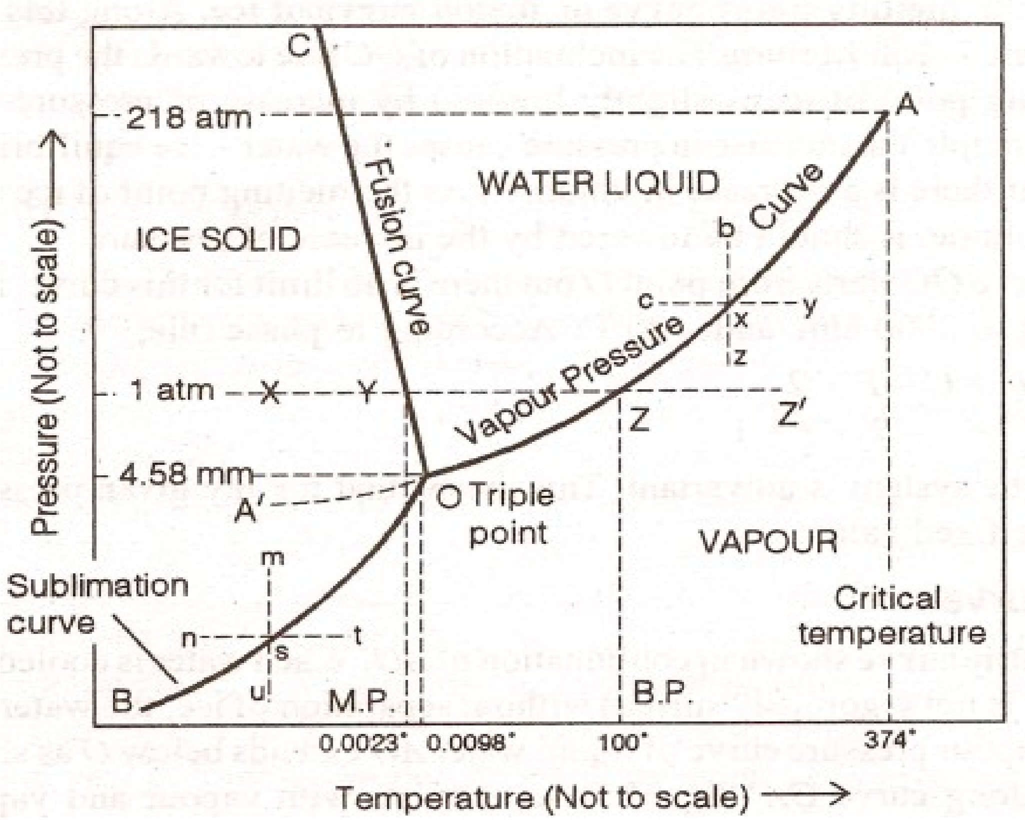
(i) Solid $\rightleftharpoons$ Liquid

(ii) Liquid $\rightleftharpoons$ Vapour

(iii) Solid ⇌ Vapour

(iv) Solid ⇌ Liquid ⇌ Vapour

The Phase diagram of water system is given as:



The phase diagram consists of :

(i) Stable curves: three *OB, OA* and *OC*

(ii) Metastable curve: one OA'

(iii) Areas: three AOB, COB and AOC

(iv) Triple point: One O

(i) Stable curves

OA : It is known as **vapour pressure curve of water**. The curve OA starts from point O i.e., freezing point of water, 0.0098°C under 4.579 mm of Hg pressure and ends at A, the critical temperature (374^0C at 218 atm.). Above critical temp. on the vapour phase exists whatever may be the value of pressure. The vapour pressure of water increases with increase in temperature.

The rate of increase of its vapour pressure with temperature is relatively higher at higher temperatures and therefore the curve OA slants upwards and slopes away from the temperature axis.

From phase rule,

$$F = C - P + 2$$

$$= 1 - 2 + 2$$

$$= 1$$

The water vapour system is univariant

OB : It is the **sublimation curve of ice**. Along this curve, solid ice is in equilibrium with its vapour.

This curve is not the prolngation of curve A but falls of more steeply. Curve OB starts From the temperature 0.0098°C above which solid water *i.e.,* ice cannot exist. The curve terminates at *B i.e.,* absolute zero (- 273°C). At this temperature, no vapour can exist and, therefore, only

ice is left. But on other points of the curve O*B,* ice is in equilibrium with vapour. Hence, there are two phases. According to phase rule,

$$F = C - P + 2$$

$$= 1 - 2 + 2$$

$$=1$$

Thus, the system is univariant. This means that for each temperature; there may be one pressure and for each pressure there may be one temperature.

OC : This curve is the **melting point curve or fusion curve of ice.** Along this curve two phases, ice and water are in equilibrium. The inclination of *OC* line towards the pressure axis indicates that the melting point of ice is slightly lowered by increase of pressure. (According to Le Chatelier's principle the increase in pressure causes the water - ice equilibrium to shift in such a direction that there is a decrease in volume.) As the melting point of ice is accompanied by decrease in volume, it should be lowered by the increase of pressure.

The curve *OC* starts from point O but there is no limit for this curve. It goes upto a point corresponding to 2000 atm. and - 20°C. According to phase rule,

$$F = C - P + 2$$

$$=1-2+2 = 1$$

Thus, the system is univariant. This means that for any given pressure, melting point must have one fixed value.

(ii) Metastable Curve

OA' : It is a metastable curve shown in continuation *of AO.* When water is cooled below its freezing point (when it is not vigorously stirred) without separation of ice, the water is said to be super cooled. The vapour pressure curve of liquid water *AO* extends below O as shown by the dotted curve *OA'.* Along curve *OA'* liquid water coexists with vapour and vapour pressures are different than over the solid. This equilibrium is called metastable equilibrium as slight disturbance brings it to the stable region *OB* of the phase diagram.

(iii) Areas

The areas give the conditions of temperature and pressure under which single phase - ice (solid), water (liquid) and vapour (gas) can exist. It is necessary to specify both temperature and pressure to define a system within this area. In the area *BOC, AOC* andAOB exists, ice (solid), water (liquid) and vapour (gas) respectively. In these areas, the degrees of freedom for the system is two or they are bivariant

(iv) The Triple point O

The point O at which the curves *AO, BO* and *CO* meet is called the triple point. At this point all the three phases *viz ,* ice, water and vapour co-exist. Thus, P =3. According to phase rule, at triple point O,

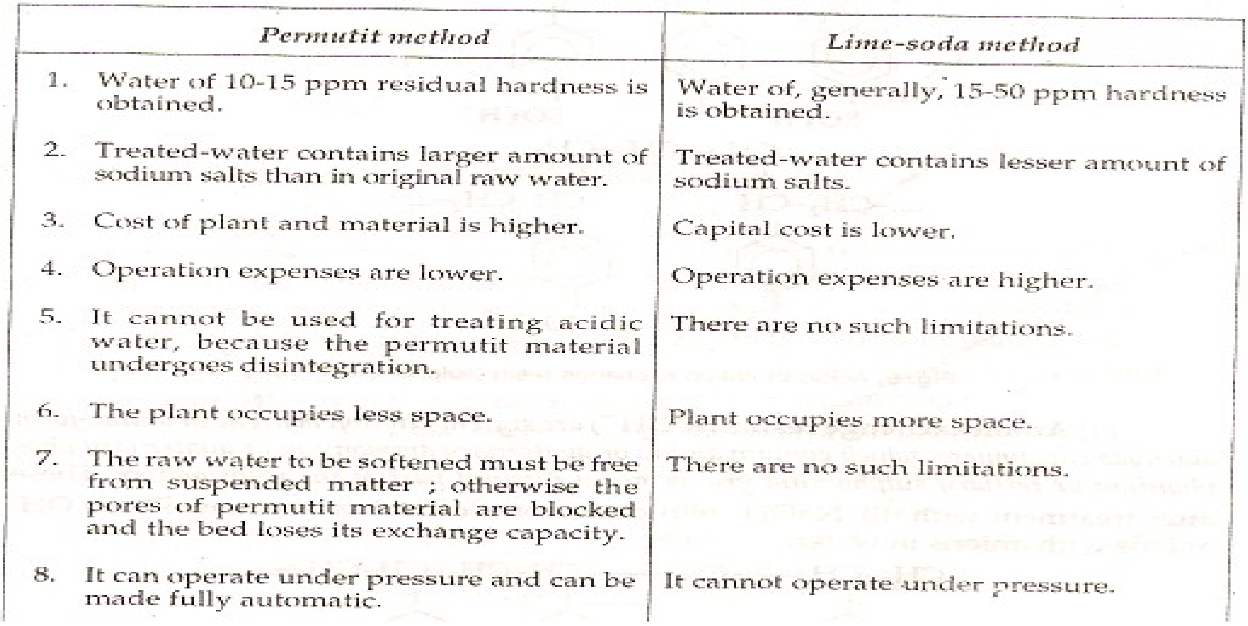
$$F = C - P + 2, \qquad =1-3+2 , \qquad F = 0$$

Thus, the degree of freedom at triple point is zero, which indicates that there is only one set of variables *P, T* at which all the three phases coexist. If any of the variables is changed, then the number of phases decreases. For example, if the temperature is raised, heat causes more and more of the solid (ice) to melt but no change in temperature or pressure of the system occurs till the whole of the solid has completely changed into liquid (water) and the system becomes a two phase system. On applying the pressure to the system, vapours start condensing to liquid or solid phase. As long as there are three phases, temperature and pressure remains same.

The triple point O is a self defined point corresponding to 0.0075°C temperature and 4.579 mm of Hg pressure (difference from the ordinary freezing point,(0.000^{0}C at 760mm pressure) because freezing temperature is lower than triple point temperature due to effect of high pressure and dissolved air).

Q 25: Differentiate between the Permutit method (ZeoliteProcess) and Lime Soda Process of water softening.

Ans:



. Comparison of permutit process with lime-soda process.

	Permutit method	*Lime-soda method*
1.	Water of 10-15 ppm residual hardness is obtained.	Water of, generally, 15-50 ppm hardness is obtained.
2.	Treated-water contains larger amount of sodium salts than in original raw water.	Treated-water contains lesser amount of sodium salts.
3.	Cost of plant and material is higher.	Capital cost is lower.
4.	Operation expenses are lower.	Operation expenses are higher.
5.	It cannot be used for treating acidic water, because the permutit material undergoes disintegration.	There are no such limitations.
6.	The plant occupies less space.	Plant occupies more space.
7.	The raw water to be softened must be free from suspended matter ; otherwise the pores of permutit material are blocked and the bed loses its exchange capacity.	There are no such limitations.
8.	It can operate under pressure and can be made fully automatic.	It cannot operate under pressure.

Unit 5

Que 1 Explain the electro chemical theory of corrosion?

Ans: Electrochemical or Wet corrosion theory :

It takes place under moist or wet conditions through the formation of short circuited galvanic cells. Electrochernical or wet corrosion is more common than dry corrosion. Electrochemical corrosion involves:

(i) Separate 'anodic' and 'cathodic' areas between which current through the conducting medium.

(ii) Occurrance of oxidation (corrosion) at anodic areas which generates metallic ions,

(iii) Non-metallic ions like OH^- or O^{2-} are formed at cathodic areas, and

(iv) Diffusion of metallic and non-metallic ions towards each other through conducting medium and formation of corrosion product somewhere between anodic and cathodic areas.

For example:

Rusting of iron in neutral aqueous solution of electrolyte in the presence of oxygen or in acidic environment with evolution of hydrogen.

Fe^{2+} ion originates at anode and OH^- ions originate from cathode. Smaller Fe^{2+} ions diffuse more rapidly than the larger OH^- ions, so corrosion occurs at the anode, but corrosion product rust deposited near cathode.

The electrons released at anode are conducted to the cathode and are responsible for various cathodic reactions like

(i) Hydrogen evolution: In absence of O_2

(a) In acidic medium: $2H^+ + 2e^- \longrightarrow H_2$

(b) In neutral or alkaline medium:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

(ii) Oxygen absorption: In presence of dissolved oxygen

(a) In acidic medium:

$$4H^+ + O_2 + 4e^- \longrightarrow 2H_2O$$

(b) In neutral or weakly alkaline medium:

$$2H_2O + O_2 + 4e^- \longrightarrow 4\,OH^-$$

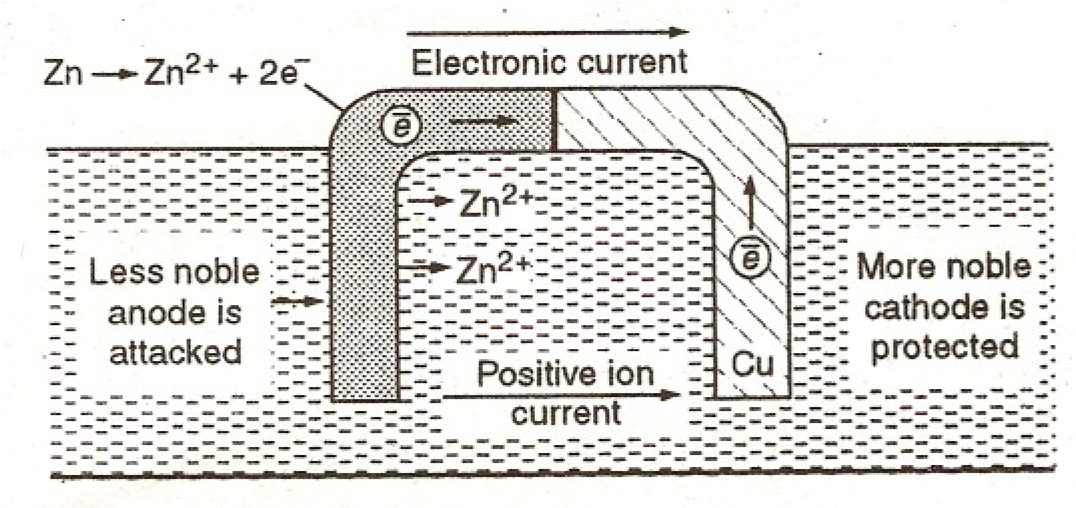
(iii) Electroplating : At cathode, metal ions collect the electrons and get deposited on the surface of cathode.

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Q.no 2 Explain Galvanic Corrosion

Galvanic corrosion :

It takes place when different metals are jointly exposed to corrosive atmosphere. The metal which is higher up in electrochemical series, with more negative electrode potential will act as anode and undergo corrosion. example, Zn and Cu; Fe and Cu; Zn and Ag. In the Zn-Cu galvanic cell, Zn act as anode where oxidation and corrosion occurs and Cu act as cathode and is protected.



Galvanic corrosion can be minimised by

(i) Avoiding galvanic couple.

(ii) Providing insulating material between the two metals.

b) Concentration cell corrosion

Concentration cell corrosion or Differential aeration corrosion :

It occurs when metallic surface is partially immersed in an electrolyte and partially exposed to air.

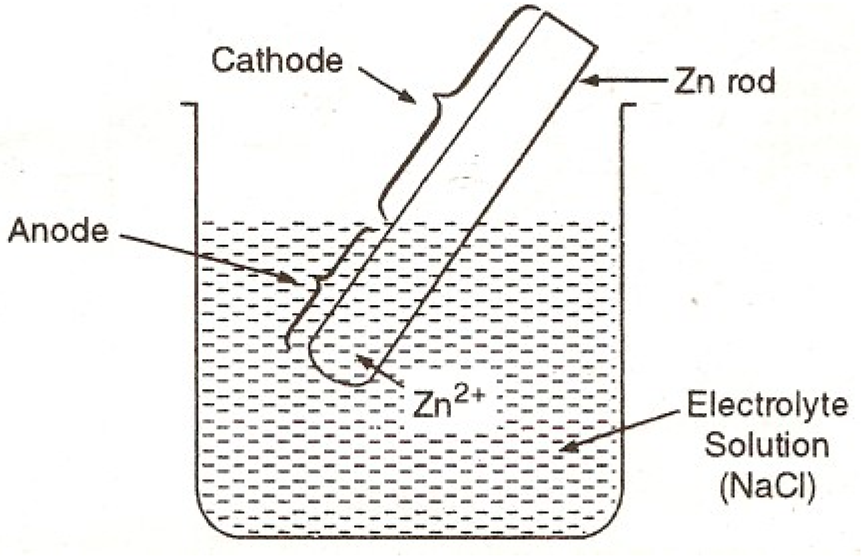
Poor oxygenated metallic part becomes anodic and undergoes oxidation.

$$Zn \qquad Zn^{2+} + 2e^-$$

Oxygen rich metallic part becomes cathodic. At the cathode, O2 takes up electrons to form OH^- ions.

$1/2O_2+H_2O+2e^-$ $\qquad$ $2OH^-$

The Zn^{2+} and OH^- ions interact to give $Zn(OH)_2$ Therefore, corrosion occurs at anode.



Q.no 3 Explain the factors influencing the corrosion?

FACTORS INFLUENCING CORROSION : The rate and extent of corrosion, depends on the following factors :

1. Nature of the metal:

(i) Position in the galvanic series: The greater the oxidation potential, when the metal is higher up in the galvanic series, greater is its tendency to become anodic and hence greater is the rate of corrosion.

(ii) Purity of metal: Lesser is the percentage purity of a metal, faster is the rate of corrosion. The impurities present in a metal cause heterogeneity and thus tiny electrochemical cells are set up at the exposed part of the impurity and corrosion of metal around the impurity takes place due to local action.

(iii) Physical state of the metal: The rate of corrosion is influenced by physical state of metal. The smaller the grain size of the metal or alloy, the greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

(iv) Nature of the oxide film: The ratio of the volumes of the metal oxide to the metal, is known as "specific volume ratio". Greater the specific volume ratio, lesser is the oxidation corrosion rate.

(v) Relative areas of the anode and cathode: When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of the cathodic part and the anodic part. When cathodic area is smaller, the demand for electrons will be less and this result in the decreased rate of disolution of metal at anodic regions.

(vi) Solubility of corrosion products: In the electochemical corrosion, if the corrosion product is soluble in corroding medium, then corrosion proceeds at a faster rate. For example, Pb in H_2SO_4 medium forms $PbSO_4$ which is insoluble in the corroding medium, hence corrosion proceeds at a smaller rate.

(vii) Volatility of corrosion products: Rapid and continuous corrosion of metal take place if corrosion product is volatile. This is due to the fact that as soon as corrosion product is formed, it volatilize, thereby leaving the underlying metal surface for further attack.

2. Nature of the corroding environment:

(i) Temperature: With increase of temperature of environment, the reaction as well as diffusion rate increase, thereby corrosion rate is generally enhanced.

(ii) Humidity of air : The greater is humidity, the greater is the rate and extent of corrosion. This is due to the fact that moisture acts as a solvent for O_2, H_2S, SO_2 and NaCI etc. to furnish the electrolyte essential for setting up a corrosion cell.

(iii) Effect of pH: Corrosions of those metal which are readily attacked by acids can be reduced by increasing the pH of the attacking environment.

(iv) Presence of impurities in atmosphere: Corrosion of metals is more in areas near to the industry and sea. This is due to the fact that corrosive gases like H_2S, SO_2, CO_2 and fumes of H_2SO_4 and HCI in the industrial areas and NaCI of sea water leads to increased conductivity of the liquid layer in contact with the metal surface, thereby increase the corrosion rate.

(v) Presence of suspended particles in atmosphere: In case of atmospheric corrosion; (a) if the suspended particles are chemically active in nature [like NaCl, $(NH_4)_2SO_4$], they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion;

(b) if the suspended particles are chemically inactive in nature *(e.g.,* charcoal), they absorb both sulphur gases, and moisture and slowly enhance corrosion rate.

Q.no 4. Give the measure preventive methods for corrosion?

Following are the methods for control of corrosion :

(i) Suitable designing: The design of the material should be such that corrosion if occurs is uniform and not localized. Following precautions must be taken :

(a) The contact of dissimilar metals in presence of corroding solution is to be avoided.

(b) The anodic material should have as large area as possible when two dissimilar metals are in contact.

(c) When two dissimilar metals in contact have to be used, they should be as close as possible in electrochemical series.

(d) An insulating filling may be used to avoid direct metal-metal electrical contact.

(e) The anodic metal should not be painted or coated because any break in coating would cause rapid localized corrosion.

(f) A suitable design should avoid presence of cracks between adjacent parts of the structure.

(g) Sharp comers are the poor design and should be avoided because they favour accumulation of solids.

(h) The equipment should be supported on legs for free circulation of air.

(i) Uniform flow of corrosive liquid is desirable.

(j) A suitable design should prevent condition subjecting some areas of structure to stress.

(ii) Using pure metal: Impurities in a metal cause heterogeneous state thereby accelerating corrosion rate. Corrosion resistance of a metal may be improved by increasing its purity. Corrosion resistance of a purified metal also depends on the nature of corroding environment.

(iii) Using metal alloys: Corrosion resistance of most metals is increased by alloying them with suitable elements. *e.g.,* Cr is the best suitable alloying metal for iron. Steel containing 13% Cr are used in surgical equipments.

(iv) Modifying the environment: The rate of corrosion also depends on corroding environment. The corrosive nature of environment can be reduced by,

(a) Deaeration: Driving out dissolved oxygen by adjustment of temperature with mechanical agitation.

(b) Deactivation: This involves addition of chemicals capable of combining with oxygen in aqueous solution.

e.g.,

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

$$N_2H_4 + O_2 \longrightarrow N_2\uparrow + 2H_2O$$

(c) Dehumidification: Reduction of moisture content of air belongs to this step. *e.g.,* alumina or silica gel can absorb moisture which are used in air-conditioning shop

Que 5: What do you mean by Sacrificial protection.

Sacrifical protection: In this method the metal to be protected is connected by a wire to a more anodic metal. The more active metal losses electrons and gets corroded slowly thereby protecting the parent cathodic metal. *e.g.,* Galvanisation process where iron is protected by covering with zinc. Some sacrificial anodes commonly employed are Mg, Zn, Al etc. Applications of this method include underground cables, water tanks etc.

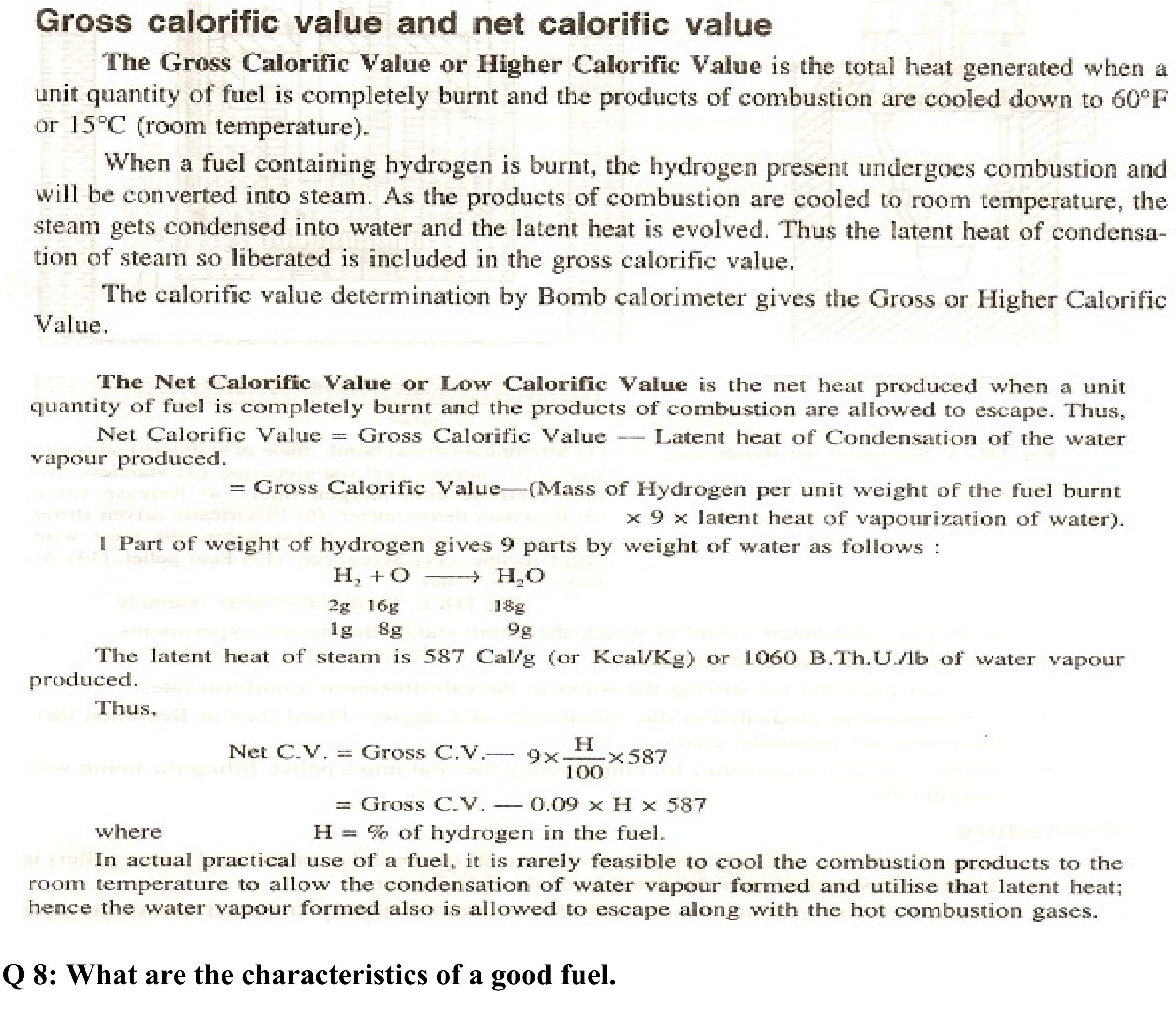
Que 6: Expalin Electrical cathodic protection:

In this method an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. The current is derived from direct sources like battery of rectifier on A.C. line with an insoluble anode (graphite, platinum).

This technique is used for long term operations.

Q 7: Explain the term Gross and Net Calorific Value of a fuel.

Ans:



Gross calorific value and net calorific value

The Gross Calorific Value or Higher Calorific Value is the total heat generated when a unit quantity of fuel is completely burnt and the products of combustion are cooled down to 60°F or 15°C (room temperature).

When a fuel containing hydrogen is burnt, the hydrogen present undergoes combustion and will be converted into steam. As the products of combustion are cooled to room temperature, the steam gets condensed into water and the latent heat is evolved. Thus the latent heat of condensation of steam so liberated is included in the gross calorific value.

The calorific value determination by Bomb calorimeter gives the Gross or Higher Calorific Value.

The Net Calorific Value or Low Calorific Value is the net heat produced when a unit quantity of fuel is completely burnt and the products of combustion are allowed to escape. Thus,

Net Calorific Value = Gross Calorific Value — Latent heat of Condensation of the water vapour produced.

= Gross Calorific Value—(Mass of Hydrogen per unit weight of the fuel burnt × 9 × latent heat of vapourization of water).

1 Part of weight of hydrogen gives 9 parts by weight of water as follows :

$$\begin{array}{ccc} H_2 + O & \longrightarrow & H_2O \\ 2g \quad 16g & & 18g \\ 1g \quad 8g & & 9g \end{array}$$

The latent heat of steam is 587 Cal/g (or Kcal/Kg) or 1060 B.Th.U./lb of water vapour produced.

Thus,

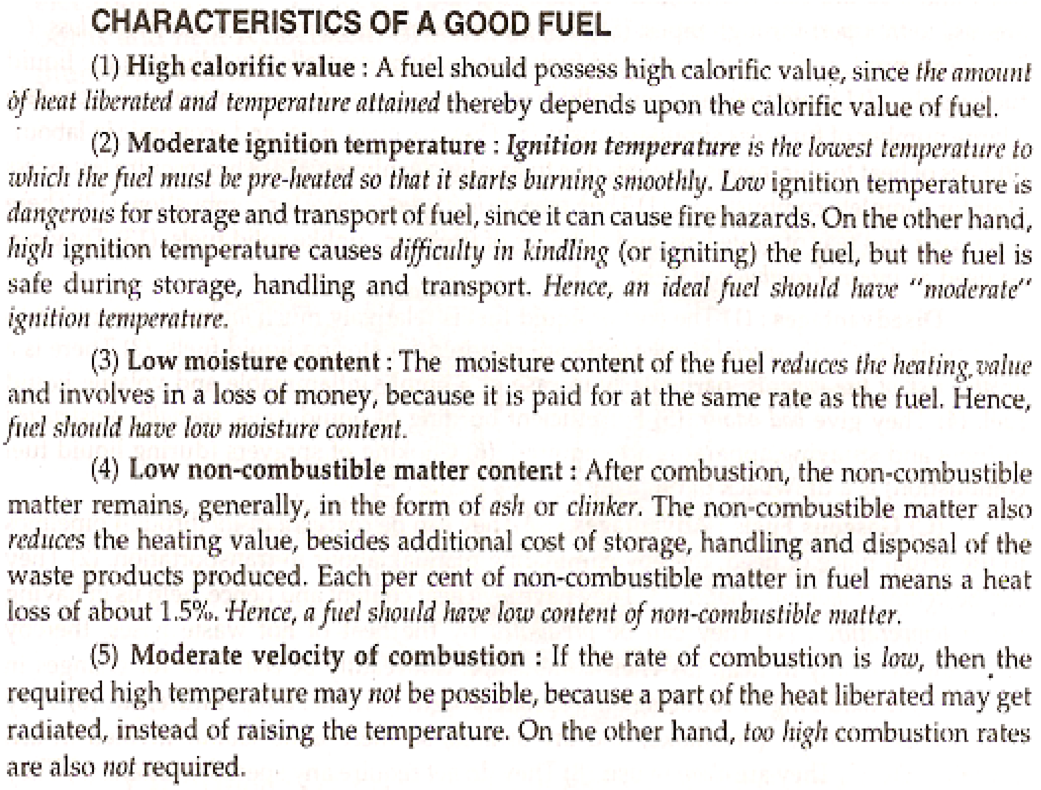
$$\text{Net C.V.} = \text{Gross C.V.} - 9 \times \frac{H}{100} \times 587$$

$$= \text{Gross C.V.} - 0.09 \times H \times 587$$

where H = % of hydrogen in the fuel.

In actual practical use of a fuel, it is rarely feasible to cool the combustion products to the room temperature to allow the condensation of water vapour formed and utilise that latent heat; hence the water vapour formed also is allowed to escape along with the hot combustion gases.

Q 8: What are the characteristics of a good fuel.



CHARACTERISTICS OF A GOOD FUEL

(1) **High calorific value :** A fuel should possess high calorific value, since *the amount of heat liberated and temperature attained* thereby depends upon the calorific value of fuel.

(2) **Moderate ignition temperature :** ***Ignition temperature*** *is the lowest temperature to which the fuel must be pre-heated so that it starts burning smoothly. Low* ignition temperature is *dangerous* for storage and transport of fuel, since it can cause fire hazards. On the other hand, *high* ignition temperature causes *difficulty in kindling* (or igniting) the fuel, but the fuel is safe during storage, handling and transport. *Hence, an ideal fuel should have "moderate" ignition temperature.*

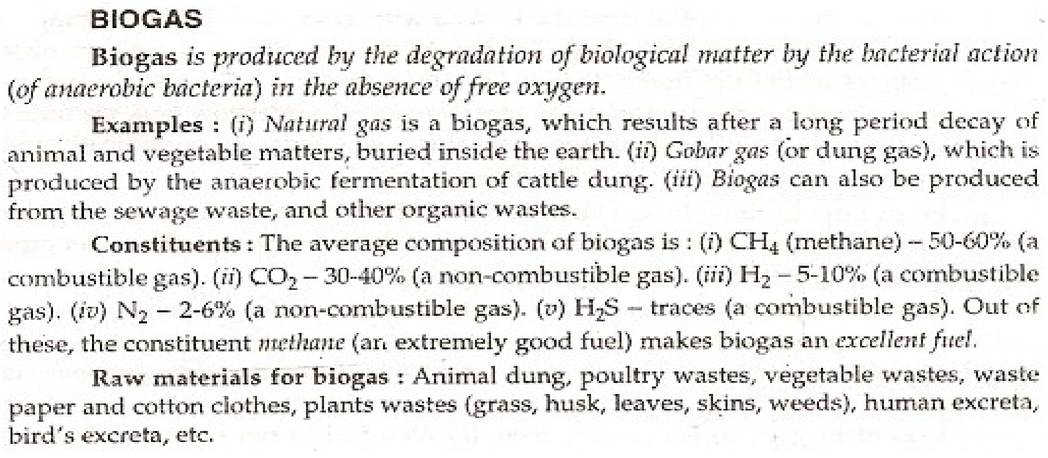
(3) **Low moisture content :** The moisture content of the fuel *reduces the heating value* and involves in a loss of money, because it is paid for at the same rate as the fuel. Hence, *fuel should have low moisture content.*

(4) **Low non-combustible matter content :** After combustion, the non-combustible matter remains, generally, in the form of *ash* or *clinker*. The non-combustible matter also *reduces* the heating value, besides additional cost of storage, handling and disposal of the waste products produced. Each per cent of non-combustible matter in fuel means a heat loss of about 1.5%. *Hence, a fuel should have low content of non-combustible matter.*

(5) **Moderate velocity of combustion :** If the rate of combustion is *low*, then the required high temperature may *not* be possible, because a part of the heat liberated may get radiated, instead of raising the temperature. On the other hand, *too high* combustion rates are also *not* required.

Q 10: Write note on biogas.

Ans:



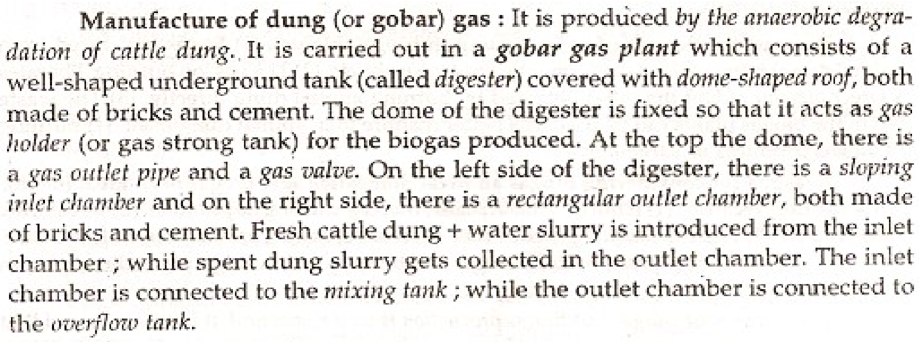
BIOGAS

Biogas *is produced by the degradation of biological matter by the bacterial action (of anaerobic bacteria) in the absence of free oxygen.*

Examples : (*i*) *Natural gas* is a biogas, which results after a long period decay of animal and vegetable matters, buried inside the earth. (*ii*) *Gobar gas* (or dung gas), which is produced by the anaerobic fermentation of cattle dung. (*iii*) *Biogas* can also be produced from the sewage waste, and other organic wastes.

Constituents : The average composition of biogas is : (*i*) CH_4 (methane) – 50-60% (a combustible gas). (*ii*) CO_2 – 30-40% (a non-combustible gas). (*iii*) H_2 – 5-10% (a combustible gas). (*iv*) N_2 – 2-6% (a non-combustible gas). (*v*) H_2S – traces (a combustible gas). Out of these, the constituent *methane* (an extremely good fuel) makes biogas an *excellent fuel*.

Raw materials for biogas : Animal dung, poultry wastes, vegetable wastes, waste paper and cotton clothes, plants wastes (grass, husk, leaves, skins, weeds), human excreta, bird's excreta, etc.



Manufacture of dung (or gobar) gas : It is produced *by the anaerobic degradation of cattle dung.* It is carried out in a ***gobar gas plant*** which consists of a well-shaped underground tank (called *digester*) covered with *dome-shaped roof*, both made of bricks and cement. The dome of the digester is fixed so that it acts as *gas holder* (or gas strong tank) for the biogas produced. At the top the dome, there is a *gas outlet pipe* and a *gas valve*. On the left side of the digester, there is a *sloping inlet chamber* and on the right side, there is a *rectangular outlet chamber*, both made of bricks and cement. Fresh cattle dung + water slurry is introduced from the inlet chamber ; while spent dung slurry gets collected in the outlet chamber. The inlet chamber is connected to the *mixing tank* ; while the outlet chamber is connected to the *overflow tank*.