Annamacharya Institute of Technology and Sciences, Tirupati
(Autonomous)

Engineering Chemistry Material
Subject Code: 20ABS9905
(AK20 Regulations)
(Common to CE and ME)

UNIT-1
WATER

Water Technology: Introduction, sources of water, types of impurities in water, hardness of water - temporary and permanent hardness, units of hardness, disadvantages of hard water. Estimation of hardness by EDTA method, boiler troubles.
Softening methods: Internal treatment, external treatment; zeolite process, ion exchange process, desalination of brackish water - reverse osmosis.

Introduction:

Water is nature's most wonderful, abundant and useful compound. Without food, human can survivefor a number of days, but water is such an essential that without it one cannot survive. Water is not only essential for the lives of animals and plants, but also occupies a unique position in industries.Probably, it's most important use as an engineering material is in the steam generation. Water is also used as coolant in power and chemical plants.

Water is widely distributed in nature. It has been estimated that about 75% matter on the earth's surface consists of water. Besides visible water on earth, there is large amount of water under earth to an average depth of over three kilometres. The air consists 12 to 15% of volume of water vapour. Water is found in living things. The body of human being consists of about 60% of water. Plants, fruits and vegetables contain 90 to 95% of water.

Sources of water:

(A) Surface water (B) Underground water

Surface water:

1. Rain water:

It is the purest form of naturel water, since it is obtained as a result of evaporation from the surface water. However, during the journey downwards, through the atmosphere, it dissolves a considerable amount of gases like $CO2$, $SO2$, $NO2$, etc. and suspended solid particles.

2. River water:

In general, the greater the greater the contact that water has with the soil, or the more soluble the minerals of the soils with which it has come in contact, the greater is the amount of dissolved impurities in river water. River water thus contains dissolved minerals of the soil such as chlorides, sulphates, bicarbonates of calcium, magnesium and iron. River water also contains the organic matter, derived from the decomposition of plants, and small particles of sand and rock in suspension. Thus,river water contains considerable amounts of dissolved as well as suspended impurities.

3. Lake water:

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

4. Sea water:

It is the most impure form of natural water. It contains, on an average, about 3.5% of dissolved salts, out of which about 2.6% is sodium chloride. Other salts present are sulphate of sodium; bicarbonates of potassium, magnesium and calcium etc.

Surface water, generally, contains suspended matter, which often contains the disease producing bacteria. Hence, such water is not considered to be safe for human consumption.

***Underground water*:**

A part of the rain water, which reaches the surface of the earth, percolates into the earth. As this water journeys downwards, it comes in contact with a number of mineral salts present in the soil and dissolves some of them. Water continues it's downwards journey, till it meet a hard rock, when it retreads upwards and it may even come out in the form of *spring or well*. In general, it is clear in appearance due to the filtering action of the soil, but contains more of the dissolved salts. Thus, water from these sources contains more hardness. Usually, underground water is of high organic purity.

***Types of impurities in water*:**

Natural water is, usually contaminated three types of impurities.

1. Physical impurities. 2. Chemical impurities. 3. Biological impurities.

***Physical impurities*:**

(a) **Colour:** Colour in water is usually caused by *metallic substances* like salts of iron, manganese, peat, industrial effluents. Usually, yellowish tinge indicates the presence of chromium and appreciable amount of organic matter. Yellowish red colour indicates the presence of iron; while red-brown colour indicate the presence of peaty matter.

(b) **Turbidity:** It is due to the colloidal, extremely fine suspension such as clay, slit, finely divided matter etc. Turbidity expresses the optical properties of water, which scatter light rather than to transmit in straight lines. Turbidity in water can be eliminated by sedimentation, followed by coagulation, filtration, etc.

(c) **Taste:**

- Bitter taste can be due to the presence of iron, aluminium, manganese sulphate or excess of lime.
- Soapy taste can be due to the presence of large amount of sodium bicarbonate.
- Brackish taste is due to the presence of unusual amount of salts.
- Palatable taste is due to the presence of dissolved gases like CO2. (d) Odour:

The causes of odour in polluted rivers are;

- Presence of inorganic and organic compounds of N, S and P and the putrefaction of proteins and other organic materials present in sewage;
- Industrial effluents containing organic substances such as alcohols, aldehydes, phenols etc.flowing into the water bodies.

***Chemical impurities*:**

(a) Acidity:

Surface water and ground water attain acidity from industrial wastes like acid, mine, drainage,pickling liquors, etc. Usually, acidity is caused by the presence of free CO2, mineral acids (H2SO4) and weakly dissociated acids. Mineral acids are released when iron and aluminium salts hydrolyse.

(b) Gases:

- All natural waters contain dissolved atmosphere CO2. It solubility depends upon temperature,pressure and dissolved mineral content of water.
- Concentration of dissolved atmosphere O2 in water depends on temperature, pressure and salt content in water. Dissolved O2 in industrial water is nuisance, since it induces corrosion reactions. On the other hand, dissolved O2 in water is essential to the life of aquatic organisms such as fishes.
- Dissolved NH3 in water arises from the decomposition of nitrogenous organic matter. Polluted water and sewage contains nitrogen in the form of nitrogenous organic compouds and urea, which are partially converted into NH3.

(c) Mineral matter:

It has origin from rocks and industrial effluents. These include Ca2+, Mg2+, Na+, K+, Fe2+, CO_3^{-2}, Mn2+,HCO^{-3} , Cl-, SO □ 24, etc. However, from industrial point of view, alkalinity and hardness are important.

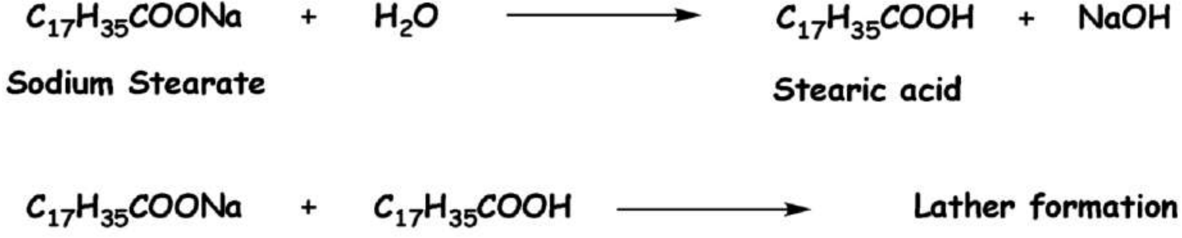
***Biological impurities*:**

These are algae, pathogenic bacteria, fungi, viruses, pathogens, parasite worms etc. The source of these contamination is discharge of domestic and sewage wastes, excreta, etc. Micro-organisms are, usually, abundant in surface water, but their count is often quite low or even nil in deep-well waters. The common type of micro-organisms from the point of treatment are algae, fungi and bacteria, which often form slime, thereby causing fouling as well as corrosion. The slime so-formed clogs the spray nozzles and screens of the circulating pumps in air-conditioning and other industrial plants. The growth of micro-organisms takes place at temperature in between 20 to 350C.In order to control the micro-organisms, chemical treatment like chlorination is done.

Hardness of water:

The water which does not produce lather with soap is called hard water. Thus, hardness in water is the characteristic, which "*prevents the lathering of soap*". On the other hand, the water which produce lather easily on shaking with soap solution, is called soft water.

The hardness of water is caused by the presence of dissolved salts such as bicarbonates, sulphates, chlorides and nitrates of divalent metal ions like calcium and magnesium. Soap is sodium or potassium salt of higher fatty acids like stearic, oleic and palmetic acids. When soap is mixed with soft water lather is produced due to stearic acid and sodium stearate.



$$C_{17}H_{35}COONa + H_2O \longrightarrow C_{17}H_{35}COOH + NaOH$$

Sodium Stearate

Stearic acid

$$C_{17}H_{35}COONa + C_{17}H_{35}COOH \longrightarrow \text{Lather formation}$$

When soap comes in contact with hard water, sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is white precipitate.

$$\underset{\text{(soluble)}}{C_{17}H_{35}COONa} + \underset{\text{(soluble)}}{Ca^{2+}} \longrightarrow \underset{\text{(insoluble)}}{Ca(C_{17}H_{35}COO)_2} + \underset{\text{(soluble)}}{2Na^{+}}$$

The different types of water are commercially classified on the basis of degree of hardness as follows;

Hardness	Name of water
0-70 mg/L	Soft water
70-150 mg/L	Moderate hard water
150-300 mg/L	Hard water
>300	Very hard water

Types of Hardness:

The hardness of water is two types;

1. Temporary hardness. 2. Permanent hardness.

1. ***Temporary hardness*** or Carbonate hardness:

This hardness is caused by two dissolved bicarbonate salts Ca(HCO3)2 and Mg(HCO3)2. The hardness is called temporary because, it can be removed easily by boiling. During boiling, bicarbonates are decomposed to yield insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2\downarrow + 2CO_2\uparrow$$

2. ***Permanent hardness*** or non-carbonate hardness:

This hardness is due to the dissolved chlorides, sulphates and nitrates of calcium and magnesium. These salts are CaCl2, MgCl2, CaSO4, MgSO4, Ca(NO3)2, Mg(NO3)2. It cannot be removed easily by boiling. Hence, it is called permanent hardness. Only chemical treatment can remove this hardness.

Total Hardness = Temporary hardness + Permanent hardness

***Expression of hardness*:**

Hardness of water is expressed in terms of calcium carbonate equivalents. The weights of different salts causing hardness are converted to weights equivalent to that of CaCO3.

If a sample of water contains two or more than two salts, their quantities are converted in equivalent to CaCO3 as mentioned above and then the sum will give the total hardness. CaCO3 was selected for expression of the degree of hardness because;

1. The Molecular Weight of CaCO3 is 100, which is easy for calculation.
2. It is an insoluble salt, and all the dissolved salts of calcium are precipitated as CaCO3.

Hardness causing salt	Molecular weight
Ca(HCO3)2	162
Mg(HCO3)2	146
CaSO4	136
CaCl2	111
MgSO4	120
MgCl2	95
Ca(NO3)2	164
Mg(NO3)2	148

Thus, 120 parts by weight of MgSO4 would react with the same amount of soap as 100 parts by weight of CaCO3. Hence, weight in terms of CaCO3 would be equal to weight of MgSO4 in water multiplied by 100/120.

The method of calculating hardness will be clear from the following formula.

Hardness of hardness causing salt in terms of CaCO3

$$= \frac{\text{Amount of the hardness causing salt x 100}}{\text{Molecular weight of hardness causing salt}}$$

Units of hardness:

There are five units in which the hardness of water is expressed.

1. Parts per million. 2. Milligrams per litre. 3. Degree Clark. 4. Degree French. 5. meq per litre.

1. <u>*Parts per million* (ppm):</u>

It is the parts of calcium carbonate equivalent hardness per 106 parts of water.

i.e. 1ppm = 1 part of CaCO3 eq hardness in 106 parts of water.

2. <u>*Milligrams per litre* (mg/L):</u>

It is the number of milligrams of calcium carbonate equivalent hardness present per litre of water.

Thus,

1 mg/L = 1 mg of CaCO3 eq hardness per1 L of water

But 1 L water = 1 kg = 1000g = 10^6 mg

1 mg/L = 1 mg of CaCO3 eq per 10^6 mg of water

= 1 part of CaCO3 eq per 106 parts of water = 1 ppm

3. *Degree Clark* (0Cl):

It is the number of grains of CaCO3 equivalent hardness per gallon of water. (or) It is the parts CaCO3 equivalent hardness per 70,000 parts of water.

1^0Cl = 1 grain of CaCO3 eq hardness per gallon of water

1^0Cl = 1 part of CaCO3 eq hardness per 70,000 parts of water

4. *Degree French* (0Fr):

It is the parts of calcium carbonate equivalent hardness per 10^5 parts of water.

i.e. 1^0Fr = 1 part of CaCO3 eq hardness in 10^5 parts of water.

Relationship between various units of hardness:

1ppm = 1 mg/L = 0.1 0Fr = 0.07 0Cl = 0.02 meq/L

Estimation of hardness by EDTA method:

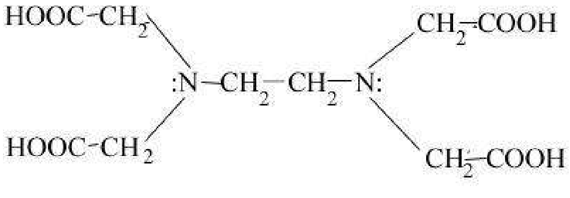
EDTA forms a colourless stable complex with Ca2+ and Mg2+ ions in water at pH10. Ammonia buffer is used to maintain the pH. In this method EBT (Eriochrome Black-T) is used as an indicator. Initially EBT forms an unstable complex with Ca2+ and Mg2+ ions, giving wine red colour to the solution.During the titration EDTA reacts with this complex (Ca-EBT or Mg-EBT complex), forms a stablecomplex (Ca-EDTA or Mg-EDTA) and releases the blue EBT into the solution. Hence the end point is wine red to blue colour.

$$M^{2+} + \text{EBT} \xrightarrow{pH=10} \underset{\text{(Wine red)}}{[\text{M-EBT}]\ \text{complex}}$$

$$\underset{\text{(Wine red)}}{[\text{M-EBT}]\ \text{complex}} + \text{EDTA} \xrightarrow{pH=10} \underset{\text{(Colour less and stable)}}{[\text{M-EDTA}]\ \text{complex}} + \text{EBT}$$

(Blue)

Where $M^{2+} = Ca^{2+}$ or Mg^{2+}



structure of EDTA

Various steps involved in this method are;

1. Preparation of standard hard water (1mg of CaCO3 per 1 mL of water).
2. *Standardization of EDTA solutions*:

   Pipette out 50 mL of standard hard water in a conical flask. Add 10-15 mL of buffer solution and 4 to 5 drops EBT indicator. Titrate with EDTA solution, till wine red colour changes to clear blue. Let volume used be V1 mL.
3. *Titration of unknown hard water*:

Titrate 50 mL of water sample just as indicated above. Let the volume used be V2 mL.

4. *Titration for permanent hardness*:

Take 250 mL of the water sample in a large beaker. Boil it, till the volume is reduced to about 50 mL. Filter, wash the precipitate with distilled water, and collect the filtrate and washings in a 250 mL measuring flask. Finally, make up the volume to 250 mL with distilled water. Then, titrate 50 mL of boiled water sample just as in step (2). Let the volume of EDTA used be V3 mL.

Calculations:

50 mL of standard hard water = V1 mL of EDTA
50 mg of $CaCO_3$ = V1 mL of EDTA
1 mL of EDTA = 50/V1 mg of $CaCO_3$
Now 50 mL of given hard water = V2 mL of EDTA

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

1 L (1000mL) of given hard water
= 1000V2/V1 mg of $CaCO_3$ eq

Total hardness of water = 1000V2/V1 mg/L = 1000V2/V1 ppm

$$\text{Now 50 mL of boiled water} = \frac{V_3 * 50}{V_1} \times \text{ mg of } CaCO_3$$

1 L of given hard water = 1000V3/V1 mg of $CaCO_3$ eq
Permanent hardness = 1000V3/V1 mg/L = 1000V3/V1 ppm
And Temporary hardness = Total hardness – permanent hardness

$$\text{Temporary hardness} = \frac{1000(V_2 - V_3)}{V_1} \text{ ppm}$$

***Disadvantages of hard water*:**

1. In domestic use. 2. In industrial use. 3. In steam generation.

1. ***In domestic use*:**

(a) Washing:

Hard water, when used for washing purpose, does not lather freely with soap. On the other hand, it produces sticky precipitates of calcium and magnesium This causes a wastage of lot of soap being used. Also presence of iron salts may cause stains on cloth.

(b) Bathing:

Hard water, does not lather freely with soap, but produces sticky scum on the bath-tub and body. Thus, the cleaning quality of soap depressed and a lot of it wasted.

(c) Cooking:

Due to the presence of dissolved hardness causing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking. Certain foods do not cook soft in hard water. Also, tea or coffee, prepared in hard water has an unpleasant taste and muddy-looking extract.

(d) Drinking:

Hard water causes bad effect on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

2. *In Industrial use*:

(a) Textile industry: Hard water causes much of the soap to go as waste. Moreover, precipitates of calcium and magnesium soaps adhere to the fabrics. These fabrics, when died later on, do not produce exact shades of colour. Iron and manganese salts-containing water may cause coloured spots on fabrics, thereby spoiling their beauty.

(b) Sugar industry: Water containing sulphates, nitrates, alkali carbonates, etc., if used in sugar refining, it causes difficulties in the crystallization of sugar. Moreover, the sugar so-produced may be deliquescent.

(c) Concrete making:Water containing chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.

(d) Pharmaceutical industry:Hard water, if used for preparing pharmaceutical product like drugs, injections and ointments etc.may produce certain undesirable products in them.

3. ***In steam generation*:**

For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as:

(i) Scale and sludge formation (ii) corrosion (iii) priming and foaming

(iv) caustic embrittlement.

DETERMINATION OF ALKALINITY OF A WATER SAMPLE

Principle: Alkalinity of water means the total content of those substances in it which causes an increased OH^- ion concentration up on dissociation or due to hydrolysis. The alkalinity of water is attributed to the presence of (i) Caustic alkalinity (Due to OH^- and CO_3^{2-}) (ii) Temporary hardness (Due to HCO_3^{2-}) Alkalinity is a measure of ability of water to neutralize the acids Determination of alkalinity OH^-, CO_3^{2-} and HCO_3^{2-} can be estimated separately by titration against standard acid using phenolphthalein and methyl orange as indicators The determination is based on the following reactions

(i) $OH^- + H^+ \longrightarrow H_2O$ (pH 8.3)

(ii) $CO_3^{2-} + H^+ \longrightarrow HCO^{3-}$ (pH 8.3)

(iii) $HCO^{3-} + H^+ \longrightarrow H_2O + CO_2$ (pH 4.5)

The titration of water sample against a standard acid up to phenolphthalein end point (P) marks the completion of reaction (i) and (ii) only. This amount of acid used thus corresponds to OH^- plus one half of the normal CO_3^{2-} present On the other hand, titration of the water sample against a standard acid to methyl orange end point (M) marks the completion of reaction (i), (ii) and (iii). Hence the total amount of acid used represents the total alkalinity.

Thus, $P = OH^- + \frac{1}{2} CO_3^{2-}$

$M = OH^- + CO_3^{2-} + HCO^{3-}$

Procedure: **Part A: phenolphthalein alkalinity**

1. Pipette out 20 ml of water sample into a conical flask. Add 1-2 drops of Phenolphthalein indicator.
2. Rinse and fill the burette with N/10 HCl
3. Titrate the water sample in conical flask with N/10 HCl till the pink colour just disappears.
4. Note down the reading and repeat to get concordant readings.
5. Calculate phenolphthalein alkalinity by using formula given below

$$\text{Phenolphthalein alkalinity} = \frac{V1 \times \text{normality of acid} \times 50 \times 1000}{20}$$

Part B: Total alkalinity (Methyl orange)

1. Take 20 ml of water sample in conical flask and add methyl orange indicator to it.
2. Titrate the water sample in conical flask with N/10 HCl taken in the burette till the yellow orange colour changes to orange red.
3. Note down the reading and repeat to get concordant readings.
4. Calculate total alkalinity by using formula given below.

$$\text{Total alkalinity} = \frac{V2 \times \text{normality of acid} \times 50 \times 1000}{}$$

DETERMINATION OF ACIDITY OF A WATER SAMPLE:

Principle: The mineral acids present in the sample which are contributing mineral acidity can be calculated by titrating with strong base NaOH at PH 4.3. The CO_2 and Bi carbonates present and contribute CO_2 Acidity in the sample can be neutralized completely by continuing the titration up to PH 8.2

Interference: Colour turbidity,iron,aluminium or Manganes and residual chlorine are Prime sources of interference,colour and turbidity can be avoided using Potentiometric titrations. Residual chlorine can be removed by adding Sodium thiosulphate iron aluminium and manganes is prevented by the addition of NaOH burette.

Procedure:

1. Take 100 ml of given sample in an Erlenmeyer flask
2. Add one drop of 0.1N $Na_2s_2o_3$ solution to remove the residual chlorine if present
3. Add 2 drops of methyl orange. The sample turns Orange
4. Proceed the titration until colour changes to yellow
5. Note down the volume of NaOH added (V1)
6. Take another conical flask containing 100 ml water sample, add 2 drops of Phenolphthalein
7. Proceed the titration until the sample turns Pink.

8. Note down the total valume of NaOH added.
Environmental Significance :
1. Acidity Interferes in the treatment of water
2.It corrodes Pipes (zinc coating of G.I pipes got dissolved)
3.Aquatic life will be affected.
4. PH is critical factor for bi-Chemical reaction.the favourable PH is 6.8 to 7.5.
5. Water contains mineral acidity more than 50 mg/l cannot be used in R.C.C works.
Application of Acidity data in Environmental Engineering Practice:-

1. The amount of CO_2 Present is an Important factor in determing whether removed by aeration or simple neutralization with lime or Sodium hydroxide will be chosen as the treatment method.

2. The size of equipment , chemical requirement storage space and cost of treatment all depend upon amount CO_2 Present.

3. CO_2 is an important consideration in estimating chemical requirements for lime or lime soda ash softening process.

4. Most industrial wastes containing mineral acidity must be eutralized be for they are subjectd to biological treatment or direct discharge into water course or sewers quantities of chemicals size of chemical feeders storage space and costs are determined from the laboratory data of acidity.

CALCULATION:

$$\text{Mineral Acidity due to mineral acids} = \frac{V1 \text{x normality of acid x } 50 \text{ x } 1000}{100}$$

$$CO_2 \text{ Acidity due to } CO_2 = \frac{V2 \text{x normality of acid x } 50 \text{ x } 1000}{100}$$

Determination of the Chloride content in water

Procedure:

Transfer 100ml of water sample into a clean conical flask. Add about 1 ml of K2CrO4 indicator solution & titrate against standard (say 0.02N) AgNO3 solution until a reddish brown color persists in the white precipitate. Record the volume of AgNO3 consumed (Let ‘a’ cm^3). Perform a blank titration taking 100 ml of distilled water. The volume of AgNO3 consumed Let ‘b’ $cm^{3.}$

Calculation:
Volume of AgNO3 required for chlorine estimation = (a-b) cm^3 = V 1000ml of
1 N AgNO3 = 35.45g/Cl^-

1 ml of 1N AgNO3 = 0.03545g/Cl^-
V ml of 0.02 N AgNO3 = 0.03545 X V X 0.02 g/Cl^-

Cl^- content in the sample = $\underline{0.03545 \text{ X } V \text{ X } 0.02}$ grams /Cl^-100

Cl^- content in the sample = $\underline{0.03545 \text{ X } V \text{ X } 0.02 \text{ X } 1000}$ mg/Cl^-100

TREATMENT OF WATER FOR DOMESTIC PURPOSE

The processes & technologies used to remove the contaminants from water & to improve its quality is recognized all over the world. The choice of which treatment to use from a great variety of available processes depends on the characteristics of the water, the type of the water quality problems to be present, & the costs of different treatments. There are different methods of water treatment the selection of which depends upon the type of source & purpose of use of water. Some of the methods are:

a) Screening
b) Plain sedimentation
c) Sedimentation by coagulation
d) Filtration
e) Disinfection

The following are different steps in treatment of water.

.REMOVAL OF SUSPENDED IMPURITIES

a) Screening : The process of removing floating matter from water is known as screening . In this process, water is passed through a screen. The floating matter is arrested by the screen and the water is free from floating matter.

b) Plain sedimentation : The process of removing big sized suspended solid particles from water is called as plain sedimentation. In this process, water is stored in big tanks for several hours. 70% of solid particles settle down due to force of gravity.

c) Sedimentation by coagulation : This is the process of removing fine suspended and colloidal impurities by adding coagulants like alum($K_2SO_4Al_2(SO_4)_3$ 24 H_2O,$FeSO_4$,$NaAlO_2$.When coagulant is added to water, floc formation takes place due to hydroxide formation which can gather tiny particles together to form bigger particles and settle down quickly.

d) Filtration: The process of passing a liquid containing suspended impurities through a suitable porous material so as to effectively removed suspended impurities and some microorganisms is called filtration. It is a mechanical process. When water flows through a filter bed, many suspended particles are unable to pass through the gaps and settle in the bed.

e) Disinfection or sterilization

The process of killing pathogenic bacteria and other microorganisms is called disinfection or sterilization. The water which is free from pathogenic bacteria and safe for drinking is called potable water. The chemicals used for killing bacteria are called disinfectants.

i) By adding bleaching powder: Water is mixed with required amount of bleaching powder, and the mixture is allowed to stand for several hours.

$CaOCl_2 + H_2O$-----------> $Ca(OH)_2 + Cl_2$

$Cl_2 + H_2O$ -----------> $HOCl + HCl$

Germs + HOCl -----------> Germs are killed

The disinfection action of bleaching powder is due to available chlorine in it. It forms hypochlorous acid which acts as a powerful germicide(disinfectant).

ii) Chlorination:

Chlorine is mixed with water in a chlorinator, which is a high tower having a number of baffle plates. Water and required quantity of concentrated chlorine solution are introduced from its top during their passage through the tower. They get thoroughly mixed and thn sterilized water is taken out from the bottom.

$Cl_2 + H_2O$ -----------> $HOCl + HCl$

Germs + HOCl -----------> Germs are killed

Advantages:

1) Storage requires less space
2) Effective and economical
3) Produce no salts
4) Ideal disinfectant

Disadvantages:

1) Excess of chlorine causes unpleasant taste and odour.
2) More effective at below pH 6.5 and less effective at higher pH values.

iii) Ozonisation:

Ozone is an excellent, disinfectant which can be prepared by passing silent electric discharge through pure and dry oxygen. Ozone is highly unstable and breaks down, liberating nascent oxygen.

$3O_2$ -----------> $2O_3$

O_3 -----------> O_2 + (O)

Advantages :

Removes colour , odour and taste.

Disadvantages:

The method is costly

Boiler troubles:

There are four important boiler troublers.
(1) Scale and sludge formation (2) Corrosion (3) Priming and foaming (4) Caustic embrittlement.

1. **Scale and sludge formation**:

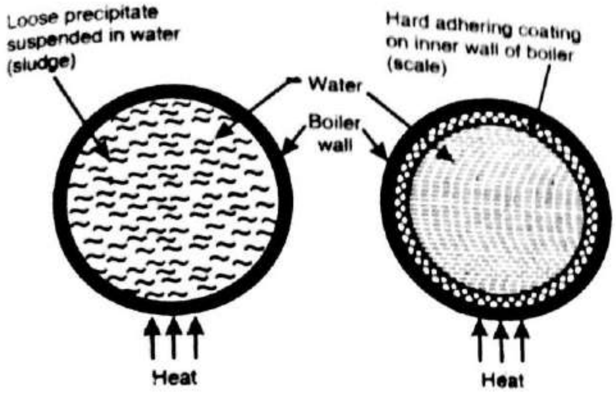
In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively. When their concentration reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. If the precipitation takes place in the form of loose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

Sludge:
It is a soft, loose and slimy precipitate formed within the boiler. Sludge can easily be scrapped off with a wire brush. It is formed at colder portions of the boiler. Sludge is formed by substances which have greater solubilities in hot water than cold water.

E.g. $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$, etc.

Disadvantages of sludge formation:
(a) Sludges are poor conductors of heat, so they tend to waste a portion of heat generated.
(b) If sludges are formed along with scales, then former gets entrapped in the latter and both get deposited as scales.
(c) Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connections.

***Prevention of sludge formation*:**
(a) By using well softened water which is free from MgCO3, MgCl2, CaCl2, MgSO4 salts.
(b) By frequent "blow-down" operation, i.e. drawing off a portion of the concentrated water.



Scale:

These are hard deposits, which stick very firmly to the inner surfaces of the boiler. Scales are difficult to remove, even with the help of hammer. These are main sources of boiler troubles. Formation of scales may be due to;

(a) *Decomposition of calcium bicarbonate*:

Due to high temperature and pressure present in the boilers, the calcium bicarbonate salt decomposes in to CaCO3, which is an insoluble salt, forms scale.

Ca(HCO3)2---------→ CaCO3 + H2O + CO2
(scale)

(b) *Deposition of calcium sulphate*:

The solubility of calcium sulphate in water decreases with rise of temperature. Thus, solubility of CaSO4 is 3,200 ppm at 150C and it reduces to 55 ppm at 2300C and 27 ppm at 320^{0}C.In other words, CaSO4 is soluble in cold water, but almost completely insoluble in super-heated water.Consequently, CaSO4 gets precipitated as hard scale on the heated portions of the boiler.

(c) *Hydrolysis of magnesium salts*:

Dissolved magnesium salts undergo hydrolysis to form magnesium hydroxide precipitate, which forms a soft type of scale.

MgCl2 + 2H2O--------→ Mg(OH)2 + 2HCl

(d) *Presence of silica*:

SiO2, even present in small quantities, deposits as calcium silicate (CaSiO3) and magnesium silicate (MgSiO3). These deposits stick very firmly on the inner side of the boiler surface and are very difficult to remove.

Disadvantages of scales:

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

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

(b) Lowering of boiler safety:

Due to scale formation, over-heating of boiler is to be done in order to maintain a constant supply of steam. This over-heating of the boiler tube makes the boiler material softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of the steam.

(c) Danger of explosion:

When thick scales crack, due to uneven expansion, the water comes suddenly in contact with overheated iron plates. This causes in formation of a large amount of steam suddenly. So sudden high pressure is developed, which even cause explosion of the boiler.

Removal of scales:

(i) With the help of scraper or wire brush, we can remove the scales, if they are loosely adhering.
(ii) By giving thermal shocks, we can remove the scales, if they are brittle.
(ii) Calcium carbonate scales can be dissolved by using 5-10% HCl. Calcium sulphate scales can be dissolved by adding EDTA, with which they form soluble complexes.
(iv) By frequent blow-down operation, if the scales are loosely adhering.

2. **Boiler corrosion**:

Boiler corrosion is “the decay of boiler material by a chemical or electro-chemical attack by its environment”.

Main reasons for boiler corrosion are:
(i) Dissolved oxygen. (ii) Dissolved carbon dioxide. (iii) Acids from dissolved salts.

(i**) Dissolved oxygen:**
Water usually contains about 8 ppm of dissolved oxygen at room temperature. At high temperature this D.O. can attack boiler material.

2 Fe + 2 H2O + O2-----------→ 2 Fe(OH)2
4 Fe(OH)2 + O2----------------→ 2[Fe2O3.2 H2O] (rust)

Removal of dissolved oxygen:

By adding calculated quantity of *sodium sulphite* or *hydrazine* or *sodium sulphide*. Thus;

2 Na2SO3 + O2--------→ 2 Na2SO4
NH2-NH2 + O2----------→ N2 + 2 H2O
Na2S + 2 O2 ----------→Na2SO4

(ii) Dissolved carbon dioxide:

CO2 + H2O---------→ H2CO3

Carbon dioxide is also released inside the boiler, if water used for steam generation contains bicarbonates.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2\downarrow + 2CO_2\uparrow$$

Removal of dissolved carbon dioxide:
By adding calculated quantity of ammonium hydroxide.

2 NH4OH + CO2-------→ (NH4)2CO3 + H2O

(iii) **<u>Acids from dissolved salts:</u>**

Water, containing dissolved magnesium salts, liberate acids on hydrolysis.

MgCl2 + 2 H2O ------→Mg(OH)2 + 2 HCl

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

Fe + 2 HCl -----→FeCl2 + H2(g)
FeCl2 + 2 H2O-------→ Fe(OH)2 + 2 HCl

Consequently, presence of even a small amount of $MgCl_2$ will cause corrosion of iron to a large extent.

3. **Priming and foaming:**

Priming:

When a boiler is producing steam rapidly, some particles of the liquid water are carried along-with the steam. This process of 'wet steam' formation, is called *Priming*.

Priming is caused by:

(i) The presence of large amount of dissolved solids.
(ii) High steam velocities.
(iii) Sudden boiling.
(iv) Improper boiler design.
(v) Sudden increase in steam-production rate.

***Priming can be avoided by*:**

(i) Fitting mechanical steam purifiers.
(ii) Avoiding rapid change in steam rate.
(iii) Maintaining low water levels in boilers.
(iv) Efficient softening and filtration of boiler-feed water.

Foaming:

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

***Foaming can be avoided by*:**

(i) Adding anti-foaming chemicals like castor oil.
(ii) Removing oil from boiler water by adding compounds like sodium aluminate.

Dis-advantages of priming and foaming:

(i) Dissolved salts in boiler water are carried by the wet steam to turbine blades, where they get deposited as water evaporates. This deposit reduces their efficiency.
(ii) Dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery.
(iii) Actual height of the water levels cannot be judged properly, thereby making The maintenance of boiler pressure becomes difficult.

4. **Caustic embrittlement**:

Caustic embrittlement is "a type of boiler corrosion, caused by using highly alkaline water in the boiler".During softening process of water (in lime-soda process), free Na_2CO_3 is usually present in small proportion in the softened water. In high pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide. This makes the boiler water 'caustic'.

$$Na_2CO_3 + H_2O \text{-------}\rightarrow 2NaOH + CO_2$$

The NaOH containing water flows into the minute hair-cracks, present in the inner side of boiler, bycapillary action. Here water evaporates and the dissolved caustic soda (NaOH) concentration increases progressively. This caustic soda attacks the surrounding area, thereby corroding the iron of boiler as sodium ferrate.

This causes embrittlement (cracking) of boiler parts, particularly stressed parts (like bends, joints), causing even failure of the boiler.

Caustic embrittlement can be explained by considering the following concentration cell;

(–) Iron at bends rivets and joints | Concentrated NaOH solution || Dilute NaOH solution | Iron at plane surfaces (+)

anode cathode

The iron surrounded by the dilute NaOH becomes the cathodic side; while the iron in contact with concentrated NaOH becomes anodic part, which consequently corroded.

Prevention of caustic embrittlement:

(i) By using sodium phosphate as softening reagent, instead of sodium carbonate.

(ii) By adding tannin or lignin to boiler water, which blocks the hair-cracks, thereby Preventing infiltration of caustic soda solution in cracks.

(iii) *By adding sodium sulphate to boiler water*:

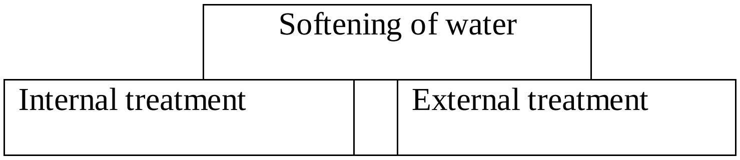
Na2SO4 also blocks hair-cracks, thereby preventing infiltration of caustic soda solution in these cracks. It has been observed that caustic embrittlement can be prevented, if Na2SO4 is added to boiler water so that the ratio:

$$\frac{\text{NaOH concentration}}{\text{Na2SO4concentration}}$$

is kept as 1 : 1, 2 : 1 and 3 : 1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

Softening methods:

Water used for industrial purpose (such as fir steam generation) should be sufficiently pure. Therefore, it should be freed from hardness producing salts before put to use. *The process of removing hardnessproducing salts from water, is known as softening of water.*
In industry, main methods employed for softening of water are two types.



Internal treatment: (Or) Conditioning of water:
The softening of water carried out inside the boiler is called internal treatment of water. In this process the hardness causing salts are removed

1. By complexing the hardness causing soluble salt by adding appropriate reagents.
2. By precipitating the scale forming impurities in the form of sludge which can be removed by blow down operation.
3. By converting the scale forming salts into other compounds which stay in 'dissolved form' and do not cause any trouble to the boilers.

The important internal conditioning methods are;

(a) Colloidal conditioning:

The scale formation in low pressure boilers can be prevented by the addition of kerosene, tannin, agaragar etc. which will be get coated over the scale forming precipitates. These forms loose, non-sticky deposits (sludge) that can be removed by blow down. This type of conditioning is called colloidal conditioning.

(b) Phosphate conditioning:

In this process, the permanent hardness causing salts in high pressure boilers will be removed by reacting with sodium phosphate. The complex formed is soft, non-adherent and easily removable.

$$3\ CaCl_2 + 2\ Na_3PO_4 \text{------}\rightarrow Ca_3(PO_4)_2 + 6\ NaCl$$

The three phosphates employed in this process are
Na_3PO_4 – tri-sodium phosphate (alkaline),
Na_2HPO_4 – disodium hydrogen phosphate (weakly alkaline) and
NaH_2PO_4 – sodium di-hydrogen phosphate (acidic).

(c) Carbonate conditioning:

The hard and strong adherent scales formed due to $CaSO_4$ are avoided by the addition of sodium carbonate to boiler water and this is called carbonate condition.

$$CaSO_4 + Na_2CO_3 \text{--------}\rightarrow CaCO_3\downarrow + Na_2SO_4$$

The $CaSO_4$ is converted to $CaCO_3$, which is loose sludge and it can be removed by blow down.

(d) Calgon conditioning:

Sodium hexameta phosphate **$Na_2[Na_4(PO_3)_6]$** or **$(NaPO_3)_6$** is called calgon. This forms solublecomplex compounds with $CaSO_4$.The treatment of boiler water with calgon is called calgon conditioning.

$$Na_2[Na_4(PO_3)_6] \text{-------}\rightarrow 2Na^+ + [Na_4P_6O_{18}]^{2-}$$
$$2\ CaSO_4 + [Na_4P_6O_{18}]^{2-} \text{--------}\rightarrow [Ca_2P_6O_{18}]^{2-} + 2Na_2SO_4$$

(e) Treatment with sodium aluminate ($NaAlO_2$):

Sodium aluminate is hydrolysed in boiler to give NaOH. The formed NaOH immediately precipitates by the reaction with some of the magnesium salts as $Mg(OH)_2$

$$NaAlO_2 + H_2O \text{-----}\rightarrow Al(OH)_3 + NaOH$$
$$MgCl_2 + 2\ NaOH \text{------}\rightarrow Mg(OH)_2\downarrow + NaCl$$

External treatment:

The treatment given to water for the removal of hardness causing salts before it is taken into the boiler is called 'external treatment'.

External treatment

Zeolite process (Or) Permutit process:

Zeolite is hydrated sodium alumina silicate, which is capable of exchanging reversibly its sodium ions for hardness-producing ions in water. Chemical formula of sodium zeolite may be represented as;

$$Na_2O.Al_2O_3.x\ SiO_2.y\ H_2O \text{ where } x = 2 – 10 \text{ and } y = 2 – 6$$

Zeolites are two types;

(i) *Natural zeolites*:

These are non-porous. Eg: Natrolite $Na_2O.Al_2O_3.4\ SiO_2.2\ H_2O$

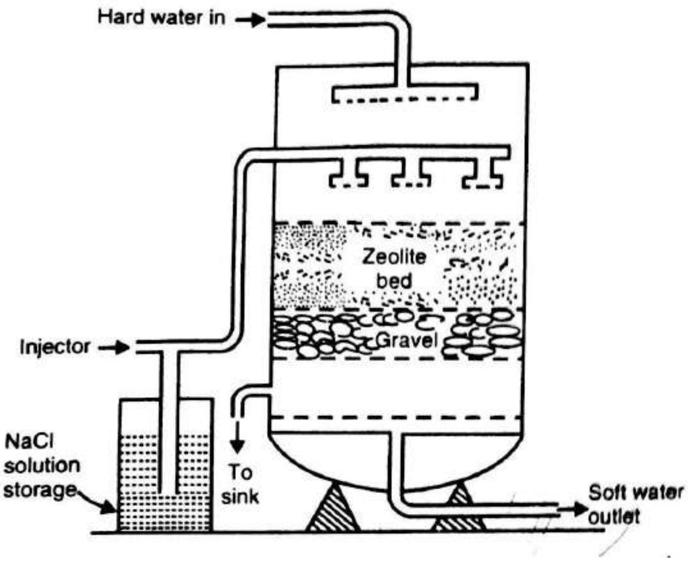
(ii) *Synthetic zeolites*:

These are porous and prepared by heating together china clay, feldspar and soda ash. Such zeolites possess higher exchange capacity per unit weight than natural zeolites.

Process:

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

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2NaHCO_3$$
$$Na_2Ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2NaHCO_3$$
$$Na_2Ze + CaCl_2 \longrightarrow CaZe + 2NaCl$$
$$Na_2Ze + MgCl_2 \longrightarrow MgZe + 2NaCl$$



Regeneration:

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

$$CaZe\ (or\ MgZe) + 2NaCl \longrightarrow Na_2Ze + CaCl_2\ (or\ MgCl_2)$$

The washings (containing $CaCl_2$ and $MgCl_2$) are led to drain and the regenerated zeolite bed thus obtained is used again for softening purpose.

Limitations of Zeolite process:

(1) If the supplied water is turbid, the suspended matter must be removed, before the water is admitted to the zeolite bed; otherwise the turbidity will clog the pores of zeolite bed, thereby making it inactive.

(2) If water contains large quantities of coloured ions such as Mn2+ and Fe2+, they must be Removed first, because these ions produce manganese and iron zeolites, which cannot be easily regenerated.

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

Advantages of zeolite process:

(1) It removes the hardness almost completely, and water of about 10 ppm hardness is produced.

(2) The equipment used is compact, occupying a small space.

(3) No impurities are precipitated, so there is no danger of sludge formation in the treated water at a large scale.

(4) The process automatically adjusts itself for variation in hardness of incoming water.

(5) It requires less time for softening.

Disadvantages of zeolite process:

(1) The treated water contains more sodium salts than in lime-soda process.

(2) The method only replaces Ca2+ and Mg2+ ions by Na+ ions, but leaves all the acidic Ions (HCO□3 and CO^{-2} 3) as such in the softened water. When such softened water (containing NaHCO3 and Na2CO3) is used in boilers for steam generation, sodium bicarbonate decomposes producing CO2, which causes corrosion; and sodium carbonate undergoes hydrolysis to sodium hydroxide, which causes caustic embrittlement.

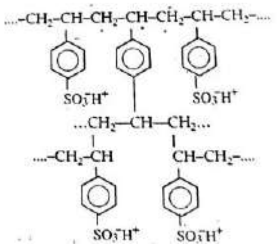
(3) High turbidity water cannot be treated efficiently by this method, because fine impurities get deposited on the zeolite bed, thereby creating problem for its working.

Ion exchange process (or) de-ionisation (or) de-mineralization process:

Ion exchange resins are insoluble, cross-linked, long chain organic polymers with a micro porous structure, and the ‘functional groups’ attached to the chains are responsible for the ion-exchange properties. Resins containing acidic functional groups (-COOH, -SO3H) are capable of exchanging their H+ ions with other cations, which comes in their contact. Resins containing basic functional groups (amino groups) are capable of exchanging their anions with other anions, which comes in their contact. Thus, ion-exchange resins may be classified as follows;

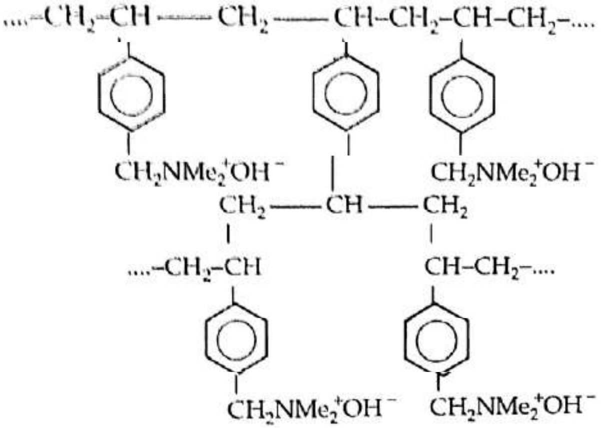
(i) Cation exchange resins (**RH+**):

These are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in their water.



(ii) Anion exchange resins (**R’OH-**):

These are styrene-divinyl benzene or amineformaldehyde copolymers, which contain amino or quarternary ammonium or quarternary phosphonium or tertiary sulphonium groups as an integral part of resin matrix. These, after treatment with dil. NaOH
solution, become capable to exchange their OHanions with anions in water.



Process:

The hard water is passed first through cation exchange column, which removes the cations like Ca2+ and Mg2+ etc from it, and equivalent amount of H+ ions are released from the column to water. Thus;

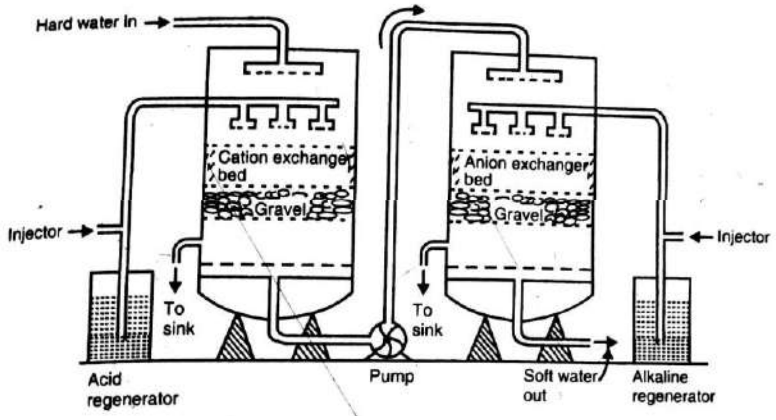
2RH+ + Ca2+-------→ R2Ca2+ + 2H+
2RH+ + Mg2+------→ R2Mg2+ + 2H+

After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like SO □ 24 , Cl -, CO2□ 3 etc. present in the water and equivalent amount of OHions are replaced from this column to water. Thus;

R'OH- + Cl-------→ R'Cl- + OH-
2R'OH+ SO □ 24-------------→R2' SO □ 24+ 2OH-
2R'OH- + CO2□3-----------→ R2' CO2□3 + 2OH

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

H+ + OH$^-$-------→ H2O



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

Regeneration:

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

The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or dil. H2SO4. The regeneration can be represented as;

R2Ca2+ + 2H+--------→ 2RH+ + Ca2+

The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as;

R2' SO □ 24 + 2OH- ---------→2R'OH- + SO □ 24

The regenerated ion exchange resins are then used again.

Advantages of ion-exchange process:

1. The process can be used to soften highly acidic or alkaline waters.
2. It produces water of very low hardness (about 2 ppm). So it is very good for treating Water used in high – pressure boilers.

Disadvantages:

1. The equipment is costly and more expensive chemicals are needed.
2. If water contains turbidity, then the output of the process is reduced. The turbidity must Be below 10 ppm. If it is more, it has to be removed first by coagulation and filtration.

ESTIMATION OF DISSOLVED OXYGEN:

The amount of oxygen present in the water in dissolved state is called dissolved oxygen

PRINCIPLE:

Dissolved oxygen can be determined by iodometric titrations. The dissolved oxygen present in water oxidizes KI liberating an equivalent amount of Iodine, which is titrated against standard hypo solution using starch as an indicator. An oxygen carrier like manganese hydroxide must be used to bring about the reaction between KI and dissolved oxygen because molecular oxygen in water is not capable of reacting with KI.

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$$

$$2\,Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2\downarrow$$

(Oxygen carrier) (Basic Manganic oxide)

$$2MnO(OH)_2\downarrow + H_2SO_4 \rightarrow MnSO_4 + (O) + 2H_2O$$

(Basic Manganic oxide) (Nascent Oxygen)

$$2KI + H_4SO_4\,(O) \rightarrow K2SO4 + H_2O + I_2$$

$$Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

(Sodium tetrathionate)

The nitrates present in water interfere with the estimation of dissolved oxygen of water, since these ions liberate iodine KI . Sodium azide is added to water which reacts with nitrate to decompose it as follows. $2NaN_3 + H_2SO_4 \rightarrow 2HN_3 + Na_2SO_4$

(Sod. Azide)

$$HN0_2 + HN_3 \rightarrow N2O \uparrow + N_2 + H_2O$$

PROCEDURE:

STEP:I PREPARATION OF STANDARD POTASSIUM DICHROMATE:

- Weigh out accurately the given pure crystalline sample of potassium dichromate and transfer into 100 ml standard (volumetric) flask provided with a funnel.
- Dissolve the dichromate in a small quantity of distilled water, and make up to the mark.
- The contents in the flask are shaken well for uniform concentration. Calculate the normality of potassium dichromate.

STEP:II STANDARDIZATION OF SODIUM THIOSULPHATE:

- Rinse the burette and fill it up with hypo solution without any air bubbles. Note the burette reading.
- Take about 20 ml of 10%KI solution in a clean conical flask and add 2 grams of sodium bicarbonate followed by 5 ml of concentrate HCl gently rotate the flask for mixing the liquids.
- Rinse the pipette with a little of potassium dichromate solution and then transfer 20 ml of the same to the conical flask. Shake it well, stopper it, and keep it in dark place for 5 minutes.
- Titrate the liberate iodine by running down hypo from the burette with constant stirring. When the solution attains a pale yellow colour add 2 ml of freshly prepared starch solution.
- The colour changes to blue. Continue the titration drop-wise till the colour changes from blue to light green indicating the end point. Repeat the titration for concurrent values.

STEP: III ESTIMATION OF DISSOLVED OXYGEN:

- Collect water sample in 300 ml capacity of BOD bottle and add 2 ml of manganese sulphate solution.
- To this add 2 ml of alkali-iodine–azide solution.
- Stopper the BOD bottle immediately.
- Appearance of brown precipitate indicates the presence of dissolved oxygen.
- Mixed well by inverting the bottle 2-3 times and allow the brown precipitate settle down.
- Add 2 ml of Conc H2SO4 to dissolve the precipitate
- Take 20 ml of the above solution in to a clean conical flask.
- Titrate the liberated iodine with standard hypo solution present in burette.
- Add 1 ml of starch solution when the color of the solution becomes blue color.
- Note the volume of the Hypo solution(v ml) repeate the titration till concurrent readings are obtained.
- Calculate the amount of dissolved oxygen present in water sample by using the formulae given below

- ➢

Dissolved oxygen in the given sample = V x Conc. of HypoX8X1000/20 PPM

Desalination of brackish water:

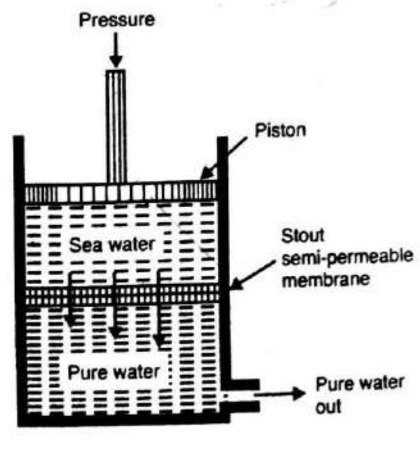
The process of removing common salt (sodium chloride) from water, is known as *desalination.* The water containing dissolved salts with a peculiar salty (or brackish) taste, is called *brackish water*.Sea water, containing on an average about 3.5% salts, comes under this category. Brackish water is totally unfit for drinking purpose.
Commonly used methods for the desalination of brackish water are;
1. Electro dialysis (out of syllabus). 2. Reverse osmosis.

Reverse osmosis:

When two solutions of unequal concentrations are separated by a semipermeable membrane, flow of solvent takes place from dilute to concentrated sides, due to osmosis.
If, however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverses, i.e. solvent is forced to move from concentrated side to diluted side across the membrane. This is the principle of *reverse osmosis*. Thus, in reverse osmosis method, pure solvent is separated from its contaminates, rather than removing contaminates from water. This membrane filtration is sometimes also called **superfiltration** or **hyper-filtration**.

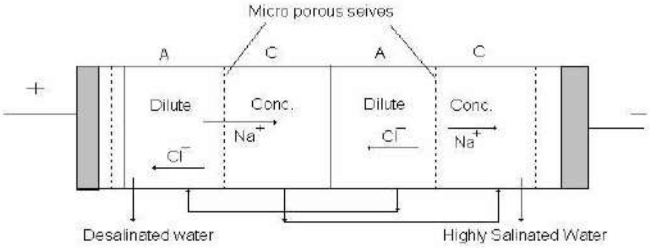
Advantages:

1. This process removes, ionic as well as non-ionic, colloidal and high molecular weight organic matter.
2. It removes colloidal silica, which is not removed by demineralization process.
3. The life time of membrane is quite high, about 2 years.
4. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.
5. Due to low cost, simplicity and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water.



Electrodialysis.

Principle: Passage of an electric current through a solution of salt results in migration of cations towards the cathode & anions towards the anode. The use of semi permeable cation or anion exchange membrane in an electrolytic vessel permits the passage of only cations or anions respectively in the solution. An electrodialyzer consists of a chamber carrying a series of compartments fitted with closely spaced alternate cation (C) & anion (A) exchange semi permeable membranes between the electrodes. An electrodialyzer unit will have 200 to 1000 compartments. The feed water is taken in the dialyzer & the electrodes are connected to a source of an electric current.



The anions pass through the anion permeable membrane towards the anode. However, these ions do not pass through the next membrane which is permeable only to cations. Similarly the cations moving in the other direction will pass through the cation exchange membrane but not the next. These anions & cations collect in the alternate chambers; the water in these is enriched with salt while that in the other compartments is desalinated. Micro porous sieves provided near the electrodes prevent the reentry of any deposit, which might have been formed on the electrodes, into the feed water. The enriched & desalinated waters are withdrawn separately. The former is rejected & the desalinated water is recycled to further reduce the salt content.

UNIT – II

ELECTROCHEMICAL CELLS and CORROSION

Syllabus:

Electrode potential, Nernst's equation, Electrochemical cells, EMF of an electrochemical cell. Reference electrodes – Standard Hydrogen Electrode (SHE), Calomel Electrode.
***Batteries**:* Introduction, Types of batteries, Ni-Cd battery, lithium ion battery. Applications.
Fuel cells: Definition, H_2 – O_2 Fuel cell, Phosphoric acid fuel cells, proton exchange membrane fuel cells, solid oxide fuel cells. Applications of fuel cells.
Corrosion: Introduction, Definition, Types of corrosion, galvanic corrosion, concentration cell corrosion, control of corrosion – Electroplating method.

Redox reactions:

Oxidation - the process which involves loss of electrons by a substance.
Reduction - the process which involves gain of electrons by a substance.
Redox reaction - The reaction in which both oxidation and reduction takes place.

OIL	RIG
Oxidation **I**s **L**oss	**R**eduction **I**s **G**ain

<u>Oxidizing agent</u> - The reactant which is an electron acceptor.

<u>Reducing agent</u> - The other reactant which is an electron donor.

It is quite apparent that if a substance loses electrons, some other substance must be involved in the reaction to accept these electrons. On the other hand, if a substance accepts electrons, some other substance must be involved in the reaction to supply these electrons. In other words oxidation and reduction must go side by side.

Examples:

1. If we place zinc metal in a copper sulphate, immediate precipitation of Cu takes place.

In this change, the zinc atom is oxidised to zinc ion, since it loses electrons; while the copper ion is reduced to copper atom, since it gains electrons.

$$\text{(a) } Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad \text{(oxidation)}$$

$$\text{(b) } Cu^{2+}(aq) + 2e \longrightarrow Cu(s) \qquad \text{(reduction)}$$

The overall reaction, obtained by adding (a) and (b), is called Redox reaction.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \qquad \text{(Redox)}$$

2. Redox reaction of dichromate ions with ferrous ions in presence of acid.

In this change, the ferrous ion is oxidised to ferric ion, since it loses electrons; while the chromium (+6) in the dichromate ion is reduced to chromium (+3) ion, since it gains electrons.

(a) $(Cr_2O_7)^{2-} + 14\ H^+ + 6e \dashrightarrow 2Cr^{3+} + 7\ H_2O$ (reduction)

(b) $6\ Fe^{2+} \dashrightarrow 6\ Fe^{3+} + 6e^-$ (oxidation)

$(Cr_2O_7)^{2-} + 6\ Fe^{2+} + 14\ H^+ \dashrightarrow 2Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$ (Redox)

Electrochemical cells:

“An electrochemical cell is a device in which a redox reaction is utilized to get electrical energy”.

Here, chemical energy is converted into electrical energy.

An electrochemical cell is also commonly referred to as Voltaic cell or Galvanic cell.

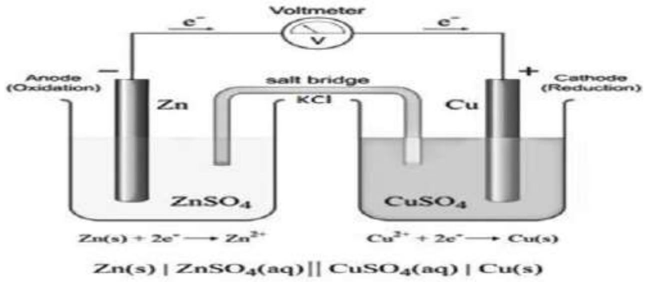
The electrode where the oxidation occurs, is called ***anode***; while the electrode where reduction occurs, is called ***cathode***. The practical application of an electrochemical cell is Daniel cell.

$$E = E_0 + nFRT\ ln\ [M^{n+}]$$

$$E = E_0 + nF2.303RT\ \log[M^{n+}]$$

Construction and working of Galvaniccell:

It consists of a copper rod dipped in $CuSO_4$ solution, which is separated by a salt bridge from a solution of $ZnSO_4$ in which a zinc rod is dipped.When the two electrodes are connected, the flow of electric current takes place and oxidation occurs at anodeand reduc tion occurs at cathode.



i.e., Zn metal passes into the solution as Zn^{+2} ions liberating two electrons (oxidation).

$Zn\ (s)\ Zn^{2+} + 2e^-$ of electric current takes place and oxidation occurs at anodeand reduc tion occurs at cathode.

The liberated electrons move through the voltmeter and then pass through the Copper rod. Then Cu^{+2} ions accepts $2e^-$ and are discharged as copper metal at copper electrode (reduction).

$$Cu^{2+} + 2e^-\ Cu\ (s)$$

Cell reaction can be represented as

$$Zn(s) + Cu^{+2}\ Zn^{+2} + Cu(s)$$

The flow of electrons in the cell is from anode to cathode (Zn electrode to Cu electrode). But flow of current in the cell is from cathode to anode. The SO_4^{2-} ions move from cathode to anode through the salt bridge. This completes the circuit of the cell. The e.m.f. of the cell is 1.1 volts. Here the salt bridge is used to maintain the electrical neutrality between the electrolytic solutions, internally.

IUPAC representation of a Cell:

$$Zn/ZnSO_4 \,||\, CuSO_4/Cu \text{ (or)}$$
$$Zn/Zn^{2+} \,||\, Cu^{2+}/Cu$$

IUPAC representation of a galvanic cell:

1. Anode is written on the left-hand side; while cathode is written on the right-hand side.
2. The electrode on the left is written by writing the metal first and then electrolyte. The two are separated by a vertical line or a semicolon.
3. The cathode of the cell is written on the right-hand side. In this case, the electrolyte is represented first and the metal thereafter. The two are separated by a vertical line or semicolon.
4. A salt bridge is indicated by two vertical lines, separating the two half-cells.

EMF of an electrochemical cell:

"The difference of potential, which causes a current to flow from the electrode of higher potential to the electrode of lower potential, is called the electromotive force (e.m.f.) of the cell". It is expressed in volts. Mathematically, the e.m.f. of an electrochemical cell is the algebraic sum of the single electrode potential. It can readily be calculated from the reduction half-cell potentials, using the following relationship.

Where,

E_{cell} = e.m.f. of cell;
$E_{cathode}$ = reduction potential of cathode;
and E_{anode} = reduction potential of anode.

We can also take, $E_{cell} = E_{right} – E_{left}$

It should be remembered that a positive value of E_{cell} indicates that the cell reaction is feasible. If however, it comes out to be negative, the cell reaction is not feasible and in actual operation of the cell, the electrodes will have to be reversed in order to bring about cell reaction.

Measurement of EMF of an electrochemical cell:

EMF can be measured in two ways.

1. Nernst's equation for a cell reaction to calculate E_{cell}:

Where

$$E_{0cell} = E_{0cathode} – E_{0anode}$$

For the Daniel cell reaction,

$$Zn(s) + Cu^{+2}\ Zn^{+2} + Cu(s)$$

The Nernst's can be written as:

$$E_{cell} = (E_{o\ Cu^{2+}/Cu} – E_{0\ Zn^{2+}/Zn}) + RT/nF\ 2.303 \log[Cu^{2+}][Zn^{2+}]$$

Here n = number of electrons = 2.

2. Measurement of EMF of electrochemical cell by potentiometer:

The e.m.f. cannot be determined accurately by connecting directly a volt meter between the two electrodes, because during such a measurement, a part of the cell current is drawn, thereby causing a change in the emf,

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

$$E_{cell} = E_{0cell} - nF2.303RT \log[\text{reactants}][\ \mathit{products}]$$

Electrode potential (E):

A metal consists of metal ions, with the valence electrons that bind them together. When a strip of this metal M is placed in a solution of its ions M^{n+}, a metal - metal ion electrode is obtained. The possible processes that can occur at the electrodes are:

(a) A metal atom on the electrode M may lose n electrons to the electrode, and enter the solution as M^{n+}, (i.e., the metal atom is oxidised).

$$M(s) \rightleftharpoons M^{n+}(aq) + ne^-$$

(b) A metal ion M^{n+} collides with the electrode, gains n electrons and gets converted into a metal atom M(i.e., the metal ion is reduced).

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$

The above processes affect the electrodes as follows:

If the metal has relatively high tendency to get oxidized, its atoms will lose electrons readily and form M^{n+} ions, which go into the solution. The electrons lost from the electrode get accumulated on the metal electrode and the electrode acquires a slight negative charge with respect to the solution. After some time, an equilibrium is established as:

$$\underset{\text{Electrode}}{M(s)} \rightleftharpoons \underset{\text{Solution}}{M^{n+}(aq)} + \underset{\text{(on electrode)}}{ne^-}$$

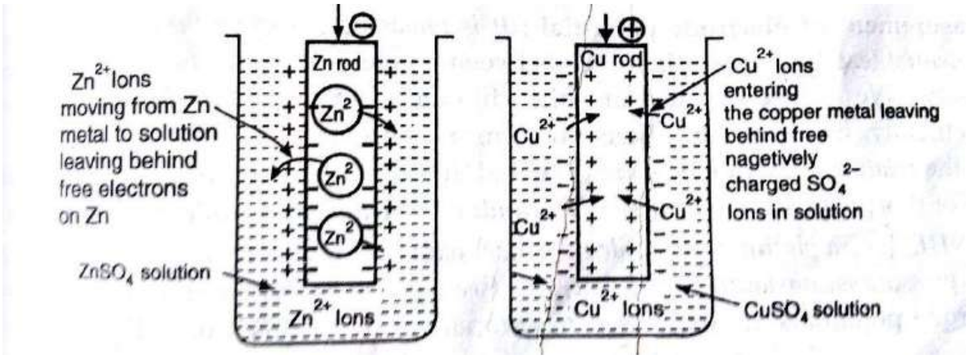
Such an equilibrium results in separation of charges (negative on the electrode with respect to the solution).

Similarly, if the metal ions have relatively greater tendency to get reduced due to electron deficiency, they will take electrons from the electrode. As a result, separation of charges occurs and a net positive charge will be developed on the electrode with respect to the solution.

Example:

(a) Zinc rod dipped in $ZnSO_4$ solution.

(b) Copper rod dipped in $CuSO_4$ solution.



Oxidation Reduction

Thus, a short layer of positive ions or negative ions is formed around the metal. This layer is called Helmholtz electrical double layer. A difference of potential is, consequently setup between the metal and the solution. At equilibrium, the potential difference between the metal and solution becomes a constant value. The equilibrium potential difference so established, is called the "electrode potential" of the metal.

Definition of Electrode potential:

The measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt is called its "*Electrode potential*".

The tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidised; and this tendency is called *Oxidation potential*.

The tendency of an electrode to gain electrons is a direct measure of its tendency to get reduced; and this tendency is known as *Reduction potential*.

It is quite obvious that the value of reduction potential is negative of its oxidation potential and vice versa.Thus, if oxidation potential of an electrode is +X volt, then its reduction potential will have a value of –X volt.

Standard electrode potential (E0):

It is the potential developed when the pure metal is in contact with its ions at one molar concentration at a temperature of 25$_o$C or 298 K.

Example: When a Zn rod of any length is dipped in 1M $ZnSO_4$ solution, standard electrode is formed and the potential developed is called standard zinc electrode potential (E_0).

In case of a gas electrode, the standard electrode potential (E_o) is defined as the potential developed at the interface of the gas and solution containing its own ions when an equilibrium is established between the gas at a pressure of 1 atm (760 mm of Hg) and the ions in solution of unit concentration.

The General Nernst Equation

The general Nernst equation correlates the Gibb's Free Energy ΔG and the EMF of a chemical system known as the galvanic cell. For the reaction

$$a\,A + b\,B = c\,C + d\,D$$

and

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

It has been shown that

$$\Delta G = \Delta G° + R\,T \ln Q$$

and

$$\Delta G = -\,n\,F\Delta E.$$

Therefore

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

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

$$\Delta E = \Delta E° - \frac{R\,T}{n\,F} \ln \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

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

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

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

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

The Nernst Equation at 298 K

At any specific temperature, the Nernst equation derived above can be reduced into a simple form. For example, at the standard condition of 298 K (25°), the Nernst equation becomes

$$\Delta E = \Delta E° - \frac{0.0592\ \mathrm{V}}{n} \log \frac{[\mathrm{C}]^c\ [\mathrm{D}]^d}{[\mathrm{A}]^a\ [\mathrm{B}]^b}$$

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

For the cell

$Zn\ |\ Zn^{2+}\ ||\ H^+\ |\ H_2\ |\ Pt$

we have a net chemical reaction of

$Zn(s) + 2\ H^+ = Zn^{2+} + H_2(g)$

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

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

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

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

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

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

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

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

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

Batteries

Definition:

"An electrochemical cell or combination of electrochemical cells connected in series, that can be used as a source of direct current at a constant voltage is called Battery".

Batteries are classified as follows,
i) Primary battery
ii) Secondary battery
iii) Fuel cell or Flow battery

***Primary battery:** (non-rechargeable)*

Primary battery is a cell in which the cell reaction is not reversible. Thus, once the chemical reaction takes place to release the electrical energy, the cell gets exhausted. Then battery become dead. These are nonrechargeable type.
Example: Dry cell, mercury cell etc.

***Secondary battery:** (rechargeable)*

Secondary battery is a cell in which the cell reaction is reversible, by passing direct current in opposite direction. Thus, these are rechargeable cells, used through a large number of cycles of discharging and charging.
Example: Lead-acid battery, Nickel-Cadmium battery, Lithium batteries etc.

$$pH = 0.0591 \quad \cdot \quad 0.2422\ {}_{cell}E$$

Fuel cell or Flow battery:

Fuel cell is the cell in which materials (reactants, products and electrolytes) pass through the battery. When the reactants are exhausted, new chemicals replace them. Here chemical energy of fuel is converted into the electrical energy.
Example: Hydrogen-oxygen fuel cell, methyl-oxygen fuel cell etc.

1) Ni- Cd battery:

This battery consists of a cadmium anode and a cathode composed of a paste of NiO(OH). These electrodes are immersed in the solution of KOH (electrolyte).

Working:

When the nickel battery operates, Cd is oxidized to Cd^{+2} ions at anode and the insoluble $Cd(OH)_2$ is formed. NiO(OH) is reduced to Ni^{+2} ions which further combines with OH^- ions to form $Ni(OH)_2$. It produces about 1.4 V. The following cell reactions occur (during discharging).

At anode $Cd (s) + 2OH^- (aq)\ Cd(OH)_2 (s) + 2e^-$
At cathode $2NiO(OH) (s) + 2H_2O + 2e^-\ 2Ni(OH)_2 (s) + 2OH$
Net reaction $Cd (s) + 2NiO(OH) (s) + 2H_2O\ Cd(OH)_2 + 2\ Ni(OH)_2$

The reaction can be readily reversed by passing the current in opposite direction, because the products, $Cd(OH)_2$ and $Ni(OH)_2$, adhere to the electrode surfaces.

Reactions during recharging:

At cathode $Cd(OH)_2\,(s) + 2e^-\; Cd\,(s) + 2OH^-\,(aq)$
At anode $2Ni(OH)_2\,(s) + 2OH^-\; 2NiO(OH)\,(s) + 2H_2O + 2e^-$
Net reaction $Cd(OH)_2 + 2\,Ni(OH)_2\; Cd\,(s) + 2NiO(OH)\,(s) + 2H_2O$

It may be noted that during discharging process cell acts as voltaic cell (chemical energy is converted to electrical energy), during recharging it acts as an electrolytic cell (electrical energy is converted to chemical energy).

Advantages of Ni-Cd battery:

1. It is portable and rechargeable cell having voltage about 1.4 V.
2. It has longer life than lead-acid battery.
3. Since no gaseous products are formed during discharging and recharging, this cell can be sealed.
4. It can be left for long periods of time without any appreciable deterioration.

Applications:

1. It is used in electronic calculators.
2. It is used in electronic flash units.
3. It is used in transistors and cordless electronic shavers.

2) Lithium batteries:

Lithium cells most popularly used cells, which are available in various configurations. These cells have following advantages.

1. These are light in weight.
2. High energy density
3. More cycle life.

Lithium has the most negative standard reduction potential (-3.05 V) of any metal, so it has lot of appeal as an anodic material. Furthermore, lithium is a very light metal, correspondingly lithium employed cell is light in weight.

Lithium batteries fall into two categories:
(a) Solid Lithium cells (primary batteries)
(b) Lithium ion cells (secondary batteries)

(a) <u>Solid lithium Batteries:</u>

One of the most common lithium primary cell is the lithium manganese dioxide battery. This cell uses a solid lithium anode and a cathode made of heat treated MnO_2. The electrolyte is a mixture of propylene carbonate and dimethyoxy ethane containing dissolved salt such as $LiClO_4$.Propylene carbonate, Dimethoxy ethane

The cell reactions are as follows:

$Li\ Li^{+}\text{----------->} + e^{-}$ (anode)

$MnO_2 + Li^{+} + e^{-}\text{---------->}MnO_2(Li)$ (cathode) (Mn^{+4} to Mn^{+3})

$Li + MnO_2\text{----------->} MnO_2(Li$ (net cell reaction)

This cell produces a voltage of about 3.4 V which is more than twice that of alkaline dry cell, and because of the light weight of lithium, it produces more than twice as much energy for a given weight.

Applications:

These cells are used in applications that require a higher current drain or energy pulses (photoflash). $H_2CCHOCOOH_3C$

(b) Lithium ion Batteries (rechargeable):

These cells do not contain metallic lithium. But they contain lithium ions. In fact, the cell's operation does not actually involve true oxidation and reduction. But it uses the transport of Li^{+} ions through the electrolyte from one electrode to the other, accompanied by the transport of electrons through the external circuit to maintain charge balance.

Initial charging:

It was discovered that Li^{+} ions are able to slip between two layers of atom in certain crystals such as graphite and $LiCoO_2$. When the cell is constructed, it is in its uncharged state with no Li^{+} ions between the layers of carbon atoms in the graphite. While the cell is initial charging, Li^{+} ions leave $LiCoO_2$ and travel through the electrolyte (usually $LiPF_6$) to the graphite (C_6).

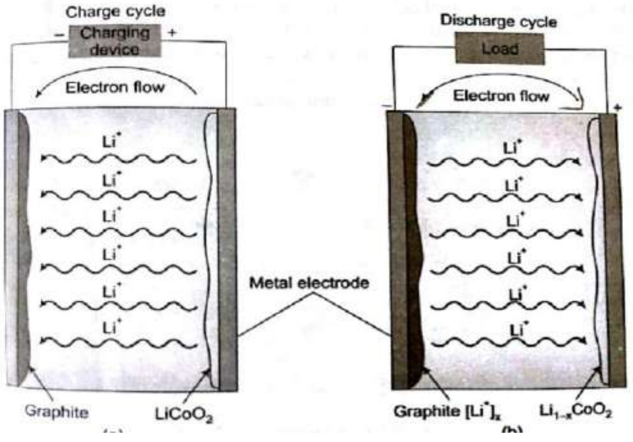
$$LiCoO_2 + \text{graphite } (C_6)\ Li_{1-x}CoO_2 + Li_xC_6$$

Discharging:

When the cell spontaneously discharges to provide electrical power, Li^{+} ions move back through the electrolyte to the Lithium cobalt oxide, while the electrons move through external circuit from the graphite electrode to the cobalt oxide electrode. If we represent amount of Li^{+} ions transferring by 'y', then the discharge reaction is represented as,

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

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



Applications:

1. Used as power suppliers in portable electronics, telecommunications, personal computerssuch as cell phones, and laptops.
2. For transportation-in electric bikes and electric cars which runs with electricity.

Fuel cells

Introduction:

We know that galvanic cells involve oxidation-reduction reaction. A workable cell forces the electrons that leave the substance being oxidized through an external conductor before they are received by the oxidizing agent. We also know that all ordinary combustion reactions are redox reactions. However, when a fuel is burned, the electron exchange take place only when the atoms of the oxidising agent (oxygen or air) come in direct contact with the atoms of the substance being oxidised (the fuel). The energy is released principally as heat. In a fuel cell, electrical energy is obtained without combustion from oxygen and a gas that can be oxidized.

The galvanic cells can only produce electrical energy for a limited time because the electrode reactants are eventually depleted. Fuel cells are electrochemical cells in which electrode reactants are supplied continuously and are able to operate without theoretical limit as long as the supply of reactants is maintained. This makes fuel cell an attractive source of power where long-term generation of electrical energy is needed. Fuel cell converts the chemical energy of the fuels directly to electricity.

Definition of Fuel cell:

An electrochemical cell in which, reactants are supplied continuously from an external source, and chemical energy of the fuel is directly converted into electricity, is called Fuel cell.

A large number of these cells are stacked together to make a battery, called fuel cell battery or fuel battery. The essential process in a fuel cell is;

Fuel + Oxygen Oxidation products + Electricity

Fuels in fuel cell are gases or liquids like H_2, CH_4, methanol etc. Oxygen acts as an oxidant.

Fuel cell Battery

- Open system
- Anode and cathode are gases in contact with a platinum catalyst.
- Reactants are externally supplied,

no recharging required.

- Closed system
- Anode and cathode are metals.
- Reactants are internally consumed,

need periodic recharging.

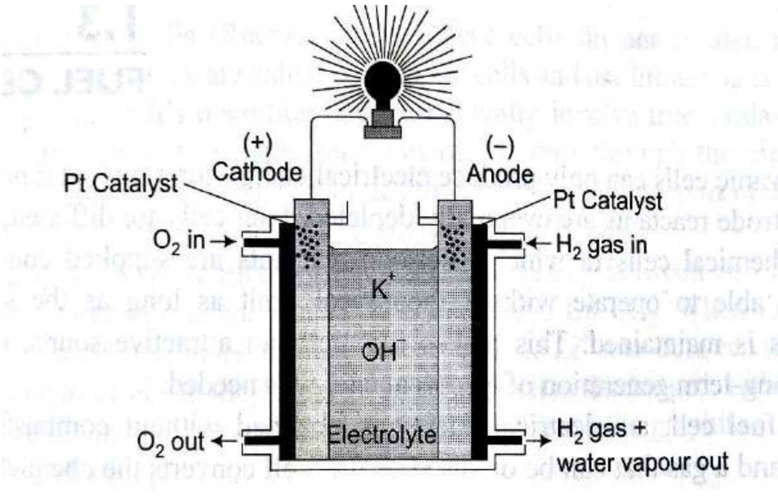
Types of fuel cells:

There are different types of fuel cells, differentiated by the type of electrolyte separating the hydrogen from the oxygen. The types of fuel cells are

1. Alkaline Fuel cells
2. Molten Carbonate Fuel cells (out of syllabus)
3. Phosphoric Acid Fuel cells
4. Proton Exchange Membrane Fuel cells
5. Solid Oxide Fuel cells

1) Alkaline fuel cells (AFCs) (or) Hydrogen- Oxygen fuel cell:

One of the simplest and successful fuel cell is hydrogen-oxygen fuel cell. It consists of an electrolyte, a hot concentrated solution of KOH in the centre compartment, and KOH is in contact with two porous carbon electrodes that contain catalyst (platinum) to facilitate the electrode reactions. Gaseous hydrogen and oxygen under pressure are circulated so as to come in contact with the electrodes.



The electrode reactions are as follows;

$$2\,H_2(g) + 4\,OH^-(aq) \text{--}\!\!\rightarrow 4\,H_2O + 4\,e^- \text{ (at anode)}$$
$$O_2(g) + 2\,H_2O + 4\,e^- \text{-------}\!\!\rightarrow 4\,OH^-(aq) \text{ (at cathode)}$$
$$2\,H_2(g) + O_2(g) \text{----}\!\!\rightarrow 2\,H_2O \text{ net cell reaction}$$

The standard EMF of the cell is 1.23 V. Generally, large number of these cells are connected in series to make a fuel battery.

Advantages:

1. These fuel cells are an attractive alternative to gasoline powered engine, because these are pollution free and the only product of the reaction is harmless water.
2. These are highly efficient (75%), converting as much as (75% of) available energy to useful work compared to the efficiency of gasoline and diesel engines (25-30%).
3. The fuel (hydrogen) and electrolyte material are available in plenty and inexhaustible unlike fossil Fuels.

Applications:

1. Hydrogen-oxygen fuel cells are used as auxiliary energy source in space vehicles, submarines, or military vehicles.
2. The weight of fuel battery is about 250 kg which is enough for 15 days in space.
3. In case of hydrogen-oxygen fuel cells, the product of water process to be a valuable source of fresh 55+water to the astronauts.

2) Proton Exchange Membrane Fuel Cells (PEMFCs):

In these fuel cells, “a polymer membrane, which is an electronic insulator, but an excellent conductor of hydrogen ions” is used as electrolyte. It consists of a fluorocarbon backbone, similar to Teflon, to which sulfonic acid groups are attached.

Ex: Nafion

The acid groups are fixed to the polymer and cannot leak out, but the protons on these acid groups are free to migrate through the membrane. The use of solid polymer electrolyte eliminates the corrosion and safety concerns associated with liquid electrolyte fuel cells. Its low operating temperature provides instant start-up. The anode and cathode are prepared by applying a small amount of platinum black to the surface of a graphitised paper. The electrolyte is then sandwiched between the anode and cathode, and the three components are sealed together under heat and pressure to produce a single “Membrane Electrode Assembly” (MEA). This MEA is the heart of the fuel cell which is less than one millimetre thick(Nafion).

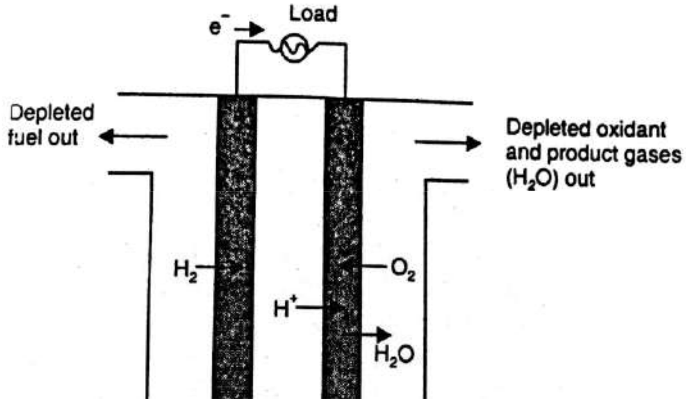
Working:

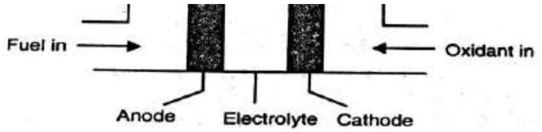
Hydrogen from the fuel gas is consumed at the anode, yielding electrons to the anode producing hydrogen ions, which enter the electrolyte. At the cathode, oxygen combines with electrons and hydrogen ions to produce water. The water does not dissolve in the electrolyte and is rejected from the back of the cathode. As the PEMFs are operating about 80_0C, the water is produced in liquid state.

At anode: $H_2 \rightarrow 2H_+ + 2e_-$

At cathode: $(1/2)O_2 + 2H_+ + 2e_- \rightarrow H_2O$

Net Reaction: $H_2 + (1/2)\,O_2 \rightarrow H_2O$





3) Solid Oxide Fuel Cells (SOFCs):

Solid oxide fuel cells work at very high temperatures, the highest of all the fuel cell types at around 800ºC to 1,000°C. They can have efficiencies of over 60% when converting fuel to electricity; if the heat they produced is also harnessed; their overall efficiency in converting fuel to energy can be over 80%.

"SOFCs use a solid ceramic electrolyte, such as zirconium oxide stabilised with yttrium oxide (or calcium
oxide), instead of a liquid or membrane".

Working:

At high operating temperatures, oxygen ions are formed at the "air electrode" (cathode). When a fuel gas containing hydrogen is passed over the "Fuel electrode" (anode), the oxygen ions migrate through the crystal lattice to oxidise the fuel. Electrons generated at the anode move out through an external circuit, creating electricity. In this cell water gas ($CO + H_2$) is used as the fuel.

Anode reaction:

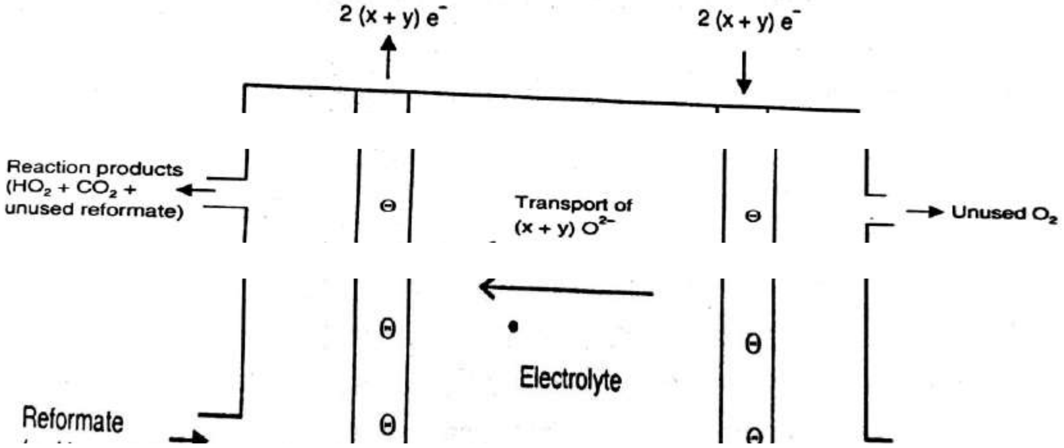
$$x\,H_2 + y\,CO + (x+y)\,O_2- \;x\,H_2O + y\,CO_2 + 2(x+y)\,e-$$

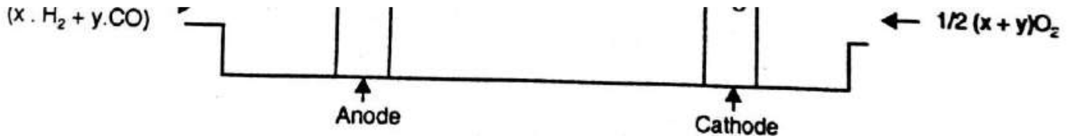
Cathodic reaction:

$$\tfrac{1}{2}\,(x+y)\,O_2 + 2\,(x+y)\,e- \;(x+y)\,O_2-$$

Net Reaction:

$$x\,H_2 + y\,CO + \tfrac{1}{2}\,(x+y)\,O_2 \;x\,H_2O + y\,CO_2$$





There are two different SOFC geometries of SOFC: planar, tubular.

- In the planar design, components are assembled in flat stacks where the air and hydrogen traditionallyflow though the unit via channels built in to the anode and cathode.
- In the tubular design, air is supplied to the inside of an extended solid oxide tube (which is sealed at one end) while fuel flows round the outside of the tube. The tube itself forms the cathode and the cell components are constructed in layers around the tube.

Advantages:

- Their high operating temperature means that fuels can be reformed within the fuel cell itself, eliminating the need for external reforming and allowing the units to be used with a variety of hydrocarbon fuels.
- They are also relatively resistant to small quantities of sulphur in the fuel, compared to other types of fuel cell, and can hence be used with coal gas.
- A further advantage of the high operating temperature is that the reaction kinetics are improved, removing the need for a metal catalyst.

Disadvantages:

- Due to the high temperature: these cells take longer to start up and reach operating temperature, they must be constructed of robust, heat-resistant materials, and they must be shielded to prevent heat loss.
- While solid electrolytes cannot leak, they can crack.
- Design Cost & choice of material.

Applications:

- Suitable for decentralized electricity production
- While the major application of SOFCs are seen in stationary plants, auxiliary power units in
- Transportation vehicles
- On-board power for aircraft
- Power packs- small enough to be carried by soldier.

Corrosion

Introduction:

Most metals (except noble metals such as Au, Pt, etc) exist in nature in combined forms as their oxides, carbonates, hydroxyl carbonates, sulphides, chlorides and silicates. These are reduced to their metallic states from their ores, during their extraction processes. During extraction of metals, considerable amounts of energy is required. Consequently, isolated pure metals can be regarded as in excited state (higher energy state) than their corresponding ores, and they have a natural tendency to revert back to combined state (lower energystate). Hence, when metals are put into use, in various forms, they are exposed to environment (such as dry gases, moisture, liquids, etc), the exposed metal surfaces begin to decay (i.e. conversion to more stable metal compounds) more or less rapidly, when they come in contact with surroundings. In other words destruction or deterioration of the metal starts at the surface. This type of metallic destruction may be due to direct chemical attack (by the environment) or electrochemical attack (i.e, similar to reactions in a Daniel cell).

REACTION:

Definition of corrosion:

"Any process of deterioration or destruction of a metal or alloy, through an unwanted chemical or electrochemical attack by its environment, starting at its surface, is called corrosion". Thus, corrosion is a process of "reverse of extraction of metals".

Examples:

1. Rusting or iron, when exposed to the atmospheric conditions. During this, a layer of reddish scale and powder of oxide (Fe_2O_3) is formed, and the iron becomes weak.
2. Formation of green film of basic carbonate [$CuCO_3 + Cu(OH)_2$] on the surface of copper, when exposed to moist-air containing carbon dioxide.

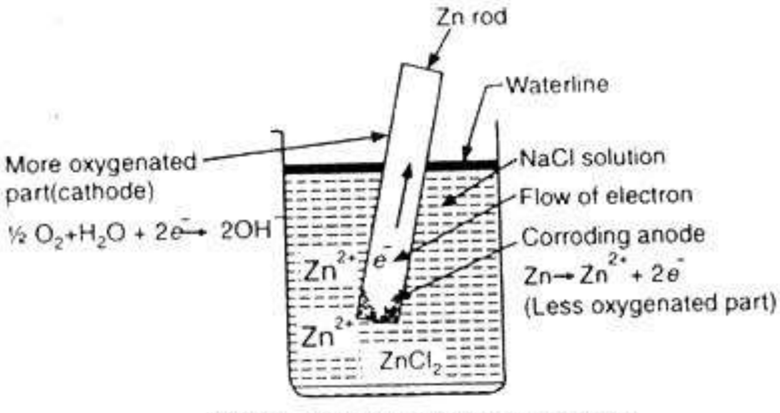
Concentration cell corrosion:

This type of corrosion is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentrations or of varying aeration. The most common type of concentration cell corrosion is Differential aeration corrosion. It occurs when one part of metal is exposed to a different air concentration from the other part. This causes a difference in potential between differently aerated areas. It has been found experimentally that "pooroxygenated parts are *anodic*". Consequently, a differential aeration of metal causes a flow of current, called differential current. It accounts for the corrosion of metals, partially immersed in a solution, just below the water line.

Explanation:

If a metal (say Zn) is partially immersed in a dilute solution of a neutral salt (say NaCl) and the solution is not agitated properly, then, the parts above and closely adjacent to the waterline are more strongly aerated, because of easy access of oxygen and hence, become *cathodic*. On the other hand, parts immersed to greater depth, which have less access of oxygen, show a smaller oxygen concentration and thus, become *anodic*. So, a difference of potential is created, which causes the flow of current between the two differentially-aerated areas of the same metal.

Zinc will dissolve at the anodic area, and oxygen will take up electrons at the cathodic area to form hydroxyl ions.



Differential aeration corrosion

$$Zn ----------> Zn^{2+} + 2e^-$$

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

The circuit is completed by migration of ions, through the electrolyte, and flow of electrons through the metal, from anode to cathode.In a similar way, iron corrodes under drops of water (or salt solution). Areas covered by droplets, having low access of oxygen, become anodic with respect to the other areas, which are freely exposed to air .

From the above, it is clear that oxygen concentration cell increases corrosion, but it occurs where the oxygen concentration is lower.

General facts about the differential aeration (concentration cell corrosion) corrosion:

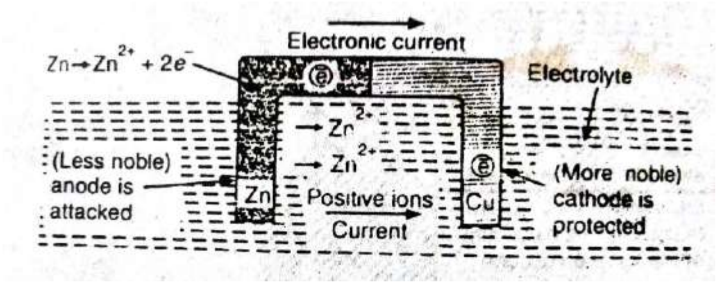
(i) Corrosion may be accelerated in apparently inaccessible places, because the oxygen deficient areas serve as anode and, therefore, cracks or crevices serve as foci for corrosion.

(ii) Corrosion is accelerated under accumulation of dirt, sand, scale or other, contamination. This is because accumulation of rust or scale or sand etc. restricts the oxygen and establishes an anode to promote still greater accumulation. The result is localized corrosion, due to non-uniform conditions.

(iii) Metals exposed to aqueous media, corrode under blocks of wood or pieces of glass, which screen that portion of metal from oxygen access. The differential aeration type of corrosion is a localized attack on some oxygen deficient areas, resulting in characteristics localized pitting. This arrack becomes more intensified with the time, because the corrosion products accumulate around a small anodic area, thereby making inaccessibility of that part more effective.

Galvanic corrosion (or bimetallic corrosion):

When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series (which is having low E_0 value) undergoes corrosion. This type of corrosion, is called “galvanic corrosion”.



Explanation:

When zinc and copper are connected and exposed to corroding environment, zinc (higher in electrochemical series) acts as anode and is going to corrode; whereas copper (lower in electrochemical series or nobler) acts as cathode.

Mechanism:

In acidic solution, the corrosion occurs by the hydrogen evolution process; while in neutral or slight alkaline solution, oxygen absorption occurs. The electron-current flows from the anodic metal i.e. Zn to the cathodic metal (Cu). Thus, it is evident that the corrosion occurs at the anodic metal; while the cathodic part is protected from attack.

$$Zn \quad Zn^{+2} + 2e^{-} \text{ (oxidation)}$$

Examples for galvanic corrosion:

1. Steel screws in a brass marine hardware.
2. Lead-antimony solder around copper wire.
3. A steel propeller shaft in bronze bearing.
4. Steel pipe connected to copper plumbing

Types of corrosion:

1. Dry corrosion (Chemical corrosion).
2. Wet corrosion (Electro chemical corrosion).

2)Wet corrosion:

According to electrochemical theory**,** corrosion of metals occurs due to the following changes, when they are exposed to the environment.

1) A large number of minute galvanic cells are formed which acts as anodic and cathodic areas.
2) At anode the metal undergoes oxidation and electrons are liberated which migrates towards cathodic region
3) Oxygen of the atmosphere undergoes reduction at cathodic area in the presence of moisture forming hydroxyl ions at the cathode

Anodic reactions*:* At anode the metal undergoes oxidation-liberating electrons

$$\underset{\text{Metal}}{M} \xrightarrow{\qquad} \underset{\text{Metal ions}}{M^{n+}} + ne^-$$

Ex: when iron is exposed to the environment it undergoes oxidation as

$$Fe \xrightarrow{\qquad} Fe^{2+} + 2e^-$$

Cathodic reactions*:* The electrons released at anode migrates to the cathodic area and reduces oxygen to hydroxyl ions.

The different cathodic reactions are,

a) ***In acidic medium:*** In acidic medium and in the absence of oxygen, hydrogen ions are reduced to hydrogen gas

$$2H^+ + 2e \xrightarrow{\qquad} H_2$$

b) ***In alkaline and in the absence of O₂:*** If the solution is alkaline and in the absence of oxygen the cathodic reaction is,

$$2\,H_2O + 2e^- \xrightarrow{\qquad} 2OH^- + H_2$$

c) ***In neutral and aerated medium:*** when the solution is neutral and aerated, hydroxyl ions are formed as follows.

$$2\,H_2O + O_2 + 4e^- \xrightarrow{\qquad} 4OH^-$$

d) ***Formation of corrosion product:*** The hydroxyl ions migrate towards anode and reacts with metal ions (M^{n+} ions) and forms corrosion product. In the case of iron OH- reacts with Fe^{2+} ions and forms an insoluble hydrated ferric oxide known as brown rust.

$$2Fe^{++} + 4OH^{-} \longrightarrow 2Fe(OH)_2$$

$$2Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2(Fe_2O_3 . 3H_2O) \text{ rust.}$$

Galvanic series:

In the electrochemical series, a metal high in the series is more anodic and undergoes corrosion faster than themetal below it. For example, Li (–3.05V) corrodes faster than Mg (–2.36V), Zn (–0.76V) corrodes faster than Fe (–0.44V), Fe corrodes faster than Sn (–0.14V), Cu (0.34V) corrodes faster than Ag (0.80V) and so on.

However, some exceptions to this generalization are known.

Examples:

1. Ti (– 1.63V) (above Ag in the electrochemical series) is less reactive than Ag (0.80V).
2. In Zn-Al couple, Zn (–0.76V) (below Al in the electrochemical series) is corroded; while Al (–1.66V)acts cathodic and is protected.These observations, exactly opposite to that predicted by the electrochemical series, are due to the fact that metals like Ti and Al develop, strongly adhering oxide layers on their surfaces, thereby making their effective electrode potential more positive (or less negative).

From the above, it is clear that electrochemical series does not account for the corrosion of all metals and alloys. Consequently, a more practical series, called *galvanic series* have been prepared by studying the corrosion of metals and alloys in a given environment like sea-water. Thus, galvanic series give real and useful information for studying the corrosion of metals and alloys.

Factors affecting the corrosion (Metal and Environment):

The main important factors, which affect on the rate of corrosion, are

a) Nature of the metal and
b) Nature of the environment

Nature of the metal:

i) ***Nature of corrosion product:***

If the nature of corrosion product forms, a protective layer on the metal surface, it prevents the further corrosion of metal .If the corrosion product is thin, invisible and doesn’t form a protective layer it leads to further corrosion of metal.

Example: In oxidizing environment metals like Al, Cr, Ti etc. forms protective metal oxide films on their surfaces which prevents further corrosion .Metals like Zn,Fe ,Mg ,etc .do not form protective layer and are readily under goes corrosion .Therefore the rate of corrosion depends on the nature of corrosion product.

ii) Electrode Potential of anode and cathode:

The rate of corrosion increases if the potential difference between anode and cathode is high and vice versa. When two different metal with large electrode potential difference (SRP values) under goes very fast corrosion

Example: The potential difference between copper and iron is 0.78 V. The potential difference between iron and tin is 0.3 V. In these two cases iron undergoes fast corrosion when it is in contact with copper than when it is in contact with tin.

iii) Anodic to cathodic areas:

If a metal has small anodic and large cathodic area the rate of corrosion increases and vice versa. This is because when anode is small the electrons liberated during oxidation are completely consumed on large cathodic surface for the reduction reactions and rate of corrosion increases.

b) ***Nature of the environment:***

i) Temperature: Increases in temperature results in an increase in the conductance of the aqueous medium and rate of corrosion also increases and vice versa.

ii) PH: In general at lower PH value the rate of corrosion is more at higher pH value (more than pH = 10) the rate of corrosion ceases due to the formation of protective coating of hydrous oxides on the metal. Corrosion rate is maximum between PH 3 and 10 in presence of oxygen

Control of corrosion:

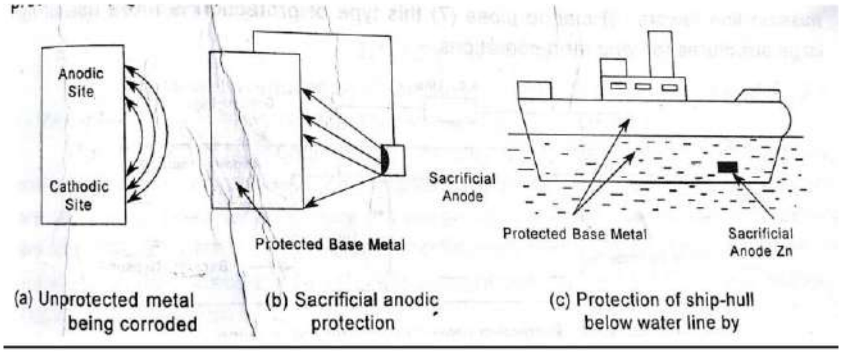
Cathodic protection (Sacrificial anodic protection)

Cathodic protection: (Sacrificial anodic protection):

It is a method of protecting metals and alloys from corrosion by making them completely The metallic structure to be protected called ‘base metal’ is connected to more anodic metal through a wire. The anodic metal undergoes corrosion slowly, while the base metal is protected. The corroded anode is called sacrificial anode, and it is replaced by a fresh one. The commonly used anodic metals are magnesium, aluminium and their alloys.

Application:

To protect marine structures and ship-hulls, which are made of steel are connected to a sacrificial anode, which undergoes corrosion leaving the base metal protected.



(a) Unprotected metal being corroded
(b) Sacrificial anodic protection
(c) Protection of ship-hull below water line by

Electroplating *(or electrodeposition):*

Definition:

The process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution, containing the soluble salt of the coating metal is called “electroplating”.

Objectives of electroplating:

(1) ***On metals:***

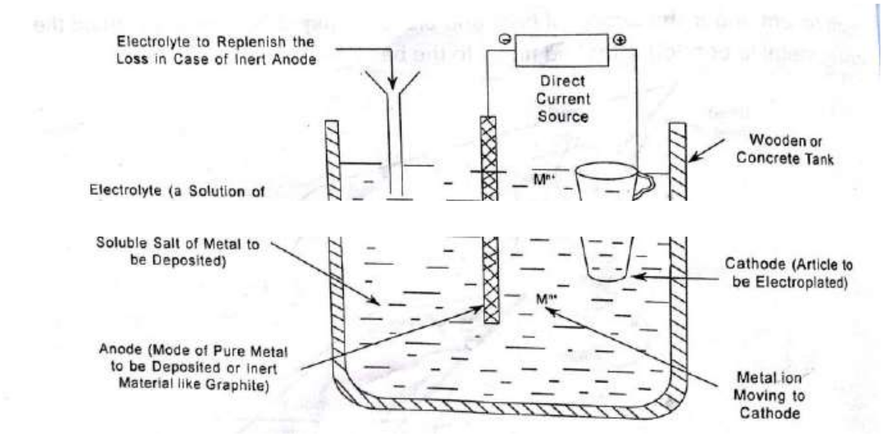
i) To increase the resistance to corrosion of the plated metal.
ii) To increase the resistance to chemical attack and wear resistance.
iii)To improve physical appearance and hardness.
iv)To improve the surface properties.
v) To increase the decorative and commercial values of the metal.

(2) ***On non-metals:***

i) For increasing strength.
ii) For preservation and decoration of the surfaces of non-metals like plastics and wood.
iii)For making the surface conductive by utilization of light-weight plastics.

Process:

In this process the base metal is made cathode and the coating metal is made anode or an inert material of good electrical conductivity is also used as anode. A direct current is passed through the electrolytic solution. If anode is made of graphite, the electrolytic salt is added continuously to maintain the proper coating metal ion concentration in the electrolyte bath.



The article to be electroplated is subjected to solvent cleaning by trichloroethylene to remove oil, greases etc. Then it is subjected to acid pickling with dil HCl or dil H_2SO_4 to remove any scales, oxides etc. The cleaned article is made cathode of the electrolytic cell and the anode can be made of the pure coating metal or graphite.The electrodes were dipped in the salt solution of the coating metal, which acts as an electrolyte. When direct current is passed, the coating metal ions migrate to the cathode and deposit on the base metal article in the form of a thin layer. For brighter and smooth deposits, conditions like low temperature, medium current density, and low metal ion concentration are used.

For example for electroplating of nickel on iron article, the following conditions are maintained.

1. Electrolytic bath solution : nickel sulphate, nickel chloride and boric acid.
2. pH maintained : 4.0 by boric acid buffer.
3. Operating temperature : 40-70$_0$C
4. Current density : 20-30 mA/cm$_2$
5. Additive agent : Saccharin/coumarin derivatives.
6. Cathode : metal article to be plated.
7. Anode : nickel pellets/pieces taken in a titanium mesh basket.

Applications:

- Electroplating is a most important and frequently used technique in industries to produce metallic coating. Both metals and non-metals can be electroplated.

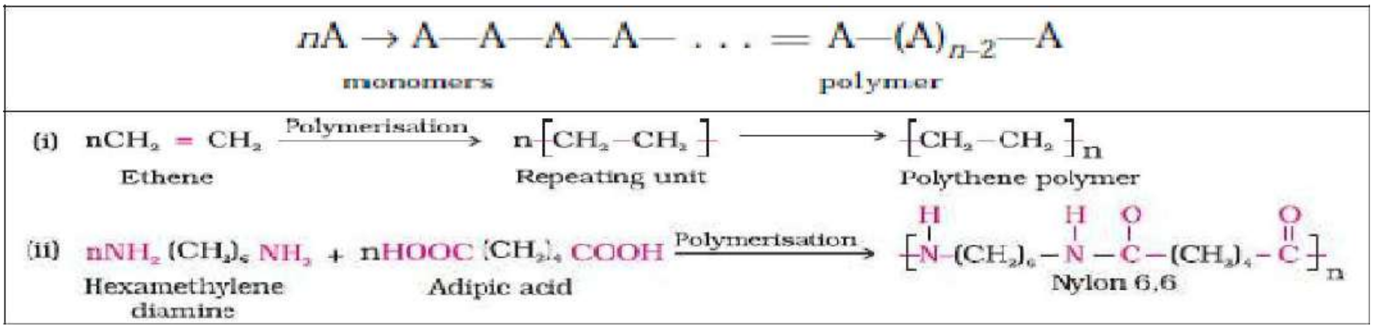
- In metals the electroplating increases resistance to corrosion, chemical attack, hardness, wear resistance, and surface properties.
- In non-metals electroplating increases strength and decorates the surface of non-metals like plastic.

UNIT III

POLYMERS

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

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



Monomers

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

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

Degree of polemerization (DP).

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

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

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

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

Molecular weight of the polythene = DP X Molecular weight of Polethene
= 100 X 28=**2800.**

Basic Concepts:

1.Functionality

The ***functionality of a monomer*** is the number of sites it has for bonding to other monomers under the given conditions of the polymerization reaction. Thus, a bifunctional monomer, i.e., monomer with functionality two, can link to two other molecules under suitable conditions.

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

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

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

$H_2C{=}CHX \rightarrow$ --- CH_2 – CHX ------

A). When the functionality of monomer is two bifunctional linear (or) straight chain polymer is formed.
Ex: (a)vinyl monomers (b)adipic acid (c)hexamethylene diamine
Example for polymer: HDPE (high density polythene)

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

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

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

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

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

2. Nomenclature of Polymers

Polymers are classified in to four types
a) Homo Polymers b) Hetero polymers c) Homo chain Polymers d) Hetero chain polymers

a) Homo Polymers : Polymers made up of with same type of monomers are called homo polymers
eg: Poly ethylene, PVC

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

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

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

N N
N N
N N

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

d) Hetero chain polymers: If the main chain consists of different type of atoms called Hetero chain Polymers

eg: Polyester, Nylon-6. –C-O-C-O-C-O-C-O-

Copolymers

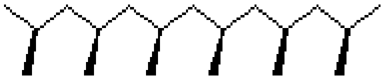
Homopolymer from a single monomer, copolymer from two (or more) monomers

chain copolymerization (different monomers incorporated during the growth of the polymer chain) can lead to:

alternating copolymer – ABABABABABABABABABABABA
block copolymer - AAAAAAAABBBBBBBBBBBBAAA
random copolymer - BAABBAABABBABABBBAABBAB
graft copolymer - branches of a different polymer are attached to a polymer chain
AAAAAAAAAAAAAAAAAAAAAAAAABBBBBBBBBBBBBBBBBB
(generate reactive site on existing polymer chain, grow new chain)

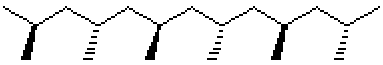
3. Tacticity – The difference in configuration due to the orientation of different functional groups with respect to the main chain is called tacticity. It is of three types

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

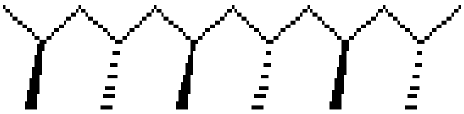


b) .Syndiotactic - If all the functional groups are arranged in the alternative fashion of main chain is

called Syndiotactic



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



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

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

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

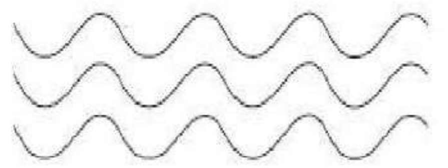
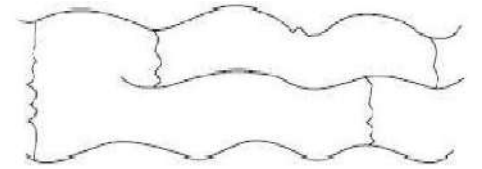
Classification Based on Backbone of the polymer chain: *Organic and Inorganic Polymers:*

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

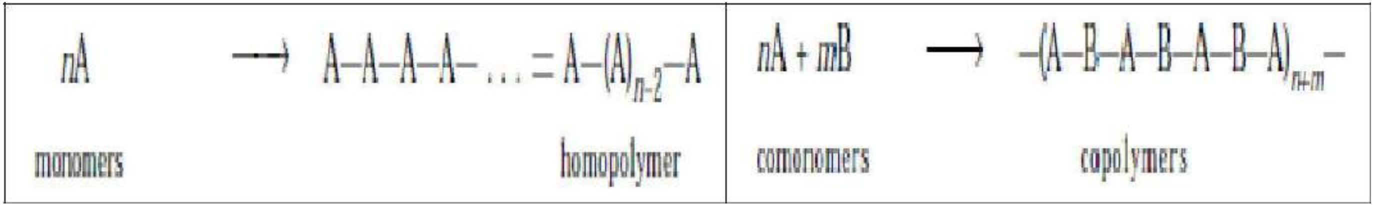
Classification Based on Structure of Polymers: [1] ***Linear Polymers***: These polymers consist of long and straight chains. The examples are high density polythen, PVC, etc.

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

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

		
Linear Polymers	Branched Polymers	Cross-linked Polymers

Classification Based on Composition of Polymers: [1] ***Homopolymer:*** A polymer resulting from the polymerization of a single monomer; a polymer consisting substantially of a single type of repeating unit.
[2] ***Copolymer:*** When two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer.

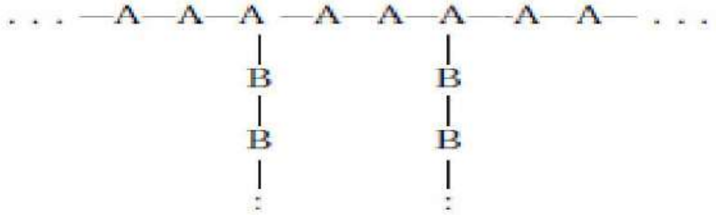


$$nA \longrightarrow A-A-A-A-\ldots = A-(A)_{n-2}-A$$

$$nA + mB \longrightarrow -(A-B-A-B-A-B-A)_{n+m}-$$

Lets imagine now two monomers(A and B) are made into a copolymer in many different ways

In an **alternating copolymer**, the two monomers are arranged in an alternating fashion
In a **random copolymer** the two monomers may follow in any order.
In a **block copolymer** all of one type of monomers are grouped together , and all of the other are grouped together
In **graft copolymer**, a block copolymer can be thought of as two homopolymers joined together at the ends: branched copolymers with one kind of monomers in their main chain and another kind of monomers in their side chains.

Alternating	—A—B—A—B—A—B—A—B—A—B—A—B—A—B—
Random	—A—A—B—A—B—B—A—B—A—A—B—B—B—A—
Block	—A—A—A—A—A—A—A—B—B—B—B—B—B—B—
Graft	

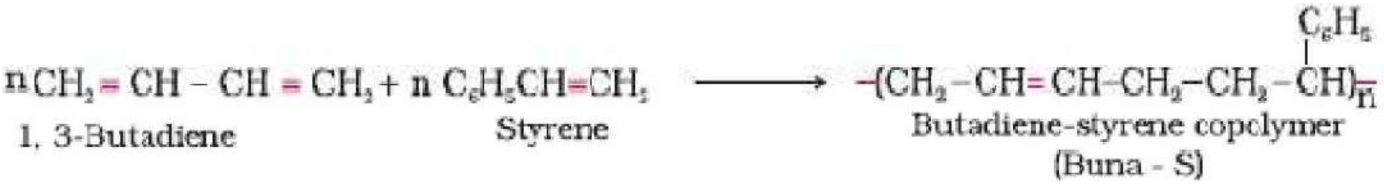
Copolymerization: A ***heteropolymer*** or ***copolymer*** is a polymer derived from two (or more) monomeric species, as opposed to a homopolymer where only one monomer is used. Copolymerization refers to methods used to chemically synthesize a copolymer. Commercially relevant copolymers include ABS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

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

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

$$\underset{\text{Ethene}}{n\,CH_2=CH_2} \longrightarrow \underset{\text{Polythene}}{-\!\!\left(CH_2-CH_2\right)\!\!-_n} \ \text{Homopolymer}$$

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



$$\underset{\text{1, 3-Butadiene}}{n\,CH_2=CH-CH=CH_2} + \underset{\text{Styrene}}{n\,C_6H_5CH=CH_2} \longrightarrow \underset{\substack{\text{Butadiene-styrene copolymer}\\\text{(Buna - S)}}}{-\!\!\left(CH_2-CH=CH-CH_2-CH_2-\overset{\overset{C_6H_5}{|}}{C}H\right)\!\!-_n}$$

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

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

Nylon 6, 6

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

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

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

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

Liquid Resins: Polymers used as adhesives, potting compound sealants, etc. in a liquid form are described liquid resins. Examples are epoxy adhesives and polysulphide sealants.

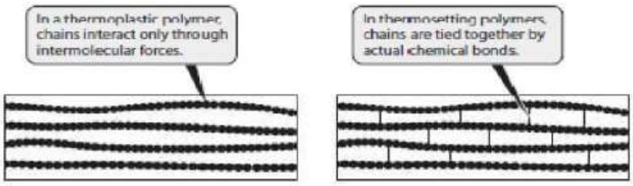
Plastics
: A polymer is shaped into hard and tough utility articles by the application of heat and pressure; it is used as a 'plastic'. Typical examples are polystyrene, PVC

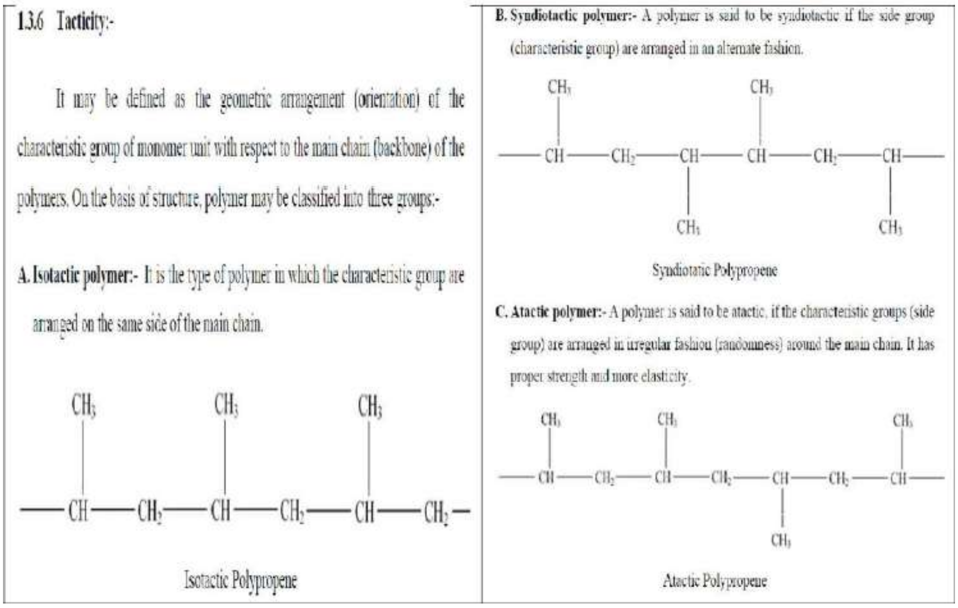
and polymethyl methacrylate.

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

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

Thermosetting Polymers: Some polymers, on the other hand, undergo some chemical change on heating and convert themselves into an infusible mass. They are like the yolk of egg, which on heating sets into a mass, and, once set, cannot be reshaped. Such polymers, that become infusible and insoluble mass on heating, are called ‘thermosetting” polymers. These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.





1.3.6 Tacticity:-

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

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

Isotactic Polypropene

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

Syndiotatic Polypropene

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

Atactic Polypropene

Types of Polymerization

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

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

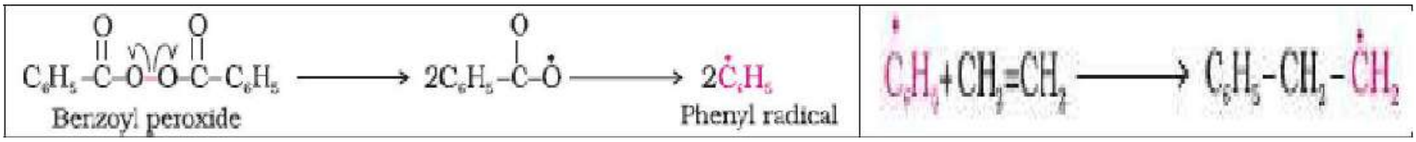
In the ***Initiation step*** an initiator molecule is thermally decomposed or allowed to undergo a chemical reaction to generate an "active species." This "active species," which can be a free radical or a cation or an anion, then initiates the polymerization by adding to the monomer's carbon-carbon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

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

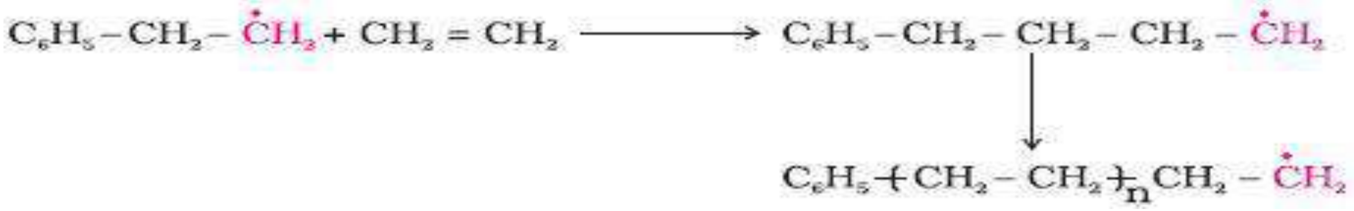
The mechanism of addition polymerisation can be divided broadly into two main classes, Free radical and Ionic polymerization and again Ionic is divided into two types Cationic and anionic Polymerisations

Free radical polymerization: A variety of alkenes or dienes and their derivatives are polymerised in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. A free radical may be defined as an intermediate compound containing an odd number of electrons, but which do not carry an electric charge and are not free ions. For example, the polymerization of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide initiator.

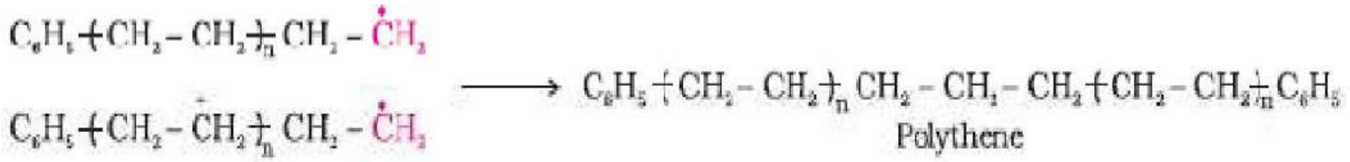
The first stage of the chain reaction is the ***initiation process***; this process starts with the addition of phenyl free radical formed by the peroxide to the ethene double bond thus generating a new and larger free radical.


$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2C_6H_5-\overset{O}{\overset{|}{C}}-\dot{O} \longrightarrow 2\dot{C}_6H_5$; $\dot{C}_6H_5+CH_2=CH_2 \longrightarrow C_6H_5-CH_2-\dot{C}H_2$

The second stage of the chain reaction is the ***propagation process***, the radical reacts with another molecule of ethene, and another bigger sized radical is formed. The repetition of this sequence with new and bigger radicals carries the reaction forward and the step is chain propagating step


$C_6H_5-CH_2-\dot{C}H_2+CH_2=CH_2 \longrightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2 \longrightarrow C_6H_5(CH_2-CH_2)_nCH_2-\dot{C}H_2$

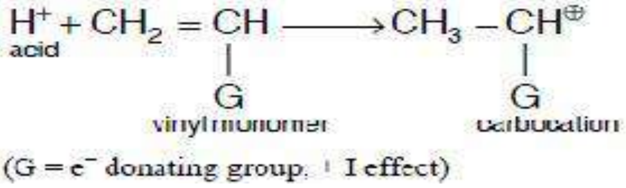
The final stage of the chain reaction is the ***termination process***; the product radical formed reacts with another radical to form the polymerised product.


$C_6H_5(CH_2-CH_2)_nCH_2-\dot{C}H_2 + C_6H_5(CH_2-CH_2)_nCH_2-\dot{C}H_2 \longrightarrow C_6H_5(CH_2-CH_2)_nCH_2-CH_2-CH_2(CH_2-CH_2)_nC_6H_5$

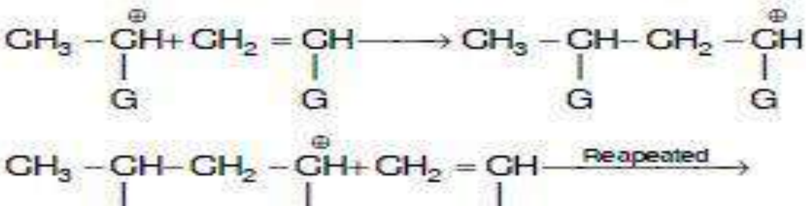
Ionic Polymerisation: The addition polymerization that takes place due to ionic intermediate is called ionic polymerization. Based on the nature of ions used for the initiation process ionic polymerization classified into two types; (a) Cationic polymerization and (b) Anionic polymerization

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

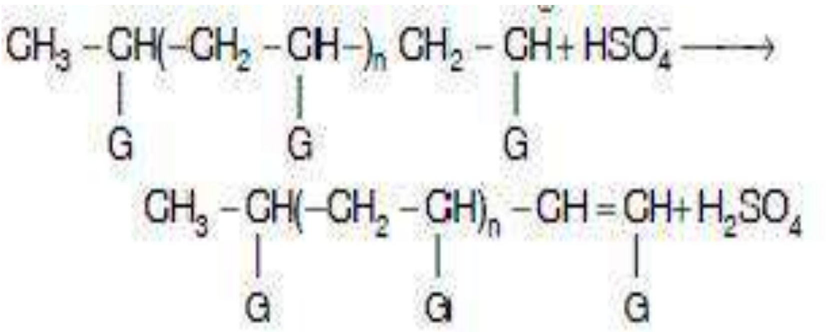
***i) Chain Initiation*:** Decomposition of the initiator is shown as $BF_3 + H_2O \rightarrow \mathbf{H^+} + BF_3(OH^-)$. The proton ($\mathbf{H^+}$) adds to C – C double bond of alkene to form stabl e carbocation.


$H^+ + CH_2=\underset{\underset{G}{|}}{CH} \longrightarrow CH_3-\underset{\underset{G}{|}}{CH^{\oplus}}$

***ii*) Chain Propagation:** Carbocation add to the C – C double bond of another monomer molecule to from new carbocation.


$CH_3-\underset{\underset{G}{|}}{\overset{\oplus}{C}H}+CH_2=\underset{\underset{G}{|}}{CH} \longrightarrow CH_3-\underset{\underset{G}{|}}{CH}-CH_2-\underset{\underset{G}{|}}{\overset{\oplus}{C}H}$

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



$$CH_3-\underset{G}{\underset{|}{CH}}(-CH_2-\underset{G}{\underset{|}{CH}}-)_n\,CH_2-\underset{G}{\underset{|}{\overset{+}{CH}}}+HSO_4^- \longrightarrow CH_3-\underset{G}{\underset{|}{CH}}(-CH_2-\underset{G}{\underset{|}{CH}})_n-CH=\underset{G}{\underset{|}{CH}}+H_2SO_4$$

Anionic polymerization depends on the use of anionic initiators which include reagents capable of providing negative ions. Typical catalysts include sodium in liquid ammonia, alkali metal alkyls, Grignard reagents and triphenylmethyl sodium [$(C_6H_5)_3C$-Na]. They are effective with monomers containing electron withdrawing groups like nitrile (–CN) or chloride (-C*l*), etc. They include acrylonitrile [CH_2=C(CN)], vinyl chloride [CH_2=C(C*l*)], methyl methacrylate [CH_2=C(CH_3)$COOCH_3$], etc.

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

where W is electron withdrawing group

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

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

Coordination polymerization: It is also a subclass of addition polymerization. It usually involve transition-metal catalysts. Here, the "active species" is a coordination complex, which initiates the polymerization by adding to the monomer’s carbon-carbon double bond. The most important catalyst for coordination polymerization is so-called Ziegler-Natta catalyst discovered to be effective for alkene polymerization. Ziegler-Natta catalysts combine transition-metal compounds such as chlorides of titanium with organometallic compounds [$TiCl_3$ with $Al(C_2H_5)_3$]. An important property of these catalysts is that they yield stereoregular polymers when higher alkenes are polymerized, e.g., polymerization of propene produces polypropene with high selectivity. Branching will not occur through this mechanism since no radicals are involved; the active site of the growing chain is the carbon atom directly bonded to the metal.

Zeigler-Nata catalysts: These are a special type of coordination catalysts, comprising two components, which are generally referred to as the catalyst and the cocatalyst. The catalyst component consists of chlorides of titanium ($TiCl_3$ and $TiCl_4$) and the cocatalysts are organometallic compound such as triethyl aluminium ($Al(C_2H_5)_3$).

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

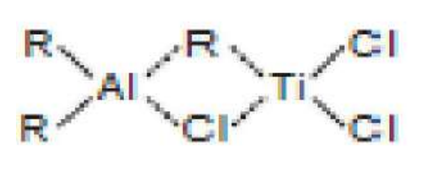
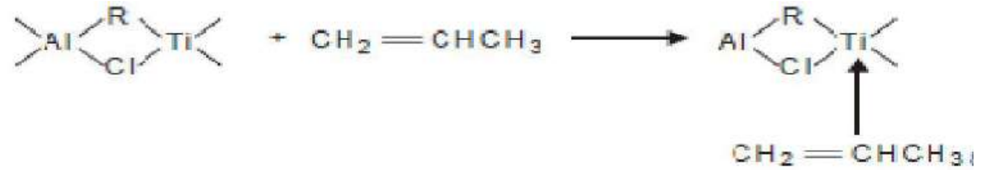
	

Figure. 1	Figure. 2

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

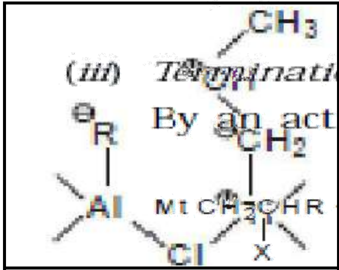
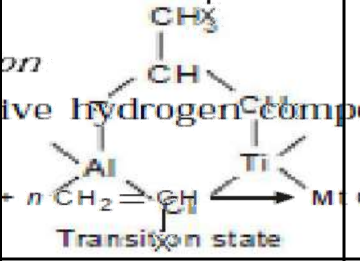
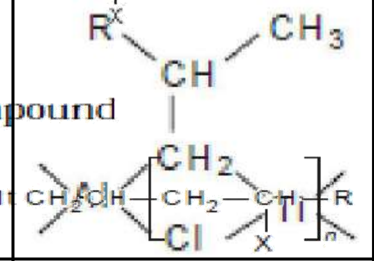
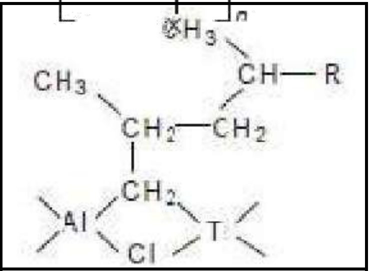
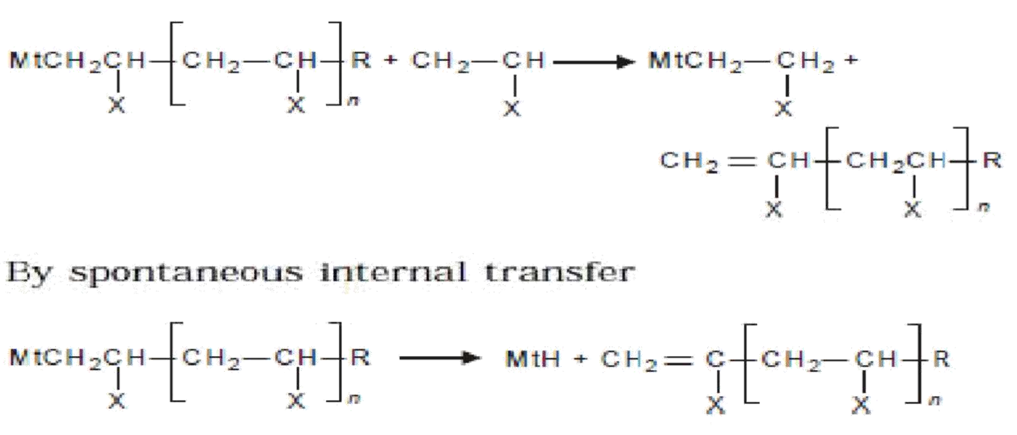
			

Figure. 3	Figure. 4	Figure. 5	Figure. 6



$$MtCH_2\underset{X}{C}H\left[CH_2-\underset{X}{C}H\right]_nR + CH_2-\underset{X}{C}H \longrightarrow MtCH_2-\underset{X}{C}H_2 + CH_2=\underset{X}{C}H\left[CH_2\underset{X}{C}H\right]_nR$$

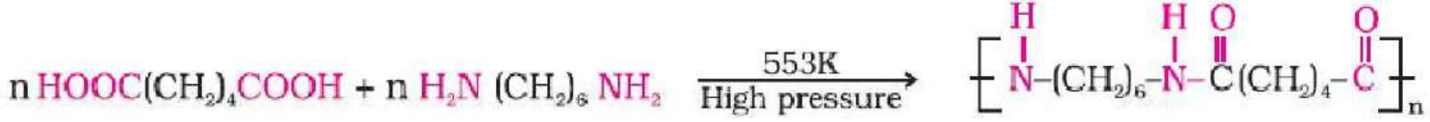
$$MtCH_2\underset{X}{C}H\left[CH_2-\underset{X}{C}H\right]_nR \longrightarrow MtH + CH_2=\underset{X}{C}\left[CH_2-\underset{X}{C}H\right]_nR$$

Condensation Polymerisation: This type of polymerisation generally involves a repetitive condensation reaction (two molecules join together, resulting loss of small molecules) between two bi-functional monomers. These polycondensation reactions may result in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers. In these reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on. Since, each step produces a distinct functionalised species and is independent of each other; this process is also called as step growth polymerisation. The type of end polymer product resulting from a condensation polymerization is dependent on the number of functional end groups of the monomer which can react.

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

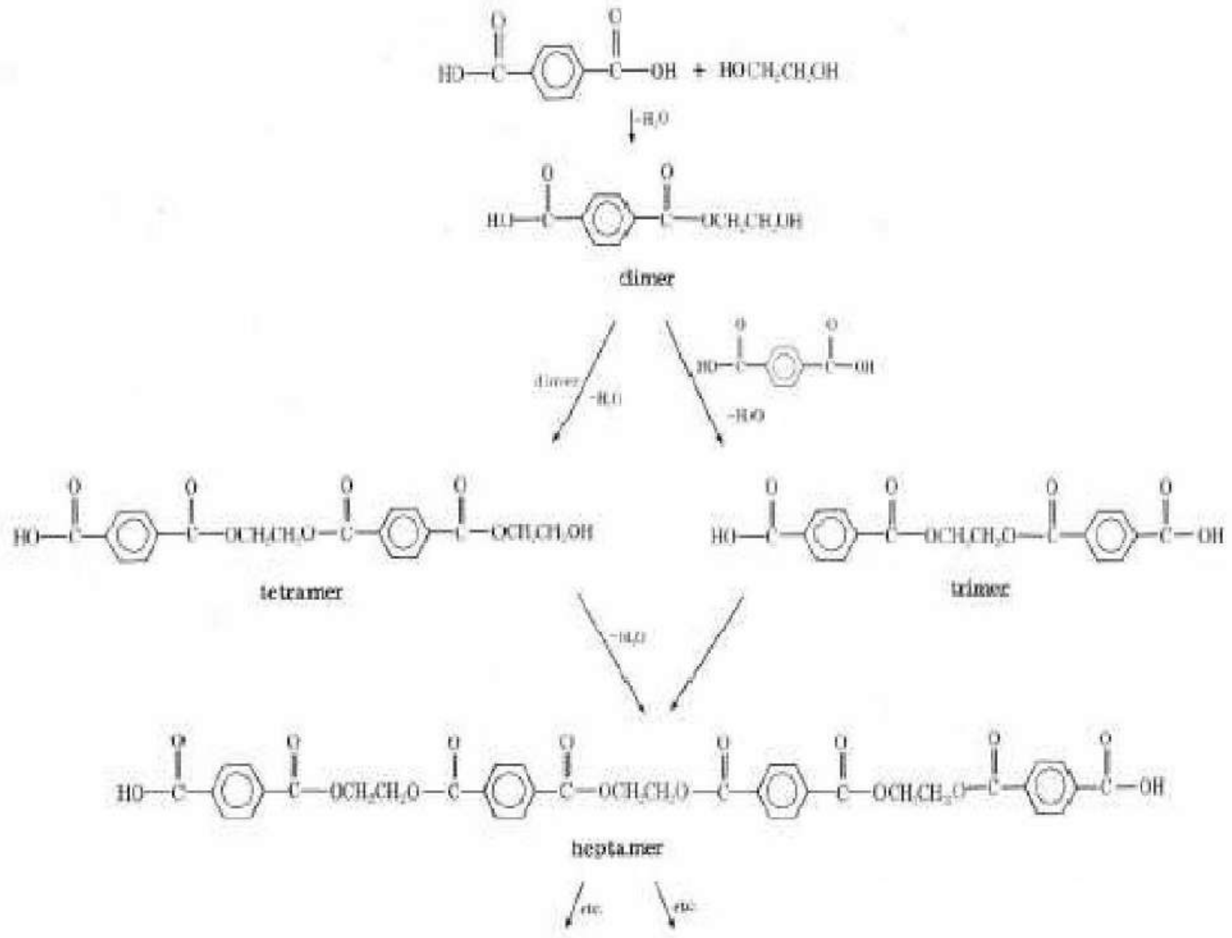
Polyester is created through ester linkages between monomers, which involve the functional groups carboxyl and hydroxyl (an organic acid and an alcohol monomer). The formation of polyester like terylene or dacron by the interaction of ethylene glycol and terephthalic acid is an example of this type of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

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



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

This type of polymerization normally employs two bifunctional monomers that are capable of undergoing typical organic reactions. For example, a diacid can be allowed to react with a diol in the presence of an acid catalyst to afford polyester. In this case, chain growth is initiated by the reaction of one of the diacid's carboxyl groups with one of the diol's hydroxyl groups. The free carboxyl or hydroxyl group of the resulting dimer can then react with an appropriate functional group in another monomer or dimer. This process is repeated throughout the polymerization mixture until all of the monomers are converted to low molecular weight species, such as dimers, trimers, tetramers, etc. These molecules, which are called oligomers, can then further react with each other through their free functional groups. Polymer chains that have moderate molecular weight can he built in this manner.



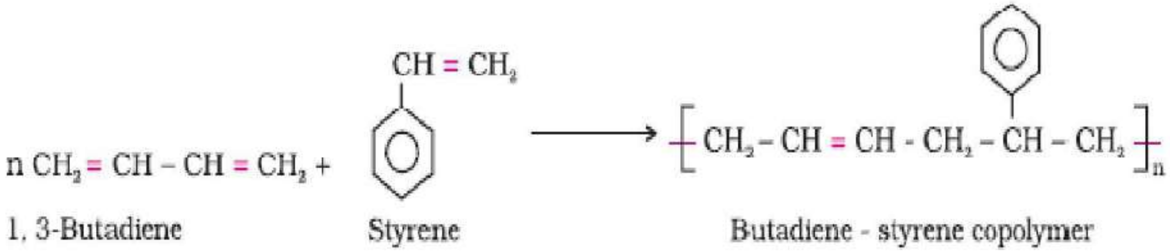
The following are several general characteristics of this type of polymerization

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

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

Copolymerization: It is a polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerize and form a copolymer. The copolymer can be made not only by chain growth polymerisation but by step growth polymerisation also. It contains multiple units of each monomer used in the same polymeric chain. For example, a mixture of styrene and 1, 3 – butadiene can form a copolymer called styrene butadiene rubber (SBR).

A reaction in which a mixture of two (or) more monomers is allowed to undergo polymerisation is known as copolymerization. The polymer is known as copolymer.



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

Plastics(Plastomers)

Plastics are the high polymers that can be molded by the application of heat and pressure. During molding process, there is no chemical change. The plastics have linear structure.

Examples: Polythene, polyvinyl chloride, polystyrene, nylons, polyesters.

Thermoplastics

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

Thermoplastics –1. These are formed by addition polymerisation

2. It consists of linear polymer chains with negligible cross-linking are soft and less brittle.
3. These are soluble in organic solvents.
4. soften on heating and hence are amenable for moulding into any shape in the hot condition on cooling, the resin becomes hard and rigid and retains the moulded shape.
5. These can be reheated and moulded into any other shape reversibly any number of times without any change in the chemical nature.

Thermosetting polymers or, Thermosets:

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

Thermosets (Thermosetting resins):

1. Are mostly formed by condensation polymerisation.
2. Are mostly branched polymer chains with potential to form a 3-dimensional structure.
3. become hard and rigid on heating during moulding process. are not soluble in common organic solvents.
4. Exhibit their characteristic properties of non-softening and non-swelling nature, hardness and brittleness.
5. Cannot be softened, reformed, reshaped once they are set. cannot be reclaimed from wastes.

Differences Between Thermoplastics and Thermosettingplastics

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

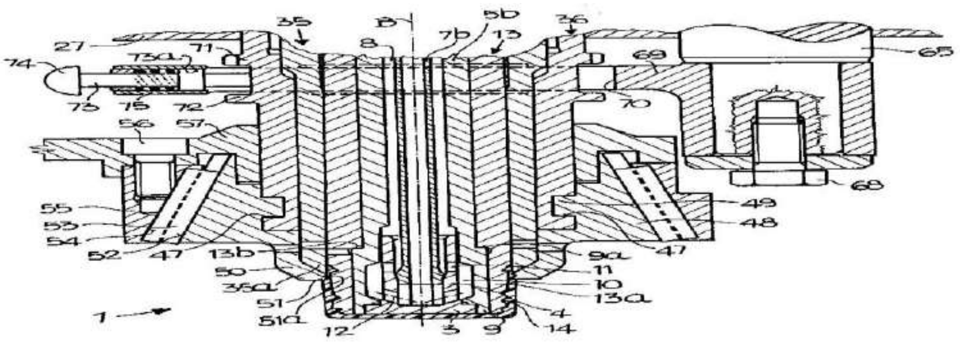
4	They soften on heating and stiffen on cooling	They do not soften on heating.
5	Low molecular weight thermoplastics are soluble in their suitable solvents.	They are insoluble in any solvent.
6	They can be remoulded, re-shaped and re-used.	They can be reclaimed from waste i.e., they can be recycled
7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

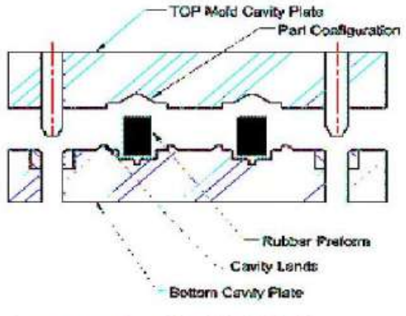
Moulding of Plastics

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

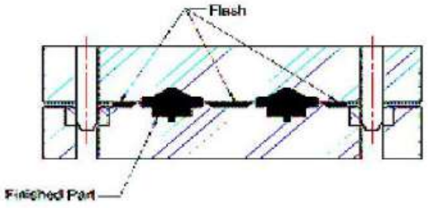
i) Compression moulding:

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





Compression Mold - OPEN

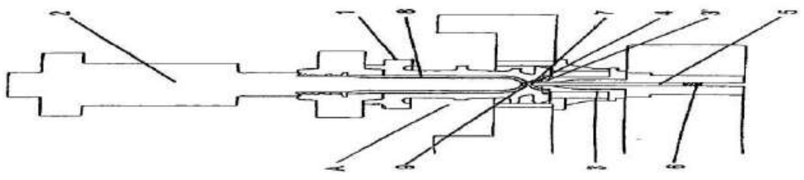


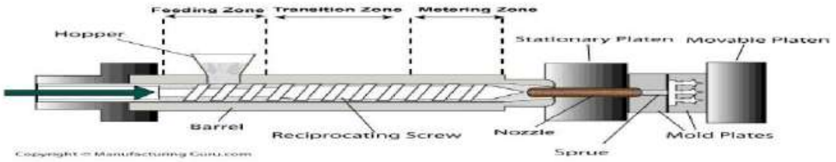
Compression Mold - CLOSED

ii) Injection moulding:

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

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





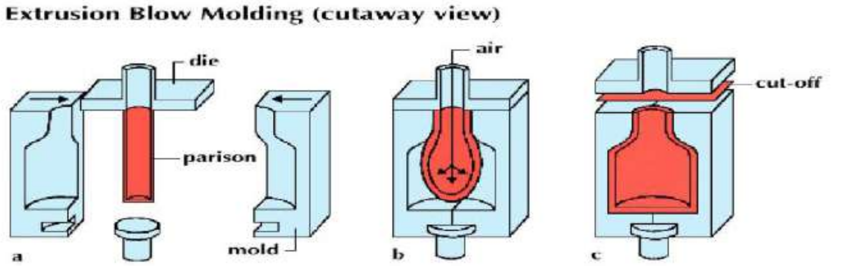
iii) Transfer moulding:

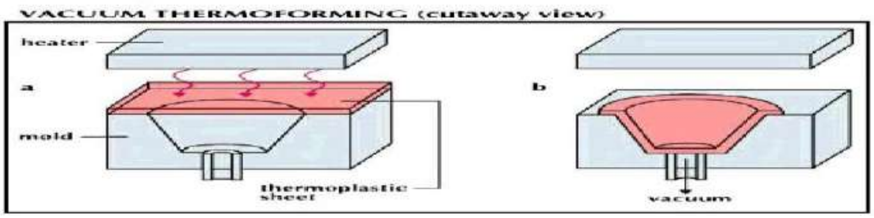
In this method, the principle is like injection moulding. The moulding powder is heated in a chamber to become plastic. Later it is injected into a mould by plunger working at high pressure through orifice. Due to this heat is developed and the plastic melts, takes the shape of the mould.

iv) Extrusion moulding:

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

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





Preparation, properties and engineering applications of some plastomers

1. Bakelite:

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

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

i) Nova lacks.

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

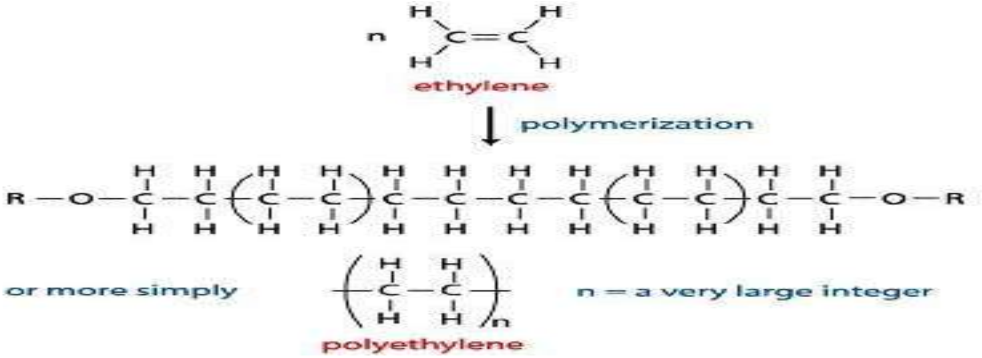
Properties.

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

Uses: Phenol formaldehyde resins are used for

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

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



Properties:

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

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

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

PVC :

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

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

$$\underset{\text{Acetylene}}{CH = CH} + HCl \text{--------}\rightarrow \underset{\text{Vinyl chloride}}{CH2 = CH\ Cl}$$

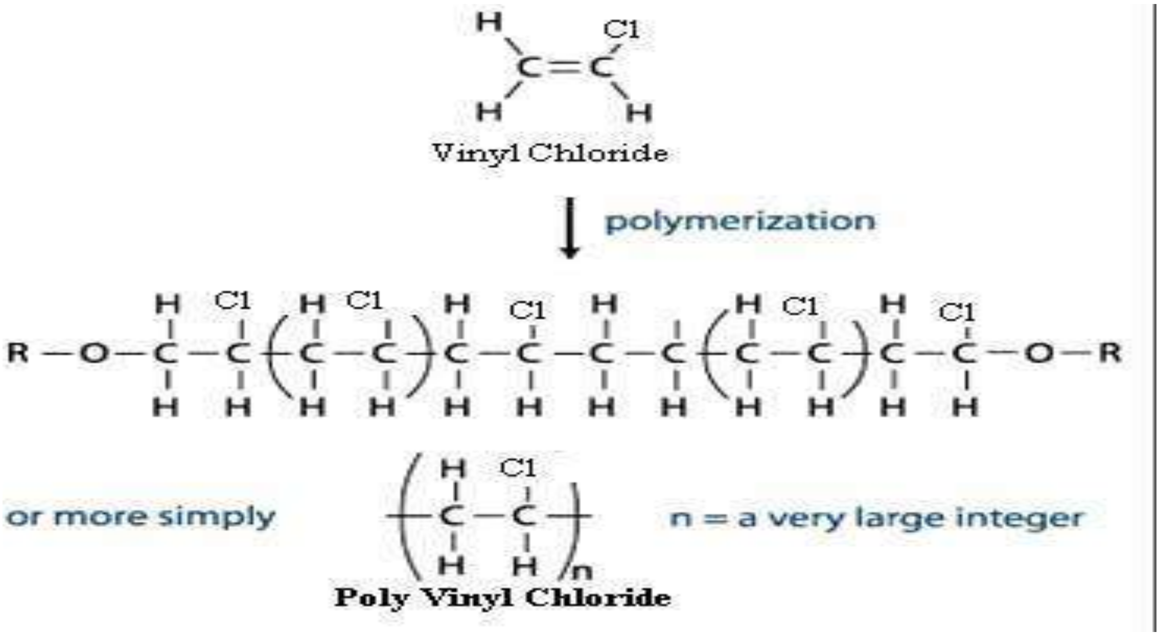
Properties:

1.It occurs as a colourless rigid mater
2. It is having high density and low softening point.
3.It is resistant to light, atmospheric oxygen, inorganic acids and alkalis.
4.It is most widely used synthetic plastic.

Uses:

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

2.It is used for manufacturing of film, sheet and floor covering.
3.PVC pipes are used for carrying corrosive chemicals in petrochemical factories.



Nylon:

Synthetic fiber forming polyamides are termed as ‘Nylons’.

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

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

2. Nylon 6.6 is also used in mechanical engineering for well known applications like gears, bearings, bushes, cans etc.,
3. Mouldings have application in medicine and pharmacy because of sterilisability.
4. Durable but costly hair combs.
5. Nylon 6.6 is also used for facketing electrical ware to provide a tough, abrasion resistant outer cover to protect the primary electrical insulation.
6. Nylon 6 is mainly used for making tyre cords.
7. Nylon 6.10 is suitable for monofilaments that are used for bristles, brushes etc.,
8. Glass reinforced Nylon plastics are used in housings and cosings of domestic

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

Nylon-6,6:

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

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

Uses:1.Nylon-6,6 is mainly used for moulding purposes for gear bearings and making car tyres, used for fibres etc.

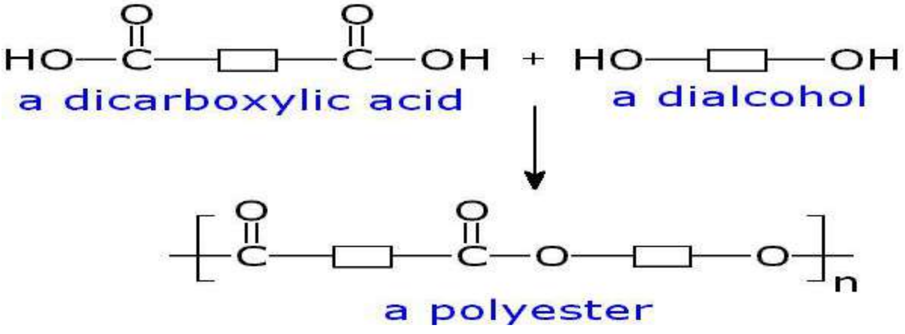
2.This is mainly used in manufacture of tyre cord. Other uses include manufacture of carpets, rope, fibre cloth etc.

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

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

POLYESTER

Terylene is a polyester fibre made from ethylene glycol and terephthalicacid. Terephtalic acid required for the manufacture of Terylene is produced by the catalytic atmospheric oxidation of p-xylene.



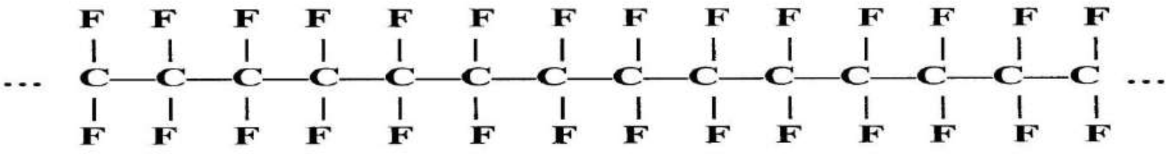
Properties: **1.**This occurs as a colourless rigid substance.
2. This is highly resistant to mineral and organic acids but is less resistant to alkalis.
3. This is hydrophobic in nature. This has high melting point due to presence of aromatic ring.

Uses: 1.It is mostly used for making synthetic fibres.
2. It can be blended with wool, cotton for better use and wrinkle resistance.
3. Other application of polyethylene terephthalate film is in electrical insulation.

TEFLON OR Poly tetra fluoro ethylene:

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

Properties:1. Due to the presence of highly electronegative fluorine atoms and the reqular configuration of the polytetrafluoro ethylene molecule results in very strong attractive forces between the different chains.
2. These strong attractive forces give the material extreme toughness, high softening point,
3. exceptionally high chemical-resistance towards all chemicals, high density, waxy touch, and very low coefficient of friction,
4. extremely good electrical and mechanical properties: It can be machined, punched and drilled.
5. The material, however, has the disadvantage that it cannot be dissolved and cannot exist in a true Molten state.
6. Around 350^0c, it sinters to form very viscous, opaque mass, which can be moulded into certain forms by applying high pressures.



TEFLON polymer (segment)

Uses: **1.**as insulating material for motors, transformers, cables, wires, fittings, etc,

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

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

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

Natural rubber:

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

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

Deficiencies of natural rubber:

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

They are –

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

Vulcanization:

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

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

Advantages of vulcanization:

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

Vulcanization:

Vulcanization discovered by Charles Goodyear in 1839.

It consists of heating the raw rubber at 100 – 140^0C with sulphur. The combine chemically at the double bonds of different rubber spring and provides cross-linking between the chains. This cross-linking during vulcanization brings about a stiffening of the rubber by anchoring and consequently preventing intermolecular movement of rubber springs. The amount of sulphur added determines the extent of stiffness of vulcanized rubber. For example, ordinary rubber (say for battery case) may contain as much as 30% sulphur.

Compounding of rubber:

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

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

The principal additives used in compounding are
a) Fillers b) Plasticizers c) Lubricants d) Accelerators e) colouring agents f) Vulcanising agents

ELASTOMERS

Definition: Elastomers are high polymers that undergo very long elongation (500 – 1000%) under stress, yet regain original size fully on released of stress.

The property of elastomers is known as elasticity. This arises due to the coiled structure of elastomers.

Characteristics of Elastomers:

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

Buna – S or STYRENE RUBBER:

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

$$nCH_2 = CH - CH = CH_2 + n\,CH_2 = CH - Ph \text{ ------> } -(-H_2C - CH = CH - CH -- CH_2 - CH - Ph-)_n-$$

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

Properties:

1. Styrene rubber resembles natural rubber in processing characteristics as well as quality of finished products.
2. It possesses high abrasion-resistance, high load-bearing capacity and resilience.
3. However, it gets readily oxidized, especially in presence of traces of ozone present in the atmosphere.
4. Moreover, it swells in oils and solvents.
5. It can be vulcanized in the same way as natural rubber either by sulphur or sulphur monochloride (S_2Cl_2).
6. However, It requires less sulphur, but more accelerators for vulcanization.

Uses:

1. Mainly used for the manufacture of motor tyres.
2. Other uses of these elastomers are floor tiles, shoe soles, gaskets, foot-wear components, wire and cable insulations, carpet backing, adhesives, tank-linings, etc.

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

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

$$mCH2{=}CH{-}CH{=}CH2\ +\ nCH2{=}CH{-}CN \xrightarrow{\text{Copolymerization}} -(-CH2-CH{=}CH-CH2-)m-(CH2-CH(CN)-)n-$$

1,3-Butadiene Acrylonitrile Poly butadiene co-crylonitrile

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

Properties:

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

USES:

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

Butyl rubber:

Preparation:

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

Properties:

1. Under normal conditions, it is amorphous but it crystallizes on stretching.
2. It is quite resistant to oxidation due to low degree of unsaturation. Due to very low unsaturation, it can be vulcanized but it cannot be hardened much.
3. It can be degraded by heat or light to sticky low-molecular weight products so stabilization is must.
4. Being non-polar, it has good electrical insulation properties.
5. Compared to natural rubber it possesses outstanding low permeability to air and other gases.
6. It does not crystallize on cooling and hence remains flexible down to $-50^{o}C$

7. Because of its hydrocarbon nature, butyl rubber is soluble in hydrocarbon solvents like benzene but has excellent resistance to polar solvents like alcohol, acetone and ageing chemicals (ex: HCl, HF, HNO_3, H_2SO_4 etc.)

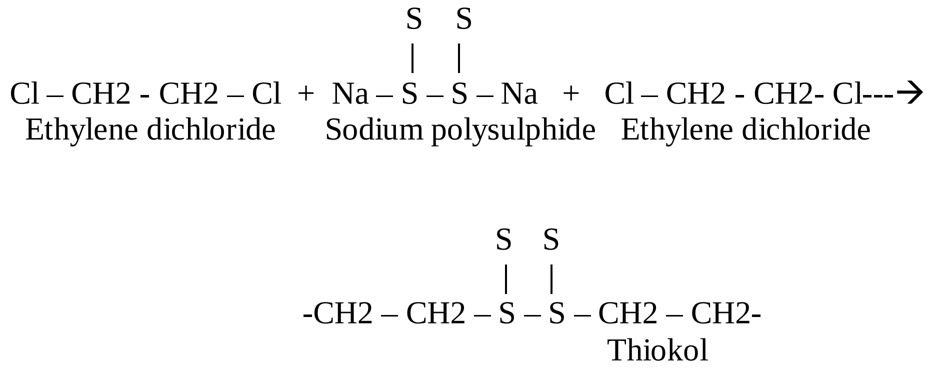
USES:

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

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

Thiokol :

This also called as polysulphide rubber (or Gr-P). It can be prepared by the condensation polymerization of sodium polysulphide (Na_2S_x) and ethylene dichloride.



$$\mathrm{Cl-CH_2-CH_2-Cl} + \mathrm{Na-\overset{\overset{S}{|}}{S}-\overset{\overset{S}{|}}{S}-Na} + \mathrm{Cl-CH_2-CH_2-Cl} \longrightarrow$$

Ethylene dichloride   Sodium polysulphide   Ethylene dichloride

$$\mathrm{-CH_2-CH_2-\overset{\overset{S}{|}}{S}-\overset{\overset{S}{|}}{S}-CH_2-CH_2-}$$

Thiokol

USES:

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

POLY URETHANES RUBBERS:

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

$$n[\mathrm{OH-(CH_2)_2-OH+O=C=N-(CH_2)_2-N=C=O}] \dashrightarrow [\mathrm{-O-(CH_2)_2-O-(CO)-NH-(CH_2)_2-NH-(CO)-}]_n$$

Properties:

1. Polyurethanes are highly resistant to oxidation, because of their saturated character.
2. They also show good resistance to many organic solvents, but are attacked by acids and alkalis, especially concentrated and hot.
3. The polyurethane foams are light, tought and resistant to heat, abrasion, chemicals and weathering

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

Silicone resins:

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

Preparation: reacting silicon with alkyl halide or silicon halide with Grignard reagent. The reaction product is fractionally distilled to get different organo-silicon chlorides, which are then polymerized by carefully controlled hydrolysis.

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

Characteristics of silicones:

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

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

Uses:

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

Conducting polymers:

Definition: A polymer that can conduct electricity is known as conducting polymer.
Classification: Conducting polymers can be classified as follows.

I) Intrinsically conducting polymers:

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

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

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

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

Applications of Conducting Polymers:-

than convensional lead storage batteries.

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

In non-linear optical materials.

10. In molecular wi

res and molecular switches.

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

Antimony oxide – Crimson

Compounding of rubber:

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

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5. To make the polymer products more pleasing and colourful. They should be cheap and sufficient in their functions.
6. They should be stable under processing and service conditions.
7. They should not impart taste or odour.
8. They should be non-toxic for food grade application of final compound after processing.
9. They should not adversely affect the properties of polymer.

Chromic oxide - Green

The principal additives used in compounding are

1) Softners and Plasticisers 2) Vulcanising Agents 3) Antioxidants 4) Accelerators
5) Fillers 6) Colouring Matter

1. **SOFTNERS AND PLASTICISERS**: These are added to give greater plasticity and flexibility to reduce the brittleness of the products eg. waxes, stearic acid and vegetable oils.
2. **VULCANISING AGENTS:** When rubber is heated with sulphur , its tensile strength,elasticity and resistance to swelling are increased.The sulphur atoms chemically bond with double bonded carbons of rubber chains and bring about excellent changes in their properties.The percentage of sulphur added variles from 0.15 to 32%. S_2Cl_2,H_2S, H_2O_2, benzoyal chloride etc., are other vulcanizing agents.
3. **ANTIOXIDANTS:** Natural rubber has tendency for oxidation. Antioxidants like phenyl naphthyl-amine and phosphites are added for preventing the oxidation of rubber.

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

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

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

Titanium oxide- White

Ferric oxide – Red

Lead chromate – Yellow

FUEL TECHNOLOGY

Definition

A fuel is defined as naturally occurring or artificially manufactured combustible carbonaceous material which serves particularly as source of heat and light and also in few cases as a source of raw material.

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Classification of fuels Fuels are classified into a two types.

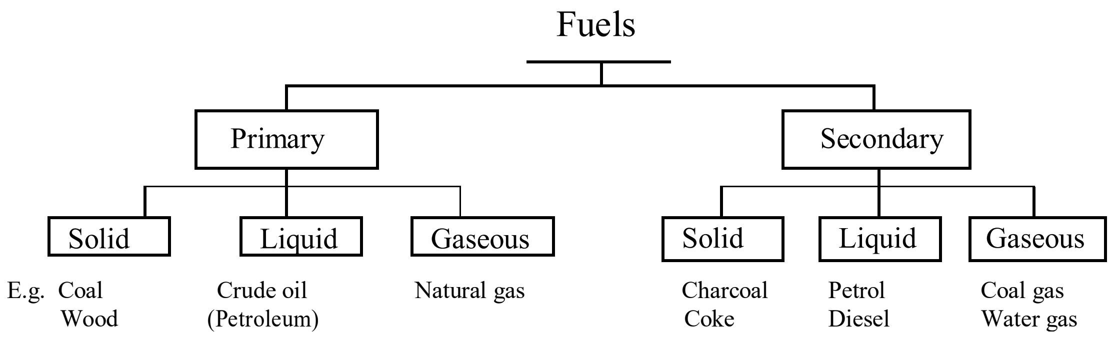
1) Based on their origin they are classified into
   a) Primary fuels
   b) Secondary fuels.

a) **<u>Primary Fuels</u>:** There are naturally occurring fuels which serves as source of energy without any chemical processing.
Ex: Wood, Coal, Crude oil, Natural gas, Peat, Lignite, Anthracite.

b) **<u>Secondary Fuels</u>: -** They are derived from primary fuels & serves as source of energy only after subjecting to chemical processing.
Ex: Charcoal, Coke, produsergas, Petrol, Diesel etc.,

Bases on their physical state fuel are classified into

a) Solid
b) Liquid
c) Gaseous fuels.



Liquid Fuels:

Liquid fuels are the important commercial and domestic fuels used in our daily life. Most of these fuels are obtained from the naturally occurring petroleum or crude oil called as primary fuel.

Advantages:

(a) They posses higher calorific value per unit mass than solid fuels.
(b) They burn without dust, ash, clinkers, etc.
(c) Their firing is easier and also fire can be extinguished easily by stopping liquid fuel supply.
(d) They are easy to transport through pipes.
(e) They can be stored indefinitely without any loss.
(f) They are clean in use and economic to handle.
(g) Loss of heat in chimney is very low due to greater cleanliness.
(h) They require less excess air for complete combustion.
(i) They require less furnace space for combustion.

Disadvantages:

(a) The cost of liquid fuel is relatively much higher as compared to solid fuel.
(b) Costly special storage tanks are required for storing liquid fuels.
(c) There is a greater risk of five hazards, particularly, in case of highly inflammable and volatile liquid fuels.
(d) They give bad odour.
(e) For efficient burning of liquid fuels, specially constructed burners and spraying apparatus are required.

Petroleum (crude oil)***:***

The crude oil or petroleum is also known as rock oil or mineral oil. It is dark colour liquid found well deep in the earth. It is mainly composed of hydrocarbons which may be solids, liquids or gases. Some optically active compounds having S and N are also present. On the average the composition of Petroleum is;

C = 79.5 – 87.1%
H = 11.5 – 14.8%
S = 0.1 – 3.5%
N and O = 0.1 – 0.5%

Refining of petroleum:

Crude oil obtained from the mine is not fit to be marketed. It contains a lot of soluble and insoluble impurities, which must be removed. Previously the purification of crude oil is done by simple fractional distillation. Further treatment of the products is done by refining.

Definition:

"The process by which petroleum is made free of impurities, followed by the separation of petroleum into different fractions having different boiling points, and their further treatment to impart specific properties" can be called as Refining of petroleum.

Various stages during the refining process are explained below

1. Removal of solid impurities.
2. Removal of water.
3. Removal of harmful impurities.
4. Fractional distillation.

1. Removal of solid impurities:

The crude oil is a mixture of solid, liquid and gaseous substances. This is allowed to stand undisturbed for some time, till the heavy solid particles settle down and gases evaporate. The supernant liquid is then centrifuged where in the solids get removed.

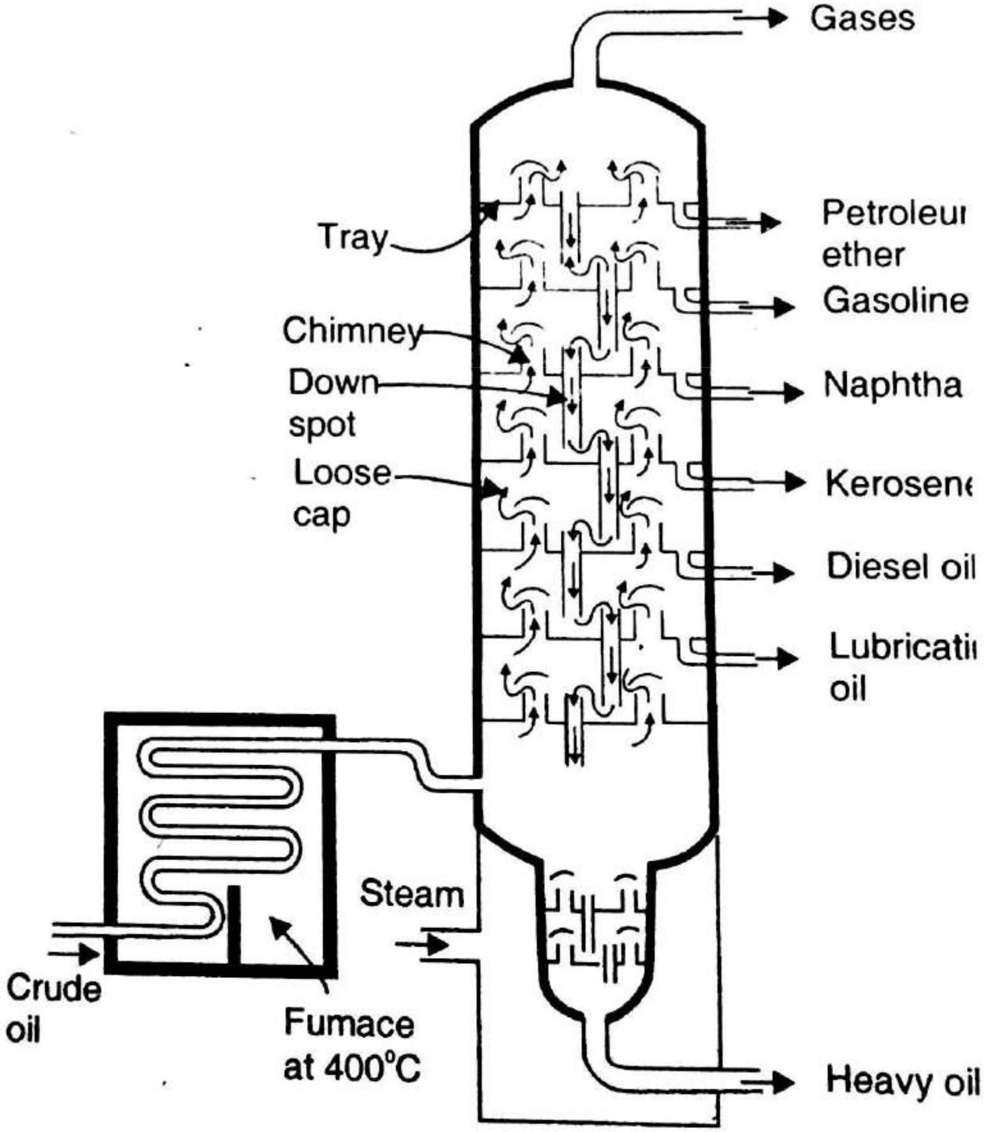
2. Removal of water by Cottrell's process:

The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine. This mixture, when passed between two highly charged electrodes, destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and get separated out from the oil.

3. Removal of harmful impurities:

In order to remove sulphur compounds in the crude oil, it is treated with copper oxide. Then, the sulphur compounds get converted to insoluble copper sulphide, which can be removed by filtration Substances like NaCl and $MgCl_2$, if present will corrode the refining equipment and result in scale formation. These can be removed by techniques like electric desalting and dehydration

Fractional distillation:



The crude oil is fractionally distilled in a fractionating still, which is a tower like structure having a bubble tower laid inside. The crude oil or the petroleum enters through the bottom of the still by an inlet. This is made to pass through a pre-heater or it can heated with steam inside the still to a temperature of about 400_0C. As we move to the top fractionating still the temperature goes on decreasing. A number of side pipes are fitted at different heights of the column or still, to collect the fractions. As petroleum enters the still, it gets vaporized and the vapours move up the bubble tower. The bubble tower consists of number of horizontal trays, and each tray is provided with a number of small chimneys through which the vapours rise. The chimneys are covered with loose caps so that the vapours bubble through and get condensed, dropping back into the trays. So as the vapours go up, they become cooler and cooler and fractional condensation of the crude oil takes place at different levels of the bubble tower.

The vapours of the liquid having the highest boiling point are the first to condense and go out and those which have the lowest boiling points go last, along with the uncondensed gases. The constituents of each fraction and the temperature at which they are obtained is given in the table.

Name of fraction	***Boiling range***	***Composition***	***Uses***
1. Uncondensed gases	Below 30_0C	C_1 to C_4	As domestic or industrial fuel under the name L.P.G.
2. Petroleum ether	30 – 70_0C	C_5 to C_7	As a solvent
3. Gasoline or petrol(11,250 kcal/kg)	40 – 120_0C	C_5 to C_9	As a motor fuel in I.C. engine
4. Naphtha (11,000 kcal/kg)	120 – 180_0C	C_9 to C_{10}	As a solvent in dry cleaning
5. Kerosene oil (11,100 kcal/kg)	180 – 250_0C	C_{10} to C_{16}	As domestic fuel and jet engine fuel
6. Diesel oil	250 – 320_0C	C_{10} to C_{18}	Diesel engine fuel
7. Heavy oil This on refraction gives; (a) Lubricating oil (b) Petroleum jelly (Vaseline) (c) Grease (d) Paraffin wax	320 – 400_0C	C_{17} to C_{30}	As lubricant In cosmetics and medicines. As lubricant In candles and wax paper
8. Residue may be either; (a) Asphalt Or	Above 400_0C	C_{30} and above	Water proofing of roofs As a fuel

(b) Petroleum coke			

Synthetic petrol:

Petrol can be synthesised by any of the following methods.

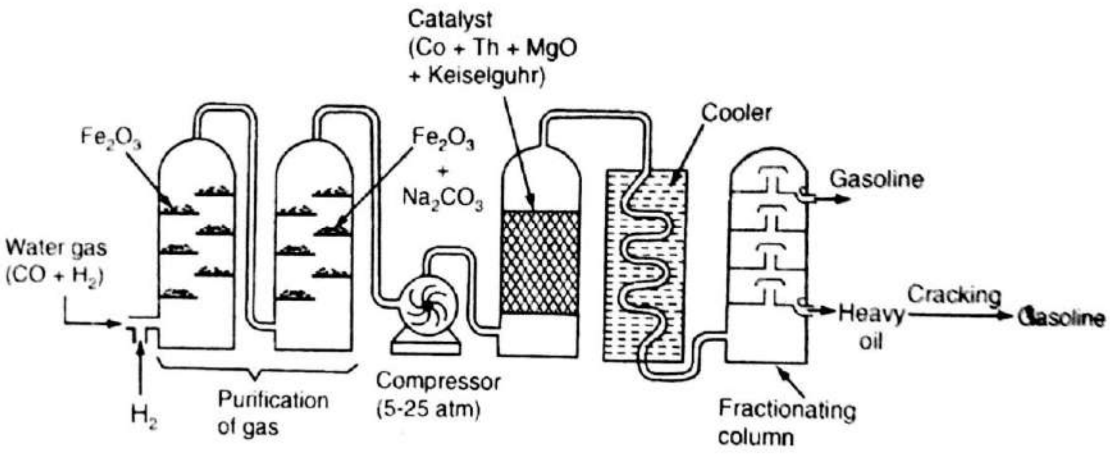
1. Fischer – Tropsch method.

2. Bergius process.

Fischer – Tropsch method:

Water gas ($CO + H_2$), produced by passing steam over heated coke, and is mixed with hydrogen. The gas is purified by passing through Fe_2O_3 to remove H_2S and then into a mixture of Fe_2O_3. Na_2CO_3 to remove organic sulphur compounds. The purified gas is compressed to 5 to 25 atm and then led through a converter, containing a catalyst.

Catalyst: It consists a mixture of 100 parts of Cobalt, 5 parts of thoria, 8 parts of magnesia, and 200 parts of keiselguhar earth. It maintained at about 200- 300^{o}C.



Then a mixture of saturated and unsaturated hydrocarbons results as follows;

$$n\,CO + 2n\,H_2 \text{--------}\rightarrow C_nH_{2n} + n\,H_2O$$

$$n\,CO + (2n+1)\,H_2 \text{--------}\rightarrow C_nH_{2n+2} + n\,H_2O$$

The reaction is exothermic, so out coming hot gaseous mixture is led to a cooler, where a liquid resembling crude oil is obtained. The crude oil thus obtained is then fractionated to yield (i) gasoline and (ii) heavy oil. The heavy oil is reused for cracking to get more gasoline.

Bergius process:

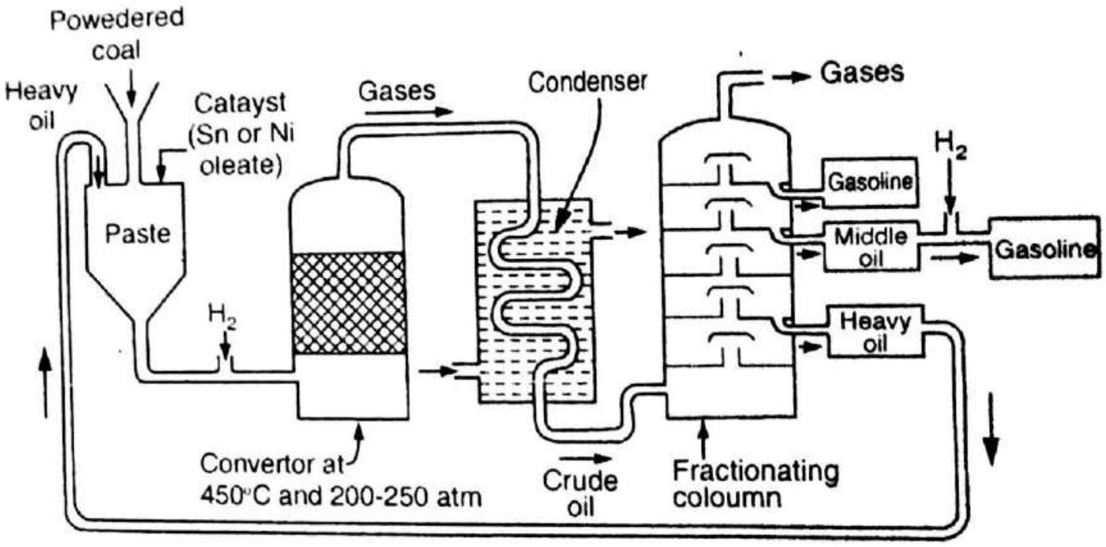
1. The low ash coal is finely powdered and made into a paste with heavy oil and then a catalyst composed of tin or nickel oleate is incorporated

2. The whole is heated with hydrogen at 450$_o$C and under a pressure 200-250 atm for about 1.5 hours, during which hydrogen combines with coal to form saturated hydrocarbons, which decompose at prevailing high temperature and pressure to yield low boiling liquid hydrocarbons.

3. The issuing gases are lead to condenser, where a liquid resembling crude oil is obtained, which is then fractionated to get (i) gasoline (ii) middle oil (iii) heavy oil.

4. The heavy oil is used again for making paste with fresh coal dust.

5. The middle oil is hydrogenated in vapour-phase in presence of a solid catalyst to yields more gasoline.



Gaseous fuels:

Gaseous fuels occur in nature, besides being manufactured from solid and liquid fuels.

The advantages and disadvantages of gaseous fuels are given below :

Advantages:

Gaseous fuels due to erase and flexibility of their applications, possess the following advantages over solid or liquid fuels :

(a) They can be conveyed easily through pipelines to the actual place of need, thereby eliminating manual labour in transportation.

(b) They can be lighted at ease.

(c) They have high heat contents and hence help us in having higher temperatures.

(d) They can be pre-heated by the heat of hot waste gases, thereby affecting economy in heat.

(e) Their combustion can readily by controlled for change in demand like oxidizing or reducing atmosphere, length flame, temperature, etc.

(f) They are clean in use.

(g) They do not require any special burner.

(h) They burn without any shoot, or smoke and ashes.

(i) They are free from impurities found in solid and liquid fuels.

Disadvantages:

(a) Very large storage tanks are needed.

(b) They are highly inflammable, so chances of fire hazards in their use are high.

Some important gaseous fuels:

Here we are going to discuss about the following gaseous fuels.

1. Natural gas 2.Water gas 3. Producer gas 4. Bio gas

5.Liquid Petroleum Gas(L.P.G.)

1. Natural gas:

It is obtained from the wells dug in the earth during mining of petroleum. It is mainly composed of methane and small quantities of ethane along with other hydrocarbons.

If the lower hydrocarbons are present, the gas is called dry gas or lean gas, but if the hydrocarbons having the higher molecular weights are present the gas is known as rich gas or wet gas.

The calorific value of this gas varies from 12000 to 14,000 kcal/m^3

Composition:

Methane – 88.5% Ethane – 5.5%
Propane – 3.7% Butane – 1.8%
Pentane, hydrogen, CO and higher hydrocarbons – 0.5%

Uses:

1. It is an excellent domestic fuel and can be conveyed over very large distances in pipelines.
2. It has recently been used in the manufacture of a number of chemicals by synthetic processes like carbon black, ammonia, methanol and formaldehyde.
3. Methane on microbiological fermentation gives synthetic proteins which are used as animal feed.
4. It is also used for generation of electricity in fuel cells as a source of hydrogen.

Producer gas: ($CO + N_2 + H_2$)

It is a mixture of combustible gases, carbon monoxide and hydrogen associated with large percentageof non-combustible gases, N_2, CO_2 etc.

Composition:

CO – 22 to 30% N_2 – 52 to 55% H_2 – 8 to 12% CO_2 – 3%

Preparation:

It is prepared by passing air mixed with little steam (about 0.35 kg/kg of coal) over a red hot coal or coke bed maintained at about 1100^{o}C in a special reactor called ‘gas producer’. It consists of a steel vessel about 3 m in diameter and 4 m in height. The vessel is lined inside with fire bricks. It is provided with a cup and cone feeder at the top and a side opening for the exit of producer gas. At the base it has an inlet for passing air and steam. The producer at the base is also provided with an exit for the ash formed.

LPG (Liquified Petroleum Gas)

Nowadays LPG has been a common fuel for domestic work and also in most of the industries. The main components of LPG or cooking gas are n-butane, isobutene, butylene and propane (traces of propene and ethane).The hydrocarbon are in gaseous state at room temperature and at atmospheric pressure but can be liquified under higher pressures. The gas can be compressed under pressure in containers and sold under trade names like Indane, Bharat, Petroleum gas, HP gas, etc.

LPG is kept in metallic cylinder attached with burner through pipe. It has two stoppers, one at the cylinder and other at burner. LPG has special odour due to the presence of organic sulphides which are added specially for safety measure. The gas is obtained from natural gas or as a by-product in refineries during cracking of heavy petroleum products.

Characteristics of LPG:

1. It has high calorific value: 27800 kcal/m$_3$, it is colourless.
2. It gives less CO and least unburnt hydrocarbons. So it causes least pollution.
3. It gives moderate heat which is very good for cooking.
4. Its storage is simple. It is colourless.
5. It has the tendency to mix with air easily.
6. Its burning gives no toxic gases though it is highly toxic.
7. It neither gives smoke nor ash content.
8. It is cheaper than gasoline. It burns with little air pollution and leaves no solid residue. Hence, it is used as fuel in auto vehicles also.
9. It is dangerous when leakage is there. It is highly knock resistant.
10. LPG can be extracted from natural gases and also from refining of crude oil. Cryogenic process is best for the extraction for natural gas.

Advantages of LPG:

1. LPG is used as domestic fuel and as a fuel for internal combustion engines.
2. It is used as a feedstock for the manufacture of various chemicals and olefins by pyrolysis.
3. LPG is used in industries as portable blow lamps, welding, annealing, hardening, steelcuttings, etc.

Knocking:

In an internal combustion engine, a mixture of gasoline vapour and air is used as a fuel. After the initiation of the combustion reaction, by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture, thereby the expanding gas drives the piston down the cylinder.The ratio of the gaseous volume in the cylinder at the end of the suction-stoke to the volume at the end of compression-stoke of the piston, is known as the ‘compression ratio’.

The efficiency of an internal combustion engine increases with the increase in compression ratio, which is dependent on the nature of the constituents present in the gasoline used. In certain circumstances (due to the presence of some constituents in the gasoline used), the rate of oxidation becomes so great that the last portion of the fuel-air mixture gets ignited instantaneously, producing an explosive violence, known as “knocking”. The knocking results in loss of efficiently.

Chemical structure and knocking:

The tendency of fuel constituents to knock is in the following order.

Straight-chain paraffins > Branched-chain paraffins > olefins > Cyclo-paraffins > Aromatics

Thus olefins of the same carbon chain length possess better anti-knock properties than the corresponding paraffins and so on.

The knocking is maximum in open chain straight paraffins and least in aromatics. Therefore a fuel to be called a good fuel for the internal combustion engine should have least knocking.

Antiknocking agents

These are the substances added to petrol in order to prevent knocking in I.C. Engines.

Ex:	TEL	Tetra Ethyl led.
	TML	Tetra Methyl led.
	MTBE	Methyl Tertiary Butyl Ether.

Leaded Petrol:

The petrol containing TEL or TML as anti knocking agents is called leaded petrol. TEL or TML are the very good anti knocking agents but has some disadvantages as follows.

a) After combustion lead is deposited as lead oxide on piston and engine walls it leads to mechanical damage.
b) Lead is a poisonous air pollutant.
c) It spoils the catalyst used in catalytic converter.

Unleaded Petrol:

The petrol, which contains antiknocking agent other than lead, is known as unleaded petrol.

Ex: MTBE is used, as an antiknocking agent in place of TEL or TML and the petrol is known as unleaded petrol.

octane number.

Octane number is defined as the percentage of isooctane present in a standard mixture of isooctane and n-heptane, which knocks at the same compression ratio as the petrol being tested.

Isooctane is the branched chain hydrocarbon has least knocking rate, hence its octane number is arbitrarily fixed as 100. N-heptane a straight chain hydrocarbon has highest tendency to knock hence its octane number is fixed as zero. Octane number of petrol is 80 means it contains 80% by volume isooctane and 20% by volume n- heptane.

Cetane number.

It is defined as the percentage of cetane present in standard mixture of a cetane and Alfa- methylnaphthalene, which knocks at the same compression ratio as the diesel fuel being tested.

Power alcohol

A mixture of ethyl alcohol and gasoline blend, which can be used as fuel in internal combustion engine, is known as power alcohol or gasohol.

Absolute alcohol is mixed with ether, benzene etc compounds and one volume of this is mixed with four volumes of petrol and is used as a fuel.

Advantages:

1. The power out put is good.
2. It has better antiknock property.
3. Ethanol is biodegradable; hence it is environmental friendly fuel.
4. The use of ethanol in alcohol increases the oxygen content of the fuels and promotes more and complete combustion of hydrocarbons in gasoline.
5. It reduces carbon monoxide emission.

Calorific value

Calorific value is defined as the amount of heat liberated when a unit mass of fuel is burnt completely in presence of air or oxygen.

Calorific value is of two types as follows:-

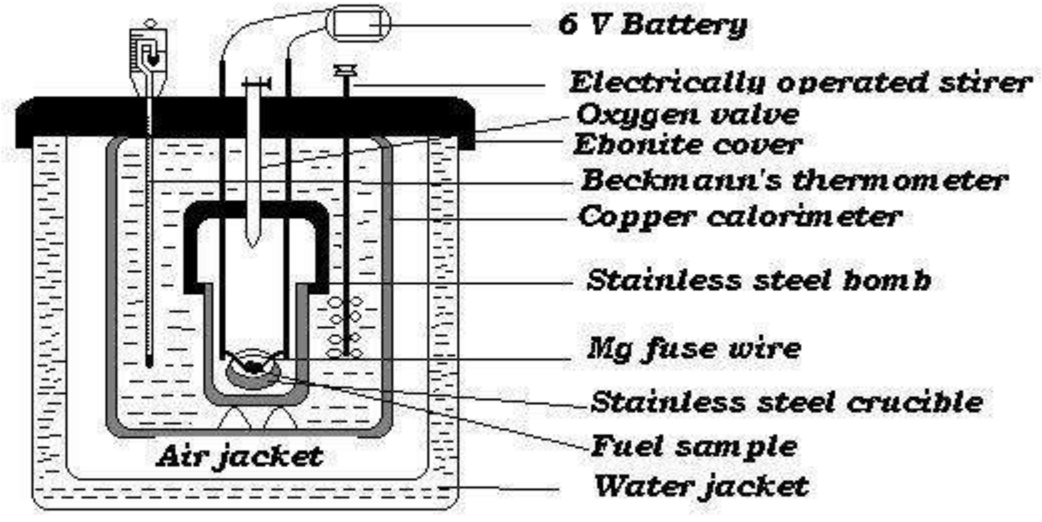
1) Higher calorific value. (HCV) or Gross calorific value. (GCV)
2) Lower calorific value. (LCV) or Net calorific value. (NCV)

1) HCV: - It is the amount of heat liberated when a unit mass of fuels burnt completely in the presence of air or oxygen and the products of combustion are cooled to room temperature. Here it includes the heat liberated during combustion and the latent heat of steam. Hence its value is always higher than lower calorific value.

2) LCV: **-** It is amount of heat liberated when a unit mass of fuel is burnt completely in the presence of air or oxygen and the product of combustion are let off completely into air. It does not include the latent heat of steam. Therefore it is always lesser than HCV.

NCV = HCV – Latent heat of steam.
= HCV –0.09X % H_2 X 587 cal/g

Determination of calorific value of solid fuel using Bomb Calorimetric method



Bomb Calorimeter

A small quantity of a fuel is weighed accurately (M Kg) and is placed in the Bomb. The bomb is placed in known amount water taken in a copper calorimeter. The initial temp of water is noted as a $t_1{}^0C$ with the help of thermometer. Oxygen gas is pumped under pressure 20 to 25 atm through the O_2 valve provided.

The fuel is ignited by passing electric current through the wires provided. As the fuel undergoes combustion and liberates heat, which is absorbed by surrounding water. The water is stirred continuously to distribute the heat uniformly and the final temp attained by water is noted $t_2{}^0C$. & gross calorific value of the fuel is calculated as follows

Calculation:

Mass of the fuel = M Kg.
Initial temp of the water = $t_1{}^0C$
Final temp of the water = $t_2{}^0C$
Change in temp = $\Delta t = (t_2 - t_1)^0$ C
Specific heat of water = S
Water equivalent of calorimeter = W Kg.

$$GCV = \frac{W \times S \times t \Delta}{M} \quad J/Kg \qquad \text{or}$$

$$GCV = \frac{(W+w) \times S \times \Delta t}{M} \quad J/Kg$$

$$NCV = GCV - 0.09 \times \%H_2 \times 587 \quad cal/g$$

PROBLEMS:

1) Calculate calorific value coal samples from the following data.

Mass of the coal = 1g.
Water equivalent of calorimeter = 2 Kg.
Specific heat of water = 4.187 J/Kg/c.
Rise of temperature = 4.8^0C.

SOLUTION:

$$GCV = \frac{W \times S \times \Delta t}{M} \; J/Kg$$

$$= \frac{2 \times 4.187 \times 4.8}{0.001}$$

$$= \mathbf{40195.2\ KJ/Kg}.$$

2) A coal sample with 93% carbon, 5% of Hydrogen and 2% Ash is subjected to combustion in a bomb calorimeter. Calculate GCV and NCV Given that. **6 Marks** Mass of the coal sample = 0.95g

Mass of water in copper calorimeter = 2000g.
Water equivalent wt of calorimeter = 700g.

Rise in temp = $2.8^{0}C$

Latent heat of = 587 cal/g. Specific heat

of water = 1 cal/g/^{0}C

$$GCV = \frac{(W+w) \text{ x } S \text{ x } \Delta t}{M}$$

$$= \frac{(2000+700) \text{ x } 10^{-3} \text{ kg x } 1 \text{ cal/g/}^{0}C \text{ x } 2.8^{0}C \text{ x } 4.184}{0.95 \text{ x } 10^{-3} \text{ kg}}$$

= 33295.83 J/kg.

NCV = GCV – 0.09 x %H_2 x 587x4.184 J/kg.

= 33295.83 J/kg – 0.09 x 5 x 587 x4.184 J/kg.

= **32190.62 J/kg**

3) When 0.84g of coal was burnt completely in Bomb calorimeter the increase in temp of 2655 grams of water was $1.85^{0}C$ if the water equivalent calorimeter is 156g Calculate GCV.

$$GCV = \frac{(W+w) \text{ x } S \text{ x } \Delta t}{M}$$

$$= \frac{(2655+156) \text{ x } 1.85 \text{ x } 10\text{-}3 \text{ x } 4.187}{0.84 \text{ x } 10\text{-}3}$$

= 25921.26 J/Kg

4) Calculate GCV and NCV of a fuel from the following data. Mass of fuel=0.75g, W=350g Δ t =$3.02^{0}C$, Mass of water = 1150, % H_2=2.8.

$$GCV = \frac{(W+w) \text{ x } \Delta t \text{ x } S}{M}$$

$$= \frac{(1150+350) \text{ x}10^{-}\text{x}^{3} \ 3.02 \text{ x } 4.184}{0.75 \text{ x } 10^{-3}}$$

GCV = **25271. 36 KJ/Kg**

NCV = GCV –0.09 x H x 587 x 4.184

= 25271.36 – 0.09 x 2.8 x 587 x 4.184

NCV = **24652.44 KJ/Kg**

5) Calculate calorific value of a fuel sample of a coal form the following data. Mass of the coal is 0.6g. Water equivalent wt of calorimeter is 2200g. Specific value 4.187 Kg/KJ/C rise in temperature = $6.52^{0}C$.

$$GCV = \frac{(W_1+W_2) \times S \times \Delta t}{M}$$

$$= \frac{(2200) \times 10\text{-}3 \times 4.184 \times 6.52}{0.6 \times 10\text{-}3}$$

= **100025.49 KJ/Kg**.

6) Calculate GCV and NCV of a fuel from the following data.

Mass of fuel =0.83g, W=3500g. , W = 385 g, t1 =29.2^{0}C, t_2 = 26.5$_{0}$C, % H_2 = 0.7 and S = 4.2 kj/kg/c

$$GCV = \frac{(W+w) \times \Delta t \times S}{M}$$

$$= \frac{(3.5 + 0.385) \times (29.2 - 26.5) \times 4.2}{0.83 \times 10^{-3}}$$

GCV = 53079.39 KJ/Kg

NCV = GCV –0.09 x H x 587 x 4.184

= 53079.39 – 0.09 x 0.7 x 587 x 4.2

NCV = **52924.07 KJ/Kg**

UNIT II

POLYMERS

Polymers

Polymers are the high molecular weight compounds obtained by repeated union of simple molecules. (Monomers).

Ex: Starch, Polyvinyl chloride, Polyethylene, Nylon 6, 6 and etc.

Classification of polymers.

Polymers are classified into two types as follows:

i) Natural Polymers.
ii) Synthetic (artificial) polymers.

i) Natural polymers: These are the polymers obtained naturally by plants and animals.

Ex: Silk, wool, natural rubber, protein, starch, cellulose, etc.

ii) Synthetic Polymers: These are artificially prepared polymers also known as man made polymers.
Ex: PVC, Nylon 6.6, Polythene, Phenol, Formaldehyde, Resin etc.,

Monomers

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

Ex: Vinyl chloride, ethene, propylene etc.

Polymerization

Polymerization is a process of chemical union of large number of monomers to form a polymer. During polymerization the monomers are linked through covalent leakages to give raise to polymer.

Based on the type of polymerization reaction, it is classified into two types as follows.

i) Addition Polymerization
ii) Condensation Polymerization

i) Addition Polymerization: It is process in which the monomers undergo simple addition reactions to give raise to a polymer without eliminating by products. Alkenes and substituted alkenes readily undergo addition polymerization reactions.

Ex: When large number of ethene molecules undergoes addition polymerization reactions, polyethylene polymer is obtained.

[redacted]

ii) Condensation Polymerization:- It is a process in which the monomers undergoes intermolecular condensation reactions to form a polymer with the elimination of simple molecules like water, HCl, ammonia, phenol etc.,

Ex: When adepic acid and hexamithylene diamine undergoes condensation polymerization reaction to form Nylon 6,6 polymer.

n.NH_2–$(CH_2)_6$-NH_2+ n.HOOC–$(CH_2)_4$–COOH Hexa $\longrightarrow$
methylene di amine Adipic acid

(NH – $(CH_2)_6$- NH -OC – $(CH_2)_4$ – CO-)n + n H_2O
Nylon 6,6

7.4 What is degree of polemerization (DP). 2 Marks

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

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

Ex: $(CH_2 – CH_2)_n$
Polythene

Here ‘n’ is the DP.

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

Molecular weight of the polythene = DP X Molecular weight of Polethene
= 100 X 28

= 2800.

7.5 Explain the free radical mechanism addition polymerization by

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UNIT – IV

Lubricants and Fuel Technology

Syllabus:

Fuel Technology

Introduction:

“Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purpose”.

E.g. Wood, charcoal, coal, kerosene, petrol, diesel, producer gas etc.

During the process of combustion of a fuel, the atoms of carbon, hydrogen etc. combine with oxygen with the simultaneous liberation of heat at a rapid rate. This energy is liberated due to the ‘rearrangement of valence electrons’ in these atoms, resulting in the formation of new compounds (like CO_2, H_2O etc). These new compounds have less energy in them and, therefore, the energy released during the combustion process is the difference in the energy of the reactants and that of the products formed.

Fuel + O_2 Products + Heat

The primary or main source of fuels are coals and petroleum oils, the amounts of which are dwindling day-by-day. These are stored fuels available in earth’s crust and are, generally, called ‘Fossil fuels’.

Classification:

Fuels can be classified into 2 types based

(a) On the basis of their occurrence.

(b) On the basis of physical state of aggregation.

(a) On the basis of occurrence, the fuels are further divided into two types.

(i) Natural or primary fuels:

Lubricants:

Definition, Functions of Lubricants, Mechanism of Lubrication, Classification of Lubricants, Properties of

Lubricants – Viscosity, Flash and Fire points, Cloud and pour points, Aniline Points, Neutralization number and mechanical strength.

Fuel Technology:

Introduction, classification, characteristics of a good fuel, calorific value, liquid Fuels, petroleum, Refining of petroleum, knocking, octane number, power alcohol, Synthetic petrol, Gaseous fuels, Important gaseous fuels.

N Nagarjuna Sarma

Fuels which found in nature are called as natural fuels.

E.g. Wood, coal, peat, petroleum and natural gas.

(ii) Artificial or secondary fuels:

Fuels which are prepared artificially from primary fuels are called artificial or secondary fuels.

E.g. Kerosene, petrol, coal gas, coke etc.

(b) On the basis of physical state of aggregation the fuels are divided into solids, liquids and gases.

Fuels

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 the 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 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.

Primary / Natural fuels Secondary / Artificial fuels

ASynthetfuels

Calorific value:

The prime property of a fuel is its capacity to supply heat. Fuels essentially consist of carbon, hydrogen, oxygen and some hydrocarbons and the heat that a particular fuel can give is due to the oxidation of carbon and hydrogen. Normally when a combustible substances burns the total heat depends upon the quantity of fuel burnt, its nature, air supplied for combustion and certain other conditions governing the combustion. Further the heat produced is different for different fuels and is termed as its calorific value.

Definition:

The calorific value of a fuel can be defined as “the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen”.

There are different units for measuring the quantity of heat. They are;

1. Calorie:

It is the amount of heat required to increase the temperature of 1 gram or water through one degree centigrade.

2. Kilocalorie:

This is the unit of heat in metric system, and is defined as “the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade”.

1 k.cal = 1000 cal

3. British thermal unit (B.Th.U.):

This is the unit of heat in English system. It is defined as “the quantity of heat required to increase the temperature of one pound of water through one degree Fahrenheit.

4. Centigrade heat unit (C.H.U.):

It is the quantity of heat required to raise the temperature of one pound of water through one degree centigrade.

Inter conversion of various units:

1 k.cal = 1000 cal = 3.968 B.Th.U. = 2.2 C.H.U.

Units of calorific value:

The calorific value is generally, expressed in “calorie / gram (cal/g)” or “kilocalorie / kg (kcal/kg)” or “British thermal unit / lb (B.Th.U/lb)” in case of solid or liquid fuels.

In case of gaseous fuels the units used are “kilocalorie / cubic metre (kcal/m^3)” or “B.Th.U/ft^3”.

There are two types of calorific values of a fuel.

Higher calorific value or Gross calorific value (HCV or GCV):

Usually all fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen gets converted to steam. If the products of combustion are condensed to the room temperature, the latent heat of condensation of steam also gets included in the measured heat, which is then called ‘Higher or Gross calorific value’.

Definition:

“The total amount of heat liberated, when unit mass or unit volume of the fuel has been burnt completely and the products of combustion are cooled down to room temperature.”

The calorific value determined by Bomb calorimeter gives the gross or higher calorific value.

Lower calorific value or Net calorific value (LCV or NCV):

Whenever a fuel is subjected to combustion, the water vapour and moisture etc. escape along with the hot combustion gases and hence there is no chance for their condensation.

So the net or lower calorific value (LCV) is defined as “the net heat produced, when unit mass or unit volume of the fuel is burnt completely and the combustion products are allowed to escape”.

LCV = HCV – Latent heat of water vapour formed

Since 1 part by mass of hydrogen produces 9 parts by mass of water as given by the equation below

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

Hence,

LCV = HCV – mass of hydrogen x 9 x latent heat of steam

Latent heat of steam is 587 k.cal/kg

Therefore,

$$NCV\ (or\ LCV) = HCV\ (or\ GCV) - 9 \times \frac{H}{100} \times 587 = HCV - 0.09 \times H \times 587$$

Where, H = % of hydrogen in the fuel.

Theoretical calculation of calorific value:

The calorific value of fuel can be approximately computed by noting the amount of the constituents
of the fuel.
The high calorific value of some important main combustible constituents of fuel such as hydrogen
is 34,000 kcal/kg, carbon is 8080 kcal/kg and sulphur is 2240 kcal/kg.
The oxygen, if present in the fuel, is assumed to be present in combined form with hydrogen, i.e. in
the form of fixed hydrogen (H_2O). So, the amount of hydrogen available for combustion
= Total mass of hydrogen in fuel – Fixed hydrogen
= Total mass of hydrogen in fuel – (
8
1) Mass of oxygen in fuel
(· 8 parts of oxygen combine with one part of hydrogen to for H_2O)
Dulong's formula for calorific value from the chemical composition of fuel is;
HCV =
100
1 [8080 C + 34,500 (H –
8
O) + 2240 S] kcal/kg
Where C, H, O, and S are the percentages of carbon, hydrogen, oxygen, and sulphur in the fuel
respectively. In this formula, oxygen is assumed to be present in combination with hydrogen as
water.
LCV = [HCV– 0.09 x H x 587] kcal/kg
This is based on the fact that 1 part of H by mass gives 9 parts of H_2O, and latent heat of steam is
587 kcal/kg.
2 g
1 g
18 g
9 g

Experimental determination of calorific value:

The calorific value of a fuel is determined by the combustion of the fuel in a special type of the
apparatus called calorimeter. The different types of calorimeters are
1. The Bomb calorimeter
2. The Boy's calorimeter and
3. The Junker's calorimeter

The Bomb calorimeter is used in finding the calorific value of solid and liquid fuels. The Boy's calorimeter and Junker's calorimeter are used for the determining the calorific values of gaseous fuels and those liquid fuels which are easily vaporized.

Liquid Fuels:

Liquid fuels are the important commercial and domestic fuels used in our daily life. Most of these fuels are obtained from the naturally occurring petroleum or crude oil called as primary fuel.

Advantages:

(a) They posses higher calorific value per unit mass than solid fuels.
(b) They burn without dust, ash, clinkers, etc.
(c) Their firing is easier and also fire can be extinguished easily by stopping liquid fuel supply.
(d) They are easy to transport through pipes.
(e) They can be stored indefinitely without any loss.
(f) They are clean in use and economic to handle.
(g) Loss of heat in chimney is very low due to greater cleanliness.
(h) They require less excess air for complete combustion.
(i) They require less furnace space for combustion.

Disadvantages:

(a) The cost of liquid fuel is relatively much higher as compared to solid fuel.
(b) Costly special storage tanks are required for storing liquid fuels.
(c) There is a greater risk of five hazards, particularly, in case of highly inflammable and volatile liquid fuels.
(d) They give bad odour.
(e) For efficient burning of liquid fuels, specially constructed burners and spraying apparatus are required.

Petroleum** (crude oil)**:

The crude oil or petroleum is also known as rock oil or mineral oil. It is dark colour liquid found well deep in the earth. It is mainly composed of hydrocarbons which may be solids, liquids or gases. Some optically active compounds having S and N are also present. On the average the composition of petroleum is; C = 79.5 – 87.1%
H = 11.5 – 14.8%
S = 0.1 – 3.5%

UNIT – IV

CEMENT AND CONCRETE CHEMISTRY

Introduction to Cement

Cement is a dirty greenish heavy powder, used as a building material. The original name of cement is concrete. It is a material which posse's adhesive & cohesive properties to bind rigid masses like stones, bricks, Building blocks etc. It has the property of setting & hardening in the presence of water i.e. hydraulic in nature. Chemically it is composed of mixture of calcium silicate & Calcium aluminate in which Calcium materials are called as calcarious&Aluminium and silica are called as argillaceous. The first cement factory in India was started in 1904 in Chennai, by the South India Industrial Ltd. which existed for a short period.

Classification of cement:- Cements are classified into following types.

(1)Natural cement
(2) Pozzolana cement
(3) Slag cement.
(4) Port land cement
(5) Expanding cement
(6) Quick getting cement

(1) Natural cement: - This is obtained by calcining& pulverizing natural rocks consisting of clay & limestone. During heating, silica & alumina present in the clay react with lime to produce calcium silicate & Calcium aluminates. Natural cement is usually used for construction of big structure such as dams.

Properties: -

(1) It is hydraulic in nature with low strength

(2) Its setting time is very less.

(2) Pozzolanacement:- It is obtained by volcanic ash. (The place Puzzouli in Italy), which consist of silicates of Ca, Fe, Al mixed with lime on heating forms pozzolana cement.

Properties: -

(1) Hydraulic in nature.

(2) Mixed with port land cement for different applications.

(3) Slag cement: - It is prepared by mixing hydrated lime + mixture of Ca, Al silicates (Blast furnace slag) in a stream of cold H_2O. It is dried & then pulverized to fine powder.Sometimes accelerators like clay or caustic soda are added for hardening process.Mainly used in making concrete in bulk construction.

Properties:-

(1) Decreased strength.

(2)The time required for setting & hardening is more i.e. a week.

(4) Portland cement:-

It is obtained by heating a mixture of lime stone &clay &crushing the resulting product to a fine powder. It is also known as magic powder. It is a mixture of Calcium silicates & aluminates with small amount of gypsum.

- William Aspidin (1824) was father of modern Portland cement Industry.
- It is a type of cement & not a brand name.

(5) Expanding cements:- Portland cement + sulphoaluminate (expanding agent)

This is obtained by burning a mixture of gypsum, bauxite & Lime stone.

(6) Quick setting cement: - This cement contains high percentage of Alumina (Al_2O_3) & takes only 5 minutes for initial& $<$ 30 seconds for final setting.

- This cement is mostly used for under water constructions.

Chemical Composition of Portland Cement:-

It is a finely powdered mixture of calcium silicate and aluminates of varying compositions. Ratio of % of lime (CaO) to that of silica (SiO_2), Alumina (Al_2O_3) and iron oxide is calculated by the formula

$$\frac{CaO}{2.8\ SiO_2 + 1.2\ Al_2O_3 + 0.65\ Fe_2O_3}$$

A good sample of Portland cement has the composition of.

Ingredient	Percentages (%)
1. CaO	60-70
2. Silica	20-29
3. Alumina	5-7.5
4.. Magnesia	2-3
5.Ferric oxide	1-2.5
6. SO_3	1-1.5
7. Na_2O	1
8.K_2O	1

Manufacture of Portland cement:-

Raw materials for manufacturing of Portland cement

(1) Calcareous: - They are rich in lime such as limestone, chalk, and cement rock.

- The limestone should not contain more than 5% of MgO, it leads to cracking.

(2) Argillaceous: - Those contain silica, alumina & iron oxide

Eg: -Clay, blast furnace slag (ashes).

(3) Gypsum: - It is added during the final grinding & it control the ratio of setting & hardening.

Methods of manufacturing process: - These are two methods for manufacturing

(1) Dry method
(2) Wet method.

The two methods differ only in the treatment of raw material. In dry process water is not added to the material during grinding. The following steps are involved in manufacture of Portland cement.

(1) Mixing of Raw material
(2) Burning
(3) Grinding
(4) Packing

(1) Mixing of Raw material:-

Dry process: This process is employed if the lime stone and clay are hard. Initially lime stone is crushed in to pieces and then it is mixed with clay in the proportion of 3:1. This mixture is pulverized to a fine powder and is stored in storage bins and later on it is introduces in to the upper end of the rotary kiln.

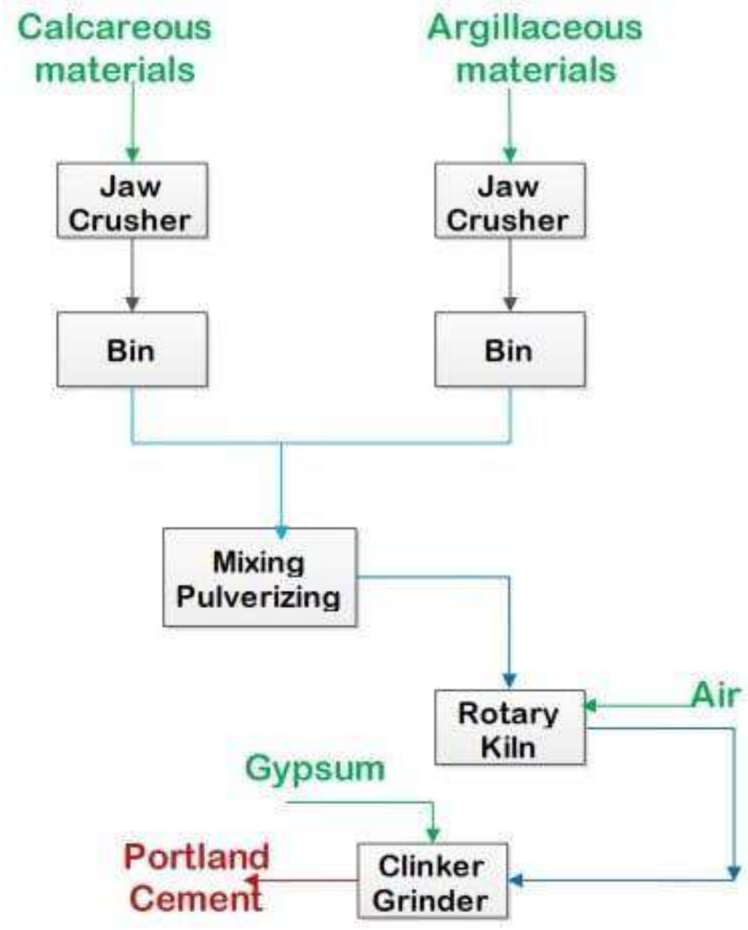


Fig: Manufacture of Cement by Dry Process

Wet process: This process is performed when the raw materials are soft. The clay is washed with water in wash mills to remove any foreign material or organic material. Powdered lime stone is then mixed with the clay paste in a proper proportion 3:1. The mixture is then finally ground and homogenized to form slurry containing about 40% water and stored in storage bins.

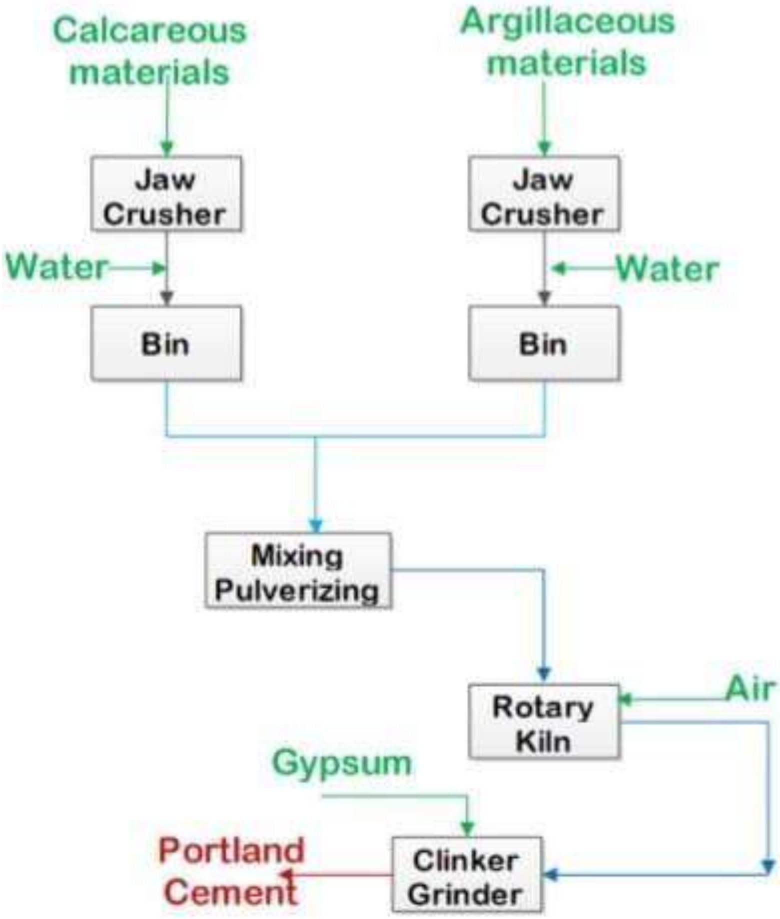


Fig: Manufacture of Cement by Wet Process

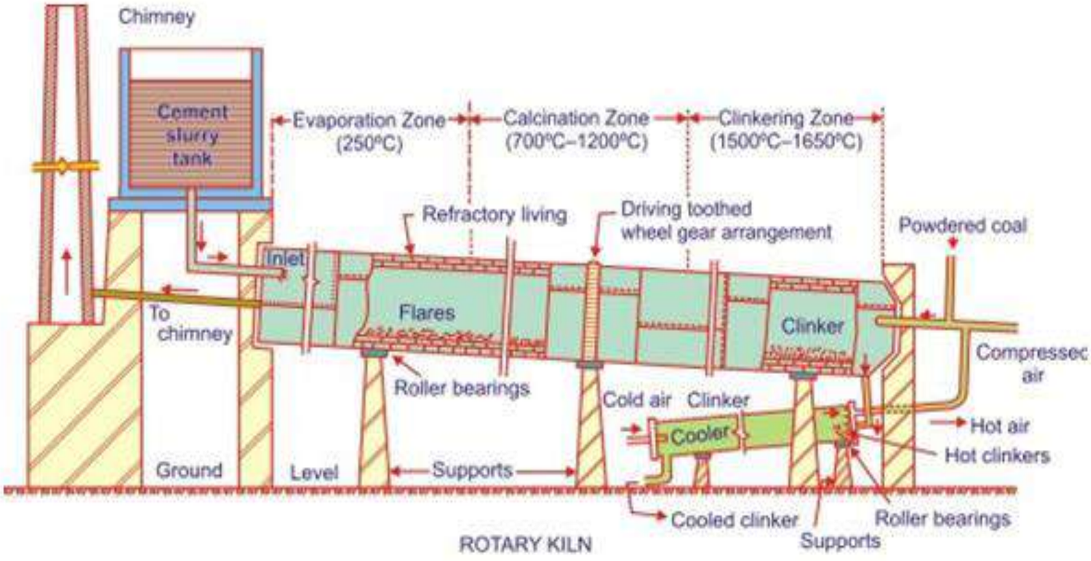


FIG. Rotary Kiln.

Difference between dry & wet process:

Dry process	**Wet process**
1. This process is adopted when the raw materials are quite hard.	1. This method is performed when the raw materials are soft.
2. It is a slow and costly process	2. Comparatively cheaper and fast process.
3. The final consumption is low, hence smaller kiln is used.	3. Fuel consumption is high so longer kiln is used.
4. The process is not suitable if the raw material has moisture content of 15% or more.	4. This process can be adopted even in wet conditions.

(2) Burning: - Rotary kilns are used for burning of cement. A Rotary kiln is an inclined steel cylinder, length is about 150—200 & diameter is about 10feet & it is lined with fire bricks.

The kiln can be rotated at desired speed,(usually 0.5 to 2 rotations/minute)as it is mounted on rollers. As the kiln rotates the raw materials passes slowly from the upper end of rotary kiln to lower end, while the burning fuel (pulverized coal, oil / natural gas)Escape after the removal of dust.

As the mixture or slurry gradually descends with increasingtemperature the following reactions take place in rotary kiln.

(a) Drying zone: -The upper part of the kiln, where the temp around 400^0 C & the slurry gets dried because of hot gases. The clay is broken as Al_2O_3, SiO2& Fe_2O_3.

(b) Calcination zone / decarbonating zone :- It is the central part of the kiln ,where the temp is around 1000^0C. In this lime stone of dry mix /slurry completely decomposed into quick lime (CaO) & CO_2.

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

(c) Clinkering zone / Burning Zone:- The lower part of the rotary kiln, the temperature is between 1500^0C to 1700^0C. In this zone lime & clay reacts to each other forming aluminates & silicates.

- $2CaO + SiO2 = Ca2SiO4$ (declaim silicate (C_2S))
- $3CaO + SiO2 = Ca3SiO5$ (tricalcium silicate (C_3S))
- $3CaO + Al2O3 = Ca3Al2O6$ (dicalcium aluminate (C_2A))
- $4CaO + Al2O3 + Fe2O3 = Ca4Al2Fe2O10$ (tetra calcium aluminoferrite (C_4AF))

These aluminates & Silicates of calcium fuse together to form hard greenish stones Called clinkers. This reaction is exothermic. The cooled clinkers are collected in trolleys.

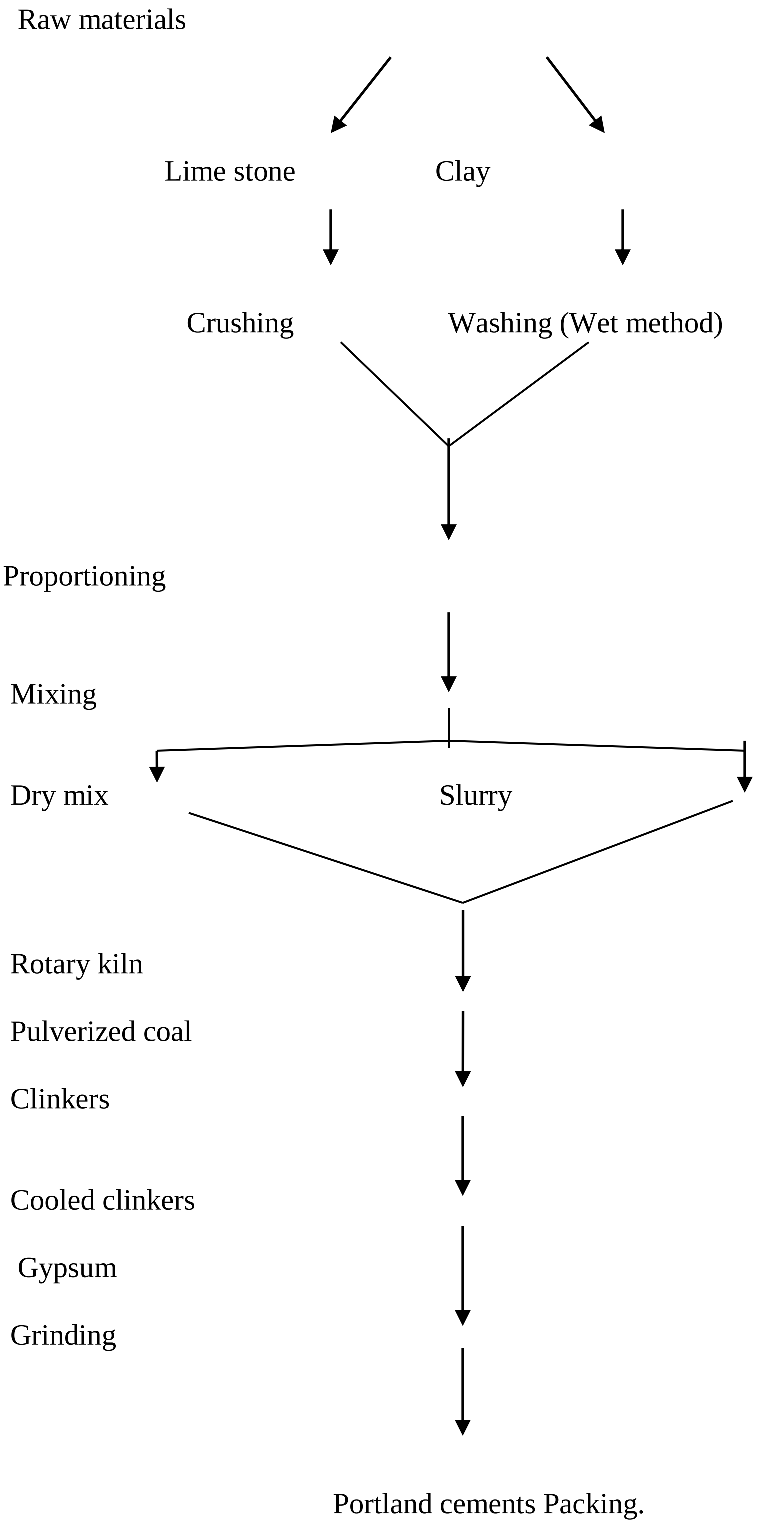
(3) Grinding / mixing of cement clickers with gypsum: - The cooled clinkers are pulverized to form powered mixture. This finely powdered clinkers set quick rapidly. So, the cement mortar will unworkable.

Therefore its setting decreases used retarders. Commonly gypsum ($CaSO_4.2H_2o$) is used as retarder. Usually about 2-6% gypsum is mixed with clinkers in long tube.

$$\text{Mixture of clinkers + 2-6\% gyps} \longrightarrow \text{Portland cement.}$$

(4) Packing: - The resulting Portland cement is stored in silos

Flow chart of manufacture of cement:-



Setting & Hardening of cement:-

When Portland is mixed with H2O, it is converted in to aplastic mass called Cement paste (initial set) which slowly loses its plasticity & becomes stiff & ultimately a rocky mass is obtained (final set).This process is called as setting.The time for the initial set should not be less than 45min and for the final set should not be more than 10 hours. After hydration, anhydrous compounds become hydrated, which have less solubility. Hence they are precipitated as insoluble gels or crystals. These have ability to surround sand, crushed stones, other inert materials & bind them strongly. Development of strength due to crystallization is called as Hardening, which continue to increase for years. The process of setting & hardening are collectively called as solidification.

⇒ Hardening of cement can be explained on the basic of 2 theories.

Crystallinetheory(given by Le – chatlier):-

Constitutional compounds after hydration form crystalline products,which undergo interlocking which is responsible for hardening of cement.

Colloidal theory (given by Michaelies):-

According to this theory hardening of cement is due to the hardening of the silicate gels, which are formed during hydration .

⇒ The main constituents of the common cement are

Name	Formula	Abbreviation	%	Setting time
Tri calcium silicate	$3CaO. SiO_2$	C_3s	45	7days
Di calcium silicate	$2 CaO.SiO_2$	C_2s	25	28days
Tricalcium Aluminate	$3 CaO. Al_2O_3$	C_3A	10	1day
Tetra calcium alumino ferrite	$4CaO.Al_2O_3. Fe_2O_3$	C_3AF	10	1day

The remainder consists of free MgO& small amounts of K_2O & Na2O & various combination of lime, Al_2O_3, SiO_2& SO_3.

Reactions involved in setting & Hardening:-

When cement mixed with water, the paste becomes quite rigid within a short time known as Initial set / flash set. This is due to rapid hydration of C_3A.

$3CaO.\ Al_2O_3 + 6H_2O \longrightarrow 3CaO.\ Al_2O_3.\ 6\ H_2O + 880$ Kj /Kg (crystals)

1. However these crystals present in the hydration reactions of other constitutional compounds form barrier over them. To decrease or retard the flash set, gypsum or plaster of paris is added during the pulverization of cement clinkers.

2. Gypsum retards the dissolution of C_3A. When it interacts with C_3A forms insoluble complex of sulphoaluminate which does not have quick hydrating property.

$3\ CaO.Al_2O_3 + x\ H_2O + Y\ CaSO_4.2H_2O \longrightarrow 3\ CaO.\ Al_2O_3.\ CaSO_4.\ 2\ H_2O. + 880$ KJ / Kg.

3. The tetra calcium alumino ferrite (C4 AF) then reacts with water forming both gels & crystalline compounds.

$4\ CaO.\ Al_2O_3.\ Fe_2O_3 + 7H_2O \longrightarrow 3\ CaO.\ Al_2O_3.\ 6H_2O + CaO.\ Fe_2O_3\ H_2O$ gels +420 Kj/Kg. crystals (gels)

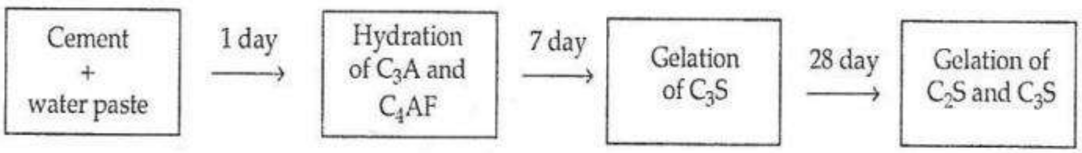
4. Now C_3S & C_2S undergo further hydration & hydrolysis reactions increase the development of greater strength .The initial setting and hardening of cement paste is due to the formation of tobermonite gel.

$2(2\ CaO.SiO_2) + 4\ H_2O \longrightarrow 3\ CaO.2SiO_2.\ 3H_2O + Ca\ (OH)_2 + 250$KJ/Kg

5. The final setting & hardening of cement paste is due to formation of tobermonite gel and crystallization of $Ca(OH)_2$.

$2(3\ CaO.SiO_2) + 6H_2O \longrightarrow 3CaO.2\ SiO_2\ 3\ H_2O + 3\ Ca\ (OH)_2 + 500$ KJ/Kg.

Sequence changes during setting & Hardening of cement:-



Sequence of changes during setting and hardening of cement.

Scheme of concrete formation:-

The manufacture of concrete is fairly simple. First, the cement (usually Portland cement) is prepared. Next, the other ingredients—aggregates (such as sand or gravel), admixtures (chemical additives), any necessary fibers, and water—are mixed together with the cement to form concrete.

Testing of cement / Analysis of cement:-

In order to maintain the quality of cement, various tests are conducted from raw material stage to packaging stage. Various cements have various compositions. But the most common cement i.e. Portland cement has the following composition.

Chemical requirements:-

Lime saturation factor :-

$$\left(\frac{CaO - 0.7SO_3}{2.8\ SiO_2 + 1.2\ Al_2O_3 + 0.65\ Fe_2O_3} \right)$$

= 0.66 to 1.02.

Ratio of Al_2O_3 / Fe_2O_3:- Not less than 0.66

Insoluble residue: - Not more than 2%

MgO: - Not more than 6%

SO_3 :- Not more than 2.75 %

Loss on ignition: - Not more than 4%

Physical Requirements :-

(1) Setting time

Initial — $<$ 30minutes

Final — $<$ 10 hrs

(2)Compressive strength

3 days not — $<$ 1.6 Kg f/mm^2

7 days not — $<$ 2.2 Kg f/mm^2

Kgf : Kilogram force = 9.807 New tons)

Phases in clinker and cement

Alite (tricalcium silicate, Ca_3SiO_5) forms the bulk of a clinker (40-70%, by mass) with crystal sizes up to about 150 µm. Alite generally displays a hexagonal crystal habit in cross section, with forms ranging from euhedral (clearly-defined crystal faces), to subhedral (poorly-defined crystal faces), to anhedral (no crystal faces). Minor oxide contents may range from about 3% to 4% by mass. Alite reacts rapidly with water and is responsible for much of the early-age (28 d) strength development.

Belite (dicalcium silicate, Ca_2SiO_4) forms 15-45% of a clinker, and displays a rounded habit with crystal sizes ranging from 5 to 40 μm. Normally the β polymorph is found in clinkers, although smaller amounts of, α, α'_H, and α'_1; polymorphs may occur with minor oxides comprising up to 5%. Light microscopy of lamellar structures on etched specimens and X-ray powder diffraction data are useful for distinguishing the belite forms. Belite is less reactive than alite but does contribute to later-age strengths (>28 d). Upon hydration, both alite and belite form a poorly-crystallized calcium silicate hydrate (C-S-H) and well-crystallized calcium hydroxide.

Tricalcium aluminate, $Ca_3Al_2O_6$, comprises 1-15% of a clinker occurring as small 1-60 μm crystals exhibiting irregular to lath-like habit, filling the area between the ferrite crystals. Tricalcium aluminate may occur as cubic or orthorhombic forms, and may contain up to 7% minor oxides. It is highly reactive with water.

Ferrite (tetracalcium aluminoferrite, $Ca_2(Al,Fe)O_5$), comprises between 0% and 18% of a clinker with crystal habits as dendritic, prismatic, and massive. Minor oxide content within ferrites may be up to 10% and ferrites exhibit variable reactivity with water. The ferrite and aluminate phases are sometimes referred to as the interstitial or matrix phases as they occur between, and appear to bind the silicate crystals.

Phases in lesser quantities, but still influential to performance, include periclase (MgO) and free lime (CaO). Periclase may exhibit a dendritic or equant crystal habit both within and between the other clinker constituents, ranging in size up to 30 µm. Free lime may occur as isolated rounded crystals or in masses with variable crystal size.

Alkali sulfates and calcium sulfates may also occur in clinker and are of interest since they have been found to affect hydration rates and strength development. Increased alkali levels in clinker are considered potentially deleterious if alkali-susceptible aggregates are used in the concrete.

Typical chemical compositions for the primary phases in cement clinkers. From

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Mn_2O_3	Fe_2O_3
Alite	0.1	1.1	1.0	25.2	0.1	0.1	0.1	71.6	0.0	0.0	0.7
Belite	0.1	0.5	2.1	31.5	0.1	0.2	0.9	63.5	0.2	0.0	0.9
Aluminate (cubic.)	1.0	1.4	31.3	3.7	0.0	0.0	0.7	56.6	0.2	0.0	5.1
Ferrite	0.1	3.0	21.9	3.6	0.0	0.0	0.2	47.5	1.6	0.7	21.4
Aluminate (orthorhombic)	0.6	1.2	28.9	4.3	0.0	0.0	4.0	53.9	0.5	0.0	6.6
Aluminate (low Fe)	0.4	1.0	33.8	4.6	0.0	0.0	0.5	58.1	0.6	0.0	1.0
Ferrite (low Al)	0.4	3.7	16.2	5.0	0.0	0.3	0.2	47.8	0.6	1.0	25.4

Parameters to Characterize the Clinker Formation

Lime saturation factor (LSF), silica ratio (SR) and alumina ratio (AR). LSF is calculated using the equation.

Lime saturation factor:

$$LS = \frac{\mathrm{CaO}}{2.8SiO2 + 1.2Al2O3 + 0.65Fe2O3}$$

The equation is based on clinker equilibrium in production and a LSF value over 1.00 indicates a presence of free lime in the cement. For modern clinkers it is typical with a LSF of 92-98.

SR is calculated using the equation:

$$SR = \frac{\mathrm{SiO2}}{Al2O3 + Fe2O3}$$

SR is empirically based and a normal value in Portland cement is 2.0-3.0. When the SR is increased, the liquid proportion is decreased making it harder to burn the clinker.

AR is calculated using the equation:

$$AR = \frac{Al2O3}{Fe2O3}$$

AR is also empirically based and has a normal value of 1.0-4.0 in Portland cement. AR impacts the properties of the cement and the formation of liquid at relatively low temperatures**.**

Chemical Admixtures

Chemical admixtures are the ingredients in concrete other than portland cement, water, and aggregate that are added to the mix immediately before or during mixing. Producers use admixtures primarily to reduce the cost of concrete construction; to modify the properties of hardened concrete; to ensure the quality of concrete during mixing, transporting, placing, and curing; and to overcome certain emergencies during concrete operations.

The effectiveness of an admixture depends on several factors including: type and amount of cement, water content, mixing time, slump, and temperatures of the concrete and air. Sometimes, effects similar to those achieved through the addition of admixtures can be achieved by altering the concrete mixture-reducing the water-cement ratio, adding additional cement, using a different type of cement, or changing the aggregate and aggregate gradation.

Five Functions

Admixtures are classed according to function. There are five distinct classes of chemical admixtures: air-entraining, water-reducing, retarding, accelerating, and plasticizers (superplasticizers). All other varieties of admixtures fall into the specialty category whose functions include corrosion inhibition, shrinkage reduction, alkali-silica reactivity reduction, workability enhancement, bonding, damp proofing, and coloring. Air-entraining admixtures, which are used to purposely place microscopic air bubbles into the concrete, are discussed more fully in Air-Entrained Concrete.

Water-reducing admixtures

Water-reducing admixtures usually reduce the required water content for a concrete mixture by about 5 to 10 percent. Consequently, concrete containing a water-reducing admixture needs less water to reach a required slump than untreated concrete. The treated concrete can have a lower water-cement ratio. This usually indicates that a higher strength concrete can be produced without increasing the amount of cement. Recent advancements in admixture technology have led to the development of mid-range water reducers. These admixtures reduce water content by at least 8 percent and tend to be more stable over a wider range of temperatures. Mid-range water reducers provide more consistent setting times than standard water reducers.

Retarding admixtures

Retarding admixtures, which slow the setting rate of concrete, are used to counteract the accelerating effect of hot weather on concrete setting. High temperatures often cause an increased rate of hardening which makes placing and finishing difficult.

Retarders keep concrete workable during placement and delay the initial set of concrete. Most retarders also function as water reducers and may entrain some air in concrete.

Accelerating admixtures

Accelerating admixtures increase the rate of early strength development, reduce the time required for proper curing and protection, and speed up the start of finishing operations. Accelerating admixtures are especially useful for modifying the properties of concrete in cold weather.

Super plasticizers

Super plasticizers, also known as plasticizers or high-range water reducers (HRWR), reduce water content by 12 to 30 percent and can be added to concrete with a low-to-normal slump and water-cement ratio to make high-slump flowing concrete. Flowing concrete is a highly fluid but workable concrete that can be placed with little or no vibration or compaction. The effect of super plasticizers lasts only 30 to 60 minutes, depending on the brand and dosage rate, and is followed by a rapid loss in workability. As a result of the slump loss, super plasticizers are usually added to concrete at the jobsite.

Corrosion-inhibiting admixtures

Corrosion-inhibiting admixtures fall into the specialty admixture category and are used to slow corrosion of reinforcing steel in concrete. Corrosion inhibitors can be used as a defensive strategy for concrete structures, such as marine facilities, highway bridges, and parking garages, that will be exposed to high concentrations of chloride. Other specialty admixtures include shrinkage-reducing admixtures and alkali-silica reactivity inhibitors. The shrinkage reducers are used to control drying shrinkage and minimize cracking, while ASR inhibitors control durability problems associated with alkali-silica reactivity.

UNIT-5

SURFACE CHEMISTRY

Introduction to surface chemistry, Colloids, Nanometals and nanometal oxides, Micelle formation, Synthesis of colloids(any two methods with examples), Chemical and electrochemical methods(not more than two methods) of preparation of nanometals and metal oxides, stabilization of colloids and nanometals by stabilizing agents, characterization of surface by physicochemical methods(SEM,TEM,X-ray diffraction), solid-gas interference, Solid- liquid interference, adsorption isotherm, BET equation(no derivation), calculation of specific surface area of solids, numerical problems, functionalization of surface of nanometals – Applications of colloids and nanometals-catalysis, medicine, sensors, etc.,.

Introduction to Surface Chemistry:

Surface chemistry is a branch in chemistry which deals with the study of the phenomenon occurring at the interface of two phases (solid–liquid interfaces, solid–gas interfaces, solid–vacuum interfaces, and liquid-gas interfaces). Surface represents the physical boundary of any condensed phase like liquid or solid. It separates one phase from the other. For example: Interfaces existing between two immiscible liquids like oil and water; between a metal and a gas like platinum and hydrogen; a liquid and a gas etc.The surface or interface between two phases is represented by a hyphen or slash. For example: Between the solid and the liquid, the interface is represented by solid/liquid. There is no interface between the gases as they are completely miscible with one another.

Definition:

Surface science is the study of chemical phenomena that occur at the interface of two phases (solid–liquid interfaces, solid–gas interfaces, solid–vacuum interfaces, and liquid-gas interfaces).

(or)

It is defined as the study of chemical reactions at interfaces.

Terminology used in Surface Chemistry:

1. **Adsorption:**

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into a higher concentration of the molecules on the surface is called adsorption. It is also called the positive adsorption. The surface on which adsorption takes place is called the adsorbent and the substance which is being adsorbed is called the adsorbate.

(Eg.) Occlusion of Hydrogen gas on Palladium where palladium is adsorbent and hydrogen gas is adsorbate.

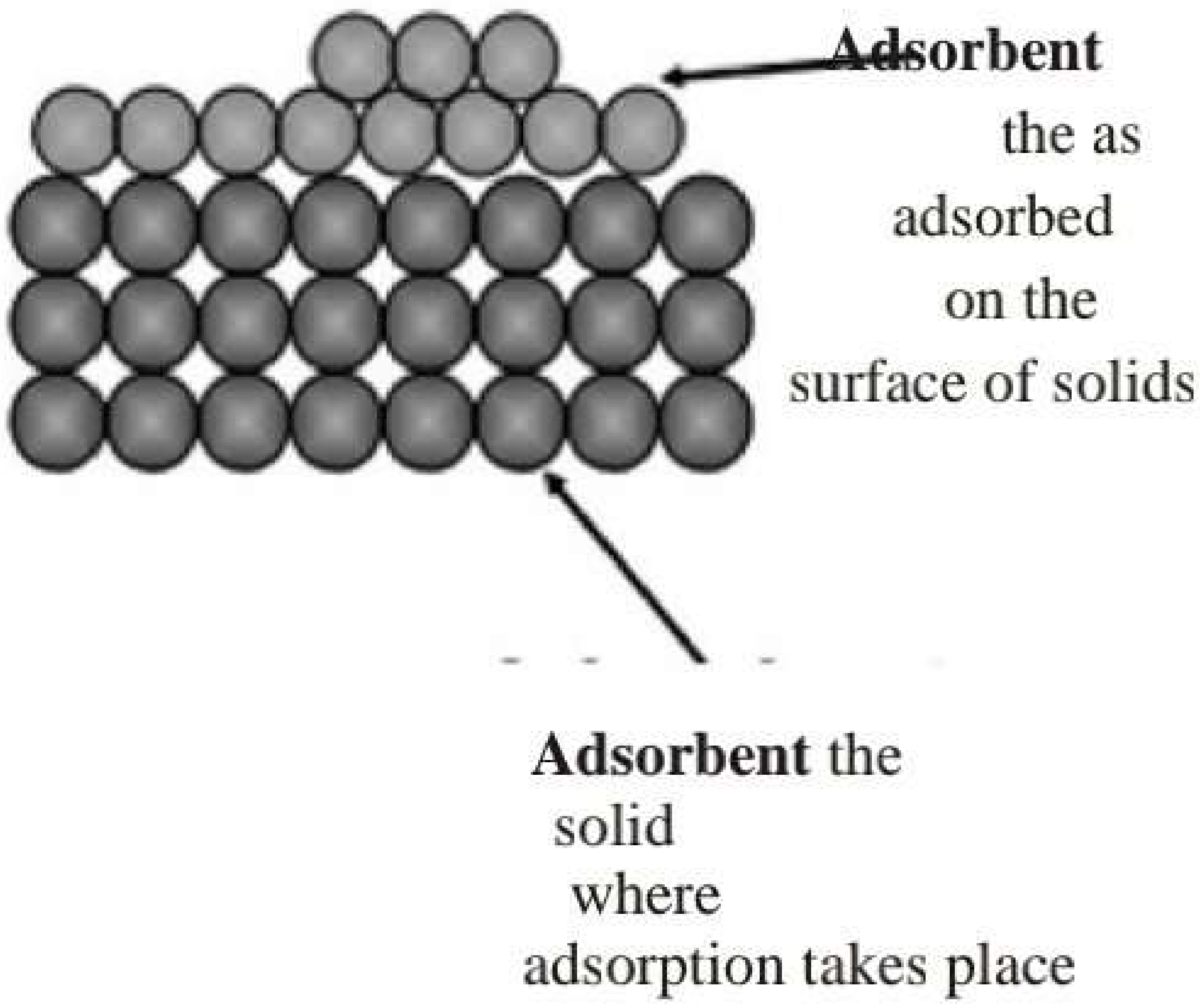


Fig. : Adsorption Process

Types of adsorption:

Adsorption is of two types:

(i) **Physical adsorption (physisorption):** The adsorption in which physical or Vander walls forces exist between adsorbate molecules and adsorbent surface without forming any chemical bond between adsorbate and adsorbent it is called physical adsorption.

E.g.: Adsorption of CO_2 gas on the surface of charcoal.

(ii) **Chemical adsorption (Chemisorption):** The adsorption in which chemical forces or chemical bond exists between adsorbate molecules and adsorbent surface of a solid by forces similar to those of a chemical bond the type of adsorption is called chemical adsorption. This type of adsorption leads to the formation of a surface compound.

E.g.: Adsorption of H_2 on platinum metal surface.

Differences between Physisorption and Chemisorptions

S.No	Physisorption	Chemisorption
1	Only van der Waals forces are present between adsorbate and surface of adsorbent.	Chemical bonds are formed between adsorbate and surface of adsorbent.
2	It usually takes place at a low temperature and decreases with increasing temperature.	It takes place at a high temperature.
3	It is reversible.	It is irreversible.
4	It forms multi-molecular layers.	It forms mono-molecular layers.
5	It does not require any activation energy.	It requires activation energy.
6	It is related to the ease of liquefaction of the gas.	The extent of adsorption not related to liquefaction of the gas.
7	It is not specific in nature	It is highly specific in nature
8	It results in to multilayer	It results into monolayer(single)
9	No surface compound formation takes place	Surface compound formation takes place

2. Positive adsorption:

When the concentration of solute adsorbed on the solid adsorbent surface is greater than in the bulk it is called positive adsorption. (E.g.) Concentrated solution of KCl is shaken with blood charcoal, it shows positive adsorption.

3. Negative adsorption:

When the solvent from the solution may be absorbed by the adsorbent so that the concentration of the solute decreases and the concentration of solution increases than the initial concentration and it is called negative adsorption. (E.g.) Dilute solution of KCl is shaken with blood charcoal it shows negative adsorption.

4. Desorption:

Desorption is the reverse of adsorption which involves the removal of the substance adsorbed from the surface. The process of desorption can be carried out by:

(i) Reducing the pressure and (ii) By heating.

5. Sorption:

In absorption, the concentration of the molecules of a substance is more in the bulk than at the surface and the molecules in the bulk are uniformly distributed. If the concentration of the molecules of a substance is more in the bulk but molecules are not uniformly distributed, then it is called negative adsorption. When both adsorption and absorption takes place together and are indistinguishable, then we use the term called Sorption.

6. Adsorbent:

The substance on the surface of which adsorption takes place is known as adsorbent.

7. Adsorbate:

The substance which gets adsorbed is called adsorbate.

8. Absorption:

The process in which a substance is uniformly distributed throughout the body of the solid or liquid is called absorption.

9. Occlusion:

When adsorption of gases occurs on the surface of metals is called occlusion.

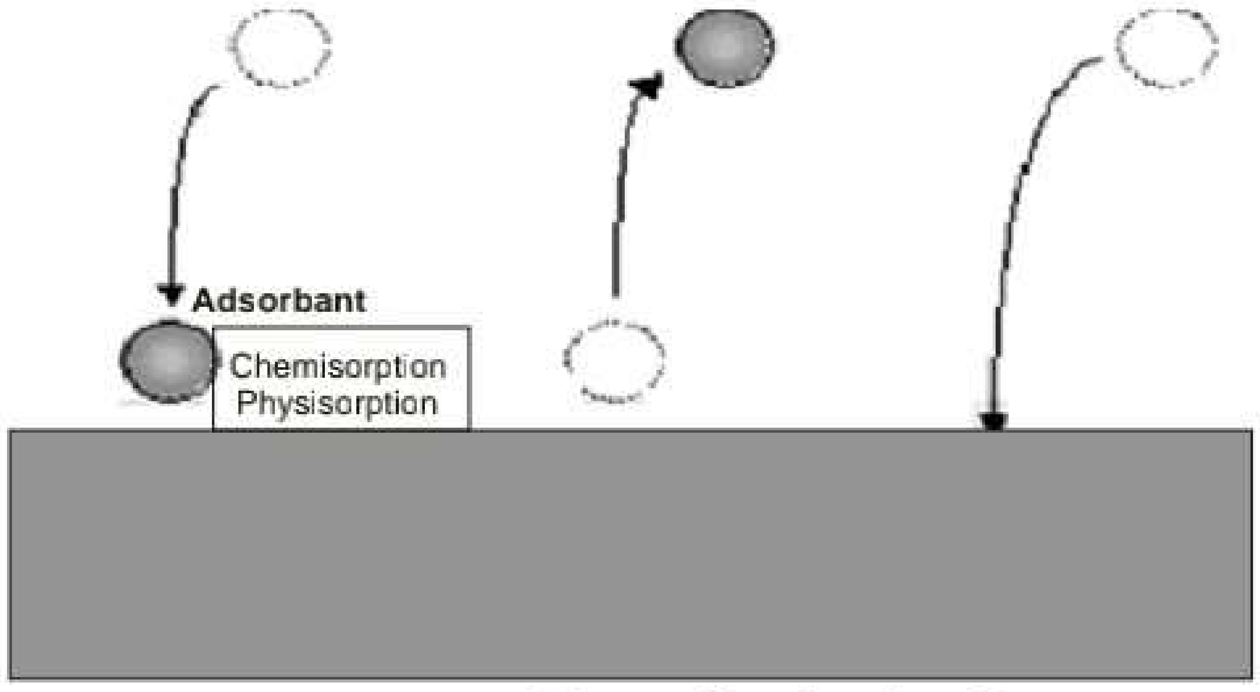


Fig. : Occlusion Process

10. Interference:

An interface is the surface of contact between any two condensed phases. It is not sharp in the sense that it cannot be clearly defined where a particular phase ends and the next begins. And unlike a mathematical surface, it is a diffused .Higher the miscibility of the two phases, higher the diffusion between the two surfaces. In the interfacial zone, there is a gradual change in density. An interface is in a sense a colloid because here we have a system in the range of or smaller.

Differences between adsorption and absorption:

S.no	Absorption	Adsorption
1.	The distribution of particles inside the bulk of the solid or liquid is uniform.	Since the gas or liquid particles do not enter inside the bulk, their concentration at the surface is higher.
2.	It is a bulk phenomenon.	It is a surface phenomenon
3.	Absorption occurs at a uniform rate.	Adsorption is rapid in the beginning and its rate slowly decreases
4.	Endothermic process	Exothermic process
5.	Attainment of equilibrium takes time.	Equilibrium is easily attained.
6.	There is no direct relation between rate of absorption and surface area.	It depends on surface area. Larger the surface area, faster is the rate of adsorption.

Colloids:

A **colloid** is a substance microscopically dispersed evenly throughout another substance. The dispersed-phase particles have a diameter between about 5 and 200 nanometres.

Examples: Milk is an emulsion, which is a colloid in which both parties are liquids.

Colloidal State:

A substance is said to be in the colloidal state when it is dispersed in another medium in the form of very small particles having diameter between 10–9 and 10–7 m that is 1 and 100 nm.

(or)

A substance in said to be in colloidal state when it is dispersed in another medium in the form of very small particles having diameter of $2*(10^{-4})$ to $1*(10^{-7})$.

Types of solution:

On the basis of the size of the dispersed particles, solutions may be of three types.

1. True solution
2. Suspensions
3. Colloidal solutions.

1. **True solution**: It is a 'homogeneous' solution that contains small solute particles (molecules or ions) dispersed through the solvent. The size of the particles is less than 1 nm and it is invisible even

under an ultra microscope. The particles can easily pass through animal or vegetable membrane. For example, solution of sodium chloride in water.

2. **Suspension**: It is a 'heterogeneous' mixture containing suspended insoluble particles. The size of the particles is greater than 100 nm. The particles in a suspension may be visible to naked eye or may be seen easily under a microscope. They cannot pass through animal or vegetable membrane or through an ordinary filter paper. For example, dirt particles in water.

3. **Colloidal solution**: It is a heterogeneous solution containing particles of intermediate size (diameter between 1 and 100 nm). Such particles are normally not visible to the naked eye but can be seen easily under an ultra microscope. The particles of a colloidal solution can pass through an ordinary filter paper but not through animal or vegetable membrane. For example, milk, starch solution, etc.

Phases of colloidal solutions:

A colloidal solution is a heterogeneous system. It consists of two essential components

Dispersed phase: It is the component present in smaller proportion just like a solute in a solvent. The dispersed phase is sometimes referred to as the inner phase or the discontinuous phase.

Dispersion medium: It is the medium in which the dispersed phase is present. It is analogous to the solvent in a solution. This phase is also referred to as the outer phase or the continuous phase.

Besides the above-mentioned phases, a colloidal solution may also contain a stabilising agent, which is a substance that tends to keep the colloidal particles apart avoiding their coalescence and consequent settling. Some colloids are self-stabilisers.

Dispersed phase + dispersion medium = dispersion system (colloidal solution). On the basis of the nature of the dispersion medium, some specific names have been assigned to the colloidal solutions

Dispersion medium	Water	Alcohol	Benzene	Air
Name of colloidal state	Hydrosols	Alcohols	Benzosols	Aerosols

The term sol is applied to the dispersion of a solid in a liquid, solid or gaseous medium. Emulsion is a system in which a liquid is dispersed in another liquid and if a colloidal system becomes fairly rigid it is termed as a gel. When gaseous particles are dispersed in a liquid or solid the colloidal system is termed as foam.

Classification of Colloids:

- Depending on the nature of the dispersed phase and dispersion medium
- Depending on the appearance:
  - (1) Sols
  - (2) Gels
- Depending on electric charge on the dispersed phase:
  1. Positive colloids
  2. Negative colloids
- Depending on the molecular size of the dispersed phase:
  1. Multimolecular colloids
  2. Macromolecular colloids
  3. Associated colloids or colloidal electrolytes
- Depending on the chemical composition:
  1. Organic colloids
  2. Inorganic colloids
- Depending on the interaction or affinity of the two phases:
  1. Lyophilic or solvent loving
  2. Lyophobic or solvent hating

Lyophilic colloids:

The word 'lyophilic' means liquid-loving. Colloidal sols directly formed by mixing substances like gum, gelatine, starch, rubber, etc., with a suitable liquid (the dispersion medium) are called lyophilic sols. An important characteristic of these sols is that if the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called reversible sols. Furthermore, these sols are quite stable and cannot be easily coagulated as discussed later.

Lyophobic colloids:

The word 'lyophobic' means liquid-hating. Substances like metals, their sulphides, etc., when simply mixed with the dispersion medium do not form the colloidal sol. Their colloidal sols can be prepared only by special methods (as discussed later). Such sols are called lyophobic sols. These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and hence, are not stable. Further, once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, these sols are also called irreversible sols. Lyophobic sols need stabilising agents for their preservation.

Characteristics of colloids:

- Continuous phase and dispersed phase
- Thermodynamically unstable but kinetically stable (i.e. they are stable indefinitely)
- Classified in terms of dispersed substance (solid, liquid, gas) in dispersing medium (solid, liquid, gas)
- Dispersed phase 10–1000 nm particles:

1. Large surface area to volume ratio
2. Size appropriate for scattering light
3. May have charged surfaces

- The name: Greek kolla = glue, eidos= like

Preparation of Colloids:

1. Preparation of lyophilic colloids: In lyophilic colloids, the dispersed phase has a strong affinity for the dispersion medium. Therefore, these colloids can be prepared easily by simply mixing the dispersed phase and the dispersion medium under ordinary conditions. For example, gum readily dissolves in water at room temperature. Colloidal solutions like gelatine and starch can be prepared by heating them with water.
2. Preparation of lyophobic colloids: Lyophobic colloids can be prepared by Condensation methods

Condensation methods: In condensation methods, particles of colloidal dimensions are obtained by condensing small particles of the dispersed phase. The following physical and chemical methods can be used.

I. Physical methods:

(a) **Solvent exchange**: Colloidal solutions of some substances can be prepared by dissolving it in a solvent in which it is soluble and then pouring it in a solvent in which it is either less soluble or insoluble. For example, colloidal solution of sulphur and phosphorus can be prepared by first dissolving them in alcohol and then pouring the alcoholic solution in excess of water. Alcohol is then removed by dialysis. Such colloidal solutions are however unstable.

(b) **Excessive cooling**: A colloidal solution of ice is obtained by freezing a mixture of water and organic solvent such as chloroform, pentane or ether.

(c) **Condensation of hot vapour under a liquid phase**: Sols of certain elements can be prepared by condensing their vapours in the cooled dispersion medium. For example, sols of mercury and sulphur are prepared by passing their vapours through cold water containing a suitable stabiliser such as ammonium salt or citrate.

(d) **Controlled condensation**: Colloidal sols of certain insoluble substances are prepared by precipitating them in the presence of some protective colloids like starch, gelatine, gum or agar-agar. For example, a sol of Prussian blue is obtained by precipitating it in the presence of starch.

II.Chemical Methods:

Oxidation: This method is used to make sols of some non-metals. For example, if H2 S gas is passed through a solution of bromine water or sulphur dioxide, a colloidal sol of sulphur is obtained.

$$H_2S + B_{r2} \rightarrow 2HBr + S \text{ (sulphur sol)}$$

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S \text{ (sulphur sol).}$$

Reduction: The colloidal solutions of metals are obtained by reduction of their compounds. For example, a solution of AuCl3 is reduced with $SnCl_2$.

$$2AuCl_3 + 3SnCl_2 \rightarrow 3SnCl_4 + \underset{\text{Gold sol}}{2Au}$$

The gold sol thus prepared has a purple colour and is called purple of cassius. Similarly, silver sol can be obtained by the reduction of AgNO3 solution containing alkaline dextrin as stabiliser with different reducing agents.

Hydrolysis: Colloidal solution of many oxides and hydroxides can be prepared by this method. For example, if a concentrated solution of ferric chloride is added drop by drop to hot water, a colloidal solution of ferric hydroxide is obtained.

$$FeCl_3 + 3H_2O \rightarrow \underset{\text{(Sol)}}{Fe(OH)_3} + 3HC$$

A beautiful red sol of ferric hydroxide can also be prepared by boiling ferric acetate in a beaker having distilled water.

$$(CH3COO)_3Fe + 3H_2O \rightarrow Fe(OH)_3 + 3CH_3COOH$$

To stabilise the sol thus obtained, excessive CH3 COOH is removed immediately by electro dialysis.

Double decomposition: This method is generally employed for preparing the sols of insoluble salts. For example, very dilute solutions of FeCl3 and K4 [Fe (CN) 6] are mixed to prepare a colloidal sol of Prussian blue.

$$3K4[Fe(CN)6] + 4FeCl_3 \rightarrow Fe4[Fe(CN)6]_3 + 12KCl \text{ Sol}$$

Similarly, by passing H_2S through dilute solution of arsenious oxide in water $A_{s2}S_3$ sol is obtained.

$$As_2O_3 + 3H2S \rightarrow \underset{\text{(Sol)}}{As_2S_3} + 3H_2O$$

Micelle formation or Mechanism of micelle formation:

A Colloidal sized particle (aggregate) formed in water by the association of simple molecules each having hydrophobic and hydrophilic end is known as micelle

Ex., Concentrated solution is an associated colloid

Mechanism:

Cloth contains Grease or fat. This is known as dirt. Dirt or grease forms an emulsion with water used for cleaning but this emulsion is not stable. Soap functions as emulsifying agent for water dirt emulsions in the cleaning process. The main function of soap is to convert the dirt or grease on the cloths into large colloidal particles (micilles). Soap (Sodium stearate) dissolves in water to give Na^+ and stearate ions. The stearate ions contain hydrophobic end (alkyl group end) called tail and contain hydrophilic end (carboxylate ion end) called head. The tail part dissolves the grease or dirt and forms the micelle. The micelle then removed by water in the cleaning process.

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

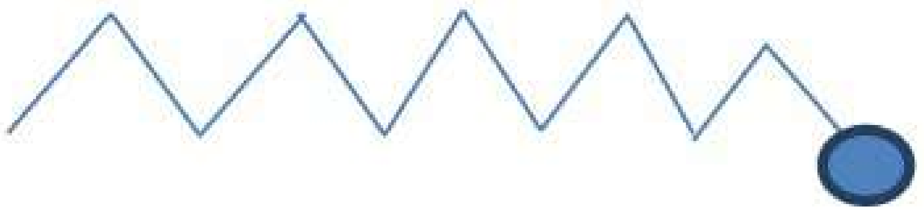


Fig: Electrically charged, hydrophilic part

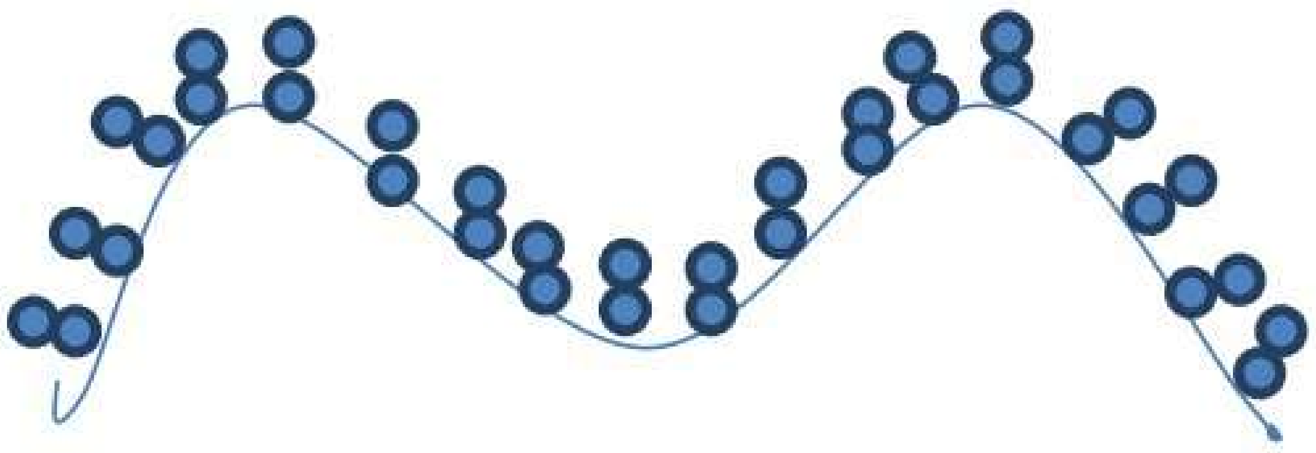
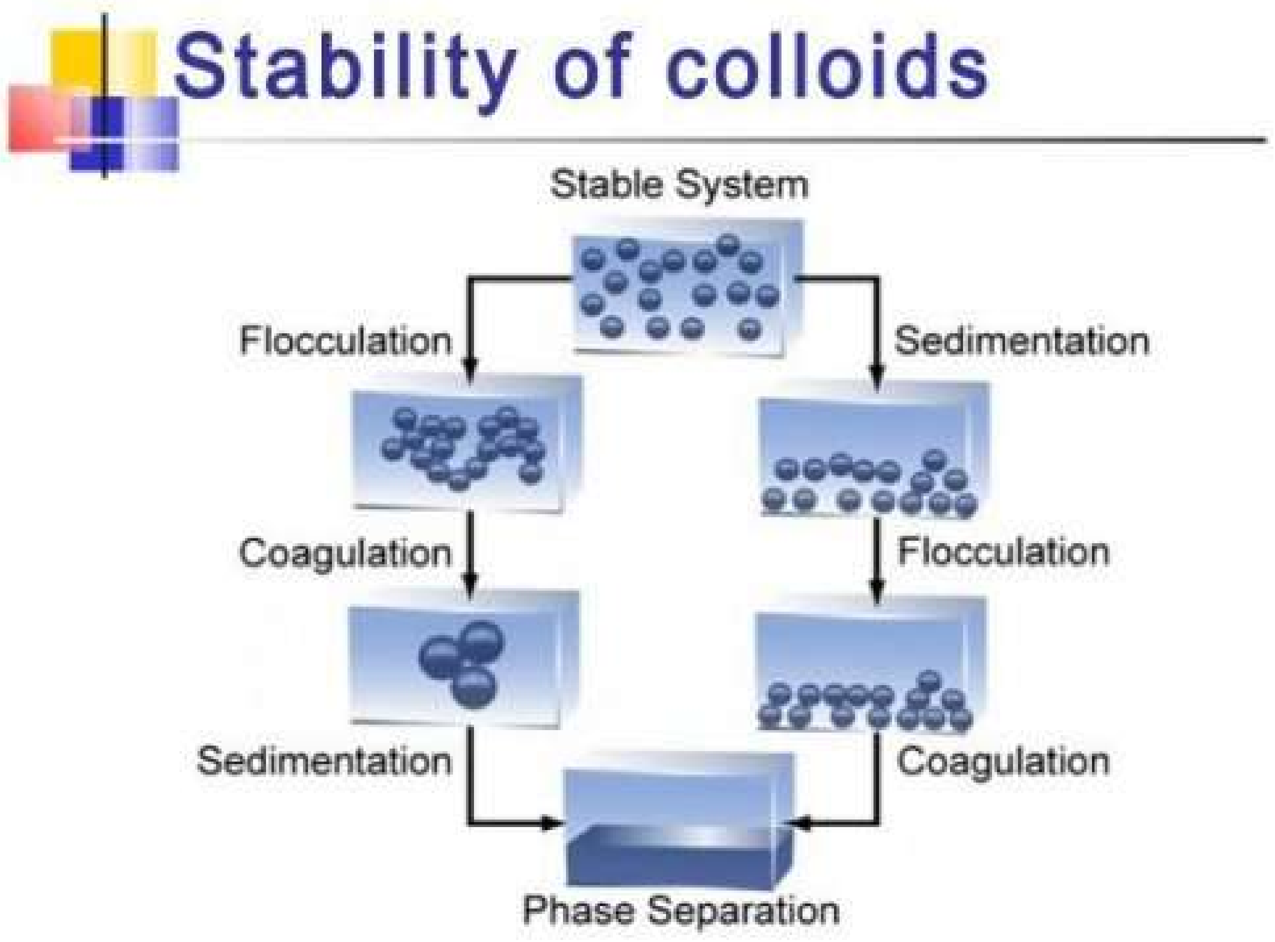


Fig: Hydrocarbon chain, hydrophobic part of soap

Stabilization of colloids:

- A stable colloidal system is one in which the particles resist flocculation or aggregation and exhibits a long shelf-life.
- Depends upon the balance of the repulsive and attractive forces that exist between particles as they approach one another. If all the particles have a mutual repulsion then the dispersion will remain stable.



- If the particles have little or no repulsive force then some instability mechanism will eventually take place e.g. flocculation, aggregation etc.

Adsorption of Gases on Solids

In adsorption of gases on solid surface, the solid surface is called the adsorbent and the gas adsorbed is called **adsorbate**. The extent of adsorption depends on many factors.

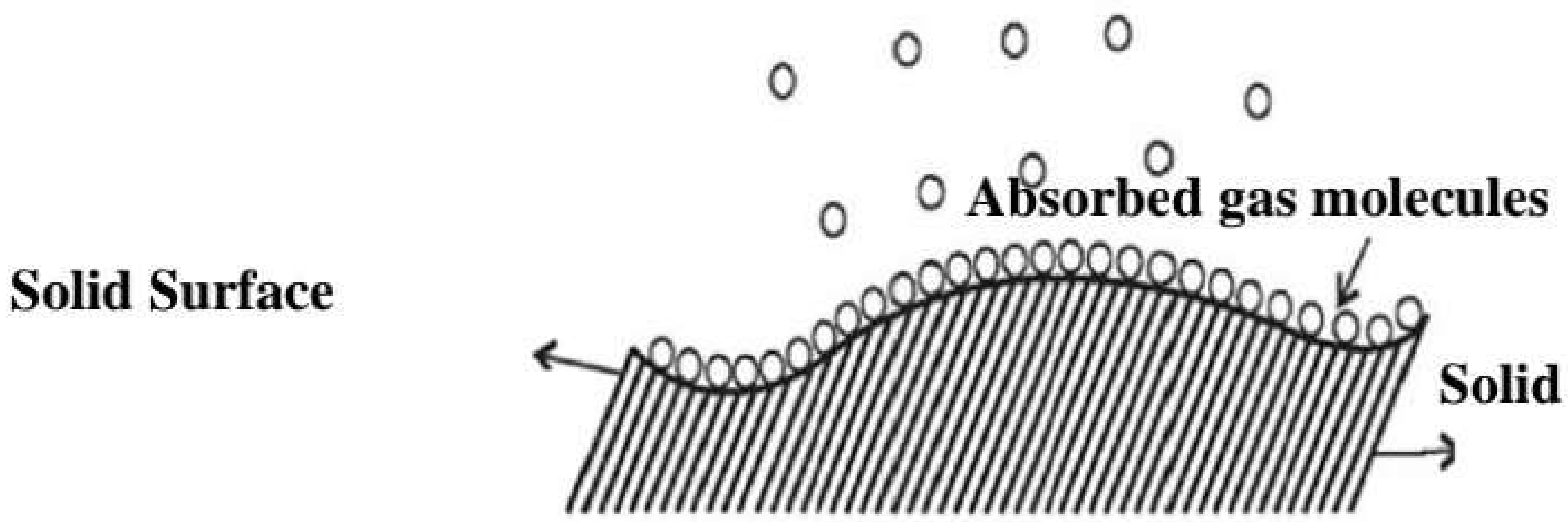


Fig. : Adsorption of gases on solids

Factors Affecting the Extent of Adsorption

(i) Nature of Adsorbent

The adsorption depends on the type of adsorbents used. When the adsorbent is highly porous the rate of adsorption increases. Activated carbon, metal oxides like aluminium oxide, silica gel and clay are commonly used adsorbents. The rate of adsorption can be increased by activation process. It helps in enhancing the pores in the adsorbent Eg. Charcoal adsorbs 0.011 gms of CCl_4 at 24°C and activated charcoal adsorbs 1.48 gm of at 24°C.

Activation of adsorbent

During activation, the adsorbent is heated in steam to about 1500°C. Heating drives out all impurities and leads to a lager free surface for adsorption. It can be done in 3 given ways

- By making the surface of adsorbent rough.
- By heating the adsorbent in vacuum so that the water vapour present in pores leave those pores.
- By increasing the surface area of adsorbent

(ii) Surface area of adsorbent

Increase in surface area of the adsorbent increases the adsorption of gases andthe extent of adsorption depends on two factors

- Greater the surface area greater the adsorption-Increase in surface area increases the number of adsorbing sites.
- Larger the porosity greater the adsorption-Finely divided and highly porous materials acts as good adsorbents.

Eg. Charcoal and silica gel (excellent adsorbents).

(iii) Nature of Gases

The amount of gas adsorbed by a solid depends on the nature of the gas. Easily liquefiable gases like HI, NH_3, CI_2, SO_2 etc., are adsorbed more easily then the permanent gases like H_2, N_2, and O_2 etc. Physical adsorption is non-specific in nature, so any gas will be adsorbed on the surface under any given conditions of temperature and pressure. Chemisorption is specific in ature so only those gases which forms chemical bonds will be adsorbed.

The nature of gas depends on two factors:

- **Critical Temperature** (maximum temperature above which the gas cannot be liquefied). Liquefactions of gases depend on critical temperature. When the critical temperature is more the gases will be liquefied and more adsorption occurs.
- **Van der Waal's forces**: Easily liquefiable gases possess greater Vander Waal's forces than permanent gases, so they are adsorbed more readily.

(iv) Exothermic Nature

Heat of adsorption is defined as the energy liberated when 1 g mol of a gas is adsorbed on a solid surface. Increase in temperature increases the kinetic energy of the gas molecules and it results in more number of collisions of gas molecules over the adsorbent surface.

(v) Pressure

When pressure is increased then the rate of adsorption increases initially. The extent of adsorption is Expressed as x/m where 'x' is amount of adsorbate; 'm' is mass of adsorbent when the dynamic equilibrium is established between free gas and the adsorbed gas. But after some time it reaches appoint where no more adsorption occurs and at this point adsorption is independent of pressure.

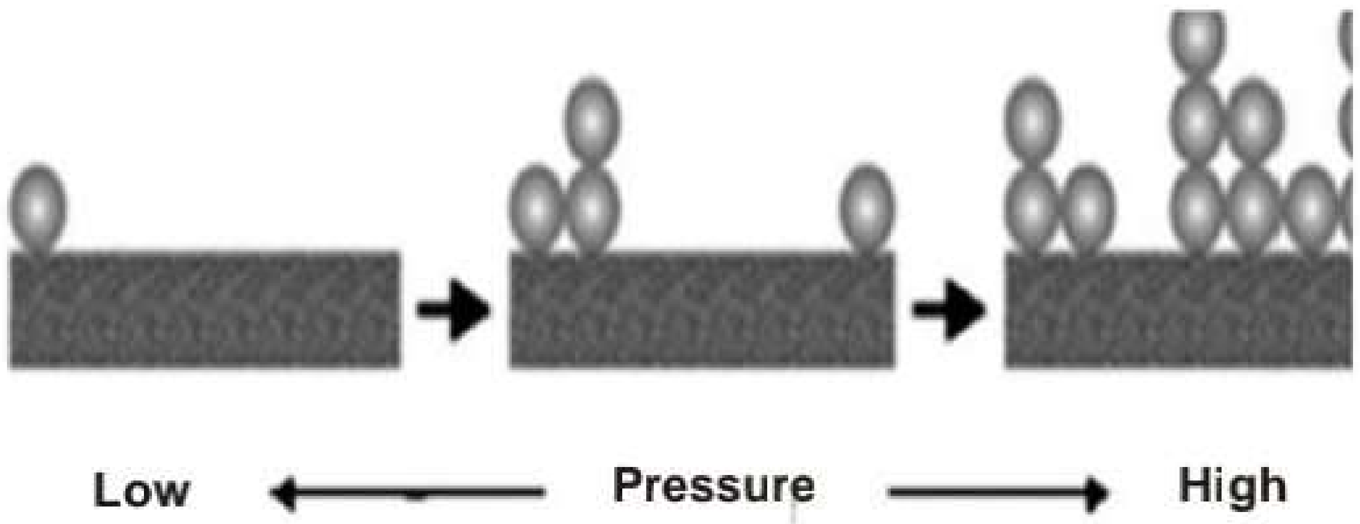


Fig. : Rate of adsorption

Adsorption of Solute from Solutions

The process of adsorption of solutes on solid surface can take place from solutions. For example the activated animal charcoal adsorbs colouring matter present in sugar solution and clarifies the sugar solution. It also has the capacity to absorb acetic acid and oxalic acid from water thereby reducing the concentration of acids in water.

There are two (or more) components present in a solution namely solute and solvent. The solute may be present in the molecular or ionic form. The extent of adsorption from solution. Depends upon the concentration of the solute in the solution, and can be expressed by the **Freundlich Isotherm**.

$$\frac{x}{m} = k \cdot c^{(1 \cdot n)}$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

where, x- is the mass of the solute adsorbed,

m -is the mass of the solid adsorbent,

c -is the concentration of the solute in the solution &

n -is a constant having value greater than one,

k -is the proportionality constant.

The value of k depends upon the nature of solid, its particle size, temperature, and the nature of solute and solvent etc. It the graph is plot between x/m against c which gives a straight line which is similar to Freundlich adsorption isotherm.

Factors Affecting Adsorption of Solutes from Solution

Nature of adsorbent

Adsorption of solute from solution is highly specific. Adsorption depends mainly on nature of adsorbent.

Temperature

Adsorption from solution decreases with rise in temperature.

Concentration of solute

Adsorption from solution decrease with decrease in concentration of solution.eg charcoal adsorbs water from dilute KCl solution whereas charcoal adsorbs KCl from concentrated KCl solution.

Factors on which Adsorption Depends Temperature

Adsorption increases at low temperature conditions. Adsorption process is exothermic in nature. According to LeChatleir principle, low temperature conditions would favour the forward direction.

Pressure: As depicted by Adsorption Isotherm, with the increases in pressure, adsorption increases up to a certain extent till saturation level is achieved. After saturation level is achieved no more adsorption takes place no matter how high the pressure is applied.

Surface Area: Adsorption is a surface phenomenon therefore it increases with increase in surface area.

Activation of Adsorbent: Activation of adsorbent surface is done so as to provide more number of vacant sites on surface of adsorbent. This can be done by breaking solid crystal in small pieces, heating charcoal at high temperature, breaking lump of solid into powder or other methods suitable for particular adsorbent.

Disadvantages

1. This equation is purely empirical and has no theoretical basis.
2. This equation is valid only up to a certain pressure and invalid at higher pressure.
3. The constants k and n are temperature dependents, they vary with temperature.
4. This isotherm fails, when the concentration of adsorbate is very high.

Adsorption Isotherm

The process of adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate (*x*) adsorbed on the surface of adsorbent (*m*) and pressure (P) at constant temperature.

$$\text{Adsorbent} + \text{Adsorbate} \Longleftrightarrow \text{Adsorption}$$

Adsorption isotherm shows the amount of molecules adsorbed on the solid surface as a function of the equilibrium partial pressure at constant temperature.

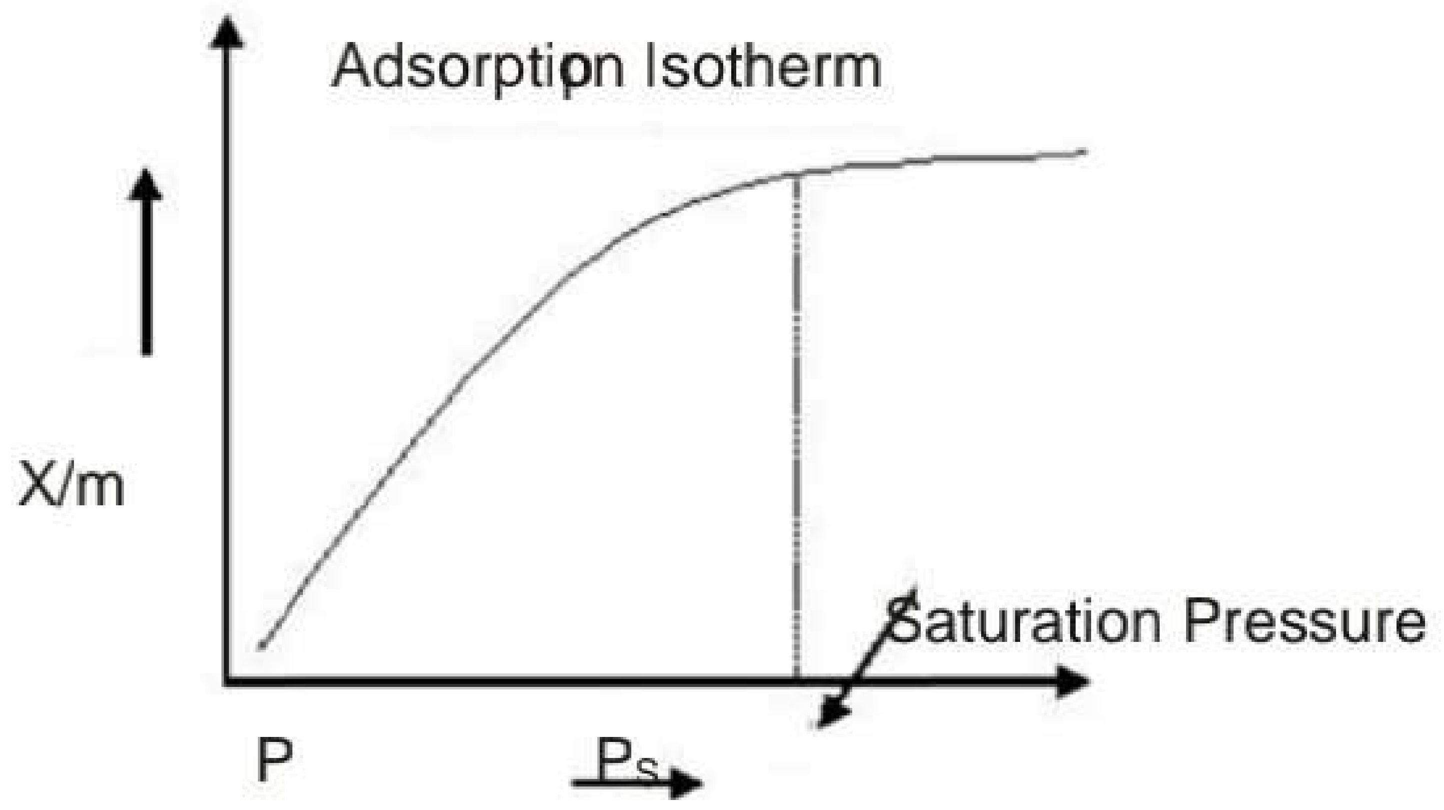


Fig. : Adsorption Isotherm

A plot of x/m vs. P is plotted to obtain adsorption at constant temperature, P_S is called the saturation pressure.

Freundlich Adsorption Isotherm

In 1909, Herbert Freundlich gave an expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. Freundlich adsorption isotherm is an empirical relation between the concentrations of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. The isotherm is given as:

$$\frac{x}{m} = kp^{\frac{1}{n}} \quad \text{or} \quad [\, n > 1 \,]$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

where x – is mass of adsorbate,

m – is mass of adsorbent,

P – is the equilibrium pressure of adsorbate, K & n – are constants.

At low pressure, extent of adsorption is directly proportional to pressure:

$$\frac{x}{m} \propto p^1$$

At high pressure, extent of adsorption is independent of pressure:

$$\frac{x}{m} \propto p^0$$

At intermediate value of pressure, adsorption is directly proportional to pressure raised to power

—

$1/n$ value is greater than 1

$$\frac{x}{m} \propto p^{(1/n)}$$

To remove proportionality a proportionality constant 'k' is used which is known as adsorption constant and we get

$$\frac{X}{m} = k.\, p^{(1/n)}$$

The above equation is known as Freundlich Adsorption equation.

Plotting of Freundlich Adsorption Isotherm

$$\frac{X}{m} = k.\, p^{(1/n)}$$

Taking log both sides of equation, we get,

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

The equation is comparable with equation of straight line, $y = m\,x + c$ where, m represents slope of the line and c represents intercept on y axis. Plotting a graph between log (x/m) and log p, we will get a straight line with value of slope equal to $1/n$ and log k as y-axis intercept.

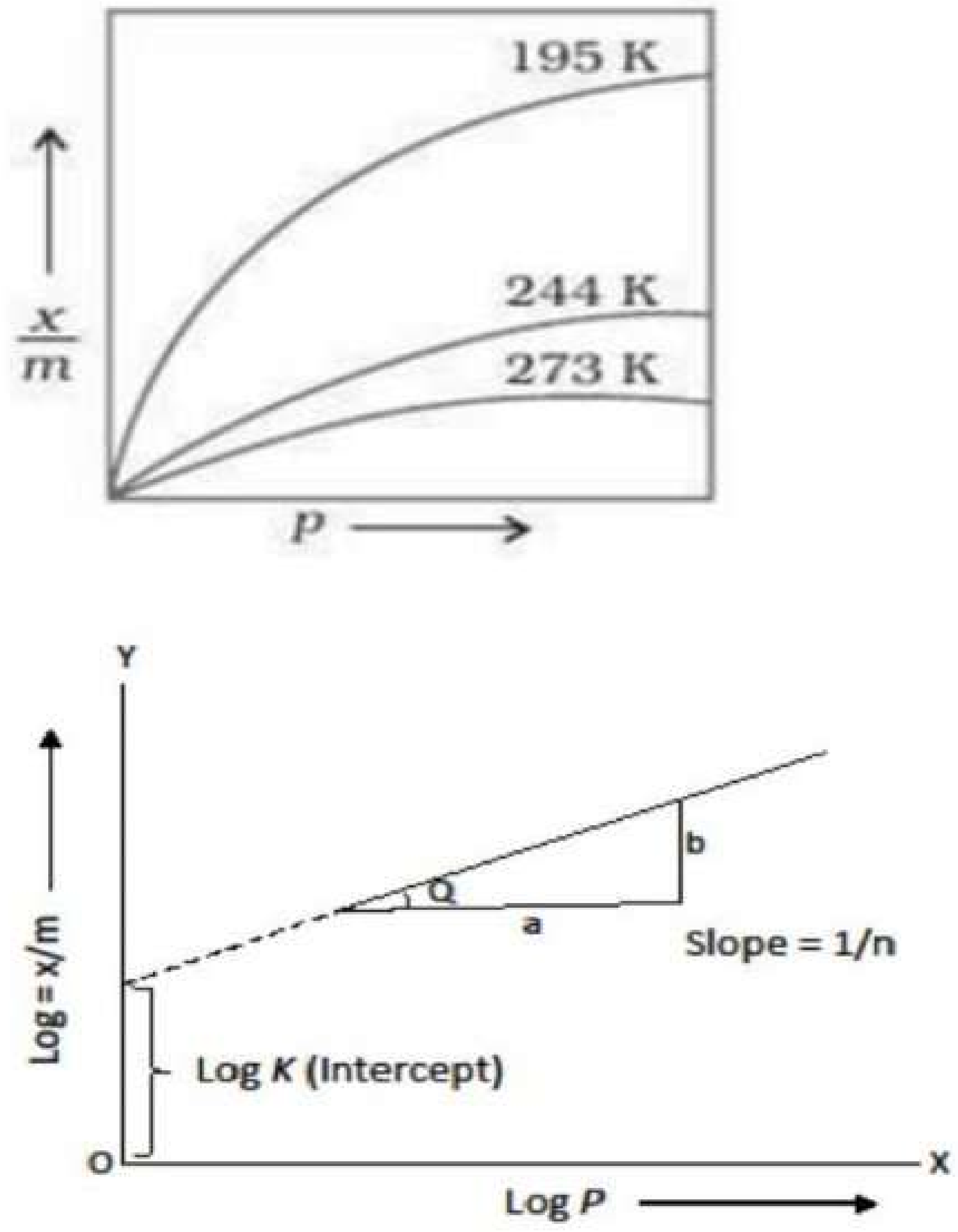


Fig. : log (x/m) vs. log p graph

Limitation of Freundlich Adsorption Isotherm

1. Freundlich equation is purely empirical and has no theoretical basis.
2. The equation is valid only upto a certain pressure and invalid at higher pressure.
3. The constants *k* and *n* are not temperature independent, they vary with temperature.
4. Frendilich's adsorption isotherm fails when the concentration of the adsorbate is very high.

Langmuir Adsorption Isotherm

In 1916, Irving Langmuir proposed another adsorption Isotherm which explained the variation of adsorption with pressure.

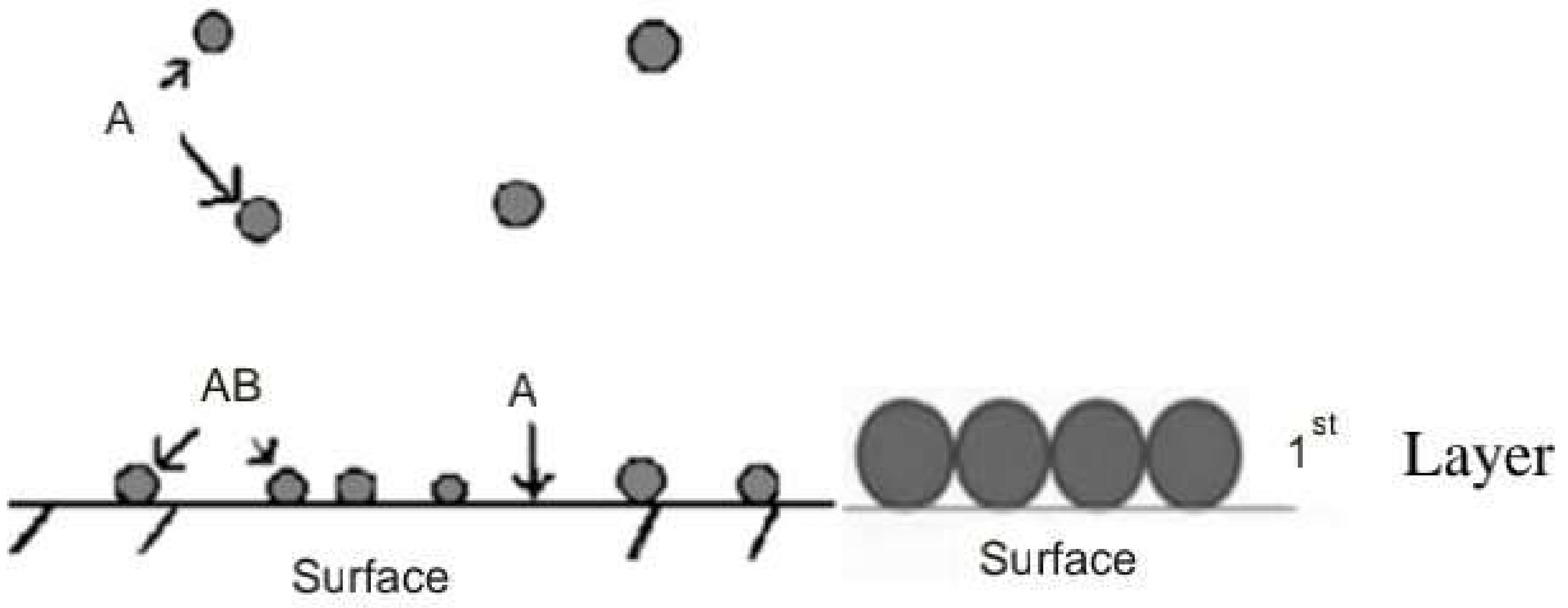


Fig. : Equilibrium between tree molecule and adsorbed molecules

Assumptions of Langmuir Isotherm

Langmuir proposed his theory by making following assumptions.

(i) Surface is energetically uniform. Fixed number of vacant or adsorption sites are available on the surface of the solid.

(ii) All the vacant sites are of equal size and shape on the surface of adsorbent.

Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released.

(iii) Heat of adsorption is constant throughout the surface and it ranges from 0 to 1.

(iv) Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

(v) Adsorption is monolayer or unilayer.

Limitations of Langmuir Adsorption Equation

(i) The adsorbed gas has to behave ideally in the vapour phase. Langmuir equation is valid under low pressure only.

(ii) Langmuir Equation assumes that adsorption is monolayer. But, monolayer formation is possible only under low pressure condition. Under high pressure condition the assumption breaks down as gas molecules attract more and more molecules towards each other.

(iii) Another assumption is the surface of solid is homogeneous but in real solid surfaces is heterogeneous.

(iv) Langmuir equation assumed that molecules do not interact with each other. This is impossible as weak force of attraction exists even between molecules of same type.

(v) In adsorption liquefaction of gases taking place, which results in decrease in randomness but the value is not zero.

Types of Adsorption Isotherm

Adsorption process is usually studied through graphs known as adsorption isotherm. After saturation pressure P_s, adsorption does not occur anymore, as there are limited numbers of vacancies on the surface of the adsorbent. At high pressure when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, adsorption is independent of pressure. There are 5 different types of adsorption isotherms and each of them has specific characteristics.

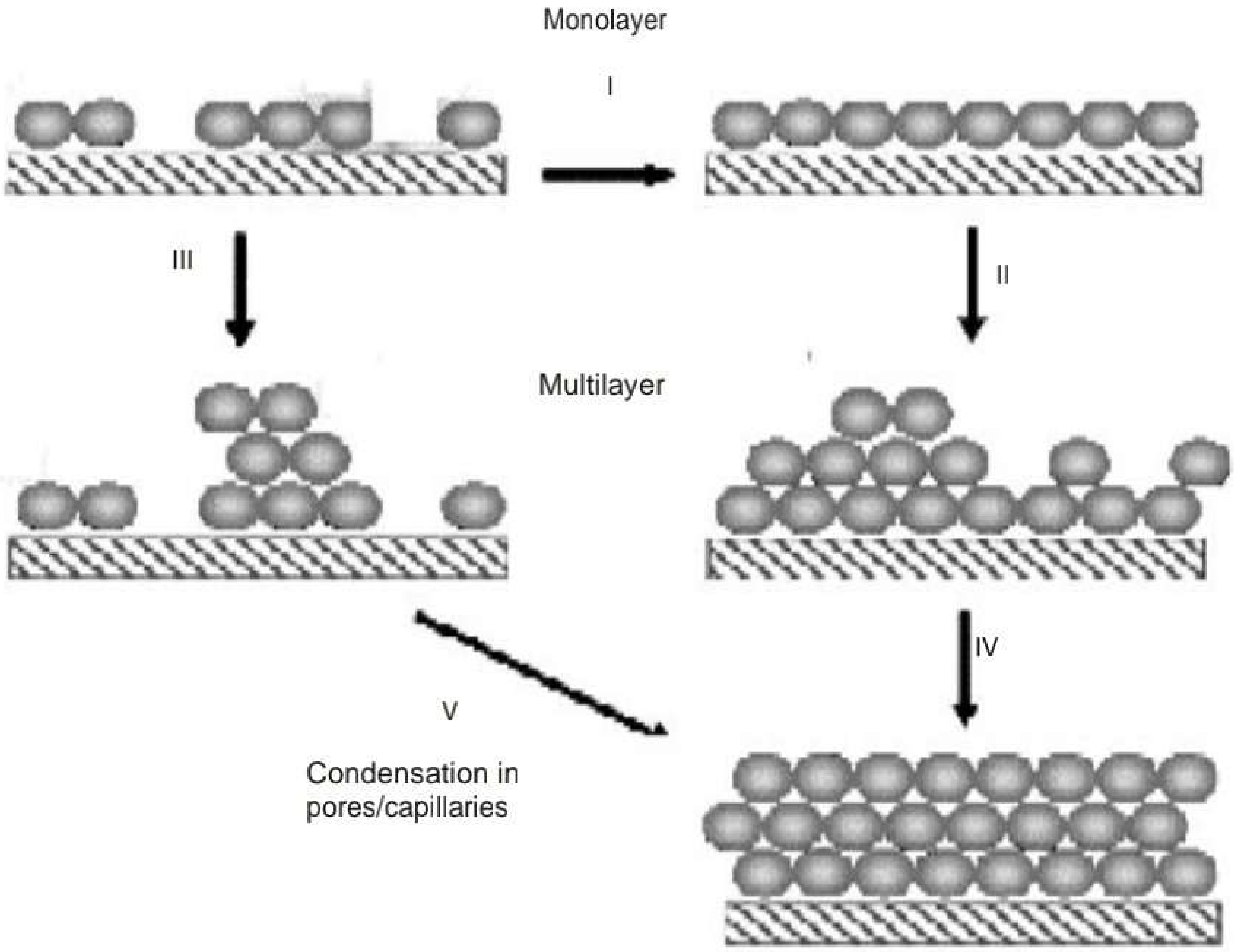


Fig. : Illustration of different types of Adsorption Isotherm

Type I Adsorption isotherm is for very small pores or micro porous adsorbents.

Adsorption occurs by filling of micropores and it mainly depicts Monolayer adsorption.
Eg. Adsorption of Nitrogen or Hydrogen on charcoal around - 1800°C.

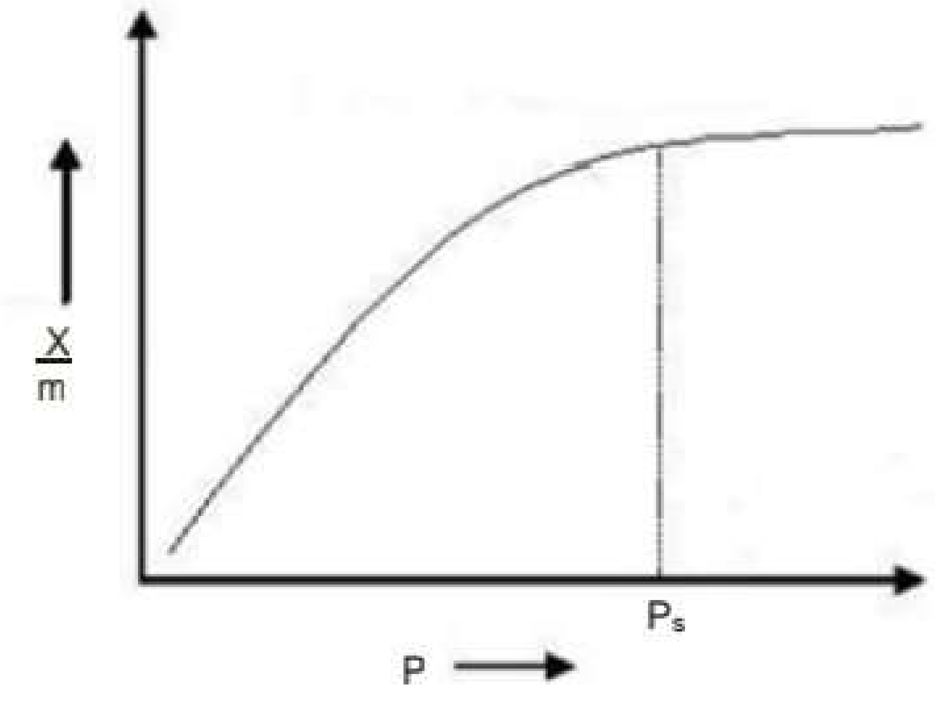


Fig. : Type I

Type II Adsorption isotherm shows large deviation from Langmuir model of adsorption. They are most frequently encountered when adsorption occurs on nonporous powders or macro porous adsorbents with unrestricted monolayer-multilayer adsorption.

The intermediate flat region in the isotherm corresponds to monolayer formation. When take place corresponding to the 'sharp knee' of the isotherms.

Eg: Iron (Fe) catalyst and Nitrogen (N (*g*)) adsorbed at -1950°C on silica gel.f
2

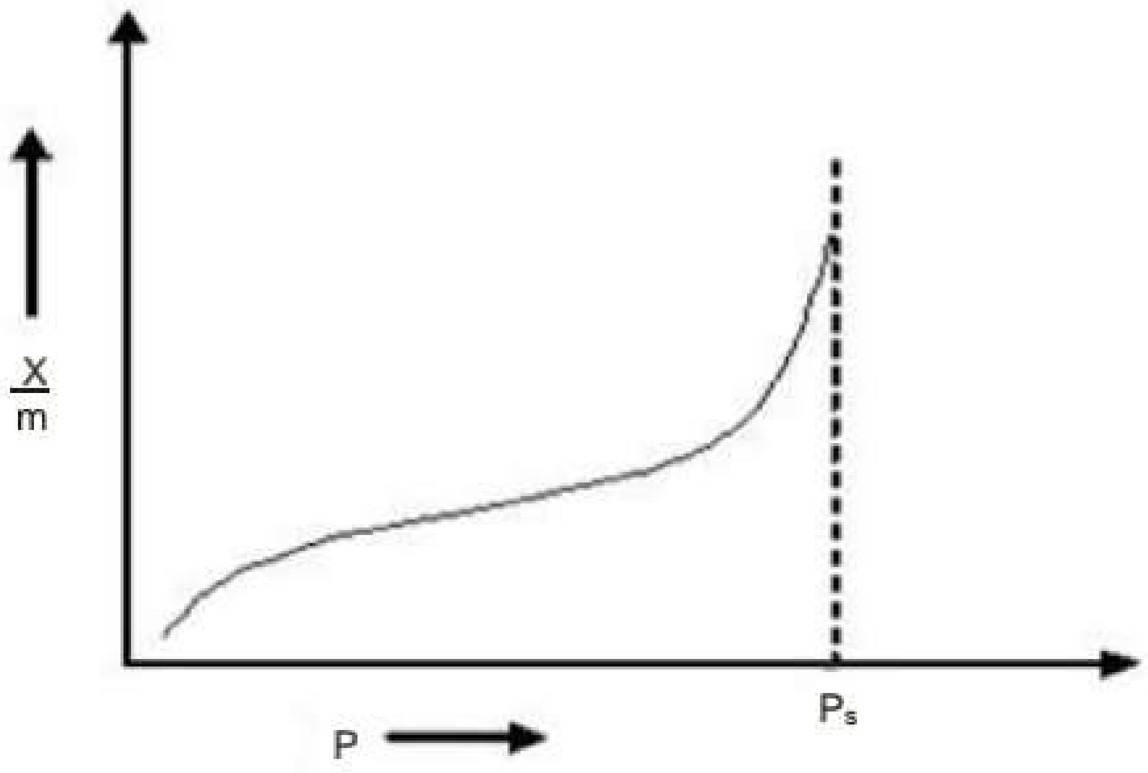


Fig. : Type II

Type III Adsorption Isotherm also shows large deviation from Langmuir model. This isotherm explains the formation of multilayer. They are characterized principally by heats of adsorption which are less than the adsorbate heat of liquefaction.

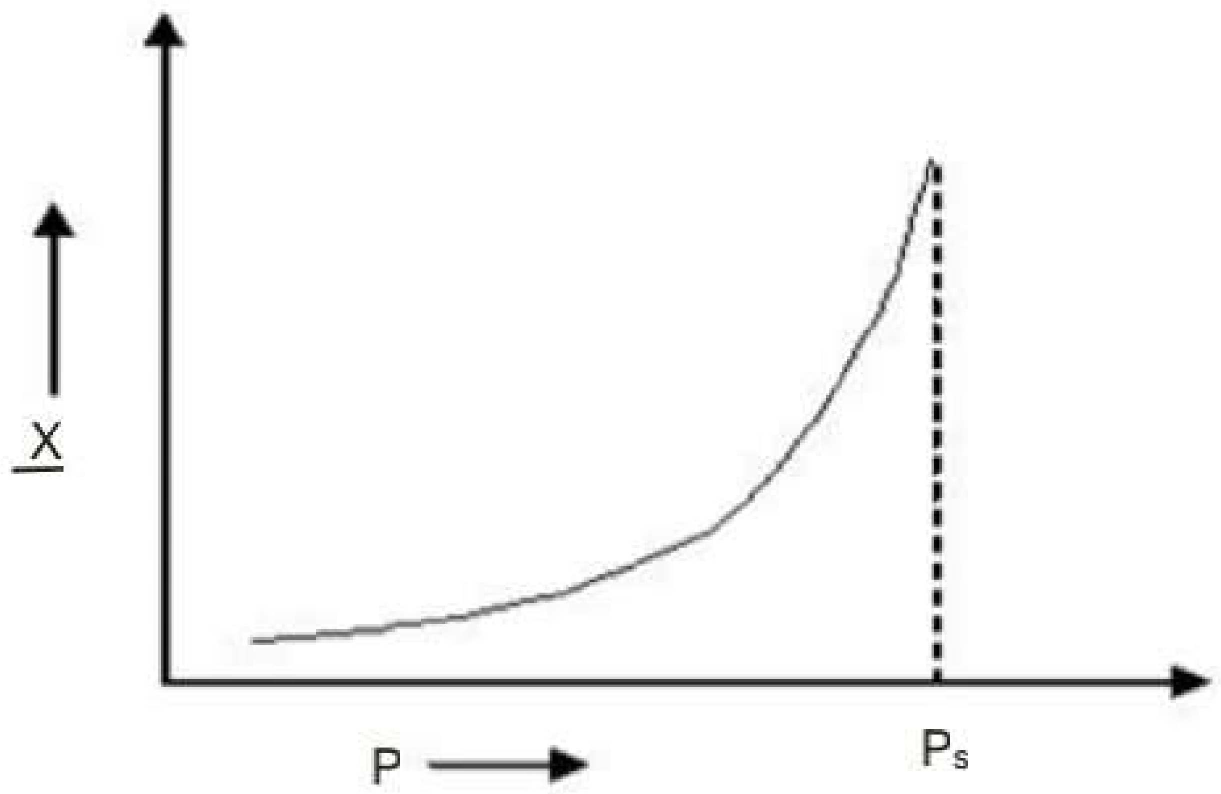


Fig. : Type III

Type IV Adsorption Isotherm occurs on porous adsorbents possessing pores in the range of approximately 15-1000 angstroms (A). At lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer.

The intermediate flat region in the isotherm corresponds to monolayer formation.

The saturation level reaches at a pressure below the saturation vapor pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure (P_S) of the gas.

Eg. Adsorption of Benzene on Iron Oxide (Fe_2O_3) at 500°C and adsorption of Benzene on silica gel at 500°C.

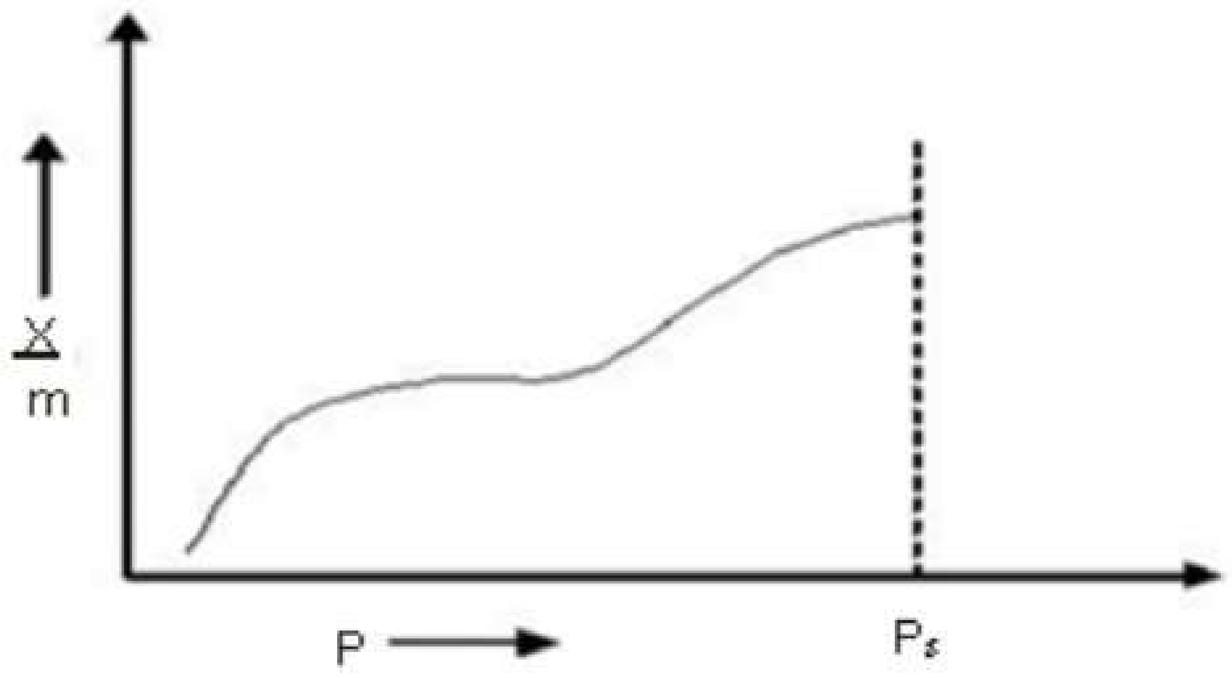


Fig. : Type IV

Type V Adsorption Isotherm results from small adsorbate-adsorbent interaction potentials similar to the Type III isotherms. However, Type V isotherms are also associated with pores in the same range as those of the Type IV isotherms.

Eg: Adsorption of Water (vapors) at 1000°C on charcoal.

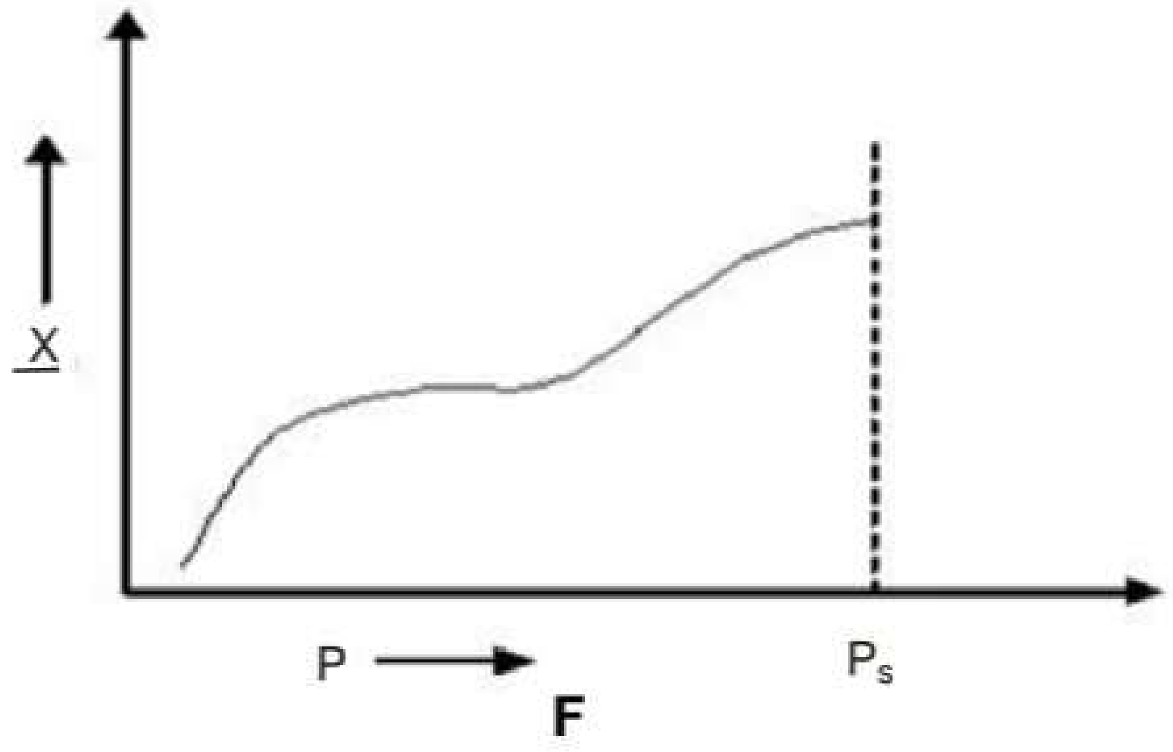


Fig.: Type V

Type III and Type V isotherms do not have the 'sharp knee' shape implying stronger adsorbate – adsorbate interactions than adsorbate-adsorbent interaction. **Type IV and V** shows phenomenon of capillary condensation of gas.

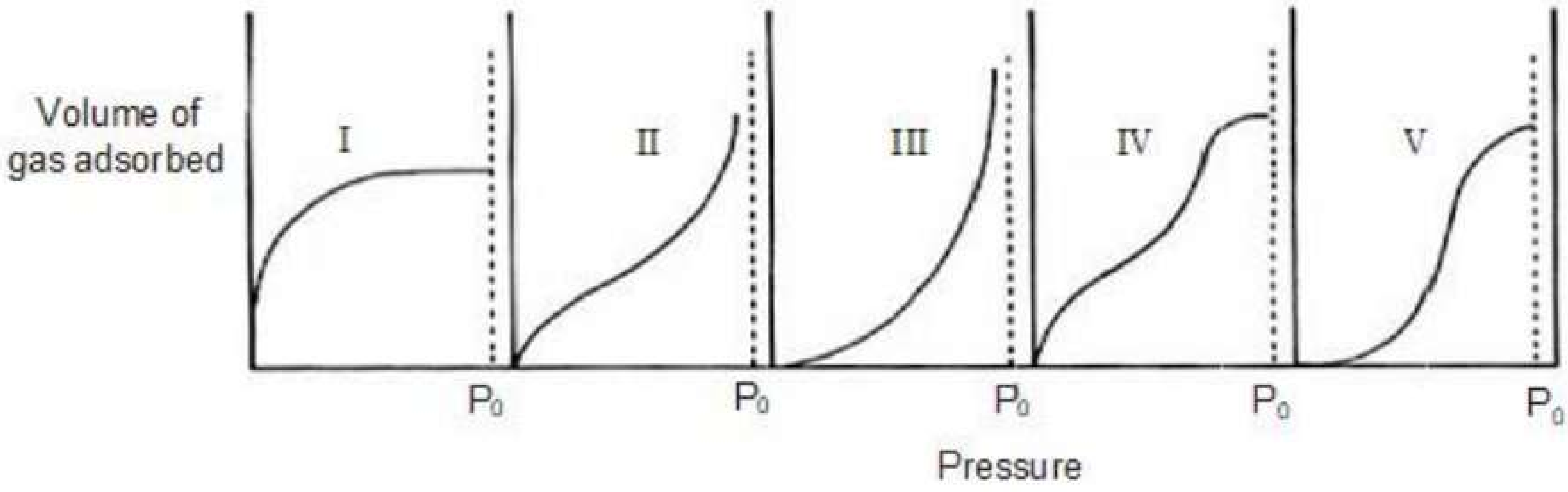


Fig.: Different types of adsorption isotherms

Application of Adsorption

Extensive application of adsorption is been listed below

1. Production of high vacuum

In Dewar flasks activated charcoal is placed between the walls of the flask so that gas entering into the annular space gets adsorbed.

2. In Gas masks

Activated carbon is used in gas masks to adsorb poisonous gases (e.g. oxide of sulphur, NOx etc.) and purifies air for breathing.

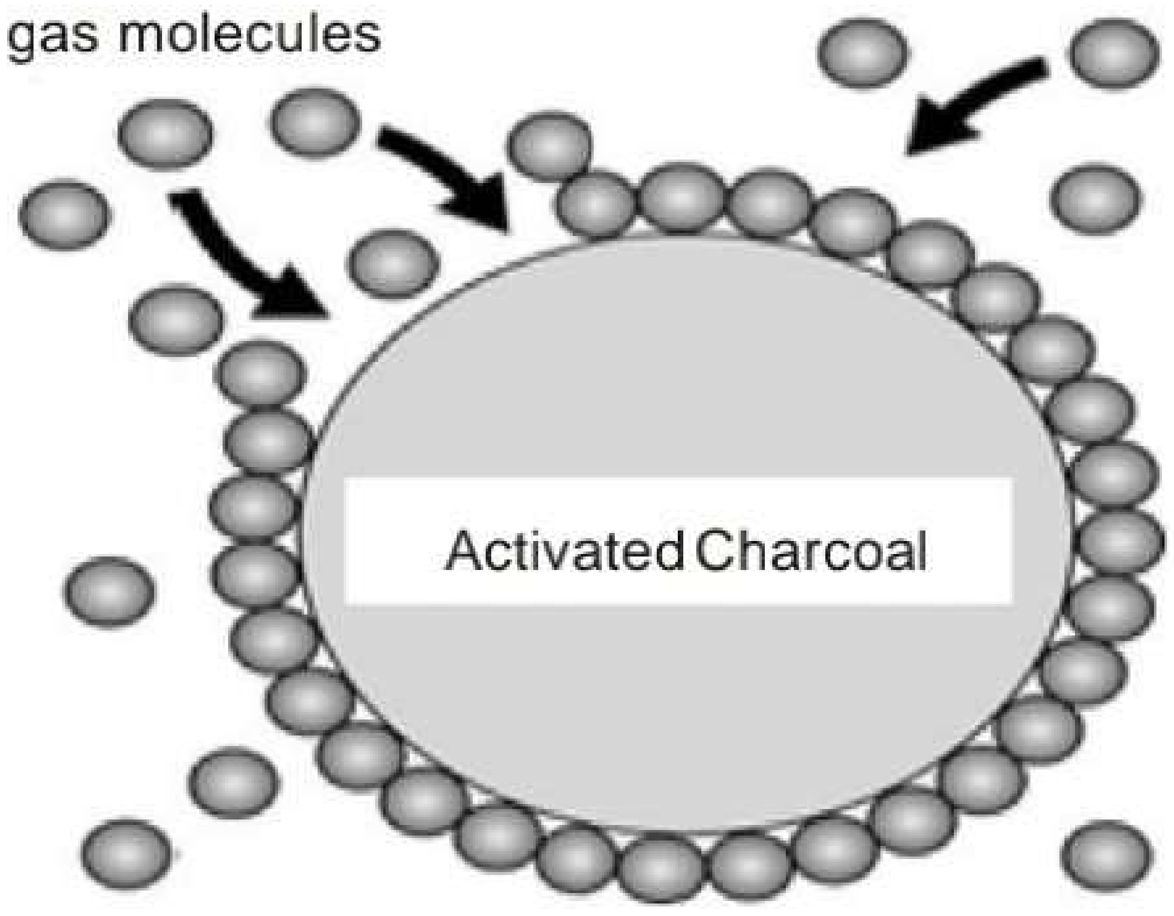


Fig. : Adsorption of poisonous gases using activated charcoal

3. In desiccation or dehumidification

Certain substances can be used to remove water vapor or moisture present in the air. Silica gel and alumina are used for dehumidification in electronic equipment.

4. In clarification of sugar

Sugar is decolorized by treating sugar solution with animal charcoal powder which removes the colour producing substances.

5. In paint industry

The paint should not contain dissolved gases as it inhibits the adherence capacity of paint to the surface to be coated. The dissolved gases are therefore, removed by suitable adsorbents. This is done by adding suitable liquids which adsorbs these films. Such liquids are called wetting agents. Eg. Use of spirit as wetting agent in furniture painting..

6. Adsorption chromatography

Analytical method, in which molecules are separated according to their adsorptive properties, where a mobile fluid phase is passed over an immobile solid adsorptive stationary phase.

7. In adsorption indicators

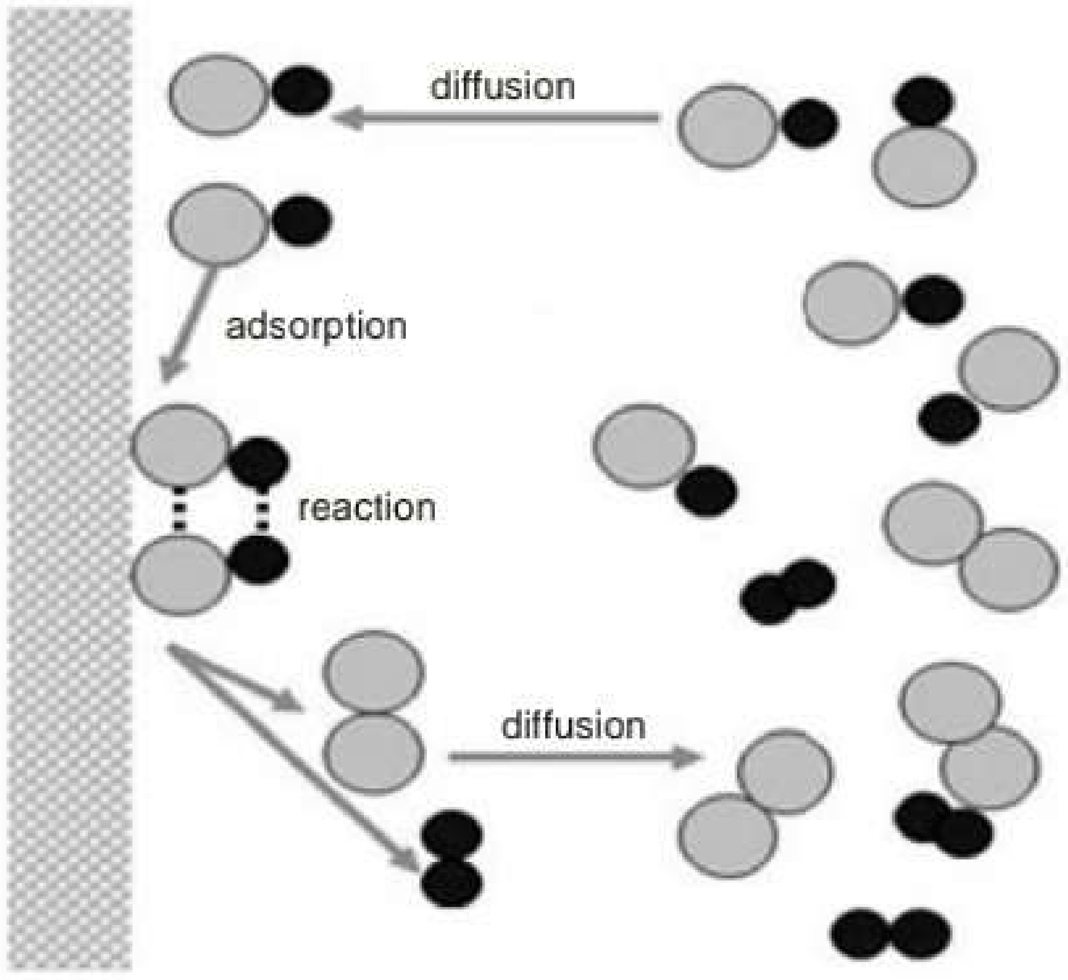
Various dyes which possess adsorption property have been introduced as indicators mainly in precipitation titrations. For example KBr is titrated with $AgNO_3$ using eosin as an indicator

8. Heterogeneous Catalysis

In heterogeneous catalytic reactions adsorption of gaseous reactants on solid catalyst occurs. The adsorption mechanism is responsible for the greater efficiency of the catalyst in the finely divided state and helps us to understand the action of catalyst promoters and poisons. eg,

1. Finely powdered nickel is used for the hydrogenation of oils.
2. In manufacture of sulphuric acid finely divided vanadium pentaoxide (V_2O_5) is used in the contact

process.



(i) **diffusion** of reactants to surface;
(ii) **adsorption** of reactants to surface;
(iii) **reaction** on the surface;
(iv) **desorption** of products from surface;
(v) diffusion of products away from the surface**.**

Fig. : Process of Heterogeneous Catalysis

9. In adsorption indicators

In many precipitation titrations many dyes are used as indicators which work on the principle ofadsorption.

10. In curing diseases

Some pharmaceutical drugs have the capacity to adsorb the germs on them and kill them and protect us from diseases.

11. Lake test for aluminium

It is based on adsorption of litmus paper by $Al(OH)_3$ precipitate

12. Separation of inert gases

Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

13. In softening of hardwater

The use of ion exchangers for softening of hard water is based upon the principle of adsorption chromatography. The ion exchange resins helps to remove hardness causing ions from water and make it useful for industrial and domestic applications.

14. Arsenic Poisoning

Colloidal ferric hydroxide is administered which adsorbs arsenic and removes it from body by vomiting

15. Formation of stable emulsions in cosmetics and syrups etc.

16. Froth floatation method

Used for concentration of sulphide ores is based on adsorption.

17. In cleaning action of soaps and detergents

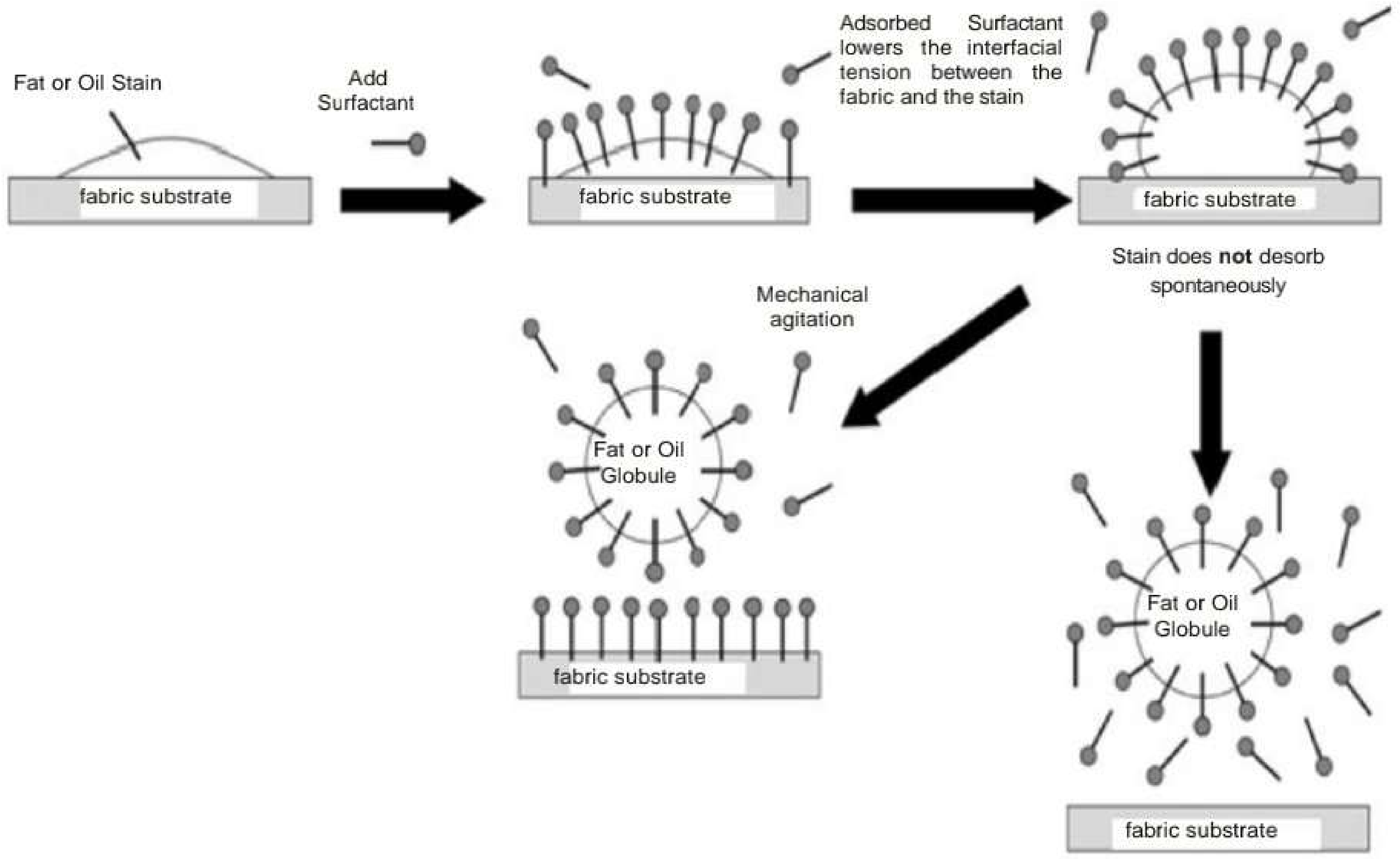


Fig. : Cleaning actions of soaps and detergents

18. Application of adsorbents on pollution abatement

- Many pollutants, both natural and synthetic, are gaseous in nature and it need to be effectively removed from the exhaust.
- Gaseous industrial pollutants include HC*l*, H_2SO_4, H_2S, SO_X, NO_X, NH_3, Ethylene, Benzene, Ethanol, and HAP's. Adsorption is a mass transfer process in which a porous solid comes in contact with a liquid or gaseous streamto selectively remove pollutants or contaminates by adsorbing them onto the solid.
- The most common adsorbents used in industry are activated carbon, silica gel, activated alumina (alumina oxide), and zeolite. Activated carbon is the most common non-polar adsorbent. Polar adsorbents have a great attraction to absorb moisture.
- Most industrial exhaust streams contain moisture the use of polar adsorbents is significantly limited for air pollution control systems. There are two main types of adsorption systems; fixed bed or continuous.

BET Equation:

Brunauer–Emmett–Teller (**BET**)equation was first published in 1938 (Brunauer, 1938), and continues to be the most widely used method to determine the number of molecules/atoms of a gas needed to form a monolayer, X_m, of adsorbed gas on a solid surface (Thommes, 2015). The BET equation (Equation 1) describes the relationship between the number of gas molecules adsorbed (X) at a given relative pressure (P/P_0), where C is a second parameter related to the heat of adsorption.

$$\frac{1}{X[(P_0/P)-1]} = \frac{1}{X_m C} + \frac{C-1}{X_m C}\left(\frac{P}{P_0}\right)$$

Equation 1: BET equation for surface area measurement

The BET equation strictly describes a linear plot of $1/[X(P_0/P)-1]$ vs. P/P_0 which for most solids, using nitrogen as the adsorbate, is restricted to a limited region of the adsorption isotherm, usually in the P/P_0 range of 0.05 to 0.35.

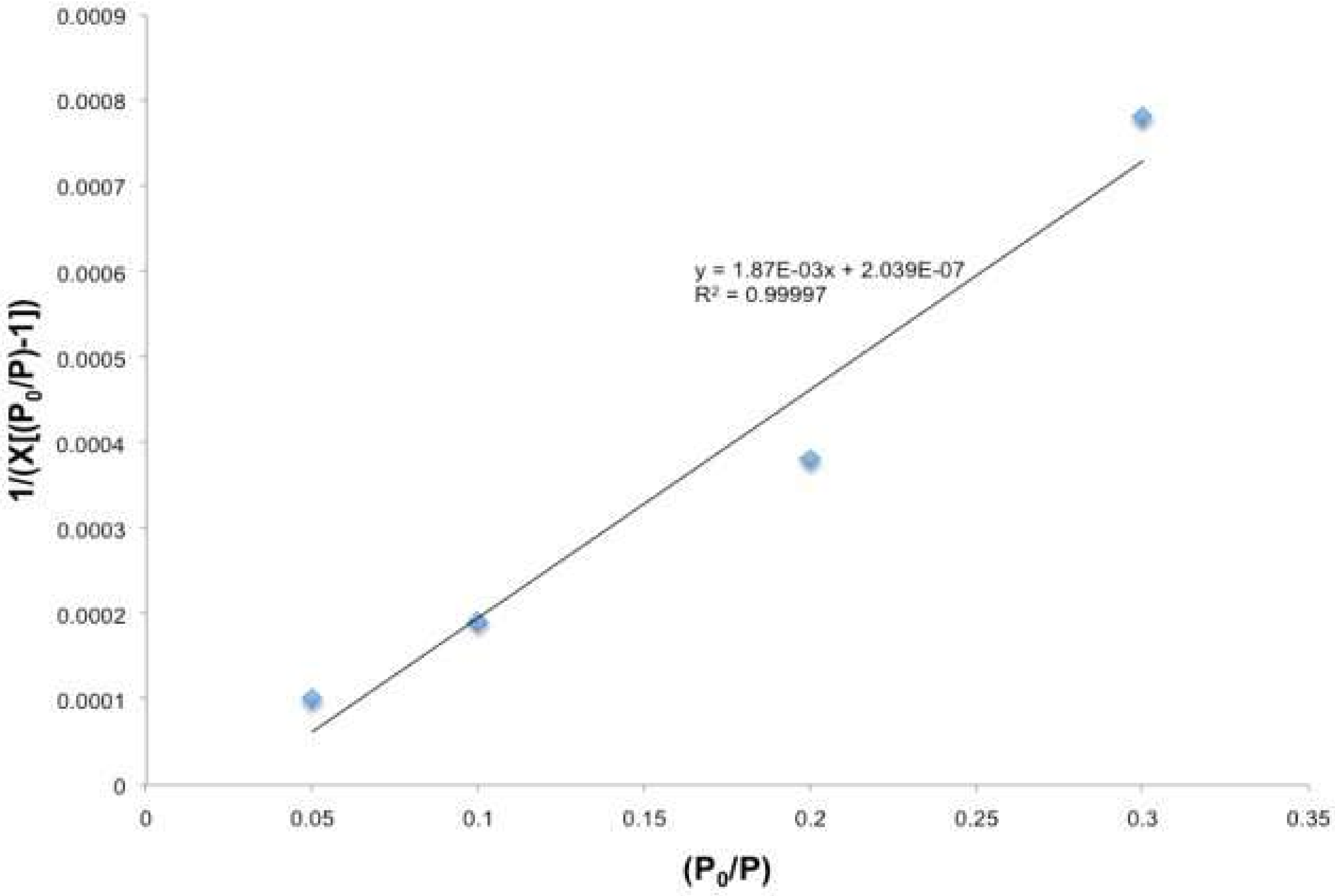


Fig: BET plot of IRMOF-13 using points collected at the pressure range 0.05 to 0.3. The equation of the best-fit line and R^2 value are shown.

The surface area, SA, is calculated from the slope and intercept according to Equation 2

$$SA = \frac{1}{slope + intercept} \cdot CSA$$

Equation 2: Surface area calculation

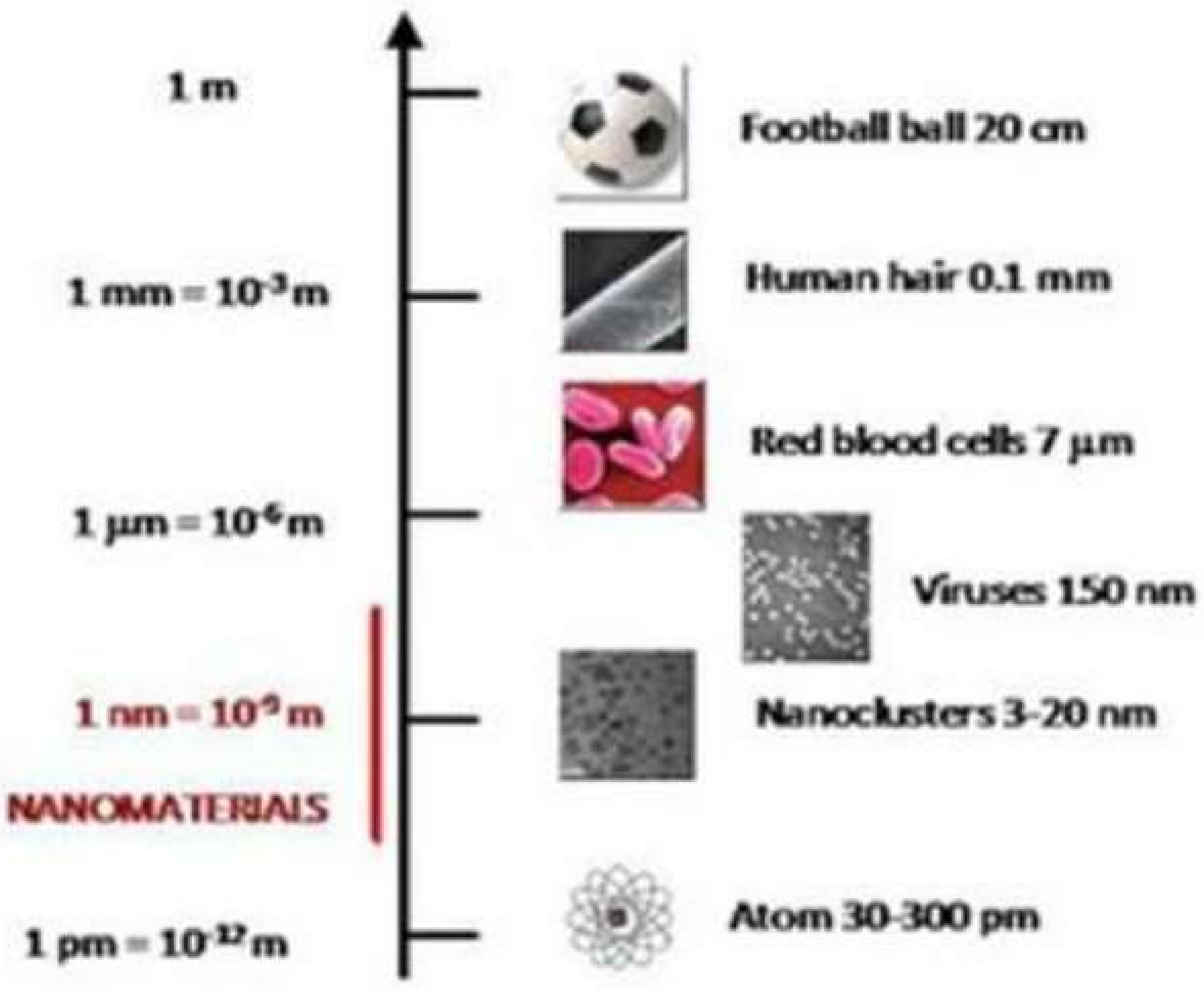
Where CSA is the cross-sectional area of the adsorbate.

Nanomaterials

Introduction

All materials are composed of grains, which in turn comprise many atoms. The visibility of these grains depends on their size. The materials possessing grains of size ranging from 1 to 100 nm, are known as **"Nanomaterials"** and the developed technology is called nano technology. This was first discovered by Feynman in 1959.

- Nano technology deals with the design, manufacturing and application of devices (or) materials which lie in the sizes of 1 to 100 nm.
- Nano means 10^{-9} (one-billionth)
- A nanometer 1nm = 10^{-9} m(one-billionth of meter)
- Nano materials are found in both biological systems and man-made structures.
- Nature has been using nano materials for millions of years.



Nano materials

All materials are composed of grains, which in turn comprise many atoms. The visibility of these grains depends on their size. The materials possessing grains of size ranging from 1 to 100 nm, are known as **"Nanomaterials".**

Examples: zno, cu-Fe alloys, Ni, Pd, Pt etc.

Classification of Nanomaterials

According to Siegel, Nanostructured materials are classified as Zero dimensional,

one dimensional, two dimensional, three dimensional nanostructures.

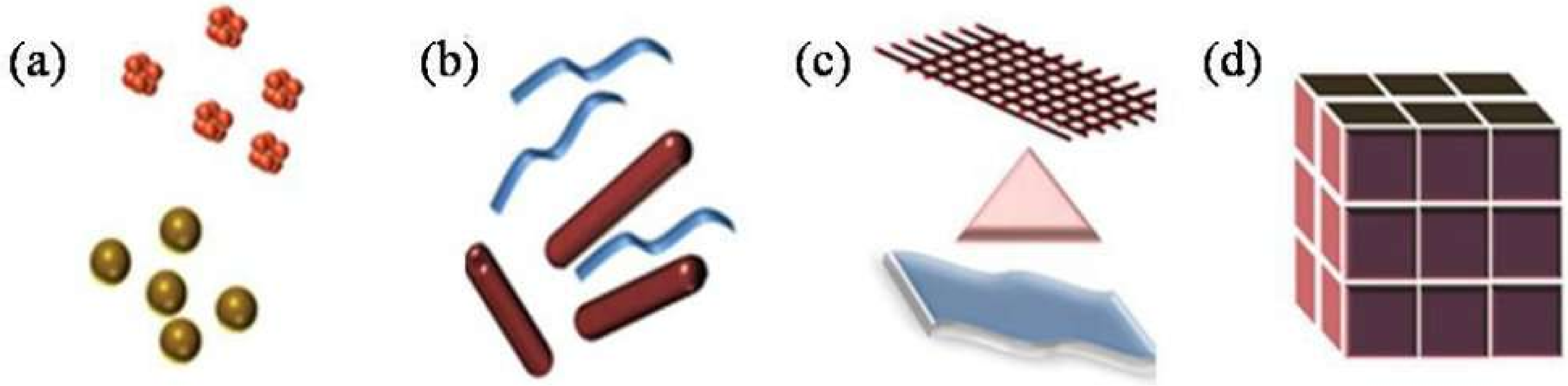


Fig: Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

- **One-dimensional Nanomaterial: -** In these Nanomaterial, grains will be layered in the form of multi-layers such as thin films or surface coatings.
- **Two dimensional Nanomaterials: -** This consists of ultrafine grains layered over layers or buried layers, which include nano wires and nano tubes.
- **Three dimensional Nanomaterials**: - This consists of nano meter sized grains.

Examples: precipitates, colloids and quantum dots.

Why the properties of nano materials are different?

(Or)

Basic principles of Nanomaterials

Two principle factors cause the properties of nano materials to differ significantly from other materials increased in surface area to volume ratio, and quantum confinement. These factors can change or enhance the properties such as reactivity, strength and electrical characteristics.

Fabrication of Nanomaterials

Nano materials can be generally fabricated in two broad ways, namely

(i) Top-down approach
(ii) Bottom – up approach

i) Top-down approach: - In which, the bulk solid materials are breaked in to nano sizes.

(ii)Bottom – up approach:-In which, the nano materials are build up from the bottom: atom by atom, molecule by molecule or cluster by cluster.

The schematic representation of the synthesis and building of nano structured materials are shown in figure.

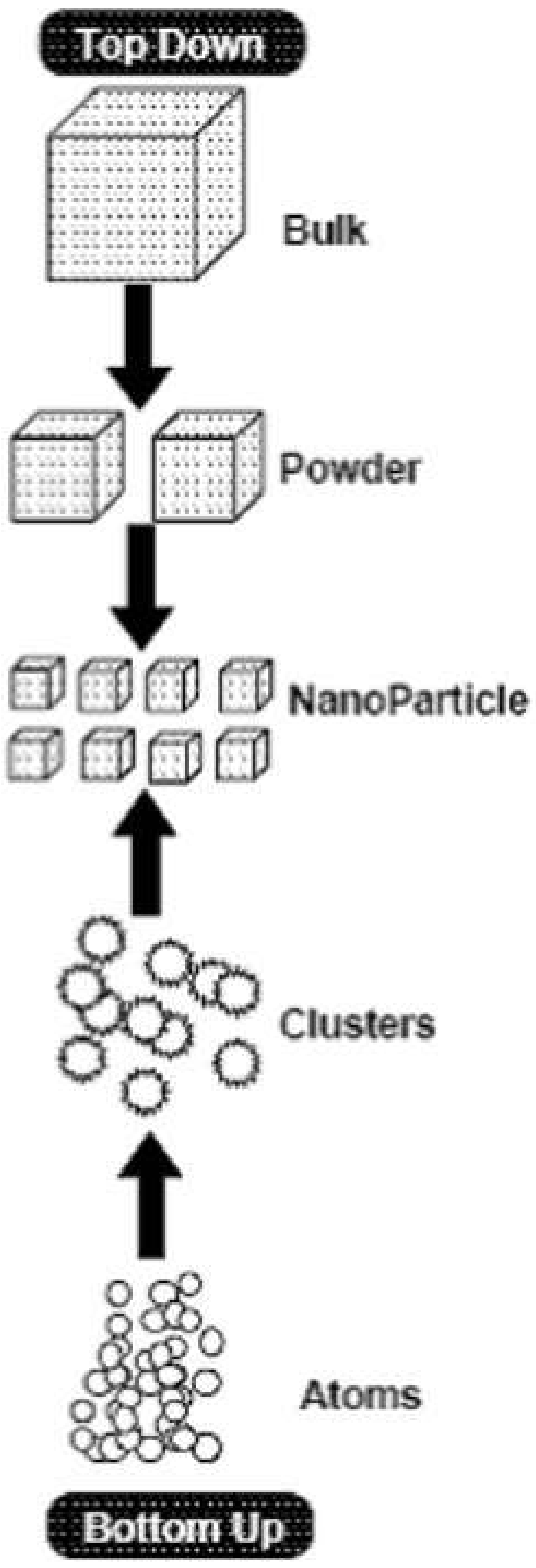


Figure: Schematic representation of the building up of Nanostructure.

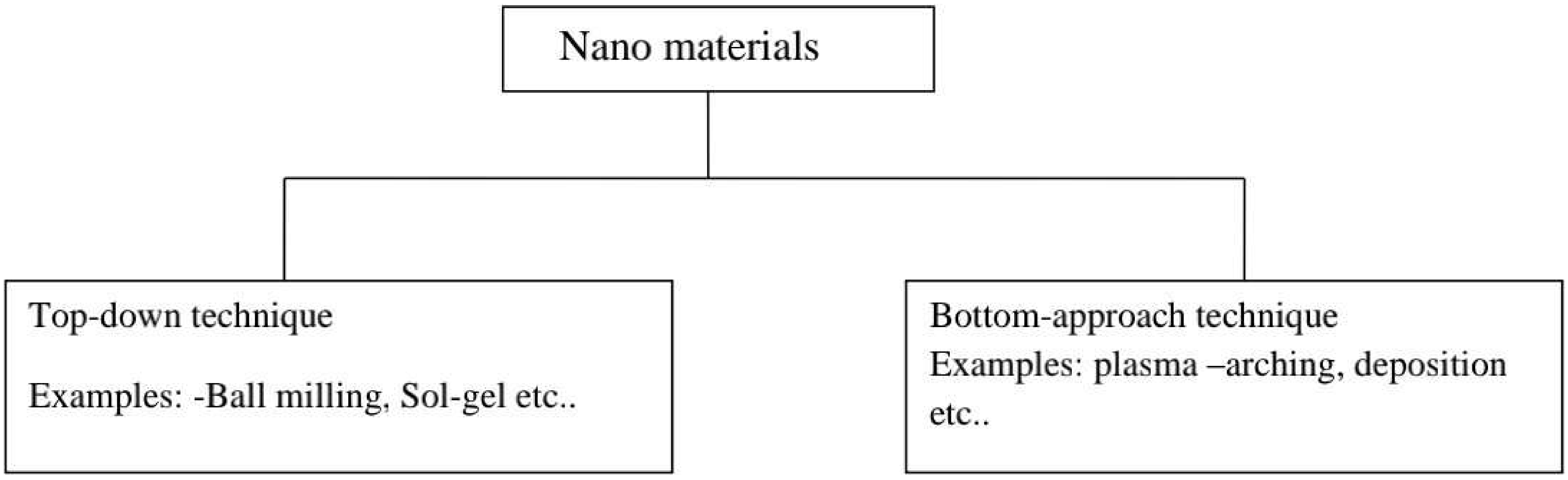


Fig:-Synthesis of nano materials.

1. Ball milling (or) Mechanical crushing:-

- The ball milling method is a typical example of top-down method of fabrication of nano materials.
- A ball mill is a type of grinder used to grind materials into extremely fine powder in order of nm.
- In this method, small balls of the material are allowed to rotate around the inside of a drum and then fall on a solid with gravity force. The balls are broken in to nano crystallites. This is also known as mechanical crushing.

- This method is used to prepare a wide range of elemental powders. For example iron nano particles of sizes 13 to 30nm can be formed.
- This method is used for produce metal oxide nano crystals (cerium oxide CeO_2 and Zinc oxide ZnO_2).

Fig: Ball milling method

Sol-gel process:

A sol is a dispersion of the solid particles (~ 0.1-1 mm) in a liquid where only the brownian motions suspend the particles. A gel is a state where both liquid and solid are dispersed in each other, which presents a solid network containing liquid components. The sol-gel process, as the name implies, involves the evolution of inorganic networks through the formation of a colloidal suspension (**sol**) and gelation of the sol to form a network in a continuous liquid phase (**gel**). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcinations of the gel produce the oxide.

Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as $Si(OEt)_4$ (tetraethyl orthosilicate, or TEOS). The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides (OR)**z** can be described as follows:

$$MOR + H2O \rightarrow MOH + ROH \text{ (hydrolysis)}$$

$$MOH+ROM \rightarrow M\text{-}O\text{-}M+ROH \text{ (condensation)}$$

Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials.

The sol-gel process can be characterized by a series of distinct steps.

Step 1: Formation of different stable solutions of the alkoxide or solvated metal precursor (the sol).

Step 2: Gelation resulting from the formation of an oxide- or alcohol- bridged network (the gel) by a polycondensation or polyesterification reaction that results in a dramatic increase in the viscocity of the solution.

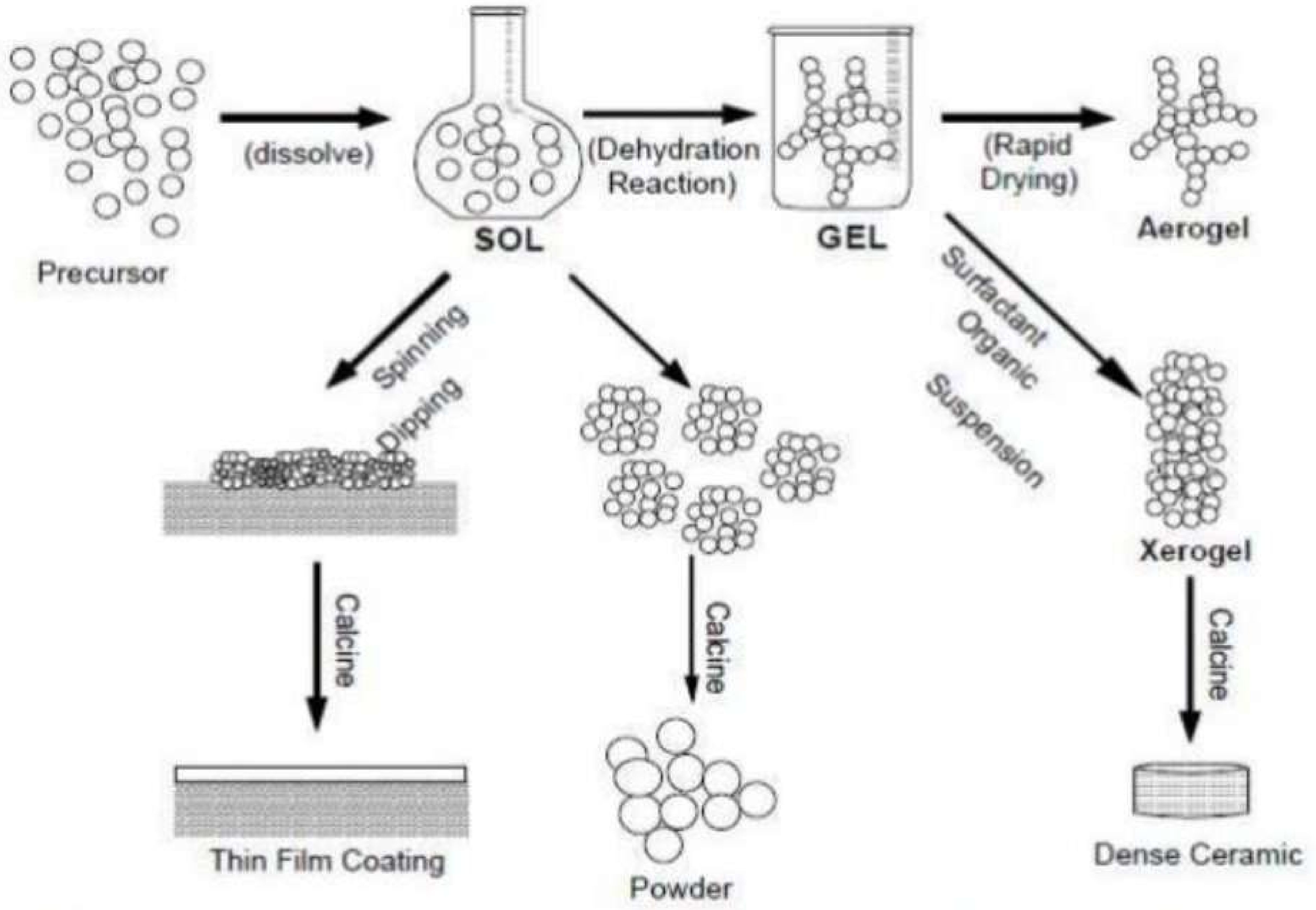
Step 3: Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. Ostwald ripening (also referred to as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with syneresis. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.

Step 4: Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rate period, (ii) the critical point, (iii) the falling rate period, (iv)the second falling rate period.

If isolated by thermal evaporation, the resulting monolith is termed a *xerogel*. If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an *aerogel*.

Step 5: Dehydration, during which surface- bound M-OH groups are removed, there by stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 800^0C.

Step 6: Densification and decomposition of the gels at high temperatures ($T>800^0$C). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.



Schematic representation of sol-gel process of synthesis of nanomaterials

Chemical vapour deposition:-

- This method is used to prepare nano powder.
- In this method nano particles are deposited from the gas phase. Material is heated to form a gas and then allowed to deposit on a solid surface, usually under vacuum condition. The deposition may be either physical (or) chemical.

  In deposition by chemical reaction new product is formed. Nano powder of oxides and carbides of metals can be formed if vapours of carbon (or) oxygen are present with the metal.
- This method can also be used to grow surfaces, i.e. suppose if an object has to be created with nano powders, then the powders, then the object has to be introduced inside the chemical vapour deposition area so that the nano powders can be deposited all over the object.

Examples: - Nano powders of oxides and carbides, Pure metal nano powders

Properties of Nano particles:-As the size of the nano particle is very less, these materials exhibits peculiar physical, electronic, magnetic, mechanical and chemical properties.

1) **Physical properties**:-

- Since the size of the particle is very less, the particles are very close to each other and hence the inter particle spacing is very less in nano materials.

- Because of its very less size, these nano materials cannot be further divided into smaller particles and it does not have any dislocation in it. Thus we can say that they have high strength, hardness and toughness.
- The melting point of nano materials will be very less.

(2) Electronic properties: -

- The energy bands in these materials will be very narrow.
- The electrical conductivity and energy band width of same materials change when they pass from bulk phase to nano particle phase. For example, bulk silicon is an insulator; it becomes a conductor in nano phase.
- Nano material semiconductors such a Ge and Si do not snow semi conducting property.

(3) Magnetic properties: - The nano materials shows variation in their magnetic property, when they change from bulk state to nano phase state. Some of the examples are listed in table (1).

S.No	Material	Bulk state	Nano-phase state
1	Iron, Ni,Cobalt	Ferro-magnetic	Super Para-magnetic
2	Sodium, Potassium	Para-magnetic	Ferro magnetic
3	Chromium	Anti-ferromagnetic	Para-magnetic

(4) Mechanical properties:-

- Mechanical properties such as hardness, toughness, elastic modulus varies from material to material.
- They exhibit super plastic behaviour.

(5) Chemical properties:-

- The nano structures in chemistry are collides and these are formed in a condensed phase having size in the range from 1 to 100nm.
- The chemical reactivity of a cluster depends on the cluster size. This is useful in the preparation of catalytic agents. Some chemically inert bulk materials become good chemical catalyst in the nano phase, for example: Platinum and gold.
- In chemical reactions, the rate of increase in mass transport increases as the particle size decreases.

(6) Carbon nano tubes :- (CNT):-

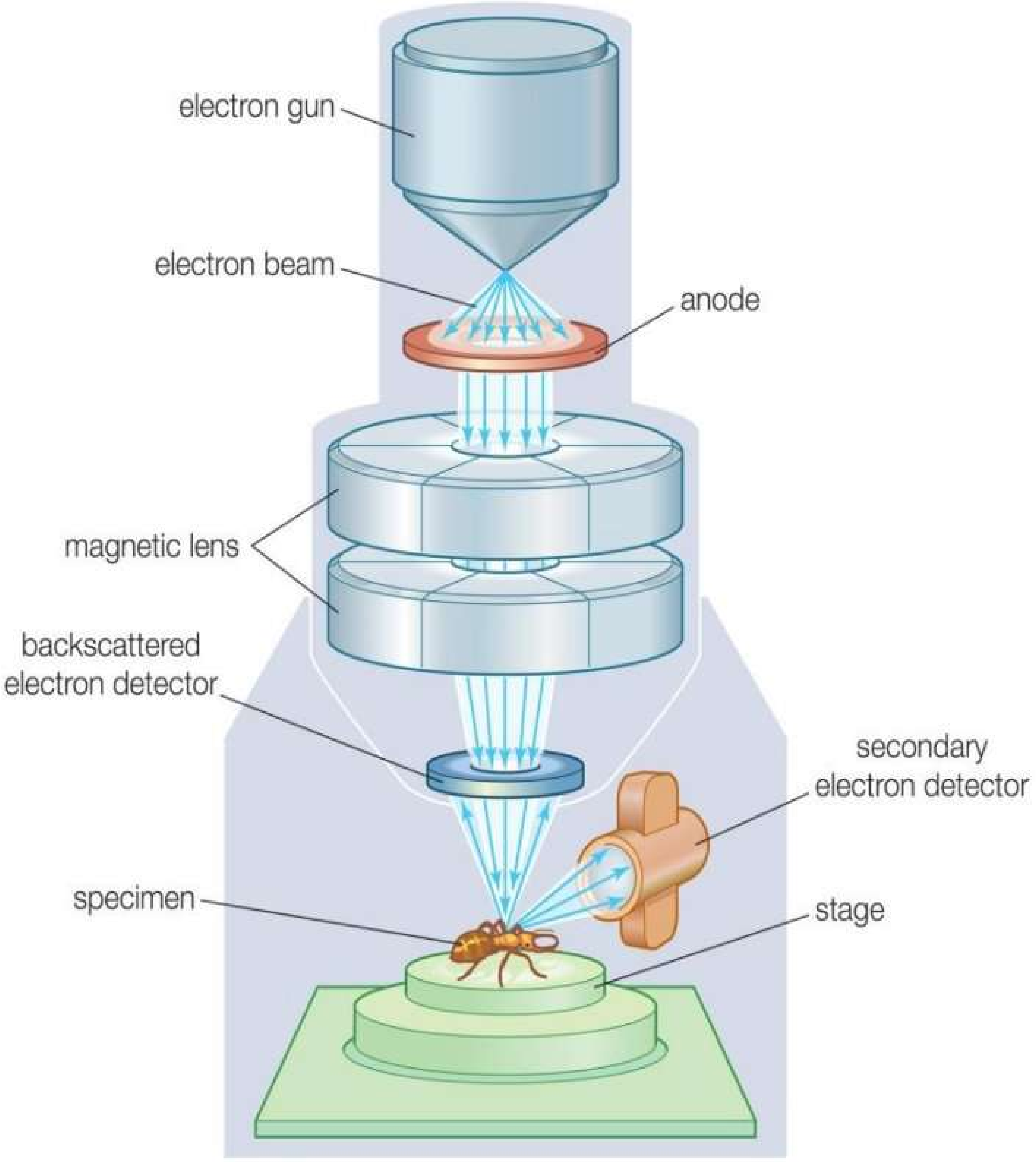
- Carbon nano tubes are hollow cylindrical tubes. The ends are closed with caps containing pentagonal rings. The carbon nano tubes are formed by rolling the graphite (or graphene) sheet into tubes with the bonds at the end of the sheet. These bonds are used to close the tube. Generally, the carbon nano tubes are formed in the range of 2 to 10nm in diameter and a length of 100μm.

Characterization of surface by physicochemical methods:

Here the three physicochemical methods are as follows:

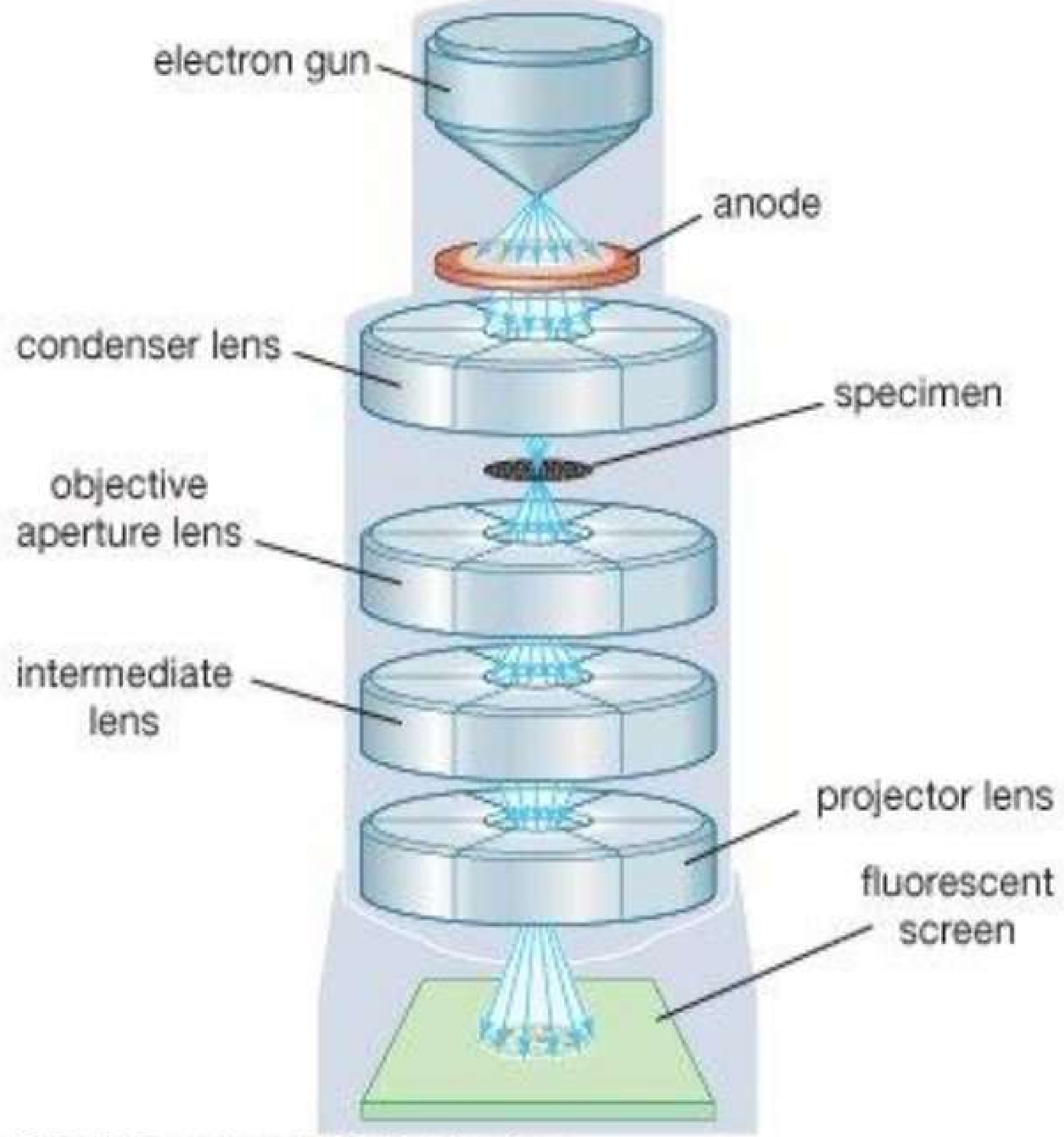
1. Scanning Electron Microscope(SEM)
2. Transmission Electron Microscope(TEM)
3. X-Ray Diffraction (XRD)

1. **Scanning electron microscope (SEM)**, type of electron microscope, designed for directly studying the surfaces of solid objects that utilizes a beam of focused electrons of relatively low energy as an electron probe that is scanned in a regular manner over the specimen. The electron source and electromagnetic lenses that generate and focus the beam are similar to those described for the transmission electron microscope (TEM). The action of the electron beam stimulates emission of high-energy backscattered electrons and low-energy secondary electrons from the surface of the specimen.



2. **Transmission electron microscope (TEM)**, type of electron microscope that has three essential systems:

1. An electron gun, which produces the electron beam, and the condenser system, which focuses the beam onto the object.
2. The image-producing system, consisting of the objective lens, movable specimen stage, and intermediate and projector lenses, which focus the electrons passing through the specimen to form a real, highly magnified image.
3. The image-recording system, which converts the electron image into some form perceptible to the human eye. The image-recording system usually consists of a fluorescent screen for viewing and focusing the image and a digital camera for permanent records. In addition, a vacuum system, consisting of pumps and their associated gauges and valves, and power supplies are required.



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3. X-Ray Diffraction (XRD)

X-ray diffraction (XRD) relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. A primary use of the technique is the identification and characterization of compounds based on their diffraction pattern.

- X-rays: Electromagnetic Radiation with typical photon energies in the range 100 eV-100 KeV.
- Short Wavelength x-rays used for diffraction : range of few 0.1 angstroms (1 KeV-120 KeV)

- Wavelength of X-rays comparable to the size of the atoms : ideal for determining the structural analysis
- Bulk structure can be determined by using x-rays that can penetrate deep in to the material.

Production of X-rays:

Source:

X-ray tubes or Synchrotron radiation; X-ray tube :primary source.

Principle:

  - Electrons collide with atoms in the target and slow down, a continuous spectrum of X-rays are emitted : Bremsstrahlung radiation
  - Commonly used targets: Cu, Mo that emits 8 KeV and 14 KeV energies with wavelengths of 1.54 and 0.8 Angstroms respectively.

Lattice Planes and Bragg's law:

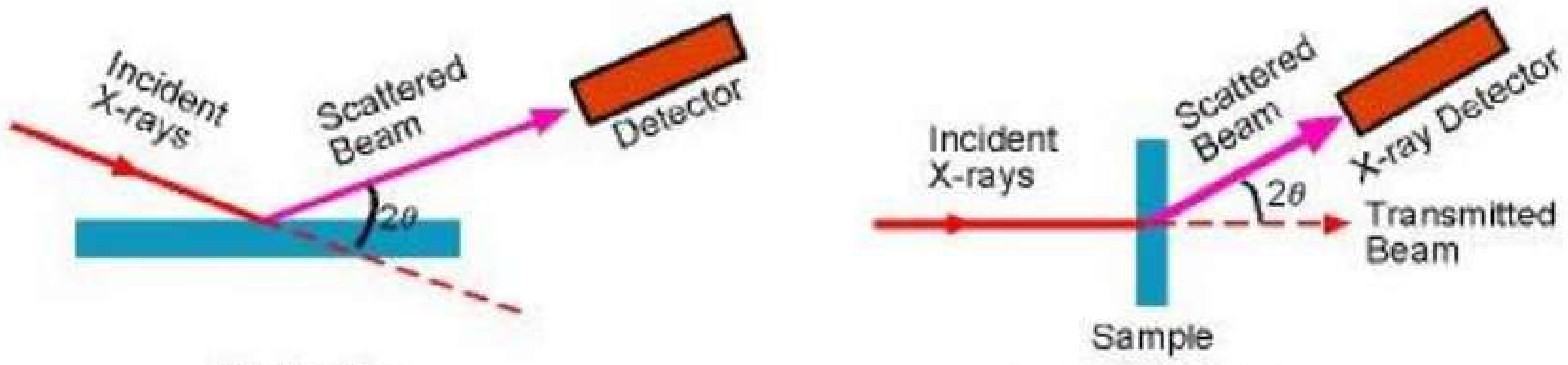
  - When X-rays collide with electrons, some photons from the incident beam will be deflected away from the direction where they original travel

Elastic or Thompson Scattering:

  - If the wavelength of these scattered x-rays did not change. Only momentum transfer takes place.

Inelastic or Compton Scattering:

  - X-rays transfer some of their energy to the electrons and scattered x-rays will have different wavelength than the incident X-rays.



Reflection

Transmission

Fig. Mechanism of X-ray diffraction

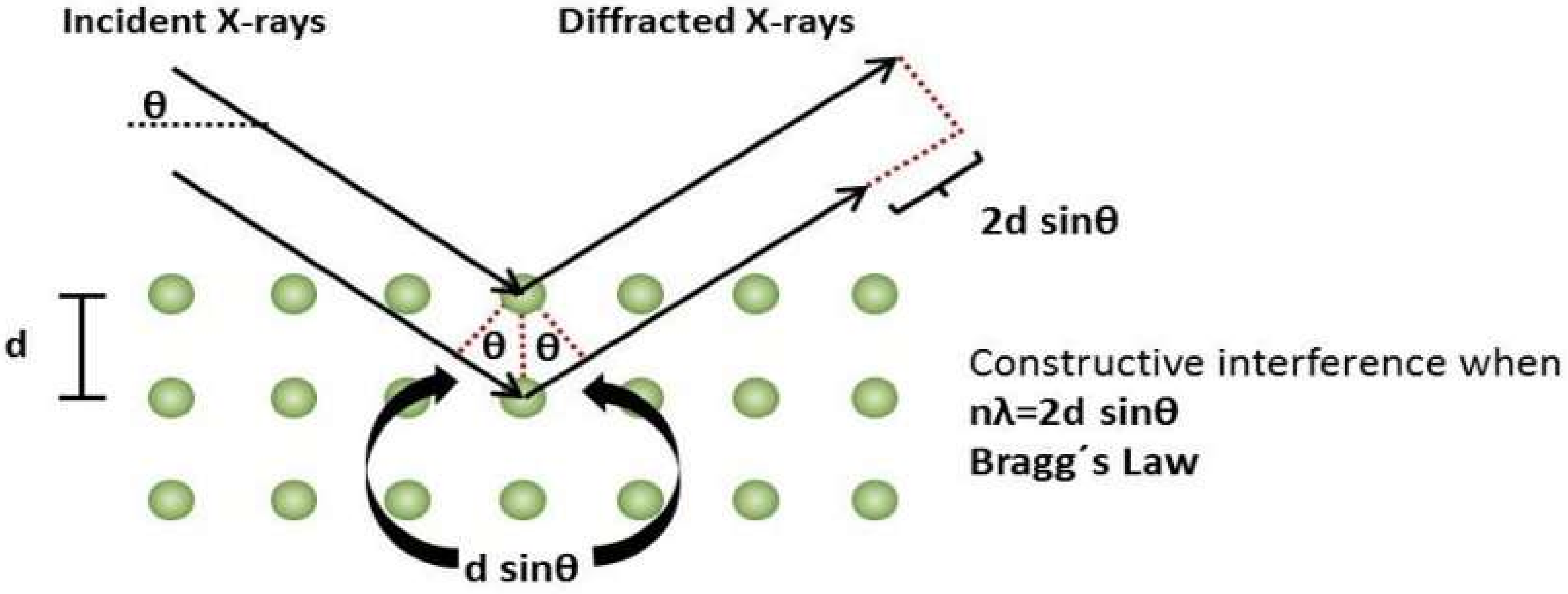


Fig. : Schematic representation of the Bragg's equation

Applications of Nano materials

Mechanical Engineering:-

- Since they are stronger, lighter etc; they are used to make hard metals.
- Nano-MEMS (Micro-Electro Mechanical Systems) are used in ICS, optical switches, pressure sensors, mass sensors etc

Electrical Electronics and Communication Engineering:-

- Orderly assembled nano materials are used as quantum electronic devices and photonic crystals.
- Some of the nano materials are used as sensing elements. Especially the molecular nano materials are used to design the robots, assemblers etc.
- They are used in energy storage devices such as hydrogen storage devices, magnetic refrigeration and in ionic batteries.
- Dispersed nano materials are used in magnetic recording devices, rocket propellant, solar cells, fuel cells etc.
- Recently nano robots were designed which are used to remove the damaged cancer cells and also to modify the neuron network in human body.

Computer Science Engineering and IT:-

- Nano materials are used to make CD's and Semiconductor laser.
- These materials are used to store the information in smaller chips.
- They are used in mobiles, lap-tops etc.
- Further they are used in chemical/ optical computer.
- Nano-dimensional photonic crystals and quantum electronic devices plays a vital role in the recently developed computers.

Bio-Medical and Chemical Engineering:-

- Consolidated state nano particles are used as catalyst, electrodes in solar and fuel cells.
- Bio-sensitive nano particles are used in the production of DNA-chips, bio- sensors etc.
- Nano-structured ceramic materials are used in synthetic bones.
- Few nano materials are also used in adsorbents, self-cleaning glass, fuel additives, drugs, Ferro fluids, paints etc.
- Nano-metallic colloids are used as film precursor.

Nano in Material Technology

- Nanocrystalline aerogel : Insulation in offices, homes etc
- Cutting tools : Harder, wear resistant and durable
- Nanocrystalline Sensors: Sensitive to changes in environment : Smoke detectors, ice detectors on air craft wings
- High energy density batteries
- Nanosized titanium dioxide and zinc oxide : sunscreens to absorb and reflect UV rays.
- Nanoparticles in paints : change in colour to the variation in temperature and reduce IR absorption and heat loss
- Water repellent and Antibacterial : Nanocoating of highly activated titanium dioxide
- Textile Industry : Breathable, water proof and stain-resistant fabrics
- Researchers are developing wires containing carbon nanotubes : lower resistance than the high-tension wires currently used in the electric grid, thus reducing transmission power loss.
- Transistors, the basic switches that enable all modern computing :smaller and smaller through nanotechnology.

Nano in Information Technology

- Data storage: Nanoscale fabricated magnetic materials
- Nano photonic crystals : Chemical optic computers
- Optoelectronic devices : Nano thickness controlled coating

Nano in Biomedicals

- Artificial Heart Valves: Nanocrystalline SiC
- Disease diagnosis, drug delivery and molecular imaging
- Nanostructured ceramics : interact with bone cells: implant material
- Nanomedicine researchers are looking at ways that nanotechnology can improve vaccines, including vaccine delivery without the use of needles.

Nano in Energy Storage

- Hydrogen storage devices
- Addition of nanoparticles to diesel : improves fuel economy: Reduces the degradation of fuel consumption
- Similarly, various nanoscience-based options are being pursued to convert waste heat in computers, automobiles, homes, power plants, etc., to usable electrical power.

Nano in Transportation

- Light weighting of cars, trucks, airplanes, boats, and space craft could lead to significant fuel savings.
- Carbon nanotube sheets are now being produced for use in next-generation air vehicles. For example, the combination of light weight and conductivity makes them ideal for applications such as electromagnetic shielding and thermal management

Nano in Machinery

- Nanostructured ceramic coatings exhibit much greater toughness than conventional wear-resistant coatings for machine parts.
- Nanotechnology-enabled lubricants and engine oils also significantly reduce wear and tear, which can significantly extend the lifetimes of moving parts in everything from power tools to industrial machinery.

Nano in Chemistry

- Nanoparticles are used increasingly in catalysis to boost chemical reactions. This reduces the quantity of catalytic materials necessary to produce desired results, saving money and reducing pollutants.

Nano in Industry: Energy Storage

- **Fuel Cells**
- Nanotechnology is being used to reduce the cost of catalysts used in fuel cells
- **Solar Cells**
- Companies have developed nanotech solar cells that can be manufactured at significantly **lower cost** than conventional solar cells.
- **Batteries**
- Companies are currently developing batteries using nanomaterials. The battery can be recharged significantly faster than conventional batteries

Nano in Industry

- **Chemical Sensors:**

- Nanotechnology can enable sensors to detect very small amounts of chemical vapors such as carbon nanotubes, zinc oxide nanowires or palladium nanoparticles can be used in nanotechnology-based sensors.

➢ **Fabric**

- Making composite fabric with nano-sized particles or fibers allows improvement of fabric properties without a significant increase in weight, thickness, or stiffness as might have been the case with previously-used techniques.

Nano in Solar Research

➢ Nanotechnology can be incorporated into solar panels to convert sunlight to electricity more efficiently, promising inexpensive solar power in the future.

➢ Nanostructured solar cells could be cheaper to manufacture and easier to install, since they can use print-like manufacturing processes and can be made in flexible rolls rather than discrete panels.

➢ Researchers are developing thin-film solar electric panels that can be fitted onto computer cases and flexible piezoelectric nanowires woven into clothing to generate usable energy on the go from light, friction, and/or body heat to power mobile electronic devices

Nano in Research

➢ Researchers have developed a nanofabric "paper towel" woven from tiny wires of potassium manganese oxide that can absorb 20 times its weight in oil for cleanup applications.

➢ Researchers have also placed magnetic water-repellent nanoparticles in oil spills and used magnets to mechanically remove the oil from the water.

➢ Many airplane cabin and other types of air filters are nanotechnology-based filters that allow “mechanical filtration,” in which the fiber material creates nanoscale pores that trap particles larger than the size of the pores. The filters also may contain charcoal layers that remove odors.

➢ Nanotechnology-enabled sensors and solutions are now able to detect and identify chemical or biological agents in the air and soil with much higher sensitivity than ever before.

➢ Another sensor has been developed by NASA as a smartphone extension that firefighters can use to monitor air quality around fires.

ALL in ALL Nano

➢ Nanoscale additives in polymer composite materials are being used in baseball bats, tennis rackets, bicycles, motorcycle helmets, automobile parts, luggage, and power tool housings, making them lightweight, stiff, durable, and resilient.

- Clear nanoscale films on eyeglasses, computer and camera displays, windows, and other surfaces can make them water- and residue-repellent, antireflective, self-cleaning, resistant to ultraviolet or infrared light, antifog, antimicrobial, scratch-resistant, or electrically conductive.
- Other computing and electronic products include Flash memory chips for smart phones and thumb drives; ultra-responsive hearing aids; antimicrobial/antibacterial coatings on keyboards and cell phone casings; conductive inks for printed electronics for RFID/smart cards/smart packaging; and flexible displays for e-book readers.