

## Unit-II POLYMERS

### INTRODUCTION:

**Polymer** (Greek poly = many; mers = units or parts): A polymer is a macromolecule (giant molecule of high molecular mass) built-up by the linking together of a large number of simple molecules (monomers).

Example: Polythene is formed by linking a large number of ethene molecules together.



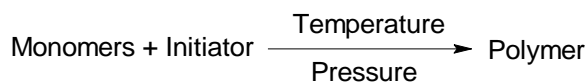
**Monomer:** A monomer is a simple molecule having two or more bonding sites through which each can link to other monomers to form a polymer chain. Monomers are often called building blocks of a polymer chain.

**Functionality:** The total number of functional groups or bonding sites present in a monomer molecule is called the functionality of the monomer. For a substance to act as a monomer, it must have at least two reactive sites or bonding sites (*bifunctional*).

Functionality of some commercial monomers:

Sl. No.	Monomers	Functional group Reactive centres	Functionality
1.	Vinyl compounds	Two reactive centres at the double bond	Two
2.	Ethylene glycol	Two alcoholic -OH groups	Two
3.	Glycerol	Three alcoholic -OH groups	Three
4.	Adipic acid	Two -COOH groups	Two
5.	Hexamethylene diamine	Two -NH <sub>2</sub> groups	Two
6.	Phenol	Three active centres at ortho and para positions	Three
7.	Formaldehyde	Two active centres	Two
8.	Bisphenol-A	Two phenolic -OH groups	Two
9.	Diisocyanate	Two isocyanate groups	Two

**Polymerization:** The chemical process by which the monomers (low molecular weight) are converted into polymers (high molecular weight) is called polymerization. All polymerization reactions need suitable initiators.



**Degree of polymerization (DP):** The number of repeating units (n) in a polymer chain is called degree of polymerization. There may be hundreds or thousands or tens of thousands or more monomer molecules linked together in a polymer molecule.



Where 'n' is the degree of polymerization.

The DP can be used to calculate the molecular weight of a polymer.

**Molecular weight of polymer = DP × molecular weight of repeat unit.**

If the DP of polyethylene is 1,000, then Mol. wt = DP × Mol. wt. of ethylene  
= 1,000 × 28  
= 28,000

**High polymers:** The polymers with high degree of polymerization (10,000 to 1,00,000) and high molecular masses (10,000 to 10,00,000) are called high polymers.

### CLASSIFICATION OF POLYMERS:

Polymers can be classified in several ways – based on their origin, structure, methods of preparation, response to heat and crystallinity.

**(a) Natural and Synthetic polymers** (based on origin): The polymers which are obtained from natural sources such as plants and animals are called natural polymers.

Eg. Cotton, Wool, Silk, Starch, Cellulose, Proteins, Natural rubber, Leather etc.

The polymers which are synthesized from simple molecules are called synthetic polymers.  
Eg. Polyethylene, Polystyrene, Teflon, PVC, Plexiglass etc.

**(b) Homopolymers, Copolymers and Linear, Branched and Crosslinked polymers** (based on structure):

A polymer may consist of identical monomers or monomers of different chemical structure and accordingly they are, called **homopolymers** and **copolymers** respectively.

-M-M-M-M-M-M-M-M- Homopolymer (Eg. Polyethylene, PVC etc.)

-M<sub>1</sub>-M<sub>2</sub>-M<sub>1</sub>-M<sub>2</sub>-M<sub>1</sub>-M<sub>2</sub>- Copolymer (eg. Nylon 66, Polycarbonates etc.)

Based on the way in which repeat units are linked, they are named as Linear, Branched and Cross linked polymers.

**A Linear polymer is one in which each monomer unit is linked only to two neighbouring units.**

-M-M-M-M-M-M-M-M- Linear homopolymer (eg. Polyethylene).

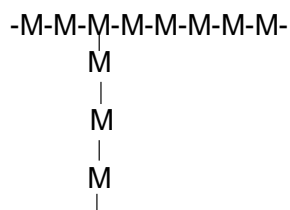
-M<sub>1</sub>-M<sub>2</sub>-M<sub>1</sub>-M<sub>2</sub>-M<sub>1</sub>-M<sub>2</sub>-M<sub>1</sub>- Linear copolymer (eg. Nylon 66).

Linear copolymers in which a block of one repeat unit is followed by a block of another repeat unit consecutively is called a **block copolymers**.

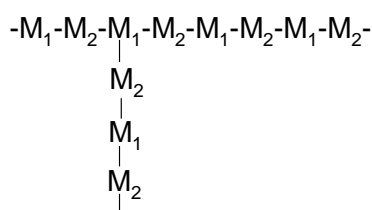
-M<sub>1</sub>-M<sub>1</sub>-M<sub>1</sub>-M<sub>1</sub>-M<sub>2</sub>-M<sub>2</sub>-M<sub>2</sub>-M<sub>2</sub>-

Where M<sub>1</sub> and M<sub>2</sub> are acrylic acid and methylmethacrylate respectively.

**A branched chain polymer** is one in which long linear chain may branched out forming a branched structure.

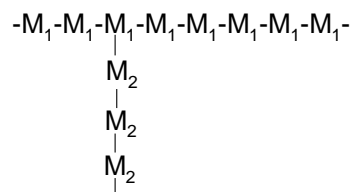


Branched chain homopolymer  
(e.g. Polyethylene at high pressure).



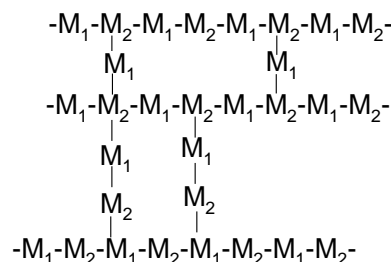
Branched chain copolymer

Branched copolymers with one kind of monomers in their main chain and another kind of monomers in their side chain are called **graft copolymers**.



Where  $M_1$  = vinyl chloride and  $M_2$  = styrene.

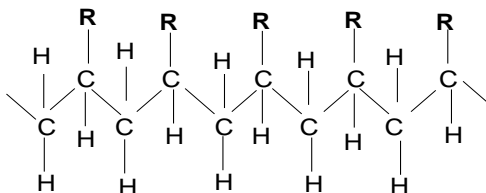
**Cross linked polymer** is formed when linear molecules under certain conditions are linked to neighbouring ones in such a way that it results in the formation of a three-dimensional structure of unlimited size.



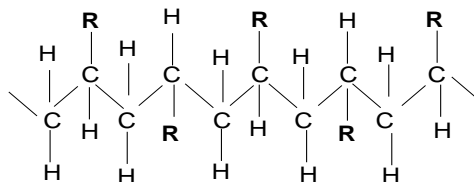
(eg. phenol-formaldehyde and urea-formaldehyde).

**(c) Stereoregular polymers or Tacticity** (based position of substituent groups in the polymer chain): Depending on the position and regularity of the repeating substituent groups, three different arrangements can be visualized, namely, isotactic, syndiotactic and atactic.

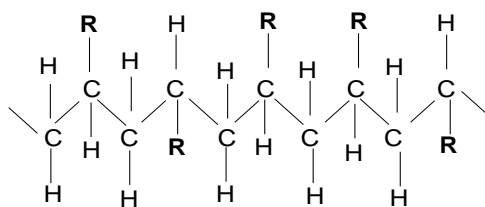
(i) The head -to-tail configuration, in which the substituent groups are all on the same side of the chain (either above or below), is called **isotactic polymer**.



(ii) If the arrangement of substituent groups are in alternating fashion (above and below), it is called **syndiotactic polymer** e.g., gutta percha.



(iii) If the arrangement of substituent groups are at random around the main chain, it is called **atactic polymer** e.g., polypropylene.



**(d) Amorphous and crystalline polymers (based on crystallinity):**

Many polymers are amorphous and have a tendency to get transformed into ordered structures when their melts are cooled. Polymers possess several crystalline and amorphous zones. The crystalline zones consist of an ordered arrangement of molecules. The polymers possessing a large number of crystalline zones (high degree of crystallinity) are referred to as crystalline polymers. Eg. fibres.

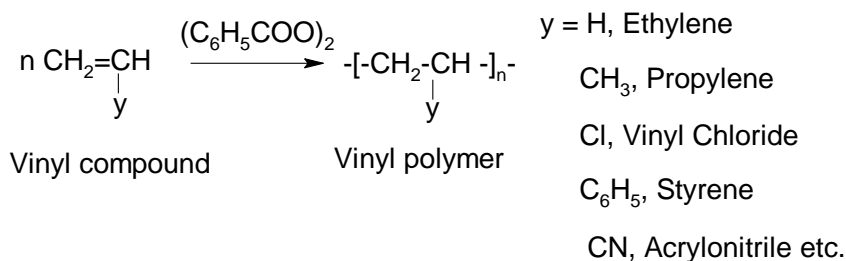
**(e) Addition and condensation polymers (based on methods of formation):**

**Addition polymers** are those formed by a process of self-addition to give polymers whose molecular masses are integral multiples of molecular mass of the monomer. Example – polyethylene, polypropylene etc.

**Condensation polymers** are formed by condensation reaction i.e., reaction between two or more monomer molecules with elimination of simple molecules like water, ammonia and hydrogen chloride etc. Example-phenol-formaldehyde resins and synthetic fibres such as polyesters and polyamides.

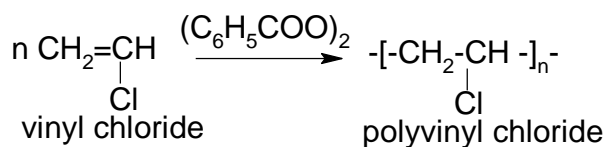
**Addition polymerization:**

**Addition polymerization** is brought about by the linking together simple unsaturated molecules such as substituted alkenes using peroxide ( $\text{H}_2\text{O}_2$  or dibenzoyl peroxide) as initiator.

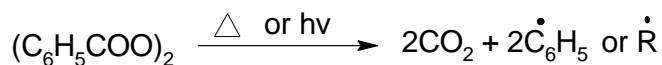


**Free radical mechanism of addition polymerization taking vinyl chloride as an example:**

The free radical mechanism of addition polymerization is illustrated in the synthesis polyvinyl chloride using dibenzoyl peroxide ( $\text{C}_6\text{H}_5\text{COO}$ )<sub>2</sub> as the initiator.



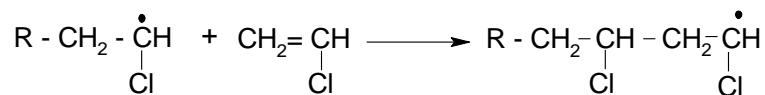
**(i) Generation of free radicals:** Initiation of chain reaction is induced by initiators which undergo thermal or photochemical decomposition generating highly reactive species referred to as free radicals.



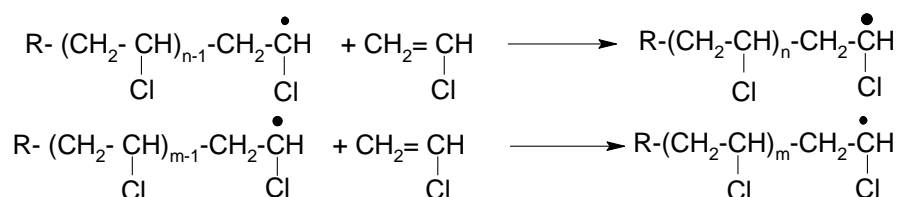
**(ii) Initiation:** The free radicals generated initiate the chain process by attacking the unsaturated monomer at the double bonds generating new free radicals.



**(iii) Propagation:** The new free radicals attack monomer molecules further in quick succession leading to chain propagation.

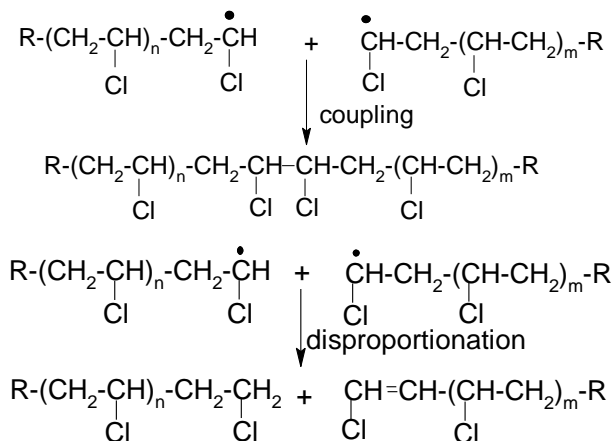


or in general,



The values of n and m varies from several hundreds to several thousands.

**(iv) Termination:** At some stage the chain propagation is terminated when the free radicals mutually combine either by coupling (combination) of two free radicals or by disproportionation. In coupling a polymer molecule of longer chain length is formed where as disproportionation results in two polymer molecules of shorter chain lengths, one of them being unsaturated. The products obtained after the termination are sometimes referred to as the dead polymers.



### GLASS TRANSITION TEMPERATURE (T<sub>g</sub>.)

**Glass transition temperature** is the temperature at which a polymer abruptly transforms from the glassy (hard) to the rubbery state (soft). This transition corresponds to the beginning of a chain reaction and is attributed to the easier molecular rotation about single bonds at T<sub>g</sub> and beyond. Below T<sub>g</sub>, polymer chain motion virtually ceases and the polymer is said to be frozen in position. Thus the polymers become associated with hardness, stiffness, brittleness and transparency – properties which are associated with inorganic glasses. The rubbery state is also referred to as viscoelastic state. On further heating the polymer melts and reaches a molten or viscofluid state.

Glassy state (Hard and brittle)  $\xrightarrow{T_g}$  Viscoelastic state (Rubbery)  $\xrightarrow{T_m}$  Viscofluid state (Polymer melt)

In the glassy state, there is neither segmental nor molecular motion. On heating beyond  $T_g$ , the polymer passes from glassy state into rubbery state. In rubbery state, there are only segmental motions while molecular mobility is forbidden. On further heating much above  $T_g$ , both segmental as well as molecular motion become possible and the polymer flows like a viscous liquid. This temperature is usually called a flow temperature since any polymer is only a mixture and has no sharp melting point. Glass transition temperature of a few amorphous polymers are given in Table- 2

**Table-2 Glass transition temperature of polymers**

Polymer	$T_g, ^\circ\text{C}$	Contributing factor
Polyethylene	- 20	Flexible backbone
Polypropylene	5	$\text{CH}_3$ groups inhibit freedom of rotation
Polyvinylchloride	80	Strong polar attraction between molecules
Polytetrafluoroethylene	115	Stiff backbone

#### **Factors influencing $T_g$ Value:**

1. **Flexibility:** A free rotational motion of the polymer chain imparts flexibility to the polymer. Linear polymer chains made of C-C, C-O and C-N single bonds have a higher degree of freedom of rotation. Presence of inherently rigid structures in the polymer chain such as aromatic or cyclic structure or bulky side groups on the backbone of C-atoms hinder the freedom of rotation thus lowering the chain flexibility and increase in  $T_g$ .

2. **Crystallinity:** The  $T_g$  value of a polymer largely depends on the degree of crystallinity. Higher the crystallinity, larger is the  $T_g$  value of a polymer. In crystalline polymer, the linear or stereoregular chains are lined up parallel to each other and are held by strong cohesive forces. This leads to a high  $T_g$  value of the polymer.

3. **Branching and cross linking:** A small amount of branching will tend to lower  $T_g$ . Increase in chain ends in branched chain polymers increase the free volume thus decreasing the  $T_g$ . On the other hand, a high density of branching brings the polymer chains closer, lowers the free volume thus reducing the chain mobility and resulting in an increase in  $T_g$ . Cross linking of chains decreases the flexibility of the polymer chain and, therefore, as the extent of cross linking increases, the  $T_g$  value increases.

4. **Molecular mass:** Generally,  $T_g$  of a polymer increases with molar mass upto a particular value and beyond that there is no change.

5. **Stereoregularity of the polymer:** A syndiotactic polymer has a higher  $T_g$  than atactic polymer which in turn has higher  $T_g$  than its isotactic stereoisomer.

**6. Presence of plasticizers:** Addition of plasticizers reduces the  $T_g$  value; for example, addition of diisooctyl phthalate to PVC reduces its  $T_g$  from  $80^\circ\text{C}$  to below room temperature.

**Significance of glass transition temperature:**

- (i)  $T_g$  can be used to evaluate the flexibility of a polymer and predict its response to mechanical stress.
- (ii) Many polymers show an abrupt change in their physical properties at their glass transition temperature. Coefficient of thermal expansion, heat capacity, refractive index, mechanical damping, modulus of elasticity and electrical properties at  $T_g$  determine the usefulness of a polymer over a temperature range.
- (iii) Polymeric materials are subjected to different processing operations such as moulding, calendring and extrusion. Knowledge of  $T_g$  is useful in choosing appropriate temperature for such processing operations.

**STRUCTURE AND PROPERTY RELATIONSHIP:**

Polymers possess a wide range of properties. They may be elastic or rigid, hard or soft, transparent or opaque. They may have the strength of steel but very light in weight. They may soften on heating and the melt may set to a hard mass on cooling. These properties may vary from one type of polymer to another and even among the polymers of the same type, there may be differences in properties. The fundamental properties which influence the structure-property relationship are molecular mass, polarity, crystallinity, molecular cohesion, and the nature of polymeric chains and stereochemistry of the molecule.

**(i) Strength:** Generally, polymers of low molecular weight are quite soft and gummy. On the other hand high molecular weight polymers are tougher and more heat resistant. High molecular masses of polymers account for their high softening temperature and tensile strength. **Cross linked ones are the stronger than their linear and less branched ones.** Tensile and impact strengths increase with molecular mass up to a certain point and then become constant (Fig.2a). The melt viscosity of the polymer initially shows a gradual increase with the molecular mass and a steep increase at higher molecular masses (Fig.2b). Low melt viscosity and high tensile and impact strengths are desirable properties for a polymer to be commercially useful.

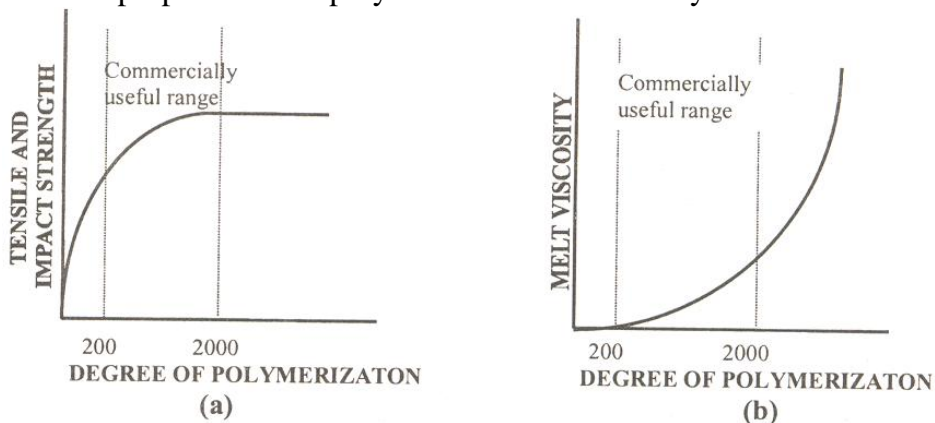


Fig.2. Influence of degree of polymerization on (a) tensile and impact strengths and (b) melt viscosity

**(ii) Crystallinity:** Polymers invariably contain both crystalline and amorphous regions. The degree of crystallinity of a polymer depends on its structure (linear, branched, with large pendent

groups in polymer chain) and configuration (stereoregular or not). Crystalline region occur when linear polymer chains without branching and carrying no bulky groups, are orderly arranged parallel and close to each other. The chains of polymers are held together by secondary forces such as Vander waal, hydrogen bonding, polar interaction, etc. Such type of close packing imparts a high degree of crystallinity. The polymers having high degree of crystallinity exhibit high tensile strength, impact resistance, high density and sharp and high melting point.

The polymers such as HDPE, stereoregular isotactic and syndiotactic isomers of polypropylene, PVC are highly crystalline. Atactic PVC, PS, polypropylene in which bulky pendant groups arranged randomly on the polymer backbone are amorphous. LDP which has extensive branching is also amorphous.

**(iii) Elasticity:** Elasticity of a polymer material is mainly because of the uncoiling and recoiling of the molecular chains on the application of force. For a polymer to show elasticity the individual chains should not break on prolonged stretching. Breaking takes place when chain slip past each other and get separated. In rubbers this is avoided by molecular engineering such as (a) introducing cross linking at suitable molecular positions (b) avoiding bulky side groups such as aromatic and cyclic structures on the repeat units and (c) introducing more non-polar groups on the chain so that the chains do not separate on stretching. The structure should be amorphous so that the material has a glass transition temperature at which it is used. This can be brought about by introducing a plasticizer molecule in the polymer chain by copolymerization or compounding the rubber with a suitable plasticizer liquid.

**(iv) Plastic deformation (rheology) of polymers:** Some polymers, on the application of heat and pressure, initially become soft, flexible rubbery matter and undergo deformation. On further heating beyond melting point, they melt and flow. Such property of polymer is called plasticity. On cooling they return to their original state. This property of plastic deformation is used in moulding operations. Thermoplastics exhibit this property. Thermoplastics are linear, stereoregular polymers. The polymer chains are closely packed and held by secondary forces such as vander waal, hydrogen bonding and dipolar interaction. Such polymers when heated, the chains acquire sufficient energy and overcome these inter chain attractive forces. They attain molecular mobility and flow like viscous fluid.

Thermosettings do not exhibit plasticity. Moulded thermosettings have three dimensional structure. All monomer units are held together through strong primary covalent bonds throughout the structure. Primary covalent bonds are not easily broken by heat. On strong heating, charring occurs instead of deformation. Therefore thermosettings do not undergo reversible plastic deformation.

**(v) Chemical resistance and nature of polymer chain:** The chemical attack on polymers involves softening, swelling and loss of strength of material. The resistance to chemical attack of a polymer depends on several factors such as (a) the presence of polar or non-polar groups (b) the degree of crystallinity and molecular mass, and (c) degree of crosslinking.

**(a) Presence of polar and non-polar groups:** A polymer is more soluble in a solvent of similar chemical structure. Polymers having polar groups such as  $\text{-OH}$  or  $\text{-COOH}$  groups are usually attacked or dissolved by polar liquids such as water or alcohols. (e.g. resol resins swell in alcohols). Polymers with non-polar groups such as  $\text{-CH}_3$  and  $\text{-C}_6\text{H}_5$  are not easily attacked by polar solvents but they easily swell and sometimes dissolve in non-polar solvents such as petrol,



benzene and carbon tetrachloride. Polymers with large number of aromatic groups dissolve in aromatic solvents such as benzene. Strong acids and alkalis attack groups such as  $\text{-NHCO-}$  and  $\text{-NHCOO-}$  present in polyamides (nylon) and polyurethanes respectively. Polyolefins, PVC, ABS plastics, and polystyrene have excellent resistance to acids and alkalis.

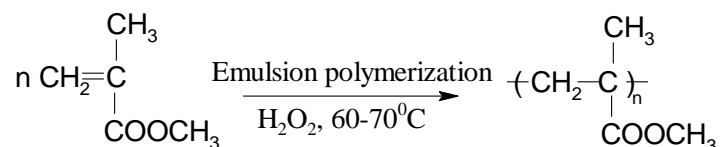
(b) *Degree of crystallinity and molecular mass*: For a given polymer, the swelling character decreases with the increase in the molecular mass. For polymers having same chemical character, the chemical resistance increases with increase in the degree of crystallinity.

(c) *Degree of cross linking*: Greater the degree of cross linking lesser is the solubility. Linear polymers readily dissolve in organic solvents and readily melt on heating. On the other hand, branched chain and cross linked polymers have very little solubility and may undergo rupture when heated.

### SOME COMMERCIAL POLYMERS:

#### a) Polymethylmethacrylate (PMMA) or Plexiglass or Lucite:

**Synthesis:** PMMA is obtained by subjecting methylmethacrylate to emulsion polymerization at  $60\text{-}70^\circ\text{C}$  in presence of hydrogen peroxide.



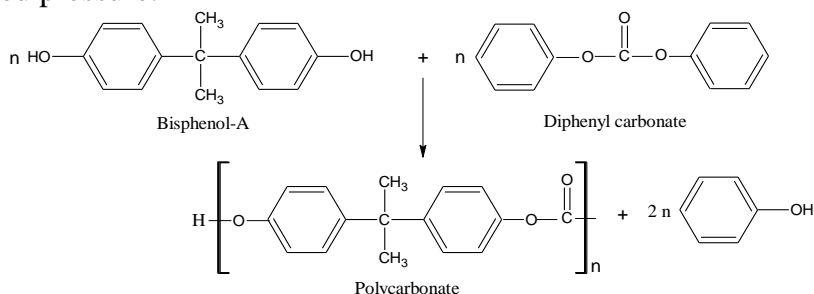
**Properties:** Plexi glass is a highly transparent thermoplastic which softens at  $120^\circ\text{C}$ . It is a hard solid which can be easily moulded and is resistant to the action of organic solvents. It has good mechanical properties and is a good substitute for glass but has a poor scratch resistance. Its characteristic feature is optical clarity. It allows  $uv$  rays to pass through it.

**Applications:** It is useful for glazing hot houses, glazing airplanes and automobiles. It is also employed in the manufacture of chemical equipment, sign boards, lenses for automobile lighting and domestic applications.

**Applications:** Polyurethanes are used as coatings, films, foams (cushions for furniture and automobiles), adhesives and elastomers. Resilient polyurethane fibres are used for foundation garments and swim-suits. They also find use as a leather substitute. They are used to cast to produce gaskets and seals.

(b) **Polycarbonates:** Polycarbonates are polymeric materials which have repeat carbonate interunit linkages ( $\text{-O-CO-O-}$ ).

**Synthesis:** They are prepared by the condensation of bisphenol-A with diphenylcarbonate at  $200^\circ\text{C}$  under reduced pressure.



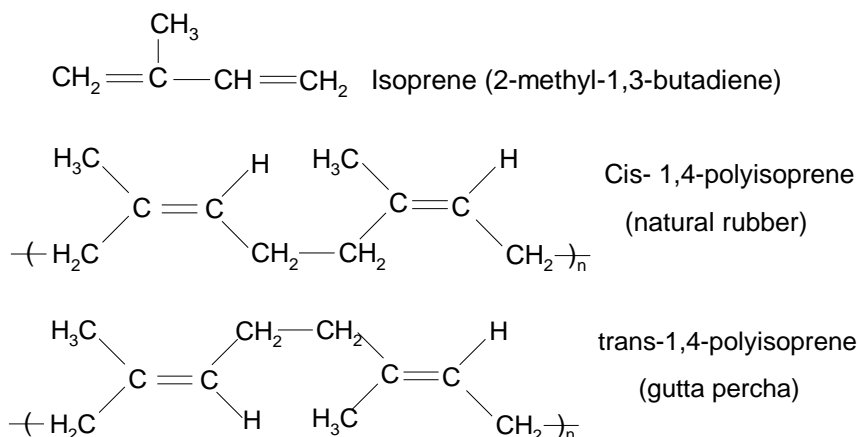
**Properties:** It is a white transparent thermoplastic. It has high melting point, tensile strength and impact resistance. It has excellent mechanical properties. However, it is soluble in acids and alkalis.

**Applications:** It is used for the manufacture of many useful articles such as telephone parts, unbreakable glazing applications, safety goggles, automobile taillight lenses, machinery housings, etc.

## ELASTOMERS: SYNTHETIC RUBBERS

**Elastomers** are high polymers which stretch easily by several times their length when subjected to an external force but readily regain their original shape when the force is removed. Rubber is an example for elastomer.

**Natural rubber** is made from the saps of wide range of plants like *havea brasillians* and *guayule*. It is a high polymer of isoprene (2-methyl-1,3-butadiene). Since polyisoprene contains C=C bonds, it exists in two isomeric structures, cis and trans forms. Natural rubber is soft and cis-configuration while 'Guttapercha' or 'Ballata' (obtained from the mature leaves of *dichopsis gutta* and *palagum gutta* trees) has trans configuration.

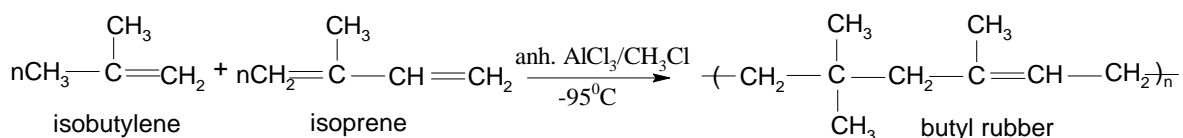


Any linear polymer may be converted into a good rubber if it meets the following characteristics.

- It is geometrically irregular polymer with a long chain at the temperature of use so that the thermal agitation will result in a coiled-type arrangement of the chains.
- It has a glass transition temperature below the working temperature range of rubber.
- There is possibility of introducing cross linking between the chains to get the required degree of rigidity.

### (a) Butyl rubbers:

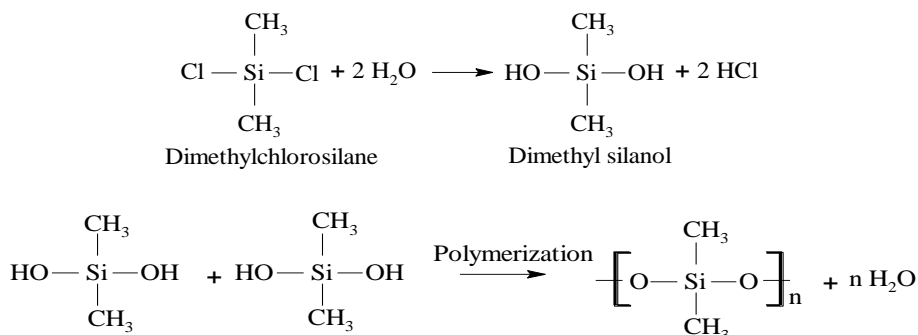
**Synthesis:** Butyl rubber is manufactured by mixing isobutylene with 1.5 to 4.5% of isoprene and methyl chloride as diluent. The mixture is placed in a reactor fitted with stirrers and cooled to  $-95^\circ\text{C}$ . The process is catalysed by the addition of anhydrous aluminium chloride dissolved in methyl chloride.



**Applications:** For making cycle and automobile tubes, automobile parts, hoses, conveyor belts for food and other materials, tank-linings, insulation for high voltage wires and cables, etc.

**(b) Silicone rubbers:** Silicone rubber (polymethyl siloxane) is an example for inorganic polymers. The silicon atoms are linked to organic groups.

**Synthesis:** Silicone rubber is formed by the condensation polymerization of dimethyl silanol, which is produced from dimethylchloro silane.



**Applications:** Silicone rubbers are used in making lubricants, used in gaskets, seals, wire and cable insulation.

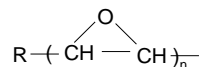
## ADHESIVES:

**An adhesive** is defined as a polymeric substance used to bind together two or more similar or dissimilar materials so that the resulting material can act or be used as a single piece.

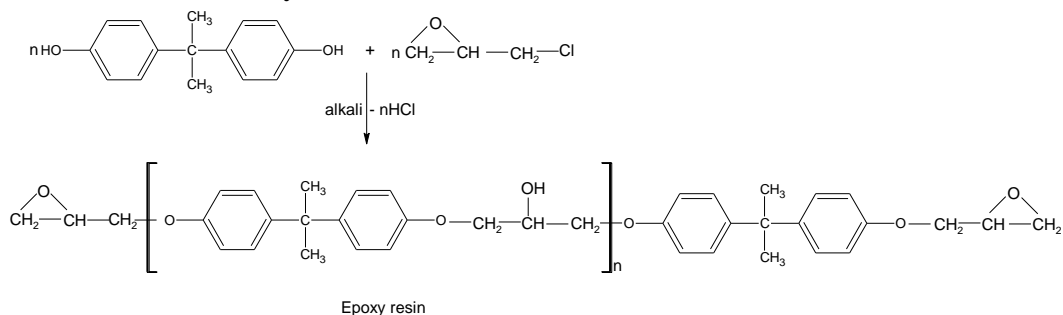
The adhesive forces may be chemical or mechanical in nature. In the former case, the adhesive reacts with parts binding them together mainly by intermolecular forces of attraction. In the later, the adhesive penetrates into the interiors of the bonded parts to produce physical cementing.

Adhesives may be broadly classified into natural and synthetic. Common gum and glues are examples of natural adhesives. Synthetic adhesives are resins. An important class of synthetic adhesives is the thermosetting resins which include phenol-formaldehyde, urea-formaldehyde, resorcinol-formaldehyde, silicones and epoxides.

**Epoxy resins (Araldite):** Epoxy resins are polymeric materials containing the epoxy group.



**Synthesis:** Epoxy resins are obtained by condensation of excess epichlorohydrin and bisphenol A, in the presence of alkali catalyst.



**Applications:** The major use of epoxy resins are as adhesives for surfaces such as glass and metals and surface coatings. They can be used both in moulding and laminating techniques to make glass fibre reinforced articles with better mechanical strength, chemical resistance and electrical insulating properties. Epoxy resins are also used in industrial flooring, highway surfacing and patching materials.

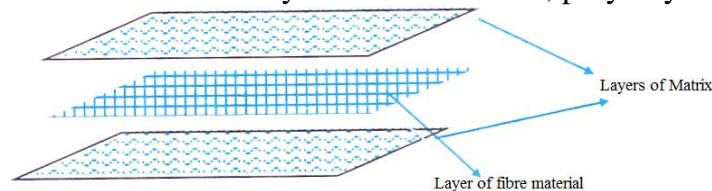
## **POLYMER COMPOSITES:**

**Introduction:** Structural materials required in various industries such as aircraft industry, should have properties such as, (i) low density (ii) high strength and stiffness (iii) abrasion and impact resistance and (iv) corrosion resistance. No single metal, alloy, ceramic or polymeric material is known which can offer the combination of aforesaid property. This is because a strong material is relatively dense and an increase in stiffness generally results in a decrease in impact strength. The search for materials possessing the above properties has led to the development of composite materials.

**Definition:** A combination of two or more distinct components to form a new class of material suitable for structural applications is referred to as composite materials. When one of the components is a polymer, the resulting composite is called a polymer composite.

While each component retains its identity, the composite material displays macroscopic properties superior to its parent constituents, particularly in terms of mechanical properties.

Polymer composites are generally made of two components, namely (i) matrix and (ii) fibre. The fibre is embedded in the matrix in order to make the matrix stronger. The matrix is usually a thermoset material such as epoxy resin or a polyamide and it holds the fibres together. Fibre is most often glass but sometimes may be a **carbon fibre**, polyethylene or **Kevlar**.

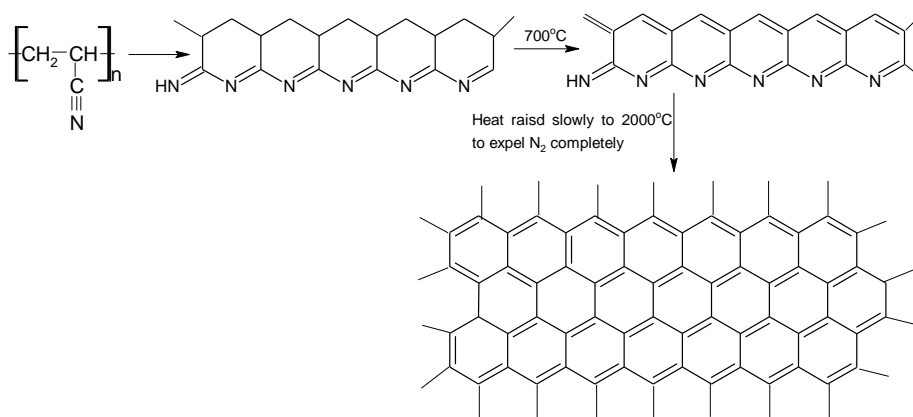


Fibre-reinforced composites are strong and light. They are often stronger than steel, but weigh much less and hence these composites can be used to make automobiles lighter, achieving more fuel efficiency and less pollution.

A common fibre-reinforced composite is fiberglass. Its matrix is made by mixing a polyester and a styrene pouring the mixture over a mass of glass fibres. The styrene and the double bonds in the polyester react by free radical vinyl polymerization to form a cross-linked resin. The glass fibres are trapped inside where they react as reinforcement. The composite may be made stronger by lining up all the fibres in the same direction. When the composite is pulled in the direction of the fibres it shows high strength. If the fibres used are in more than one direction (such as in a woven fabric), the resulting composite will be strong in all directions.

**Carbon fibre:** Carbon fibre is a fibre made up of carbon. Carbon fibre is very thin strands of carbon even thinner than human hair. When bound together with plastic polymer resin with heat, pressure or vacuum, a composite material is formed that is both strong and light weight. The strength of carbon fibre depends on the weave. The more complex the weave the more durable the composite will be.

**Preparation:** Carbon fibre is made by heating polyacrylonitrile (PAN) carefully and slowly when the polymer cyclizes through the cyano groups to form a polycyclic chain. The resulting solid is heated gradually so that hydrogen is expelled and rings become aromatic. It is then roasted at 600-700°C when the adjacent chains join together losing more hydrogen gas. Then the temperature is gradually raised to 2000°C to get wider ribbon-like mass. The temperature is maintained around 2000°C till all the nitrogen is expelled leaving behind wider ribbon-like pure carbon fibre in the graphite form.



#### **Properties:**

- i) Carbon fibre reinforced composites are very strong and are often stronger than steel but lighter.
- ii) Good corrosion resistance.
- iii) Very low coefficient of thermal expansion.
- iv) Low impact resistance.

#### **Applications:**

- i) In aerospace and automotive fields, as well as in sailboats.
- ii) In modern bicycles and motorcycles.
- iii) In consumer goods such as laptops, tripods, finishing rods, golf clubs, tennis rackets etc.

### **CONDUCTING POLYMERS:**

**Conducting polymers** are generally obtained by doping an oxidizing or a reducing agent into organic polymers with conjugated backbone consisting of alternating double and single carbon-carbon bonds.

**Mechanism of conduction in polyacetylene:** The neutral polymer would have band model identical to that of an insulator. The polymer may be transformed into a conductor by doping it with an electron donor (reductive dopant such as sodium naphthalide) or an electron acceptor (oxidizing dopant such as iodine,  $\text{AsCl}_3$ ,  $\text{FeCl}_3$ ). This resembles doping of Si with As or Ga. However, this doping would not produce donor level close to the conduction band and acceptor level close to the valence band as in the case of Si with As or Ga. In doped conjugated polymers, there are two types of  $\pi$ -electron energy bands- the  $\pi$ -bonding MOs constitute the valence band, while  $\pi^*$ -anti-bonding MOs form the conduction band.

**The oxidative doping of a polyacetylene,** (Fig. 6) leads to the removal of an electron from  $\pi$ -system of the backbone producing free radical and a positive charge. This combination of charge site and a radical is referred to as polaron, which could be a radical cation. This would create new localized electronic states in the forbidden gap being occupied by a single unpaired electron. Upon further oxidation, the free radical of the polaron is removed, creating a new defect called bipolaron (solitons). Due to the formation of soliton, a new localized electronic state appears in the middle of the energy gap. When doping is high, several charged solitons form

soliton band. This can later merge with edges of valence and conduction bands exhibiting conductivity.

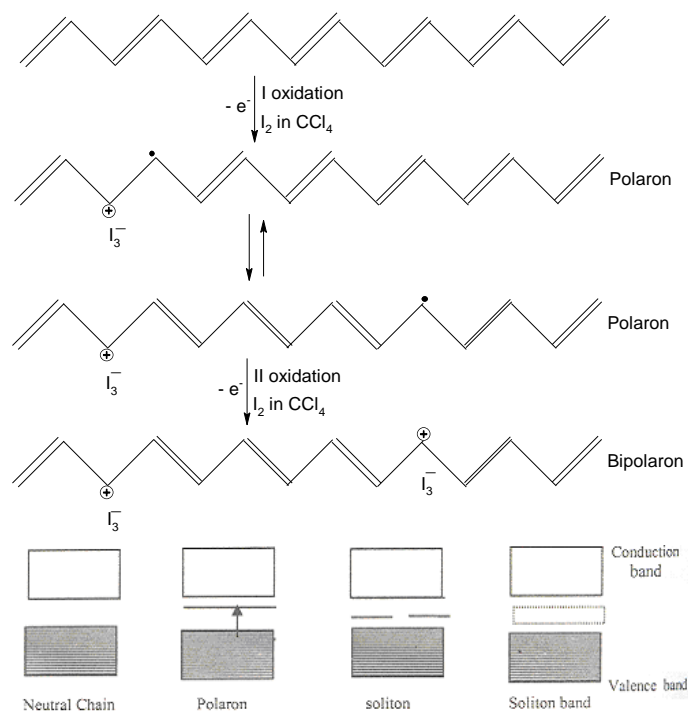


Fig.6. Band diagram of polyacetylene as the amount of oxidative dopant is increased

**Polyaniline:** Polyaniline is considered as one of the most useful conducting polymers because of its ease of preparation, its stability under aqueous conditions and the facility to fine-tune electrical, optical and chemical properties through substituent effects. It shows a conductivity of greater than  $10^5 \text{ s}^{-1} \text{ m}^{-1}$ . As a comparison Teflon has a conductivity of  $10^{-16} \text{ s}^{-1} \text{ m}^{-1}$  and that of copper is  $10^8 \text{ s}^{-1} \text{ m}^{-1}$ .

**Applications:** Conducting polymers are highly promising materials to be used in electric and electronic applications. Some of the applications are

- (i) As electrode material for rechargeable batteries, for higher power to weight ratio (coin type materials).
- (ii) As conductive tracks on printed circuit boards.
- (iii) As sensor- humidity sensor, gas sensor, radiation sensor, biosensor for glucose, galactose etc.
- (iv) In electrochromic display windows. (v) In information storage devices.
- (vi) As film membranes for gas separations. (vii) In light emitting diodes.
- (vii) In fuel cells as the electrocatalytic materials

\*\*\*\*\*

## WATER CHEMISTRY

### Natural sources of water:

#### (a) Surface water:

**1. Rain water** is probably the purest form of natural water, since it is obtained as a result of evaporation from the surface water. However, during the journey downwards through the atmosphere, it dissolves a considerable amount of industrial gases (like  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NO}_2$  etc.) and suspended solid particles, both of organic and inorganic origin.

**2. River water:** Rivers are fed by rain and spring waters. Water from these sources flow over the surface of land, dissolves the soluble minerals of the soil and finally falls in rivers. River water thus contains dissolved minerals of the soil such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium, and iron. River water also contains the organic matter, derived from decomposition of plants, and small particles of sand and rock in suspension. Thus, river water contains considerable amounts of dissolved as well as suspended impurities.

**3. Lake water** has a more constant chemical composition. It usually, contains much lesser amounts of dissolved minerals than even well water, but quantity of organic matter in it is quite high.

**4. Sea water** is the most impure form of natural water. Rivers join sea and throw in the impurities carried by them. Moreover, continuous evaporation of water from the surface of sea makes sea water continuously richer in dissolved impurities. Sea water contains, on an average, about 3.5% of dissolved salts, out of which 2.6% sodium chloride. Other salts present are sulphate of sodium; bicarbonates of potassium, magnesium and calcium; bromides of potassium and magnesium and a number of other compounds.

Surface water generally contains suspended matter, which often contains the disease-producing (or pathogenic) bacteria's. Hence, such waters as such are not considered to be safe for human activities.

**(b) Underground water:** A part of the rain water, which reaches the surface of the earth, percolates into the earth. As this water journeys downwards, it comes in contact with a number of mineral salts present in the soil and dissolves some of them. Water continues its downward journey, till it meets a hard rock, when it retards upwards and it may even come in the form of spring.

Spring and well water (or underground water), in general is cleaner in appearance due the filtering action of soil, but contains more of the dissolved salts. Thus water from these sources contains more hardness. Usually, underground water is of high purity.

#### Impurities in water:

The water found in nature is never pure and contains a large number of impurities in varying amounts. The major types of impurities found in water are of the following type:

**(i) Dissolved gases:** Most water contains dissolved gases such as oxygen, carbon dioxide, sulphur dioxide, ammonia and oxides of nitrogen all of which are derived from atmosphere.

**(ii) Dissolved solids:** Dissolved solids mainly consist of bicarbonates, chlorides and sulphates of calcium, magnesium and sodium. In addition, small amounts of nitrates, nitrites, silicates, ammonia and ferrous salts are also present.

**(iii) Suspended impurities:** The suspended matter may be inorganic or organic nature. The inorganic materials include particles such as sand, clay, silica, hydroxides of iron and aluminium

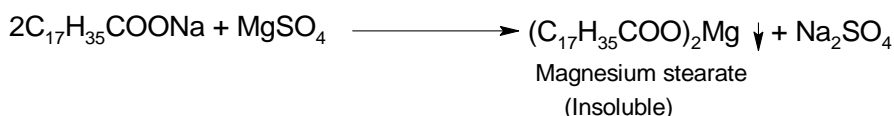
etc. derived from erosion of soil. Some of these particles have large size and therefore settle down readily. Others are fine particles and colloidal in nature. Such particles do not settle down easily. The organic suspensions are decaying vegetable matter and due to microorganisms. These are also colloidal form. The presence of suspended matter, particularly the colloidal particles impart turbidity to water.

**(v) Microscopic matter:** Many pathogenic bacteria and microorganisms are also present in water. They are main causes for the water borne diseases.

### Water analysis:

**Hardness of water:** Hardness in water is that characteristic, which “prevents the lathering of soap”. This is due to presence of certain salts of calcium, magnesium and other heavy metals dissolved in it.

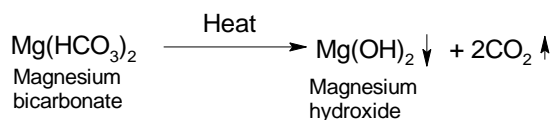
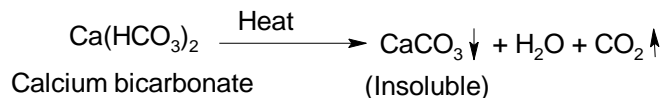
A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but on the other hand forms a white scum or precipitate. This precipitate is formed, due to the formation of insoluble soaps of calcium and magnesium.



Thus, water which does not produce lather with soap solution readily, but forms a white curd, is called hard water. On the other hand, water which lathers easily on shaking with soap solution is called soft water. Such water, consequently, does not contain dissolved calcium and magnesium.

Hardness of can be classified as temporary and permanent hardness.

**(i) Temporary or carbonate hardness** is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and carbonate of iron. Temporary hardness is mostly destroyed by mere boiling of water, when bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel. Thus:



**(ii) Permanent or non-carbonate hardness** is due to the presence of chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Unlike permanent hardness is not destroyed on boiling.

The sum of temporary and permanent hardness is referred to as total hardness of water.



**Equivalents of calcium carbonates:**

The concentration of hardness as well as non-hardness constituting ions are, usually, expressed in terms of equivalent amount of  $\text{CaCO}_3$ . The choice of  $\text{CaCO}_3$  in particular is due to its molecular weight is 100 (equivalent weight = 50) and moreover, it is the most insoluble salt that can be precipitated in water treatment. The equivalents of  $\text{CaCO}_3$  equal to

$$\frac{\left[ \text{Mass of hardness producing substance} \right]}{\text{Chemical equivalent of hardness-producing substance}} \times \left[ \text{Chemical equivalent of } \text{CaCO}_3 \right]$$

$$\frac{\text{Mass of hardness producing substance} \times 50}{\text{Chemical equivalent of hardness-producing substance}}$$

**Units of hardness:**

(i) **Parts per million (ppm)** is the parts of calcium carbonate equivalent hardness per  $10^6$  parts of water, i.e., 1 ppm = 1 part of  $\text{CaCO}_3$ eq hardness in  $10^6$  parts of water.

(ii) **Milligrams per litre (mg/L)** is the number of milligrams of  $\text{CaCO}_3$  equivalent hardness present per litre of water. Thus:

1mg/L = 1 mg of  $\text{CaCO}_3$  eq. hardness of 1 L of water

But 1L of water weighs = 1kg = 1000g =  $1000 \times 1000$  mg =  $10^6$  mg.

Therefore 1 mg/L = 1 mg of  $\text{CaCO}_3$  eq per  $10^6$  mg of water.

= 1 part of  $\text{CaCO}_3$ eq per  $10^6$  parts of water = 1ppm.

**Determination of Hardness of water by EDTA (Complexometric) method:**

**Principle:** The hardness of water can be determined by titrating a known volume of water against standard EDTA solution at pH of 10 using Eriochrome black-T indicator. The colour of the free indicator at pH 10 is blue. Eriochrome black-T forms a wine red complex with  $\text{M}^{2+}$  ions. On titration, EDTA first gets complexed with all the free  $\text{M}^{2+}$  ions and then with  $\text{M}^{2+}$  ions of  $\text{M}^{2+}$ -indicator complex. Thus the indicator gets freed and consequently gives a colour change from wine red to blue at the equivalence point. Since the reaction involves the release of  $\text{H}^+$  ions, a buffer mixture ( $\text{NH}_4\text{OH-NH}_4\text{Cl}$ ) is used to maintain a pH of 10.

The total hardness is determined by titrating a known volume of water sample against EDTA. To determine the temporary hardness, another sample of the same volume of water is boiled to convert the bicarbonates to carbonates and precipitated calcium carbonate is filtered off. The filtrate, after cooling, is titrated against EDTA in the same away. This gives permanent hardness. The difference between the total hardness and the permanent hardness gives the temporary hardness.

**Procedure: (i) Total hardness:** 25 ml of given hard water is pipetted out into a clean conical flask. 5 ml of  $\text{NH}_4\text{OH-NH}_4\text{Cl}$  buffer and 3 drops of Eriochrome black-T indicator are added. The resulting wine red coloured solution is titrated against EDTA (0.01M) until clear blue without any reddish tinge is obtained. Let the volume of EDTA required be  $V_1$  ml.

**(ii) Permanent hardness:** 25 ml of given hard water is pipetted out into a clean 500 ml beaker and boiled for 20-30 minutes. It is cooled and filtered directly into a 250 ml conical flask. 5 ml of  $\text{NH}_4\text{OH-NH}_4\text{Cl}$  buffer and 3 drops of Eriochrome black-T indicator are added. The resulting wine red coloured solution is titrated against EDTA (0.01M) until clear blue without any reddish tinge is obtained. Let the volume of EDTA required be  $V_2$  ml.

**Calculations:** 1000 ml of 1M EDTA  $\equiv$  100 g CaCO<sub>3</sub> (Mol. Wt. of CaCO<sub>3</sub> = 100)

$$1\text{ml of 1M EDTA} \equiv \left(\frac{100}{1000}\right) \text{ g of CaCO}_3$$

$$V_1 \text{ ml of 0.01M EDTA} \equiv \frac{V_1 \times 0.01 \times 100}{1000} \text{ g of CaCO}_3$$

$$25 \text{ ml of sample water contains } \frac{V_1 \times 0.01 \times 100}{1000} \text{ g of CaCO}_3$$

$$10^6 \text{ (1 million) ml of water sample} \equiv \frac{V_1 \times 0.01 \times 100}{1000 \times 25} \times 10^6 \text{ ppm of CaCO}_3$$

$$= 40 \times V_1 \text{ ppm of CaCO}_3$$

$$\text{Total hardness of water sample} = 40 \times V_1 \text{ ppm of CaCO}_3 \text{ equivalent}$$

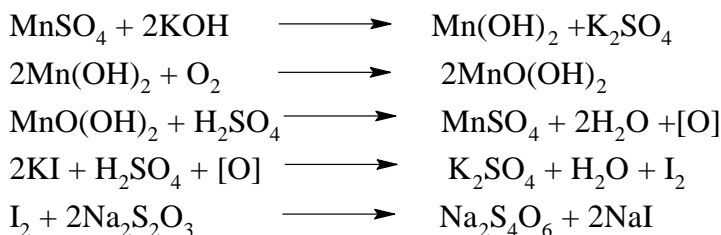
$$\text{Similarly, Permanent hardness} = \frac{V_2 \times 0.01 \times 100}{1000 \times 25} \times 10^6 \text{ ppm of CaCO}_3$$

$$= 40 \times V_2 \text{ ppm of CaCO}_3$$

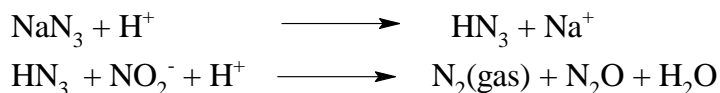
$$\text{Temporary hardness} = 40 (V_1 - V_2) \text{ ppm of CaCO}_3 \text{ equivalent.}$$

### Determination of Dissolved Oxygen by Winkler's method:

**Principle:** The principle involved in the determination of dissolved oxygen is that the divalent manganese solution along with a strong alkali is added to water sample. The DO present in water sample oxidizes divalent manganese to tetravalent manganese. The basic manganese oxide formed acts as oxygen carrier to enable the dissolved oxygen in molecular form to take part in the reaction. Upon acidification, tetravalent manganese reverts to divalent state with the liberation of nascent oxygen, which oxidizes KI to I<sub>2</sub>. The liberated iodine is titrated against sodium thiosulphate solution using starch indicator.



KI is added as alkaline KI which consist of a solution of sodium azide, KI and KOH in water. Sodium azide destroys the nitrites in water and thereby reduces the error due to nitrites.



**Procedure:** 250 cm<sup>3</sup> of water sample is collected in a BOD bottle (avoiding the contact with air, as far as possible). Immediately 2 cm<sup>3</sup> of manganese sulphate is added by means of pipette (dipping the end well below the water level). Similarly, 2 cm<sup>3</sup> of alkaline iodide-azide mixture is added carefully. The bottle is stoppered and shaken thoroughly. 2 cm<sup>3</sup> of conc. H<sub>2</sub>SO<sub>4</sub> is added slowly into it. The bottle is stoppered and shaken thoroughly.

100 cm<sup>3</sup> of the solution pipetted into a clean conical flask from the bottle and titrated against Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution using 1 cm<sup>3</sup> starch as indicator near the end point. End point is colour change from blue to colourless.

**Calculations:**

100.0 cm<sup>3</sup> of water sample (iodine)  $\equiv$  V ml of 0.01 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.

1000 cm<sup>3</sup> of 1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution  $\equiv$  8 g of oxygen

Therefore, V cm<sup>3</sup> of 0.01N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution  $\equiv \frac{V \times 0.01 \times 8}{1000}$  g of oxygen

$\therefore$  The amount of oxygen present in 10<sup>6</sup> cm<sup>3</sup> of water  $\equiv \frac{V \times 0.01 \times 8}{1000 \times 100} \times 10^6$

$\therefore$  The dissolved oxygen present in the water = 0.8V ppm

**BOILER FEED WATER AND BOILER PROBLEMS:**

**Scale and sludge formation in boilers:** In boilers, water evaporates continuously, and the concentration of the dissolved salts increases 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 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<sub>3</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, MgSO<sub>4</sub>, etc.

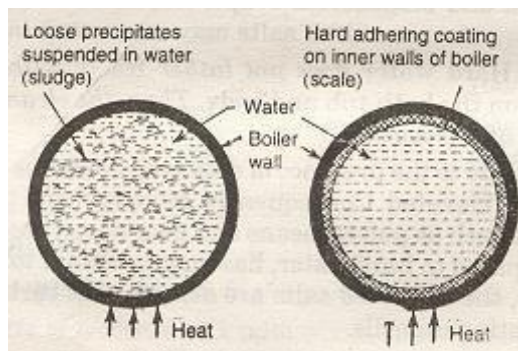


Fig.1. Scale and sludge in boilers

**Disadvantages of sludge formation:**

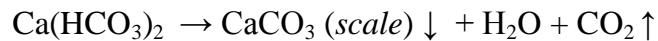
(i) Sludges are poor conductor of heat, so they tend to waste a portion of heat generated. (ii) If sludges formed along with scales, then former gets entrapped in the latter and both get deposited as scales.

(iii) 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.

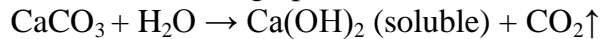
**Prevention of sludge formation:** (i) By using well softened water (ii) Drawing off a portion of the concentrated water.

**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 sources of boiler troubles. Formation of scales may be due to:

(1) *Decomposition of calcium bicarbonate:*



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,  $\text{CaCO}_3$  is soluble.



(2) *Deposition of calcium sulphate:* The solubility of calcium sulphate in water decreases with rise of temperature (solubility of calcium sulphate is 3,200 ppm at  $15^\circ\text{C}$  and it reduces to 55 ppm at  $230^\circ\text{C}$  and 27 ppm at  $320^\circ\text{C}$ ). In other words,  $\text{CaSO}_4$  is soluble in cold water, but almost completely insoluble in super heated water. Consequently,  $\text{CaSO}_4$  gets precipitated as hard scale on the heated portions of the boiler. This is the main cause of scales in high-pressure boilers.

(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.



(4) *Presence of silica:* ( $\text{SiO}_2$ ), even present in small quantities, deposits as calcium silicate ( $\text{CaSiO}_3$ ) and /or magnesium silicate ( $\text{MgSiO}_3$ ). 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 steady supply of heat to water, excessive or overheating is done and this causes increase in fuel consumption.

(2) *Lowering of boiler safety:* Due to scale formation, overheating of boiler is to be done in order to maintain a constant supply of steam. The over-heating of the boiler tube makes the material softer and weaker, and this causes distortion to 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 overheated 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 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, with which they form soluble complexes.

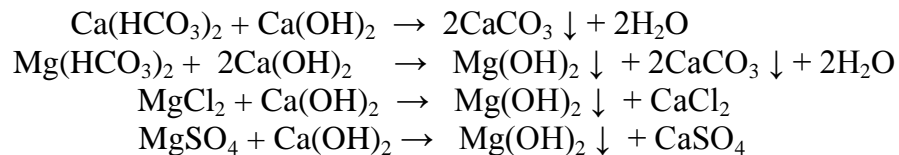
(vi) By frequent blow-down operation, if scales are loosely adhering.

**Prevention of scales formation: (1) External treatment and (2) Internal treatment.**

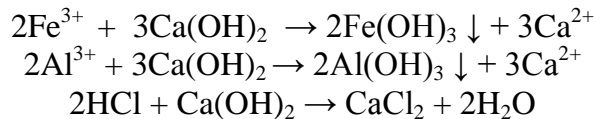
**1) External treatment:** It includes efficient softening of water. The process of removing hardness producing salts from water is known as *softening of water*.

**(A) Hot Lime-soda process:** In this method, the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime  $[\text{Ca}(\text{OH})_2]$  and soda  $[\text{Na}_2\text{CO}_3]$ . Calcium carbonate  $[\text{CaCO}_3]$  and magnesium hydroxide  $[\text{Mg}(\text{OH})_2]$ , so-precipitated, are filtered off.

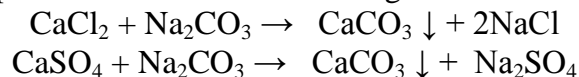
**Function of lime -  $\text{Ca}(\text{OH})_2$ :** The lime removes carbonate (temporary) hardness of calcium and magnesium. It also removes noncarbonate (permanent) hardness of magnesium. But equivalent non-carbonate hardness of calcium is introduced.



In addition to this, lime removes hardness due to heavy metal ions  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  as their hydroxides, and acids by neutralization.



**Function of soda- $\text{Na}_2\text{CO}_3$ :** Soda ash ( $\text{Na}_2\text{CO}_3$ ) removes noncarbonate (permanent) hardness originally present in water plus the one introduced during above reactions.



**Process:** It involves in treating water with softening chemicals at a temperature of 80 to 150°C. A typical hot lime-soda water softening unit is shown in Fig.2, which includes a reaction cum settling tank and a filter. The calculated amounts of lime and soda are mixed with raw water in a reaction tank and the mixture is heated by injecting super heated steam. The softening reactions start soon after mixing and tend to be completed before it enters the sedimentation tank. The large and heavy precipitates of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  settle down as sludges in sludge tank and are removed through the sludge outlet. The softened water containing some unsettled particles leaves sedimentation tank and is next passed through conventional sand filter which retains all the suspended precipitates. Filtered soft water finally flows out of the filter which is ready to feed into boilers for steam production.

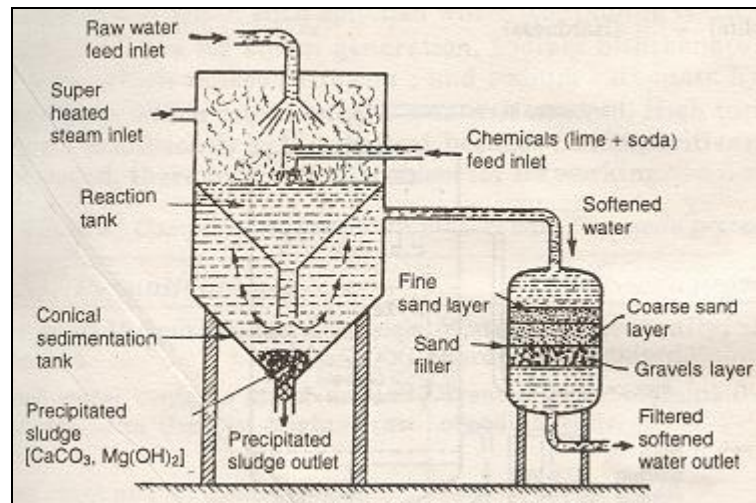


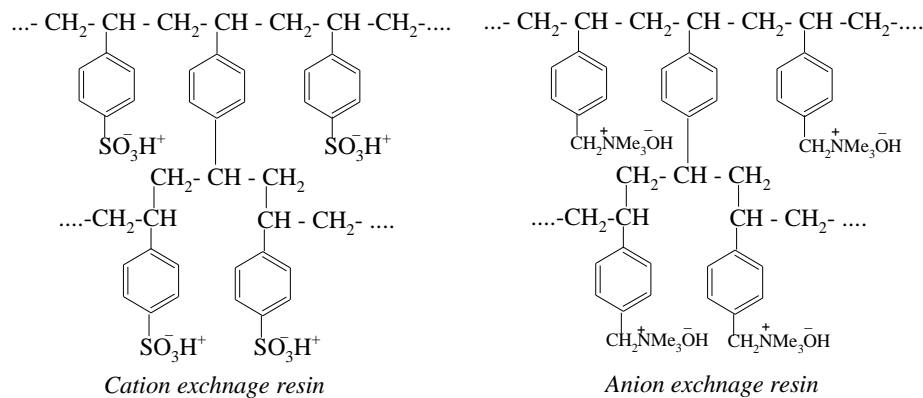
Fig.2. Continuous hot lime-soda process

### (B) Ion-exchange method (Demineralization):

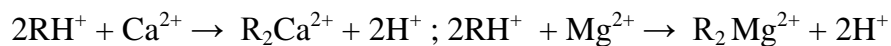
Ion exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure, and functional groups are attached to the chains are responsible for the ion exchange properties. The ion exchange resins may be classified as:

(i) **Cation exchange resins ( $RH^+$ )** are mainly styrene-divinyl benzene copolymers containing acidic functional groups ( $-COOH$ ,  $-SO_3H$  etc.) are capable of exchanging their  $H^+$  ions with other cations, which comes in their contact.

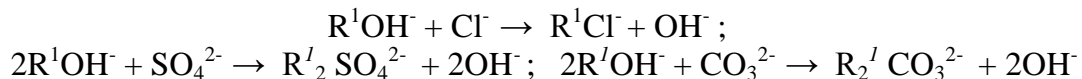
(ii) **Anion exchange resins ( $R^+OH$ )** are styrene-divinyl benzene or amine-formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups with  $OH^-$  capable of exchange their  $OH^-$  ions with anions in water.



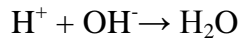
**Process:** The hard water is passed through cation exchange column, which removes all cations like  $Ca^{2+}$ ,  $Mg^{2+}$  etc. from it, and equivalent amount of  $H^+$  ions are released from this column to water.



After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like  $SO_4^{2-}$ ,  $Cl^-$ , etc. present in the water and equivalent amount of  $OH^-$  ions are released from the column to water.



$H^+$  and  $OH^-$  ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecule.



Thus, the water coming from the exchanger is free from cations as well as anions, Ion-free water, is known as deionised or demineralised water.

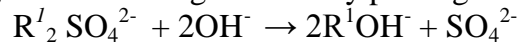
**Regeneration:** When capacities of cation and anion exchangers to exchange  $H^+$  and  $OH^-$  ions respectively are lost, they are then said to be exhausted.

The exhausted cation exchange column is regenerated by passing through dil.HCl or dil. $H_2SO_4$



The column is washed with deionised water and washing (which contains  $Ca^{2+}$ ,  $Mg^{2+}$ , etc and  $Cl^-$  or  $SO_4^{2-}$  ions) is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dil.NaOH.



The column is washed with deionised water and washing (which contains  $Na^+$  and  $SO_4^{2-}$  or  $Cl^-$  ions) is passed to sink or drain. The regenerated ion exchange resins are then used again.

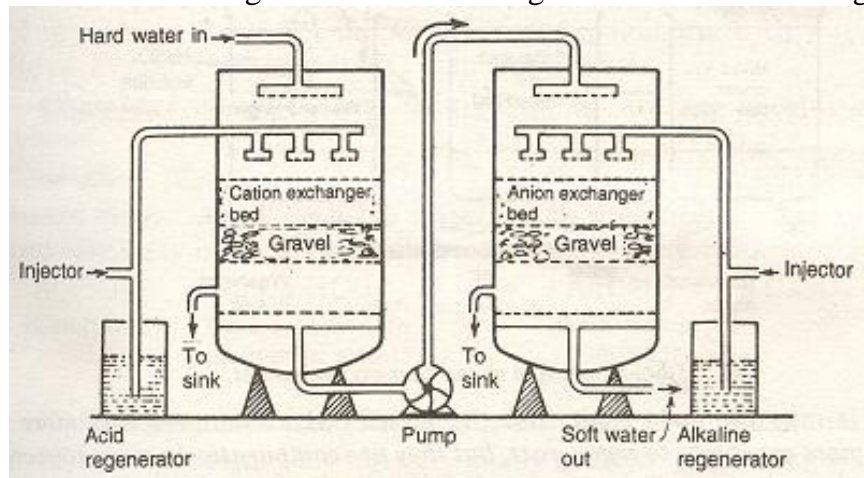


Fig.3. Demineralization of water.

**(2) Internal treatment.** Internal treatment consists of adding chemicals directly to the water in the boilers for removing dangerous scale forming salts which were not completely removed in the external treatment for water softening.

The objectives of internal treatment can be achieved by one of the following methods.

i) The scale forming calcium and magnesium ions are precipitated as sludges and the precipitates are removed from boiler by blow-down operation. ii) The scale forming ions are held in solutions by converting them in soluble complexes.

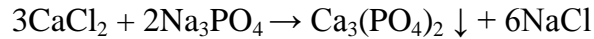
Important internal conditioning/treatment methods are

**(A) Colloidal conditioning:** In low-pressure boilers, scale formation can be avoided by adding organic substances like kerosene, tannin, agar-agar, etc. which get coated over the scale forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by pre-determined blow-down operations.

**(B) Phosphate conditioning:** In high-pressure boilers, scale formation can be avoided by adding sodium phosphate, which reacts with hardness of water forming non-adherent and easily

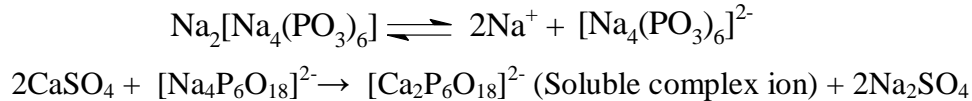


removable, soft sludge of calcium and magnesium phosphates, which can be removed by blow-down operation, e.g.,



The main phosphates employed are: (i)  $\text{NaH}_2\text{PO}_4$ , sodium dihydrogen phosphate (acidic); (ii)  $\text{Na}_2\text{HPO}_4$ , disodium hydrogen phosphate (weakly alkaline); (iii)  $\text{Na}_3\text{PO}_4$ , trisodium phosphate (alkaline).

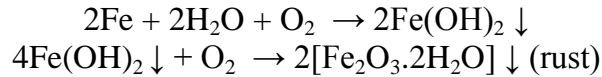
**(C) Calgon conditioning** involves in adding calgon [sodium hexa meta phosphate] to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with  $\text{CaSO}_4$ .



### BOILER CORROSION:

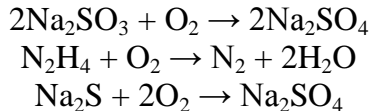
Boiler corrosion is decay of boiler material by a chemical or electrochemical attack by its environment. Main reasons for boiler corrosion are:

**(A) Dissolved oxygen:** Water usually contains about 8 mg of dissolved oxygen per litre at room temperature. Dissolved oxygen in water, in presence of prevailing high temperature, attacks boiler material:



#### **Removal of dissolved oxygen:**

(a) By adding calculated quantity of sodium sulphite or hydrazine or sodium sulphide. Thus



(b) By mechanical de-aeration, i.e., water spraying in a perforated plate-fitted tower, heated from sides and connected to vacuum pump (Fig.4). High temperature, low pressure and large exposed surface (provided by perforated plates) reduces the dissolved oxygen in water.

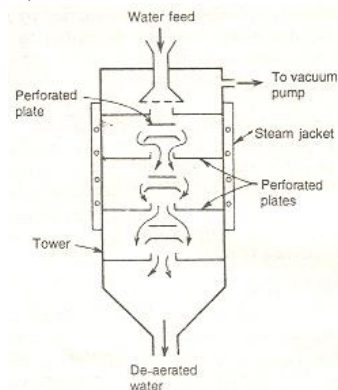


Fig.4. Mechanical de-aeration of water

**(B) Dissolved carbon dioxide:** ( $\text{CO}_2$ ) is carbonic acid

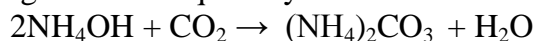


which has a slow corrosive effect on the boiler material. Carbon dioxide is also released inside the boiler, if water used for steam generation contains bicarbonate e.g.,



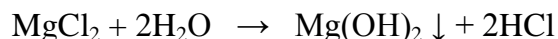


**Removal of  $\text{CO}_2$ :** (a) By adding calculated quantity of ammonia. Thus

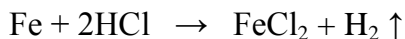


(b) By mechanical de-aeration process along with oxygen

**(C) Acids from dissolved salts:** Water containing dissolved magnesium salts liberate acids on hydrolysis, e.g.,



The liberated acid reacts with iron (of the boiler) in chain-like reactions producing HCl again and again. Thus:



Consequently, presence of even a small amount of  $\text{MgCl}_2$  will cause corrosion of iron to a large extent.

## DESALINATION:

The process of partial or complete demineralization of highly saline water such as the sea water is referred to desalination. In partial demineralization, the amount of dissolved salts is reduced to such a level, that water is rendered potable. Several methods such as reverse osmosis and electrodialysis are available for desalination and are described below.

### i) Reverse osmosis:

**Principle:** When two solutions of unequal concentrations are separated by a semi-permeable membrane (which selectively does not permit the passage of dissolved solute particles, i.e., molecules, ions, etc.), flow of solvent takes place from dilute to concentrated sides, due to osmosis. If, however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverses (i.e., solvent is forced to move from concentrated side to dilute across the membrane). This is the principle of reverse osmosis. This membrane filtration is some –times also called “super-filtration” or hyper-filtration”.

**Process:** In this process, pressure (of the order 15 to 50  $\text{kg}/\text{cm}^2$ ) is applied to the sea-water/impure water (to be treated) to force its pure water out through the semi-permeable membrane; leaving behind the dissolved solids (both ionic as well as non-ionic). The principle of reverse osmosis, as applied for treating saline/sea water, is illustrated in Fig.6. The membrane consists of very thin films of cellulose acetate, polymethacrylate or polyamide, affixed to either side of a perforated tube.

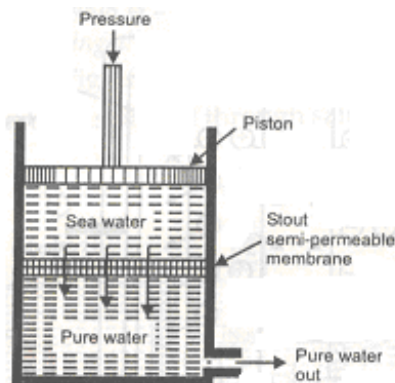


Fig.6. Reverse osmosis cell

## ii) Electro-dialysis:

**Principle:** Electro-dialysis is a method in which the ions (of the salts present) are pulled out of the salt water by passing direct current, using electrodes and thin rigid plastic membrane pair (natural or synthetic). When direct electric current is passed through the saline water the sodium ions ( $\text{Na}^+$ ) start moving towards the negative pole (cathode): while the chloride ions ( $\text{Cl}^-$ ) start moving towards the positive pole (anode), through the membrane, as a result, the concentration of brine decreases in the compartment; A cation-selective membrane is permeable to cations only, because of the presence of charged fixed functional groups such as  $\text{RSO}_3^-$  or  $\text{RCOO}^-$ , which rejects anions. Similarly, anion-selective membrane is permeable to anions only, because of the presence of positively charged fixed functional groups such as  $\text{R}_4\text{N}^+\text{Cl}^-$ , which rejects cations.

**Process:** An electro-dialysis cell (Fig.7) consists of a large number of paired sets of rigid plastic membranes. Saline water is passed under pressure (of about  $5\text{--}6\text{ kg/m}^2$ ) between membrane pairs and an electric field is applied perpendicular to the direct of water flow. The fixed positive charges inside the *anion selective membrane* repel positively charged ions ( $\text{Na}^+$ ), yet permit negatively charged ions ( $\text{Cl}^-$ ) to pass through. Similarly, the fixed negative charges inside the *cation selective membrane* repel negatively charged ions ( $\text{Cl}^-$ ), yet permit positively charged ions ( $\text{Na}^+$ ) to pass through. Therefore, water in one compartment of the cell is deprived of its salts: while the salt concentration in adjacent compartment is increased. Thus, we get alternate streams of pure water and concentrated brine.

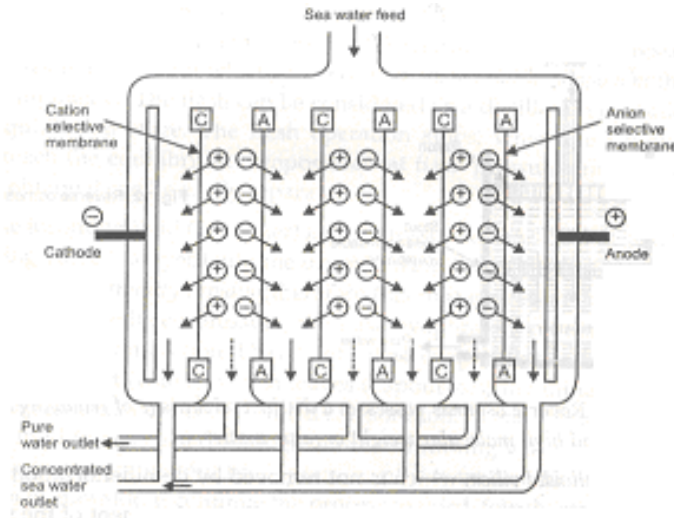


Fig.7. Electrodialysis cell

**Treatment of domestic sewage:** The treatment of sewage is carried out in three stages.

### (a) Primary (Physical and chemical) treatment:

The removal of coarse solids in the sewage water is effected by means of screens (removes large suspended or floating matter), grit chambers (removes sand, broken glass etc.) and skimming tanks (removes oils and grease). Then water is passed into a sedimentation tank where it is allowed to settle. The non-settleable solids are removed by coagulation by treatment with coagulating agents like alum, ferric chloride or lime.

**(b) Secondary (Biological) treatment:**

**Activated sludge process:** The waste water after the primary treatment is allowed to flow into large tanks (Fig.8) where biological treatment is carried out. Activated sludge containing microorganisms (from a previous operation) is sprayed over the water. The microorganisms present in the sludge form a thin layer and thrive on the organic wastes in the sewage. Air is passed vigorously from the centre of the tank in order to bring good contact between the organic wastes and bacteria in presence of air and sunlight. Under these conditions, aerobic oxidation of organic matter occurs. The sludge formed is removed by settling or filtration. A part of the sludge is reused and rest is used as fertilizer. The residual water is chlorinated to remove bacteria and finally discharged into running water or used for watering plants. The activated sludge process operates at 90-95% efficiency of BOD treatment.

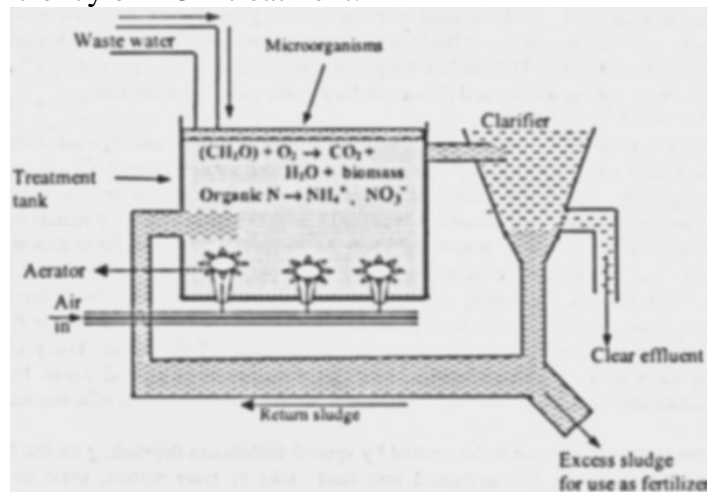


Fig.8. Activated sludge process

**(c) Tertiary treatment:** If the treated water contains a high concentration of phosphates, heavy metal ions, colloidal impurities and non-degradable organic compounds, the water is subjected to tertiary treatment. The process includes

- (i) Treatment with lime for the removal of phosphates as insoluble calcium phosphates.
- (ii) Treatment with  $S^{2-}$  ions for the removal of heavy metal ions as insoluble sulphides.
- (iii) Treatment with activated charcoal to absorb remaining organic compounds.
- (iv) Treatment with alum to remove the colloidal impurities not removed in the previous treatments to further reduce BOD level.

\*\*\*\*\*

## NANOMATERIAS

**Nanomaterials** are materials which have at least one of their dimensions in the nanometer ( $1\text{ nm} = 10^{-9}\text{ m}$ ) range. It is concerned with the unique properties associated with assemblies of atoms or molecules on a scale between that of the individual building blocks and the bulk material (1 to 1000 nm). Nanostructures include quantum dots, clusters, nanocrystals, nanowires, nanotubes and so on. The physical and chemical properties of nanomaterials can differ significantly from those of their bulk counterparts. Suitable control of the properties and response of nanostructures can lead to new devices and technologies. The nanoscience field has matured so rapidly that it is probably hard to find a segment of any technical subject where the implications of nanomaterials have not been explored at least to a preliminary extent.

### CLASSIFICATION

The classification is based on the number of dimensions which are not confined to the nanoscale range ( $< 100\text{ nm}$ ).

- (i) **Zero dimensional:** Materials wherein all the dimensions are within the nanoscale range are called as 0-D nanomaterials. The most common representation of 0-D nanomaterials are nanoparticles.
- (ii) **One dimensional:** Here two dimensions are at nanoscale range, other dimension is not. This leads to needle like-shaped nanomaterials. Eg. Nanotubes, nanorods, nanowires.
- (iii) **Two dimensional:** One dimension is at nanoscale range, other two dimensions are not. They exhibit plate-like shapes. Eg. Nanocoatings, nanofilms.
- (iv) **Three dimensional:** These materials are not confined to the nanoscale in any dimension. Thus these materials are characterized by having three arbitrarily dimensions above  $100\text{ nm}$ . They are also called as bulk nanomaterials. Bulk nanomaterials can form a nanocrystalline structure by multiple arrangement of nanosize crystals, most typically in different orientations. 3-D nanomaterials can contain dispersions of nanoparticles, bundles of nanowires/nanotubes as well as multilayers.

### PROPERTIES OF NANOMATERIALS:

Nanomaterials have the structural features in between of those of atoms and the bulk materials. While most microstructured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials. This is mainly due to the nanometer size of the materials which render them: (i) large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk materials.

The total surface area (or) the number of surface atom increases with reducing size of the particles

(i) **Thermal properties:** Nanomaterials have a significantly lower melting point or phase transition temperature due to a huge fraction of surface atoms in the total amount of atoms. Atoms or molecules on a solid surface possess fewer nearest neighbours or coordination numbers and number of bonds formed by each of the surface atoms is less than that formed by the atoms in the bulk. Therefore, the number of bonds need to be broken per atom during melting is less in nanomaterial than in macromaterial.

(ii) **Mechanical properties:** At nanoscale, surface and interfacial forces become dominant. For example, adhesion forces, capillary forces and strain forces can exceed forces that that normally

prevail at macroscopic length scales. This results in changes in ductility, malleability and plasticity. Cu shows reduced Yong's modulus in the nano state. Nanophase ceramics are more ductile at elevated temperatures as compared to the coarse-grained ceramics. Cold welding properties combined with ductility make them suitable for metal-metal bonding especially in the electronic industry.

**(iii) Magnetic properties:** The large surface area to volume ratio results in a substantial proportion of atoms having different magnetic coupling with neighbouring atoms leading to different magnetic properties. Bulk gold and platinum are non-magnetic but at the nano size they act as magnetic particles. Au nano particles become ferromagnetic when they are capped with appropriate molecules such as thiol. Magnetic nanoparticles are used in a range of applications like imaging, bioprocessing, refrigeration as well as high storage density magnetic memory media.

**(iv) Optical properties:** Crystal structure of microstructured materials and nanostructured materials of the same chemical composition are different. Eg.,  $Y_2O_3$ - nano (monoclinic), conventional (cubic). A change in zone structure leads to a change in absorption and luminance spectra. Bulk gold appears yellow in colour whereas nanosized gold appears red in colour. The particles are so small that electrons are not free to move about as in the bulk gold. Because of this restriction in movement, the particles react differently with the light. Nanostructured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties like luminescence in silicon powders and silicon germanium quantum dots used in infrared optoelectronic devices. In ZnO, the luminescence spectra show a blue shift, that is as the particle size reduces the wavelength of the emitted light shifts towards lower wavelengths. Nanostructured semiconductors are used as window layers in solar cells.

**(v) Electrical properties:** Nanoparticles array shows environment dependent electrical properties (conductivity). These properties are modified by the chemical species present in its vicinity. The conductivity of nanoparticles is believed to occur due to (i) Tunneling of electrons through the metal core. (ii) Hopping of the electrons along the atoms constituting the chain of the legend molecule encapsulating the nanoparticle.

By changing the parameters of the nanoparticle such as its particle diameter, space between the particles and the number of layers, the conductivity of the system can be altered. The analyte can be made to interfere with any one of the processes and hence can help vary the conductivity. This could lead to a sensing of the analyte.

**(vi) Catalytic activity:** Due to their high surface to volume ratio, nanomaterials exhibit better catalytic activity. They find applications as precursors for new type of heterogeneous catalysts such as cortex catalysts where active catalytic material can be supported on solid nanooxides.

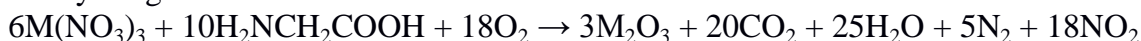
## **PREPARATION METHODS:**

**Nanochemistry** deals with the synthesis, characterization, reactions and application of nanoparticles and their compounds. Nanomaterials can be synthesized by two different approaches, namely "Bottom-up" approach and "Top-down" approach. These two approaches

can be explained in a simplified manner by taking an example of powder production. The synthesis of powder using chemicals represents the “bottom-up” approach whereas crushing of chunks represents the “top-down” approach. Thus in “bottom-up” approach atoms or molecules are used as building blocks to produce nanomaterials whereas in the other approach, large pieces of materials are broken down into nanosize by mechanical or chemical methods.

**(i) Combustion method:**

Combustion synthesis is preferred because of its potential advantages like low processing time, low external energy consumption, self-sustaining instantaneous reaction, and high yield of nano-sized particle. In this method, metal nitrates are mixed together with glycine in water. The water is evaporated by boiling, and when sufficiently dry, the remaining slurry self-ignites, to produce very fine metal oxide powder. The reaction is very rapid and the short reaction time limits the crystal growth.



**(ii) Microwave method:**

This method has recently been widely used due to its advantages like rapid volumetric heating, higher reaction rate, reducing reaction time and higher yield of products.

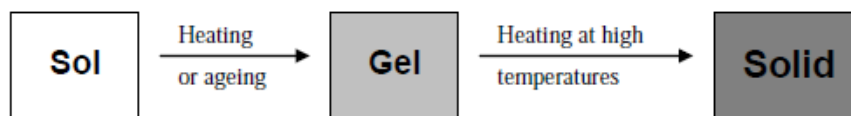
Microwaves are electromagnetic waves. Microwaves directly couple with the molecules of the entire reaction mixture. The energy from the microwave is transferred to the molecules either by dipole rotation or ionic conduction. Since this energy transfer occurs in less than a nanosecond, the molecules are unable to relax completely. This results in rapid rise in temperature leading to superheating.

**(iii) Sol-gel method:** Sol-gel approach is most widely used for nanocomposite fabrication due to its simple processing steps, the flexibility of solution chemistry, the low temperature treatments and small investment in equipment.

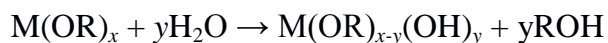
A sol is a stable suspension of colloidal solid particles in a liquid. A gel is a porous, three-dimensional, continuous solid network surrounding a liquid phase. The sol-gel process usually consists of four steps:

- a) Preparation of a precursor solution: The desired colloidal particles are dispersed in a liquid to form a sol.
- b) Deposition of the sol onto a substrate: The sol solution is coated on a substrate by spraying, dipping or spinning.
- c) Formation of gel: The particles in the sol are polymerized through the removal of the stabilizing components. This can be done by either heating the sol at a low temperature or allowing it to stand for certain duration. This results in the formation of a three dimensional continuous network (Gel).
- d) Heat treatment: The gel is heated at higher temperature wherein the organics or inorganics get evaporated/decomposed and form a crystalline coating.

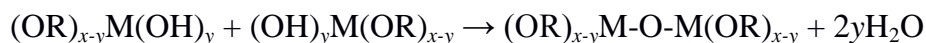




The precursors generally used for the formation of sol are metal alkoxides (say silica, alumina and others). This is mainly because alkoxides readily react with water. A catalyst may be used to start the reaction as well as to control the pH. The first reaction to occur is the hydrolysis which makes the solution active.



This is followed by condensation polymerization resulting in the formation of 1, 2 or 3-dimensional network of [M-O-M] bonds accompanied by the liberation of water molecules. These reactions increase the molecular weight of the oxide polymer.



The gel so formed is further processed by sintering.

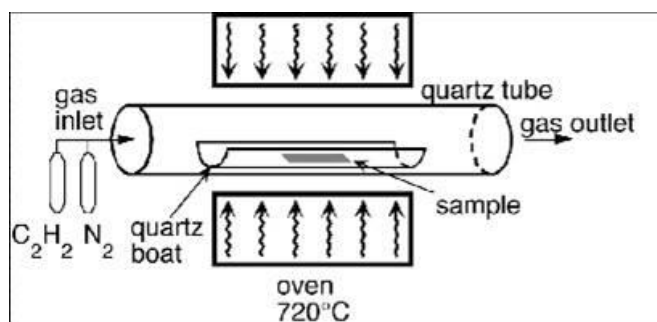
**(iv) Vapor deposition:** Vapor deposition refers to any process in which materials in a vapor state are condensed through chemical reactions or conversion to form a solid material. Vapor deposition processes generally take place within a vacuum chamber. There are two categories of vapor deposition processes. (i) *Physical Vapor Deposition (PVD)* and (ii) *Chemical Vapor Deposition (CVD)*:

***Chemical Vapor Deposition (CVD):***

In CVD processes, substrates are heated to the growth temperature. During heating, it is common to flow gases appropriate for substrate conditioning (i.e., for removal of surface oxides and contamination). After a certain time period, precursor gases are introduced into the reaction chamber. Given appropriate system conditions (temperature, pressure, etc.) these precursors lead to formation of films of surface-bound material. Growth is carried out for a certain period of time, after which precursor supply is terminated. Heating is then switched off and the substrate cooled to a temperature at which it can be safely removed. CVD schemes are employed widely for various processes throughout the semiconductor industry.

***Synthesis of carbon nano tubes by Chemical vapour deposition method:***

In 1993, Chemical vapor deposition (CVD) technique was first reported to produce MWNTs (Multi walled nano tubes) by Endo and his research group. CVD technique can be achieved by taking a carbon source in the gas phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. The CVD process uses hydrocarbons as the carbon sources including methane, carbon monoxide and acetylene. The hydrocarbons flow through the quartz tube being in an oven at a high temperature (~ 720 C). Schematic diagram of the chemical vapor deposition apparatus is shown in Fig. 1. At high temperature, the hydrocarbons are broken to be the hydrogen carbon bond, producing pure carbon molecules. Then, the carbon will diffuse toward the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it will bind. Carbon nanotubes will be formed if the proper parameters are maintained.



**Fig. 1** Schematic diagram of the chemical vapor deposition apparatus

**Applications of nanomaterials:** Nanomaterials have unique, beneficial chemical, physical and mechanical properties and these properties are used for a wide range of applications in the industrial environment. These applications include, but are not limited to the following:

**Automotive Industry:** Nanomaterials are used for light weight construction, painting (fillers, basecoat, and clear coat), catalysts, tires (fillers), and sensors, coatings for windscreen and car bodies in the automotive industry.

**Chemical Industry:** Nanomaterials are used as fillers for paint systems, coating systems based on Nanocomposites, impregnation of papers, switchable adhesives and magnetic fluids in the chemical industry.

**Electronic Industry:** Nanomaterials are used for data memory (MRAM, GMR-HD), displays (OLED, FED), laser diodes, glass fibers, optical switches, filters (IR-blocking), conductive and antistatic coatings in the electronic industry.

**Construction Industry:** Nanomaterials are used for construction materials, thermal insulation, flame retardants, surface-functionalized, building materials for wood, floors, stone, facades, tiles, roof tiles, etc., facade coatings and groove mortar in the construction.

**Textile/Fabrics/Nonwovens Industry:** Nanomaterials are used for surface-processed textiles and smart clothes in the Textile/fabrics/nonwovens industry.

**Energy:** Nanomaterials are used for fuel cells, solar cells, batteries and capacitors in the power industry.

**Cosmetics:** Nanomaterials are used for sun protection, lipsticks, skin creams and tooth paste in the cosmetics industry.

**Food and Drinks:** Nanomaterials are used for package materials, storage life sensors, additives, clarification of fruit juices in the food and drinks industry.

**Household:** Nanomaterials are used for ceramic coatings for irons, odors catalyst, cleaner for glass, ceramic, floor and windows in the household.

**Sports/Outdoor:** Nanomaterials are used for ski wax, antifogging of glasses/goggles, antifouling coatings for ships/boats, reinforced tennis rackets and balls in Sports /outdoor.

**Electronic, Optoelectronic Magnetic Applications:** Nanomaterials have a wide range of applications in Chemical–mechanical polishing, Electro conductive coatings, Magnetic fluid seals and recording media, Multilayer capacitors, Optical fibers, Phosphors and Quantum optical devices.

**Biomedical and Pharmaceutical Applications:** Nanomaterials have a wide range of applications in Antimicrobials, Bio-detection and labeling, Bio-magnetic separations, Drug delivery, MRI contrast agents, Orthopedics/implants, Sunscreens and thermal spray coatings.

\*\*\*\*\*