

**LECTURE NOTES**  
**ON**  
***Engineering Chemistry***  
**B.TECH I YEAR- I SEMESTER**  
**(R19)**



**DEPARTMENT OF HUMANITIES & SCIENCES**

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**(Approved by AICTE, New Delhi, Affiliated to JNTUA Ananthapuramu,**  
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# UNIT-1

# WATER TECHNOLOGY

## Introduction:

Water is one of most abundant and widely distributed substance but is also most misused one. It covers 3/4<sup>th</sup> of earth's surface and essential for all organisms like animals, plants, human beings. It is not only essential for organisms but also used in engineering side for steam generation. In addition to it, it is used in domestic purposes like drinking, washing, bathing, cooking used in industries like production of paper, rayon, textiles, tires, irrigation, atomic energy, steel etc...

**Sources of water:** Based on their availability, sources of water are broadly divided into 2 types

- 1) Surface water
- 2) Underground water

## **I. Surface water:**

### **1. Rain Water:**

- It is the purest form of water. It is obtained from evaporation of surface water.
- During the downward movement through the atmosphere it dissolves considerable amount of industrial gases (CO<sub>2</sub>, SO<sub>2</sub>) and suspended particles (organic & inorganic).

### **2. River water:**

- Rivers are fed by rain water and spring water. Water from these sources flow over the surface of earth and dissolves soluble minerals present in the soil.
- River water also contains organic matter derived from decomposition of plants and small particles of sand and rock in suspension i.e. it contains both dissolved and suspended impurities.

### **3. Lake water:**

- It belongs to still water type. It contains constant chemical composition.
- It consists of much lesser amounts of dissolved impurities than well water.
- It has high concentration of organic matter.

### **4. Sea water:**

- It is the most impure form of natural water. All rivers join sea along with their impurities.
- It contains 3.5% dissolved salts of which 2.6% is NaCl and other salts are sulphates of Na<sup>+</sup>, bicarbonates of K<sup>+</sup>, Mg<sup>+2</sup>, Ca<sup>+2</sup> and bromides of K<sup>+</sup> and number of other compounds.

## **II. Underground water:**

- The rain water passed down to the lower layers of earth continuously until it comes in contact with rocks. It comes out of the earth in the form of spring water.
- Well and spring water has high organic purity and consists of more amount of dissolved salts. It has more hardness.

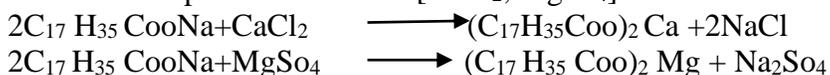
## **Impurities of Water:**

Water has following impurities. They are

1. Inorganic Impurities
2. Organic Impurities
3. Biological impurities

## **Hardness of water:-**

- Hardness is the characteristic property of water, which prevents formation of lather with soap.
- This is due to the presence of certain salts of Ca, Mg, Fe & heavy metals dissolved in water.
- When a sample of hard water is treated with soap it forms a white precipitate called **Scum** instead of lather.
- Soaps are Na/K salts of higher fatty acid like palmitic acid, stearic acid, oleic acids.
- Reactions of soap with hard water [CaCl<sub>2</sub>, MgSO<sub>4</sub>] are as follows:-



- Based on hardness present or not, water is classified in to two types. They are

**Soft water:-** A sample of water which produce lather easily with soap is called as soft water. This doesn't have salts of Ca, Mg, Fe& heavy metals.

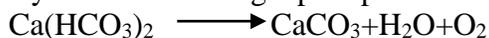
**Hard water:** The water which doesn't give lather easily with soap is called hard water. This water contains dissolved salts present in it.

**Types of Hardness:-** Hardness of water is of two types

- 1) Temporary hardness
- 2) Permanent hardness

### 1. Temporary or carbonate hardness:

- It is caused by the presence of bicarbonates of Calcium, Magnesium, heavy metals and carbonates of Fe.
- It can be removed by boiling. On boiling the soluble bicarbonates are converted to insoluble carbonates and hydroxides which get precipitated and can be removed by filtration.



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

- It is caused due to the presence of chlorides, sulphates of Ca, Mg and heavy metals. Unlike temporary hardness it cannot be removed by boiling.

**Disadvantage of hard water:** - There are several disadvantages with hard water when used in domestic & industrial purposes and also in boilers.

1. Domestic use
2. Industrial use
3. Boilers

## I. Domestic Use:

**Drinking:** - If hard is used for drinking, it destroys the digestive system and it also forms Calcium Oxalates (Stones) in urinary track and Kidneys.

**Washing:** - When hard water is used for washing, it does not produce lather freely with soap and produces sticky precipitates of it. A lot of soap gets wasted and a sticky precipitate get adhered on to the fabrics of cloth giving spots and presence of Fe salts may cause staining of cloth.

**Bathing:** - Wastage of soap takes place and forms sticky scum on the bath tub and body.

**Cooking:-** Due to the presence of calcium and magnesium salts, water boiling point gets elevated, hence more time and fuel are required for cooking. Certain foods such as pulses, peas are not cooked soft with hard water if it is used to making of tea and coffee it exhibits unpleasant odour and muddy looking extract.

## II. In industrial use:

**Textile industry:** - The precipitates of Ca and Mg soaps adheres on the fabric and do not produce correct shapes to fabric and iron stain the cloth and produces spots on fabric. Hard water destroys the beauty of fabrics.

**Sugar industry:** -  $\text{SO}_4^{-2}$ ,  $\text{NO}_3^{-2}$ , Alkali, carbonates of hard water arise the problem in crystallisation of sugar. The resulting sugar may be deliquescent.

**Dying industry:** - Hard water gives improper shades to the cloth in dying industry due to the presence of precipitates of Ca and Mg.

**Paper industry:** - Chlorides and sulfates of Ca and Mg affect the quality of paper.

**Laundry:** - A lot of soap was wasted in laundry due to the formation of precipitates of Ca and Mg.

**Concrete making:** - Chlorides and sulfates of hard water affect the hydration of cement and final strength of the hardened concrete.

**Pharmaceuticals:** - Hard water may form some undesirable products while preparation of the pharmaceuticals (drugs, ointments, injections)

### **III. For Steam making in boilers:** -

Boilers are used for steam generation. If hard water is used in boilers it may lead to the following boiler troubles

- |   |   |                 |
|---|---|-----------------|
| 1. Formation of scales & sludges.<br>2. Boiler corrosion<br>3. Caustic embrittlement.<br>4. Priming & foaming | } | Boiler troubles |
|---|---|-----------------|

### **Degree of Hardness:**

Hardness of water is expressed in terms of CaCO<sub>3</sub> equivalents. The molecular weight of CaCO<sub>3</sub> is 100 and its equivalent weight is 50 which is easy for calculation and CaCO<sub>3</sub> is the most insoluble salt present in hard water. All the dissolved salts present in hard water are converted in to CaCO<sub>3</sub> equivalents.

$$\begin{aligned} \text{CaCO}_3 \text{ equivalent} &= \frac{\text{Weight of the salt} \times \text{Equivalent of CaCO}_3 (50)}{\text{Eq wt of that salt}} \\ &\text{OR} \\ &= \frac{\text{Weight of the salt} \times \text{Molecular weight of CaCO}_3 (100)}{\text{Mol wt of that salt}} \end{aligned}$$

**Units of hardness:** - The following units are used to measure hardness. They are

1. Parts per million (PPM)
2. Milligrams per liter (mg/L)
3. Degree Clark (<sup>o</sup>Cl)
4. Degree French (<sup>o</sup>Fr)

**1. PPM:** - PPM is the parts of CaCO<sub>3</sub> equivalent hardness present per one million parts of water i.e .10<sup>6</sup> parts of water.

1PPM = 1 part of CaCO<sub>3</sub> equivalent hardness in 10<sup>6</sup> parts of water.

**2. Milligrams per liter:** - It is defined as number of milligrams of CaCO<sub>3</sub> equivalent hardness present per liter of water.

1mg/L = 1mg of CaCO<sub>3</sub> equivalent hardness present in one liter of water.

1 liter water weighs 1 kg = 1000g = 1000 x 1000 = 10<sup>6</sup> mg

There fore 1 mg/L = 1mg of CaCO<sub>3</sub> Equivalent hardness per 10<sup>6</sup> mg of water.

$$\mathbf{1ppm = 1mg/L}$$

**3. Degree Clark (<sup>o</sup>Cl):-** It is defined as number of parts of CaCO<sub>3</sub> equivalent hardness present in 70,000 parts of water or one gallon of water.

1<sup>o</sup> Cl = 1 part of CaCO<sub>3</sub> eq: hardness per 70,000 parts of water.

$$\mathbf{1PPM = 0.07 ^oCl.}$$



### **B. Estimation of total hardness: -**

- Take 50ml of given hard water.
- To this add 5 ml of buffer and few drops of EBT indicator and then titrate with EDTA solution until end point.

**Let the volume of EDTA used be  $V_2$  ml**

### **C. Estimation of permanent hardness: -**

- Take 250ml of hard water sample in to a beaker and evaporate it until final volume becomes nearly 50 ml (all bicarbonates are converted to carbonates and hydroxides).
- Filter, wash and make up the filtrate to 250ml with distilled water.
- From this pipette out 50ml boiled water.
- To this add buffer and few drops of indicator.
- Titrate with EDTA until wine red color changes to deep blue.

**Let the volume of EDTA used be  $V_3$  ml**

### **CALCULATIONS:**

#### **Standardization of EDTA: -**

1ml of standard hard water = 1mg of  $\text{CaCO}_3$  equivalent

50 ml of standard hard water =  $V_1$ ml of EDTA

50 mg of  $\text{CaCO}_3$  =  $V_1$  ml of EDTA

**1 ml of EDTA =  $50/V_1$  mg of  $\text{CaCO}_3$  eq.**

#### **Estimation of total hardness:-**

50 ml of given hard water =  $V_2$  ml of EDTA

50 ml of given hard water =  $V_2 \times 50 / V_1$  mg of  $\text{CaCO}_3$  eq

1 ml of given hard water =  $V_2 / 50 \times 50 / V_1$  mg of  $\text{CaCO}_3$

1 liter of given hard water =  $V_2 / V_1 \times 1000$  mg/L

**Total hardness =  $V_2 / V_1 \times 1000$  mg/L**

#### **Estimation of permanent hardness:-**

50 ml of given boiled  $\text{H}_2\text{O}$  =  $V_3$  ml of EDTA

=  $V_3 \times 50 / V_1$  mg of  $\text{CaCO}_3$  eq

1 ml of given boiled  $\text{H}_2\text{O}$  =  $V_3 / 50 \times 50 / V_1$  mg of  $\text{CaCO}_3$  eq

1 liter of given boiled  $\text{H}_2\text{O}$  =  $V_3 / V_1 \times 1000$  mg/L

**Permanent hardness =  $V_3 / V_1 \times 1000$  mg/L**

#### **Estimation of temporary hardness:-**

Temporary hardness = Total hardness – Permanent hardness

=  $(V_2 / V_1 \times 1000 - V_3 / V_1 \times 1000)$

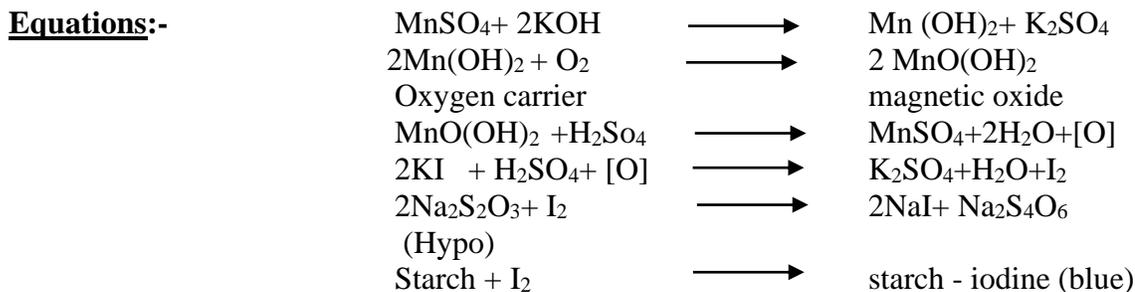
=  $(V_2 - V_3 / V_1) \times 1000$  PPM

**Temporary hardness =  $(V_2 - V_3 / V_1) \times 1000$  mg/l.**

### **Analysis of water –Estimation of dissolved $\text{O}_2$**

At room temperature and pressure the amount of dissolved oxygen in water is about 8mg/l. dissolved oxygen is essential for aquatic organisms and it also serve as an indicator of the extent of water pollution by impurities. Hence the determination of dissolved oxygen content is important both for environmental and industrial point of view. The amount of dissolved oxygen in water is determined by ‘**WINKLER’S METHOD**’.

**Principle: -** The determination of dissolved  $\text{O}_2$  is based on the oxidation of KI by dissolved  $\text{O}_2$ . The liberated iodine is titrated against standard sodium thio sulfate (Hypo) solution using starch as indicator blue color disappears. The dissolved molecular oxygen is unable to react with KI in water. Hence the carrier  $\text{Mn}(\text{OH})_2$  carries oxygen and brings about the reaction between KI and  $\text{O}_2$ .  $\text{Mn}(\text{OH})_2$  is produced by KOH and  $\text{MnSO}_4$ .



**Preparation of solutions:-**

**1. MnSO<sub>4</sub> solution:-** 400 gm of MnSO<sub>4</sub> dissolved in 1 liter of water .

**2. Alkaline KI solution:-** 150 gm of KI , 500gm of NaOH , 20 gm of sodium azide (NaN<sub>3</sub>) which destroys impurities in water, all are dissolved in 1 liter of water.

**3. Standard Hypo (N/100):** - 2.48 gm of Hypo dissolved in 1 liter water.

**Method / procedure:** - 250 ml of water is collected in bottle avoiding as far as possible contact with air, immediately add 2 ml MnSO<sub>4</sub> & 2 ml of alkaline KI solution. Stopper the bottle & shake it thoroughly for 10 – 15 minutes and allow to stand for few minutes to settle precipitate .Repeat this process of shaking and settling at least 3 times. Add 20 ml of conc. H<sub>2</sub>SO<sub>4</sub> , stopper and shake to dissolve precipitate . Pipette out 100ml of solution in conical flask & titrate against standard Hypo using freshly prepared starch as indicator. End point is disappearance of blue color.

**Calculation: -**

$$N_1V_1 = N_2V_2$$

$N_1$  = Normality of Hypo ,

$N_2$  = Normality of dissolved O<sub>2</sub>

$V_1$  = volume of Hypo,

$V_2$  = volume of dissolved O<sub>2</sub>

$$\text{Weight of dissolved O}_2 = \frac{N_1V_1 \times 8 \times 10^6}{100 \times 1000} \text{ PPM.}$$

**Treatment of water for domestic purpose:**

For domestic purposes, the required water is collected from natural sources like rivers, lakes, ponds etc. However this water contains organic, inorganic & suspended impurities. Hence it must be purified before using. The domestic used water should have the following features:

1. It should be clear & odor less.
2. It should be pleasant in taste.
3. It should be perfectly cool.
4. Its turbidity should not exceed 10PPM.
5. It should be free from dissolved gases like hydrogen sulfide, minerals like lead, arsenic, chromium & manganese salts
6. It should be free from disease causing micro organisms.
7. Its alkalinity shouldn't be high and its pH should be about 8.
8. It should reasonably soft.
9. Its total dissolved solids content should be less than 500ppm.

**PURIFICATION OF WATER FOR DOMESTIC USE:**

Purification of water for domestic purpose involves two steps. They are

- I. Removal of suspended impurities
- II. Removal of micro organisms/Sterilization

**I. Removal of suspended impurities**

1. Screening
2. Sedimentation
3. Filtration.

**1. Screening:** - This method is used for removing of suspended impurities. The process of removing floating matter from water with the help of screens is known as screening. In this process water is passed through a screen. The movement of floating matter is stopped by the screen and the water is free from floating matter.

**Sedimentation:** - Sedimentation is a process of allowing water to stand in big tanks. Then most of the suspended particles settle down at the bottom due to force of gravity. It is of two types

- 1) Plain sedimentation
- 2) Sedimentation by coagulation.

**2. Plain sedimentation:** - This process is mainly used for sedimentation of big size suspended particles. In this process water is stored in big tanks for several hours. 70% of solid particles settle down due to gravitational force of attraction.

**3. Sedimentation by coagulation:** - It is the process of removing finely suspended and colloidal impurities by addition of requisite amount of chemicals called **coagulants** to water before sedimentation. When coagulant is added to water, it forms an insoluble gelatinous, flocculent precipitate which gathers tiny particles to form bigger flocks which settle down easily.

Eg:

Name	Formula
Alum	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Sodium aluminates	$NaAlO_2$
Ferrous sulfate	$Fe SO_4 \cdot 7H_2O$

### **3. Filtration: -**

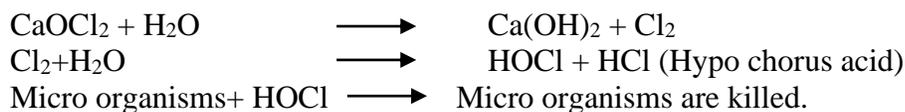
- Even though water is subjected to screening & sedimentation, it contains fine clay, colloidal matter and also micro organisms. At that time filtration is used for purification of water.
- Water is passed through filters that contain pore size smaller than the size of the particles that are to be removed. Then the particles get accumulated on the surface of filter and water moves through the filter.

**II. Sterilization:** - When water is subjected to sedimentation, coagulation & filtration still it contains a small percentage of micro organisms. Pathogenic micro organisms cause the water not suitable for drinking. Hence they also should be removed. The process removing or killing of pathogenic micro organisms using chemical substances is called as **sterilization or Dis-infection**. This is done by the following three methods.

1. Addition of bleaching powder
2. Chlorination
3. Ozonization

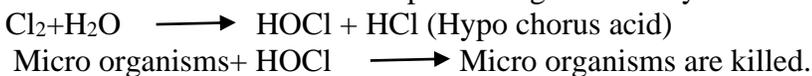
#### **1.Addition of Bleaching powder:**

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



The disinfection action of bleaching powder is due to available chlorine in it. It forms hypo-chlorous acid which acts as a powerful germicide.

**2.Chlorination:** - Treatment of water with chlorine is called chlorination, which is one of best methods for sterilization of water .Chlorine is a powerful germicide by means of HOCl.



#### **Mechanism: -**

Chlorination is done in apparatus called chlorinator which is large tower containing a number of baffel plates & two inlets for chlorine and water & one outlet for sterilized water. Water and proper quantity of conc. Chlorine solution are introduced to its related inlets. During their passage through the tower they get thoroughly

mixed. Then chlorine reacts with water and releases HOCl, which kills germs. The treated water is collected at the bottom.

<u>Advantages</u>	<u>Disadvantages</u>
<ol style="list-style-type: none"> <li>1. It is most effective &amp; economical.</li> <li>2. It requires very little place for storage.</li> <li>3. It is stable &amp; doesn't deteriorate on keeping.</li> <li>4. It can be used at low and also high temp.</li> <li>5. It doesn't introduce salt impurities in treated water.</li> <li>6. It is most ideal des infect ant</li> </ol>	<ol style="list-style-type: none"> <li>1. Excess of chlorine used for purification produces unpleasant odor and taste.</li> <li>2. Excess produces irritation on mucous membrane.</li> <li>3. The quantity of free chlorine in treated water shouldn't exceed 0.1 to 0.2 PPM</li> <li>4. It is less effective at higher pH values.</li> </ol>

### 3. Ozonization:-

Treatment of water by ozone is called ozonization. Ozone is an excellent disinfectant, which is produced by passing silent electric discharge through cold & dry oxygen.



Ozone is highly unstable and break down liberates nascent oxygen which is powerful oxidizing agent & kills all the bacteria as well as oxidizes the organic matter present in water.



<u>Advantages</u>	<u>Disadvantages</u>
<ol style="list-style-type: none"> <li>1. It simultaneously removes color, odor and taste without giving any residue.</li> <li>2. Its excess is not harmful since it is unstable and decomposes in to oxygen.</li> </ol>	<ol style="list-style-type: none"> <li>1. This method is quite expensive hence not employed for disinfection of municipal water supply.</li> </ol>

## WATER FOR INDUSTRIAL USES

### Water for steam generation:-

Water is used for making steam. Such water should be free from dissolved salts, gases, suspended impurities, oils & silica etc... Usually boilers are used for of steam generation. The boilers are heated with fuels such as coal. The steam generated rotates the blades of turbines fast to produce electricity. This electricity produced by making use of water in boiler. The turbine is a magnet wounded by coil wire.

### Boiler Troubles :-

If hard water is used in boilers the following problems arise

1. Priming and foaming
2. Boiler corrosion
3. Formation of scales and sludge's
4. Caustic embrittlement.

**(I) Priming & foaming (or) Carry over:-** The process of formation of wet steam is called as priming or carry over. The steam carrying water droplets is called as wet steam.

**(A) Priming:** The phenomenon of steam production along with water droplets by rapid boiling of water is nothing but priming.

### Reasons:-

1. Very high steam velocity.
2. Sudden boiling.
3. Improper boiler design.
4. High water levels.
5. Presence of large amounts of dissolved salts.

### Prevention:-

1. Maintaining low water levels
2. Using softened water
3. Fitting mechanical steam purifiers.

#### 4. Using well designed boiler

**(B) Foaming:** - The production of persistent bubbles or foam in boiler water surface is called foaming.

**Reasons:** -

1. The presence of oily or soapy substances.
2. Certain dissolved salts.

**Prevention:-**

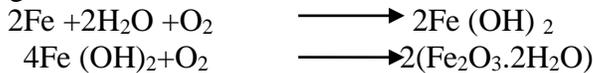
1. It can be avoided by adding anti-foaming agents like cotton seed oil & castor oil
2. By adding  $\text{NaAlO}_2$  which coagulates oily or soapy substances.

**(II) Boiler corrosion:** - The decay of boiler material by chemical or electro chemical attack by its environment is called boiler corrosion.

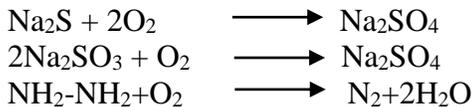
**Reasons:** -

1. Due to presence of dissolved  $\text{O}_2$
2. Dissolved  $\text{CO}_2$
3. Acids from dissolved salts.

**1. Dissolved  $\text{O}_2$ :**- At room temperature one liter water consists eight mg of dissolved  $\text{O}_2$ . It attacks boiler material causing rust formation.



**Removal:** - Dissolved oxygen is eliminated by adding calculated quantity of sodium sulphate and sodium sulphide or hydrazene.

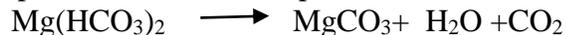


Among these the hydrazene method is ideal method for removal of dissolved oxygen. The liberated is not harmful to boilers.

**2. Dissolved  $\text{CO}_2$ :**-It gives carbonic acid with water. This carbonic acid has corrosive effect on boiler material.



Carbon dioxide is also produced from decomposition of bicarbonate salts usually present in water.



**Removal:** - It is removed from water by adding calculated quantity of  $\text{NH}_3$  in the form of  $\text{NH}_4\text{OH}$  to produce ammonium carbonate.



**3. Acids from dissolved Salts:** Acids that are produced from dissolved salts are also mainly responsible for corrosion. Certain salts like magnesium chloride, calcium chloride etc...produce acids by their hydrolysis.



The liberated HCl reacts with Fe produces HCL again and finally leads to formation of rust.

**Removal:** - It can be removed by neutralizing acids with alkali.



**(iii) Scales & Sludge's:** - In boilers, water evaporates continuously and the concentration of dissolved salts increase progressively. When their concentration reach saturation point they are thrown out of water in the form of precipitates on the surface or inner walls of boilers. The precipitation takes place in two ways.

1. Scales
2. Sludge's

**1. Sludge's:** - 1. Sludge's are soft, loose, slimy non – stick precipitates produced due to higher conc. of dissolved salts.

2. It can easily be scrapped off by wire brush.

**Reason:** - Sludge's are formed by substances which have greater solubility in hot water than in cold water.

Eg;  $\text{MgCl}_2$ ,  $\text{Mg}(\text{CO}_3)_2$ ,  $\text{MgSO}_4$ ,  $\text{CaCl}_2$  etc.

**Disadvantages:** - 1. Sludge's are bad conductors of heat, hence it wastes portion of heat generated.

2. Excessive sludge formation reduces the efficiency of boiler.
3. It settles in the region of poor circulation areas such as pipe connection,

Plug opening, gauze glass connection leading to checking of the pipes.

**Prevention:** - 1. By using well softened water.

2. Frequently carried out blow down operations (removal of conc. water from the Bottom of boiler).

**2. Scales:** - 1. Scales are hard, sticky deposits formed on inner walls of boiler.

2. The main source of boiler troubles are scales and are very difficult to remove once they are deposited on the inner walls of boiler.

**Disadvantages:-**

1. Wastage of fuel.

2. Decrease in efficiency.

3. Low boiler safety & danger of explosion (at high temp. cracks may be formed on boilers scale leading to explosion).

4. Scales are bad conductor of heat.

**Removal of scales:-**

1. Scales are not easily removed by wire brush, scrappers or wiped piece.

2. Scale can be removed by thermal shocks (sudden heating and cooling).

3. Using certain chemicals to removal of scales

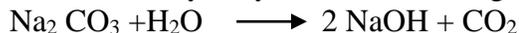
a .5-10% of HCl - used to removal of CaCO<sub>3</sub> scales.

b. EDTA- removal of CaSO<sub>4</sub> scales.

c. MgO - removal of silica

4. By adding of anti -coagulants (removal of silica scales)

**IV. Caustic Embrittlement:** - It is at type of corrosion produced by caustic alkalinity (NaOH). Usually water consists of Na<sub>2</sub>CO<sub>3</sub> which is hydrolyzed to alkali at high temp.



The NaHCO<sub>3</sub> present in water produce Na<sub>2</sub>CO<sub>3</sub> which in turn give NaOH. This NaOH passes in to the small cracks or stress areas on the boiler by capillary action and attacks the surrounding area and dissolves the Fe of boilers as sodium ferroate.



This causes embrittlement of boiler parts particularly at joints, bends, pipes etc.

**Disadvantage:-** Failure of boiler.

**Prevention :-**

1. Neutralizing the alkali with very small quantity of acid.

2. By adding sodium phosphate as softening agent to water.

3. By adding sodium sulphate, lignin to boiler water which blocks hair cracks.

### **WATER TREATMENT FOR BOILERS:**

Water treatment is used for prevention of scales & softening of water. They are two types.

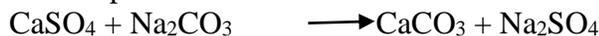
1. Internal treatment used to remove scales

2. External treatment for softening water.

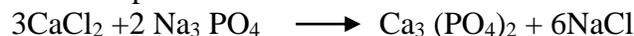
**Internal treatment:** - The following internal conditioning methods are used prevention of scales.

**1. Colloidal conditioning:** - When certain chemicals like tannin , agar - agar , kerosene are added to water, these substances coat the outer surfaces of crystalline ppts, and thus forms colloidal non - sticky, sludge like ppt which can be easily removed by mechanical methods like blow - down operation.

**2. Carbonate conditioning:** - In low pressure boilers scale formation can be avoided by treating boiler water with Na<sub>2</sub>CO<sub>3</sub> .The scale forming salts like CaSO<sub>4</sub> are partially converted to CaCO<sub>3</sub> (loose sludge) , which can be removed by blow down operation .



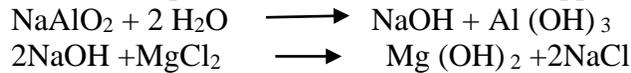
**3. Phosphate conditioning:-** In high pressure boilers Na<sub>2</sub>PO<sub>4</sub> reacts with water forms loose ppt .when can be easily removed by blow down operation .



**4. Calgon conditioning:** -  $\text{Na} [\text{Na}_4 (\text{PO}_3)_6]$  [calgon] is added to boiler scales forms soluble complex with  $\text{CaSO}_4$ .



**5.  $\text{NaAlO}_2$  conditioning:** - In water sodium aluminate gives aluminum hydroxide &  $\text{NaOH}$ . This  $\text{NaOH}$  reacts with magnesium salts to form  $\text{Mg} (\text{OH})_2$  ppt. This hydroxide interacts with finely divided particles and neutralizes the charge on colloidal particles and forms loose, soft ppt. removed by blow down operation.



**2. External treatment:** - This is used for softening of water. The removal of hardness causing salts from water is nothing but softening of water. The most important method for softening is ion exchange process and Zeolite process.

**Ion – exchange process / Demineralization / Deionization:-**

Ion exchange resins are used for softening of water. Resins are insoluble, cross linked, long chain, organic polymers with a micro- porous structure, and their functional groups are attached to the chains responsible for the ion –exchanging properties. These Resins are two types.

1. Cation exchanger
2. Anion exchanger

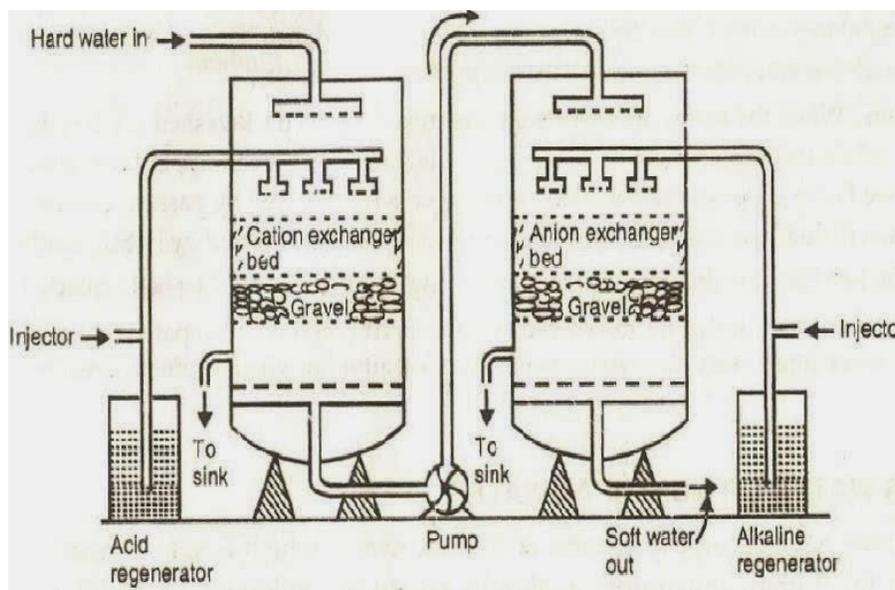
**Cation exchanger ( $\text{RH}^+$ ):** These resins contain acidic functional groups ( $\text{COOH}/\text{SO}_3\text{H}$ ). These are capable of exchanging their  $\text{H}^+$  ions with cations of the dissolved salts which comes in their contact. They are represented by the general formula  $\text{RH}^+$ .

R—Structure of the resin,  
 $\text{H}^+$ -- exchangeable with cation.

Usually they are styrene di vinyl benzene copolymers.

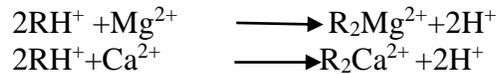
**Anion exchanger ( $\text{ROH}^-$ ):** R— general structure of resin Styrene divinyl benzene (or) amino formaldehyde (or) phenol formaldehyde copolymers which contain amino or quaternary ammonium or quaternary their  $\text{OH}^-$  ions with any anion present in the dissolved salts. These are represented by the formula  $\text{ROH}^-$ . phosphate or ternary sulphonium groups as an internal part of the resin matrix. These resins exchange

R—Structure of the resin,  
 $\text{OH}^-$ -- exchangeable with anion.



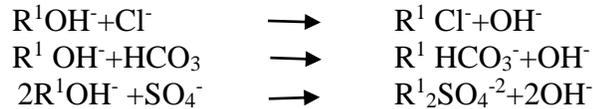
**Process:** - In demineralization plant the first chamber is filled with cation exchange resin and second one is with anion exchange resin.

**Step 1:-** When hard water is passed through bed of cation exchange resin, it exchanges  $H^+$  ions with  $Ca^{+2}$ ,  $Mg^{+2}$ ,  $Na^+$  of hard water



Thus hardness producing cations are removed.

**Step2:-** Then the water is passed through anion exchange resin, it exchanges anions like  $Cl^-$ ,  $HCO_3^-$ ,  $SO_4^{2-}$  which enter from 1<sup>st</sup> chamber to 2<sup>nd</sup>.



Thus hardness causing anions are removed.

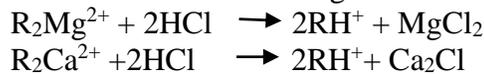
**Step 3 :-** The  $H^+$  ions that are produced from 1<sup>st</sup> chamber combine with  $OH^-$  ions produced from 2<sup>nd</sup> chamber to form water.



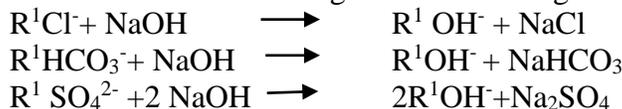
Hence the water produced from ion exchange process is completely free from all cations & anions of hard water.

**Regeneration of resins:** - After deionization of certain amounts of water, the cationic and anionic exchangers will be exhausted. Hence they are employed to regeneration for further uses.

1. The exhausted cationic exchange resin can be regenerated by passing dil. HCl.



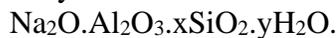
2. The exhausted anionic exchange resin can be regenerated by passing dil. NaOH.



Advantages	Disadvantages
1. Highly acidic or alkaline water can be treated by this method. 2. It produces very low hardness nearly 2ppm. 3. the softened water is completely free from salts and fit for use in boilers.	1. This equipment is costly. 2. More expensive chemicals are required for regeneration. 3. Turbid water cannot be treated by this method.

### Zeolite or Permutit Process:

Zeolite is hydrated sodium aluminosilicate. Its general formula is



Here  $x = 2-10$   $y = 2-6$

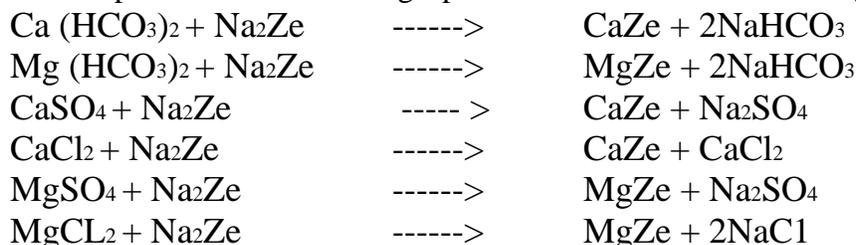
Eg: Natrolite  $Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$ .

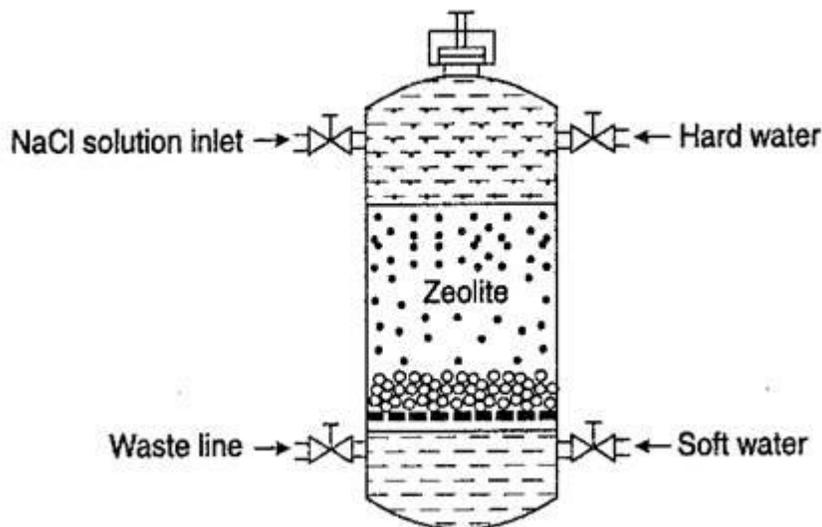
Natural zeolite are generally non porous. The artificial zeolite is called Permutit. They are prepared by heating together with china clay, feldspar and soda ash. These are porous and have greater softening capacity than natural zeolite. They exchange  $Na^+$  ions with the hardness producing ions ( $Ca^{+2}$ ,  $Mg^{+2}$  etc.) in water. Sodium zeolite is denoted as  $Na_2Ze$ .

### Process:

In this process hard water is passed through a bed of zeolite at ordinary temperature.

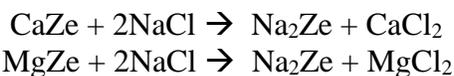
The hard water percolates  $Ca^{+2}$  and  $Mg^{+2}$  present in hard water are exchanged with  $Na^+$  ions.





### **Regeneration:**

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



The washings are led to drain and the regenerated zeolite bed thus obtained is used again for softening process.

### **Advantages:**

- i. The equipment is small and easy to handle.
- ii. It requires less time for softening.
- iii. Water obtained from this process contains a residual hardness up to 10ppm.
- iv. Easy to regenerate.
- v. No sludge is formed in this process.

### **Demineralization /Desalination Of Brackish Water: -**

#### **Reverse Osmosis:**

Reverse osmosis is used for desalination of sea water. The process of removal of salts from sea water is nothing but desalination. Sea water contains an average of about 3.5% of salts. This water is totally unfit for drinking and other domestic uses.

A semi permeable membrane is used for desalination which is made of cellulose acetate, polymethacrylate, polyamide polymers which don't allow dissolved solute particles, molecules, salts, ions etc... By osmosis solvent flow from low conc. to high conc. at constant pressure. However an excess of osmotic pressure is applied to sea water, so that the solvent flow in reverse direction i.e solvent is forced to move from high conc. to low conc. across the membrane. This means semi permeable membrane doesn't allow dissolved salts of sea water through it. This process is called reverse osmosis & this membrane filtration is called super/hyper filtration.

#### **Advantages: -**

1. It is used for removal of ionic, non-ionic, colloidal, high molecular weight organic matter.
2. Removes colloidal silica which is not removed by ion exchange process.
3. The life span of semi permeable membrane is about 2 years.
4. The membrane can be replaced within few minutes.
5. This method is a simple, economical, & highly reliable.



# UNIT-II

# UNIT – I

## ELECTRO CHEMISTRY

**Electro chemistry:** This is a branch of physical chemistry that deals with conversion of chemical energy into electrical energy and vice versa.

**Electrolyte:**-A Substance, which decomposes as a result of passage of electric current, is called “Electrolyte”.

**Electrolysis:**-The phenomenon of decomposition/ breakdown/ lysis of electrolyte by passing electricity is called electrolysis.

**Electric current:**-The flow of electrons that are generated by a battery when the circuit is complete is called electric current.

**Electric conductor:**-Any substance which allows or passes electric current through it is called as ‘electric conductor’.

**Anode:** It is an electrode at which Oxidation occurs.

**Cathode:** It is an electrode at which Reduction occurs.

**Types of Electrolytes:** Electrolytes may be classified into

1. Strong electrolytes
2. Weak electrolytes

**1. Strong electrolytes:** It is a substance that gives a solution in which almost all the molecules are ionized and having increasing value of equivalent conductance at low dilution.

Eg:     Strong acids     : HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HBr etc  
       Strong bases     : NaOH, KOH, Ca (OH)<sub>2</sub>, Mg (OH)<sub>2</sub> etc.  
       Salts             : NaCl, KCl, AgCl<sub>2</sub>

**2. Weak electrolytes:** The electrolytes which ionize to a small extent on dilution are called weak electrolytes. They are poor conductors in solution.

Eg:     Weak acids       : All organic acids like Acetic acid, Propionic acid etc.  
       Weak bases       : Alkyl amines, NH<sub>4</sub>OH  
       Weak salts        : HgCl<sub>2</sub> and Lead acetate.

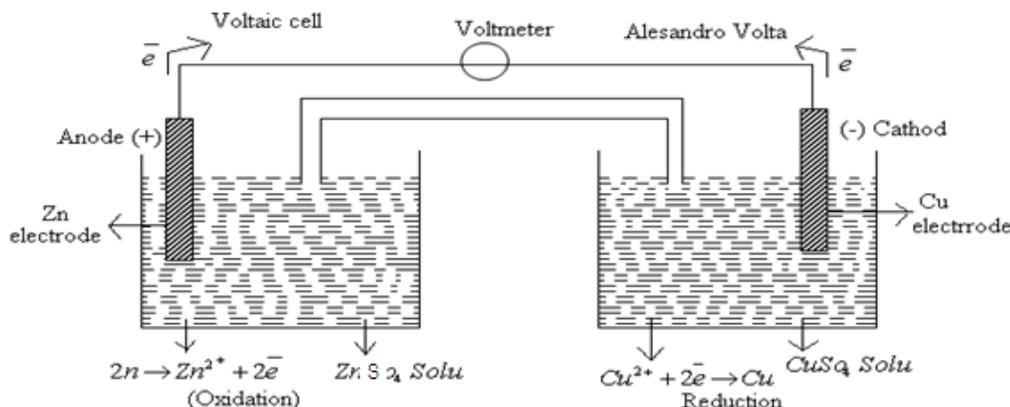
**Galvanic Cells or Voltaic Cells:-**

- A Voltaic cell is a device which is used for converting chemical energy into electrical energy. A redox reaction is utilized to get electrical energy.
- In galvanic cells electric current results from a redox reaction in which oxidation occurs at one electrode and reduction at the other.
- The substance which loses electrons is called **oxidized** and the process is called **Oxidation** and the substance which gains electrons is called **Reduced** and the process is **Reduction**.

- The apparatus that provides electricity through redox reaction is called galvanic cell, invented by Luigi Galvani (1737-1798) and also called as voltaic cell (Alessandro Volta (1745-1827).

- Ex: Daniel Cell

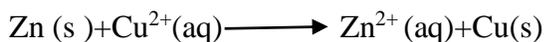
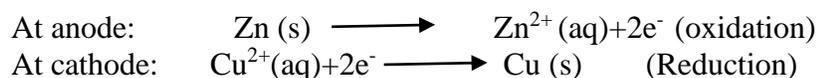
- **Daniel Cell:** A Daniel cell is made up of two half cells (an individual oxidation and reduction takes place at two electrodes).
- On the left Zinc electrode dips into a solution of ZnSO<sub>4</sub> (oxidation) and on the right a Copper electrode dips into a solution of CuSO<sub>4</sub> (Reduction).
- The two electrodes are connected by an external electrical circuit and two solutions are connected by a salt bridge.



**Reactions occurring in the cell:** The electrode reactions are:

**At anode:** Oxidation takes place in the Zn electrode by the liberation of electrons. This electrode is negative electrode or anode.

**At Cathode:** Reduction takes place in the Cu electrode by the acceptance of electrons. This electrode is positive electrode or Cathode.

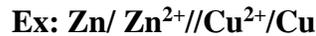


- When these reactions takes place, electrons left behind by oxidation of the Zinc travel through external circuit to the other electrode where they are transferred to the Cu ions and are reduced to Cu metal.
- The overall reaction that takes place in a galvanic cell is called **cell reaction**.
- Electric current flows from positive electrode to negative electrode.
- The flow of electrons from one electrode to other electrode in a galvanic cell indicates that the electrodes have different potentials.
- The difference of potentials which causes electrons to flow or current from one electrode which is at higher potential to another electrode which is at lower potential is called **Electro motive force (EMF)** of the cell.

Representation of a galvanic cell:

- A galvanic cell consists of two electrodes- Anode and Cathode
- The anode is written on the left side while the cathode is written on the right hand side.

- Anode must be written writing electrode metal first and then electrolyte. These two are separated by a vertical line.
- The cathode may be written by writing electrolyte first and then the electrode metal. These two are separated by a vertical line.
- The two half cells are separated by a salt bridge which is indicated by two vertical lines.



**Electrode potential:**

- Metal ions have a tendency to go into solution as metal ions. This tendency is called ‘**electrode potential**’ of that metal.
- Electrode potential can be defined as the tendency of metal atoms to go in to solution in the form of metal ions.
- The electrode equilibrium is represented as



- Electric current flows between two electrodes if the contact is established between two metals.
- The flow of current from one electrode to another electrode in a galvanic cell indicates that the two electrodes have different potentials.
- The difference of potential which causes the flow of current from one electrode which is at higher potential to another electrode which is at lower potential is called “EMF of the cell”

**Nernst Equation for EMF of a cell:**

Electrode potential for the electrode reaction,



Relative to hydrogen electrode is given by a simple form of the Nernst equation as

$$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{RT}{nF} \ln (M^{n+})$$

Here

$E^{\circ}_{M^{n+}/M}$  = Standard electrode potential for a molar solution of a metal ion at 298°K  
(This is determined by using the standard hydrogen electrode )

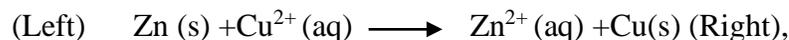
R= Universal gas constant (8.31 J/K/mol)

T= Temperature in Kelvin

n= Number of moles of electrons

F= Faraday (96500 C/mol)

In the Daniell cell,



The electrode potential of the right hand electrode is written as:

$$E_{Cu^{+2}/Cu} = E^{\circ}_{Cu^{+2}/Cu} + \frac{RT}{nF} \ln [Cu^{+2} (aq)]$$

The electrode potential of the left hand electrode is written as:

$$E_{Zn^{+2}/Zn} = E^{\circ}_{Zn^{+2}/Zn} + \frac{RT}{nF} \ln [Zn^{+2} (aq)]$$

∴ The cell potential  $E_{cell}$  = Electrode potential of right hand electrode –

Electrode potential of left hand electrode

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

$$\begin{aligned} \therefore E_{\text{cell}} &= \left\{ E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} + \frac{RT}{nF} \ln [\text{Cu}^{+2}(\text{aq})] \right\} - \left\{ E^{\circ}_{\text{Zn}^{+2}/\text{Zn}} + \frac{RT}{nF} \ln [\text{Zn}^{+2}(\text{aq})] \right\} \\ &= (E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} - E^{\circ}_{\text{Zn}^{+2}/\text{Zn}}) + \frac{RT}{nF} \ln \frac{[\text{Cu}^{+2}(\text{aq})]}{[\text{Zn}^{+2}(\text{aq})]} \end{aligned}$$

$$E_{\text{Cell}} = E^{\circ}_{\text{cell}} + \frac{RT}{nF} \ln \frac{[\text{Cu}^{+2}(\text{aq})]}{[\text{Zn}^{+2}(\text{aq})]} \quad (\because E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} - E^{\circ}_{\text{Zn}^{+2}/\text{Zn}})$$

$E^{\circ}_{\text{cell}}$  is cell potential in standard state. By converting natural logarithm to the base 10, and substituting the values R, T (298K) and F, we get

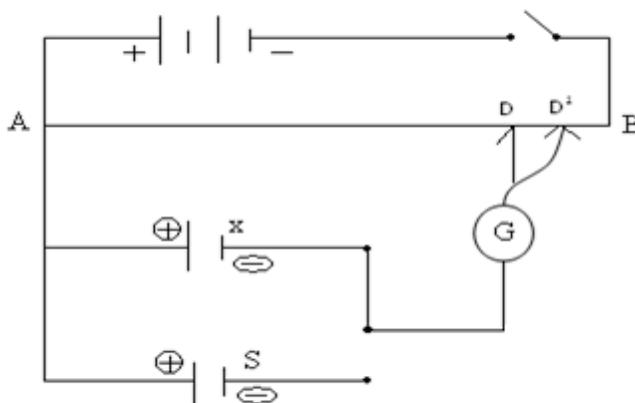
$$E_{\text{Cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{2} \log \frac{[\text{Cu}^{+2}(\text{aq})]}{[\text{Zn}^{+2}(\text{aq})]}$$

In general Nernst Equation is

$$E_{\text{Cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{n} \log \frac{\text{Right hand side electrode}}{\text{Left hand side electrode}}$$

### EMF measurement (Electro motive force):-

- An EMF of a cell can be measured by connecting two electrodes to the two terminals of a voltmeter.
  - EMF of the cell can be measured without disturbing the chemical equilibrium by using **Poggendorff's compensation principle**.
  - In this technique the EMF is measured using potentiometer where principle is EMF to be measured is balanced by equal and opposite EMF from another cell or battery and there is no net flow of current in the circuit.
  - The electrical assembly used is called **Potential meter**.
  - Potentiometer consists of a uniform wire AB of high resistance, connected to a storage battery of constant EMF which should be longer than the EMF of cell to be measured.
  - The Cell 'X' whose EMF is to be determined is connected to the positive pole 'A' and then through a galvanometer 'G' to a sliding contact D.
- S = Standard cell EMF.



- The sliding contact 'D' is moved along the wire AB till there is no current flow in the galvanometer. The position 'D' is then noted.
- The EMF of cell ( $E_x$ ) is proportional to the distance AD  

$$E_x \propto AD$$
- The cell 'X' is now replaced by standard cell 'S', whose EMF  $E_s$  is known.

- The position of sliding contact is readjusted by moving it over the wire AB till the point of no current in the Galvanometer i.e. the 'null point', indicated as 'D<sup>1</sup>'

$$E_s \propto AD^1$$

$$\Rightarrow \frac{E_x}{E_s} = \frac{AD}{AD^1}$$

$$\Rightarrow E_x = \frac{AD}{AD^1} \times ES$$

Knowing the  $E_s$ ,  $E_x$  can be calculated easily.

- The standard cell must be capable of giving constant and reproducible emf and its variation with temperature should be negligibly small.

### **Standard electrode potential :-( $E^0$ cell)**

- The tendency of an electrode to lose or gain electrons when it is in contact with a solution of its own salt is called "Electrode potential".
- The potential difference between the metal and its salt solution in which it is dipped is called single electrode potential.
- When this electrode potential is measured under standard conditions like 25°C, 1.0 M solute concentration and a pressure of 1 atm, then the electrode potential is called '**Standard Electrode Potential**'.
- The SEP is represented by  $E^0_{\text{cell}}$ .
- When 2 half cells are connected to make galvanic cell, one half cell having larger standard electrode potential (the one with the greater tendency to undergo reduction) accepts electrons from the half cell with lower standard electrode potential (greater tendency to undergo oxidation).

$$E^0_{\text{cell}} = (\text{SEP of the reduced substance}) - (\text{SEP of the oxidized substance})$$

- The values of standard electrode potentials arranged in the decreasing order is called "**Electro chemical series**".
- These values are on Hydrogen Cycle because standard hydrogen electrode is used as the reference electrode and its value is taken as zero.

Elements	Electrode Reaction	$E^{\ominus}_{red}$ (volts)
	<i>Oxidised Form + ne<sup>-</sup> → Reduced Form</i>	
Li	$\text{Li}^+(aq) + e^- \longrightarrow \text{Li}(s)$	- 3.05
K	$\text{K}^+(aq) + e^- \longrightarrow \text{K}(s)$	- 2.93
Ba	$\text{Ba}^{2+}(aq) + 2e^- \longrightarrow \text{Ba}(s)$	- 2.90
Ca	$\text{Ca}^{2+}(aq) + 2e^- \longrightarrow \text{Ca}(s)$	- 2.87
Na	$\text{Na}^+(aq) + e^- \longrightarrow \text{Na}(s)$	- 2.71
Mg	$\text{Mg}^{2+}(aq) + 2e^- \longrightarrow \text{Mg}(s)$	- 2.37
Al	$\text{Al}^{3+}(aq) + 3e^- \longrightarrow \text{Al}(s)$	- 1.66
Zn	$\text{Zn}^{2+}(aq) + 2e^- \longrightarrow \text{Zn}(s)$	- 0.76
Cr	$\text{Cr}^{2+}(aq) + 3e^- \longrightarrow \text{Cr}(s)$	- 0.74
Fe	$\text{Fe}^{2+}(aq) + 2e^- \longrightarrow \text{Fe}(s)$	- 0.44
	$\text{H}_2\text{O}(l) + e^- \longrightarrow \frac{1}{2} \text{H}_2(g) + \text{OH}^-(aq)$	- 0.41
Cd	$\text{Cd}^{2+}(aq) + 2e^- \longrightarrow \text{Cd}(s)$	- 0.40
Pb	$\text{PbSO}_4(s) + 2e^- \longrightarrow \text{Pb}(s) + \text{SO}_4^{2-}(aq)$	- 0.31
Co	$\text{Co}^{2+}(aq) + 2e^- \longrightarrow \text{Co}(s)$	- 0.28
Ni	$\text{Ni}^{2+}(aq) + 2e^- \longrightarrow \text{Ni}(s)$	- 0.25
Sn	$\text{Sn}^{2+}(aq) + 2e^- \longrightarrow \text{Sn}(s)$	- 0.14
Pb	$\text{Pb}^{2+}(aq) + 2e^- \longrightarrow \text{Pb}(s)$	- 0.13
<b>H<sub>2</sub></b>	<b><math>2\text{H}^+ + 2e^- \longrightarrow \text{H}_2(g)</math> (standard electrode)</b>	<b>0.00</b>
Cu	$\text{Cu}^{2+}(aq) + 2e^- \longrightarrow \text{Cu}(s)$	+ 0.34
I <sub>2</sub>	$\text{I}_2(s) + 2e^- \longrightarrow 2\text{I}^-(aq)$	+ 0.54
Fe	$\text{Fe}^{3+}(aq) + e^- \longrightarrow \text{Fe}^{2+}(aq)$	+ 0.77
Hg	$\text{Hg}_2^{2+}(aq) + 2e^- \longrightarrow 2\text{Hg}(l)$	+ 0.79
Ag	$\text{Ag}^+(aq) + e^- \longrightarrow \text{Ag}(s)$	+ 0.80
Hg	$\text{Hg}^{2+}(aq) + 2e^- \longrightarrow \text{Hg}(l)$	+ 0.85
N <sub>2</sub>	$\text{NO}_3^- + 4\text{H}^+ + 3e^- \longrightarrow \text{NO}(g) + 2\text{H}_2\text{O}$	+ 0.97
Br <sub>2</sub>	$\text{Br}_2(aq) + 2e^- \longrightarrow 2\text{Br}^-(aq)$	+ 1.08
O <sub>2</sub>	$\text{O}_2(g) + 2\text{H}_3\text{O}^+(aq) + 2e^- \longrightarrow 3\text{H}_2\text{O}$	+ 1.23
Cr	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + e^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+ 1.33
Cl <sub>2</sub>	$\text{Cl}_2(g) + 2e^- \longrightarrow 2\text{Cl}^-(aq)$	+ 1.36
Au	$\text{Au}^{3+}(aq) + 3e^- \longrightarrow \text{Au}(s)$	+ 1.42
Mn	$\text{MnO}_4^-(aq) + 8\text{H}_3\text{O}^+(aq) + 5e^- \longrightarrow \text{Mn}^{2+}(aq) + 12\text{H}_2\text{O}(l)$	+ 1.51
F <sub>2</sub>	$\text{F}_2(g) + 2e^- \longrightarrow 2\text{F}^-(aq)$	+ 2.87

- The table shows that Fluorine has maximum positive value of SEP and hence it has maximum tendency to accept electrons and get reduced to Fluoride ion.
- The negative sign indicates that the half-cell reaction occurs in the opposite direction, the reduced form has a greater tendency to get oxidized and leave electrons.
- Li has maximum negative value of the electrode potential and hence it has the maximum tendency to lose electrons and get oxidized to Li<sup>+</sup> ions.

### Applications of SEP:

There are many applications to standard electrode potential.

#### (A) Calculation of standard EMF ( $E^{\ominus}_{cell}$ ) of a galvanic cell and determination of cell reaction:-

- $E^{\ominus}_{cell}$  is equal to the standard electrode potential of the right hand electrode minus standard electrode potential of the left hand electrode.

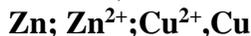
$$E^{\ominus}_{cell} = E^{\ominus}_R - E^{\ominus}_L$$

- The electrode at the right is written in the order : **Ion-electrode** ( $\text{Cu}^{2+}$ , Cu) and the left electrode is written in the order: **Electrode- Ion** ( $\text{Zn}:\text{Zn}^{2+}$ ).
- Half-cell reaction taking place at left hand electrode is oxidation reaction and at right, the half cell reaction is reduction reaction. The complete cell reaction is given by the sum of these two half-cell reactions.

**(B) Predicting spontaneity or feasibility of the cell reaction:-**

- If the standard emf of the cell is +Ve, the cell reaction is spontaneous or feasible.

Ex:-Let us consider Zn-Cu cell, the cell is represented as

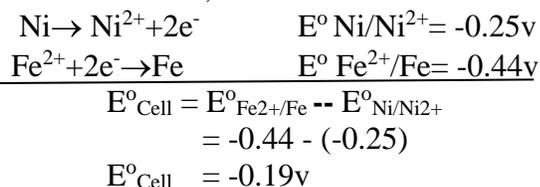


$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{R}} - E^\circ_{\text{L}} \\ &= E^\circ(\text{Cu}^{2+}, \text{Cu}) - E^\circ(\text{Zn}^{2+}, \text{Zn}) \\ &= 0.34 - (-0.76) = +1.10 \text{ volts.} \end{aligned}$$

The positive value indicates that the redox reaction is spontaneous in the forward direction.

- If the standard emf of the cell is -Ve, the cell reaction is not spontaneous or not feasible.

Ex: - Let us consider,

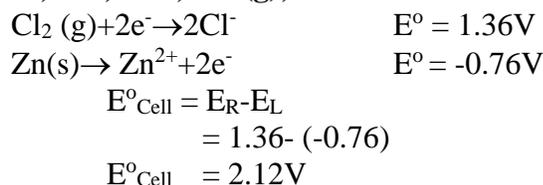


Since the EMF of above cell is negative, the cell reaction is non- spontaneous.

**(C) Designing of cells:**

- The standard electrode potential data is helpful in designing of the cells through which required voltage can be withdrawn.

Ex:-  $\text{Zn}^{2+}, \text{Zn}; 2\text{Cl}^-, \text{Cl}_2(\text{g}); \text{Pt}$



**(D) Change of electrodes:**

- From the standard Electrode Potentials, a non-spontaneous electrode can made to spontaneous by suitable changes in the sign of electrode.

Eg: -  $\text{Fe}^{2+}(\text{aq}) + \text{Ni}(\text{s}) \longrightarrow \text{Fe}(\text{s}) + \text{Ni}^{2+}(\text{aq})$  – Non- spontaneous.

$\text{Ni}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + \text{Ni}(\text{s})$  - has a Cell potential of +0.19V, - Spontaneous.

**(E)** An oxidizing agent with a higher reduction potential will oxidize any reducing agent with a lower reduction potential.

**(F)** A reducing agent with a lower reduction potential will reduce any oxidizing agent with a higher reduction potential.

**(G)** No two substances on the same side (left or right) will react with each other.

## **Batteries:-**

- A battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage.
- A cell contains only one anode and cathode where as a battery contains many anodes and cathodes.
- They are of 3 types.
  1. Primary cells
  2. Secondary Cells
  3. Fuel cells

### **1. Primary cells: -**

- In these cells the cell reaction is not reversible.
- When the reactants are converted in to products, further no more electricity is produced and the battery becomes dead. Hence they cannot be recharged.

Eg: - **i) Voltaic cell** (Cu and Zn electrodes dipped in  $H_2SO_4$ )

**ii) Daniel cell** (Zn in  $ZnSO_4$  and Cu in  $CuSO_4$  separated with porous diaphragm).

**iii) Dry (Laclanche) cell:** - This is a cell without fluid component. It is the most familiar of all batteries. In these Anode is 'Zn can' with  $NH_4Cl$  or  $ZnCl_2$  and  $MnO_2$  as electrolytes and to which starch is added to make it thick paste to prevent leakages and a 'carbon/graphite rod' serve as cathode which is immersed in the centre of electrolyte. Dry cell is cheap and gives a voltage of 1.5V. It is used in flash lights, transistor, radios, calculators etc,

### **2. Secondary cells: -**

- In these cells, the cell reaction can be reversed by passing direct electric current in opposite direction. They can be used again and again by recharging the cell.

Eg: - Ni-Cd storage cell,

Mercury battery,

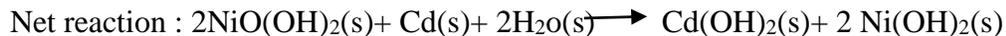
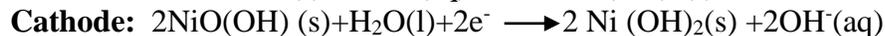
Ni—metal hydride lithium batteries.

### **1. Lead Storage cell or Acid storage cell:**

- It is secondary battery which can be used as a voltaic cell and as an electrolytic cell.
- It acts as a voltaic cell and supplies electrical energy and becomes run down. During recharge the cell acts as an electrolytic cell.
- It consists of a number of voltaic cell 3-6.
- It provides a voltage of 6-12V.
- Anode is made up of Pb and  $PbO_2$  acts as a cathode.
- Many anodes and cathodes are connected in parallel and are separated by insulators like rubber or glass fiber.
- Then the entire combination is immersed in dil. $H_2SO_4$  having a density of 1.30g.ml.
- The cell may be represented as



**Ni—Cd storage cell / Ni-Cad battery:** - This is recently developed, portable, rechargeable cell and its voltage is fairly constant (about 1.4V). It consists of 'Cd' anode, a cathode composed of a paste of 'NiO(OH)<sub>2</sub>'(s).



- This reaction can be readily reversed, because the reaction products, Cd(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> adhere to electrode surfaces.
- They are mainly used in electronic calculators, CD players, electronic cars, cordless electronic shavers and transistors.
- They have long durability without any maintenance.

**Lithium Batteries:** - The cells having lithium anodes are called lithium cells, irrespective of the cathode used. It is very light metal. It belongs to two categories.

(a) Lithium primary batteries

(b) Rechargeable cells / Li<sup>+</sup> Ion cells.

**a) Li primary cells: -**

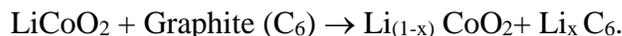
- The most common Li primary cell is the lithium manganese dioxide battery (LiMnO<sub>2</sub>).
- Anode is Li and Cathode is MnO<sub>2</sub> which is heated above 300<sup>0</sup>C to remove H<sub>2</sub>O before incorporating it in the cathode. This increases the efficiency of cell.
- A mixture of propylene carbonate and dimethoxy ethane containing dissolved salt such as LiClO<sub>4</sub> is taken as electrolyte.



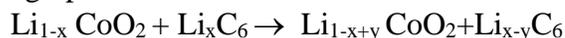
- This cell produces a voltage of about 3.4v, which is more than twice that of dry cell due to light weight of Li.
- They are widely used in applications that require higher current drain like fully automatic cameras, electronic devices such as calculators and watches.

**b) Lithium Ion cells or Rechargeable cells:**

- These cells do not contain metallic 'Li' instead it contains lithium ions (Li<sup>+</sup>).  
Anode: Carbon compound, graphite  
Cathode: Lithium Cobalt oxide
- In these cells the true oxidation/ reduction does not takes place, instead of that transport of Li<sup>+</sup> ions through the electrolyte from one electrode to the other takes place.
- When the cell is constructed, it is in its uncharged state with no Li<sup>+</sup> ions between the layers of 'C' atoms in the graphite.
- When the cell is charging, Li<sup>+</sup> ions leave LiCoO<sub>2</sub> and travel through the electrolyte to the graphite C<sub>6</sub>.



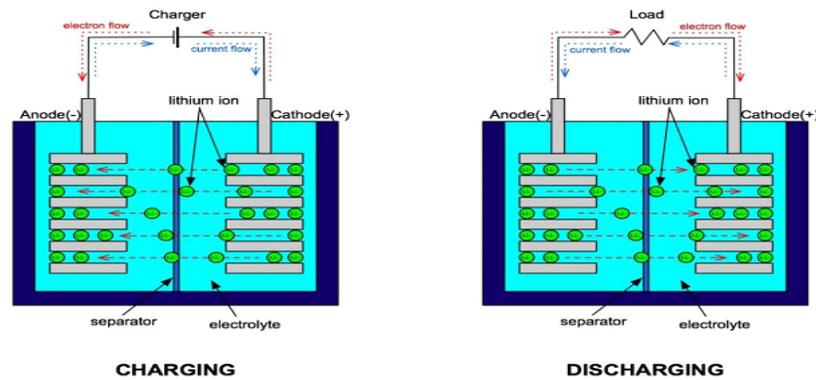
- When the cell spontaneously discharges to provide electrical power, Li<sup>+</sup> ions move back through the electrolyte to the cobalt oxide while electrons move through the external circuit from the graphite electrode to the cobalt oxide electrode.



Y=amount of Li<sup>+</sup> transferring from Li<sub>x</sub>C<sub>6</sub> . LiCoO<sub>2 1-x</sub>

X= transferring amount of  $\text{Li}^+$  from  $\text{LiCoO}_2$  to graphite.

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



### Fuel cell/Flow battery: -

- The reactants are continuously supplied from an external source to the cell and the reaction products continuously removed, such cells are called as fuel cells.
- In a fuel cell electrical energy is obtained without combustion from  $\text{O}_2$  and gas can be oxidized. Hence fuel cell converts chemical energy of the fuel directly to electricity.

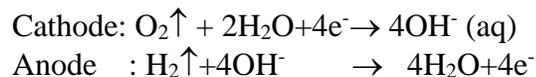
The important steps in the fuel cell

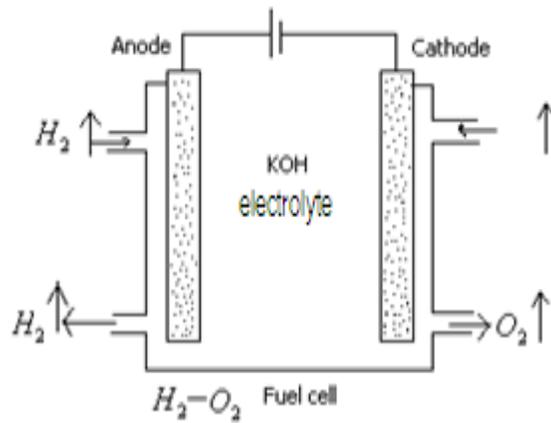


- In which fuel is gas/liquid and oxygen being oxidized. In fuel cell the chemical energy is provided by fuel and easily converts to electrical energy.
- Fuel cells are characterized by,
  - (1) High efficiency
  - (2) Low noise levels
  - (3) Free from vibration, heat transfer.
- The most important fuel cells are
  - (1)  $\text{H}_2\text{-O}_2$  fuel cell
  - (2) Methanol fuel cell

**(1) $\text{H}_2\text{-O}_2$  fuel cell/ alkaline fuel cell:** - It is successful and simplest cell.

- **Electrodes:** - Porous Platinum electrode, electrolyte -- 35-40% KOH.
- It consists of hot concentration KOH electrolyte solution and 2 porous Pt electrodes are dipped in KOH solution.
- At anode  $\text{H}_2$  gas and at cathode  $\text{O}_2$  gas is supplied, which are come in contact with electrodes and shows following reactions.





### Applications:-

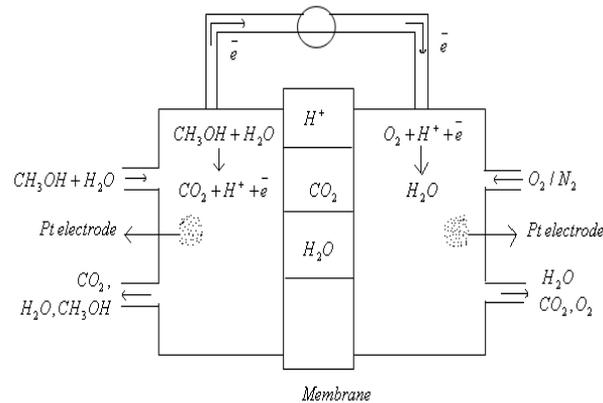
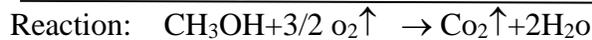
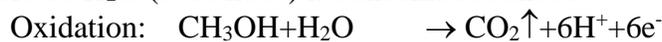
- (1) They are used as energy source in space vehicles, submarines or military vehicles.
- (2) The reaction product is water, which is harmless and used as source of fresh water to the astronauts.
- (3) The weight of fuel battery for 15 days is about 250 Kg.

### Disadvantages:-

- (1) Energy cost of generating H<sub>2</sub> fuel.
- (2) Difficult in storage and distribution of highly flammable.
- (3) Availability of alternative fuels.

### (2)Methanol fuel cell/proton exchange fuel cells:-

- **Electrodes:-** Porous Pt electrodes, separated by proton transport membrane.
- **Anode:** Oxidation of CH<sub>3</sub>OH and H<sub>2</sub>O absorbed on catalyst to form CO<sub>2</sub> with loss of H<sup>+</sup> (Protons) and electrons.
- **Cathode:** - H<sub>2</sub>O is liberated by reduction of O<sub>2</sub>, which accepts electrons and protons. Protons are transported from anode to cathode through proton transport membrane, while electrons transport through electric circuit.
- The liberated H<sub>2</sub>O (at cathode) is consumed at anode.



### Advantages:-

(1) Storage of methanol is much easier than  $H_2$  (does not high pressure or low temperature) since methanol is liquid form  $-97.0^{\circ}C$  to  $64.7^{\circ}C$  ( $-142.6^{\circ}F$  to  $148.5^{\circ}F$ )

(2) The energy density of methanol is greater than  $H_2$ .

**Disadvantages:-**

(1) During methanol oxidation, CO formed which is strongly adhere on to pt catalyst, reducing, the surface area and lowering the performance.

(2)  $CH_3OH$  is toxic and flammable and so utmost care is necessary.

(3) Limited power is produced by them.

**PREVIOUS QUESTIONS**

1. (a) What is meant by specific conductance and equivalent conductance? What are its units?

(b) Equivalent conductance of an electrolyte increases; where as specific conductance decreases. Explain?

2. (a) Explain the relationship between cell constant, conductivity, conductance?

(b) Define the specific resistance of a solution? Explain the specific conductance with diagrammatic illustrate of specific conductivity. What are its units?

3. (a) Define the cell constant of a conductivity cell? Explain how it is measured? What are its units.

(b) Resistance of N/2 solution of an electrolyte in a well was found to be 50 ohms. Calculate the equivalent conductance of the solution, if the electrodes in cell are 2.2cm apart and with an area of 3.8 sq.m.

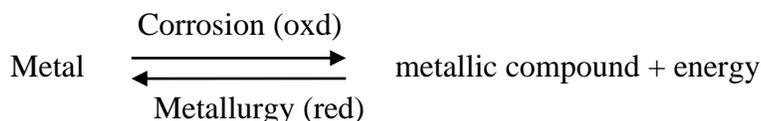
4. (a) Discuss the titration curve obtaining conductometric titration of weak acid and strong base?

(b)What are the limitations of conductometric titrations?

## SCIENCE OF CORROSION

**Introduction:** Most of the metals (except noble metals like Au, Pt, and Ag) occur in nature in combined form of their oxides, hydroxides, sulphides, chlorides, carbonates and silicates. All these metals have natural tendency to revert back to combined state for stability.

The natural combined form of metal is more stable than the other metals. So metals after extraction from its ore tends to revert back to the stable natural combined form when it comes in contact with other elements in the environment. That is why metal after extraction from its ore tends to revert back to the stable natural combined form. So corrosion is reverse process of metallurgy.



The surface of all metals begin to decay when exposed to atmospheric gases, water & other reactive liquid medium as a result they are converted to oxides, hydroxides, carbonates, nitrates, sulphates etc. This natural process is called corrosion.

**Definition:** - The process of gradual decay or deterioration / eating of metal from its surface by unwanted chemical / electro-chemical attack by its surrounding environment is called corrosion.

### Example for corrosion:-

- A reddish brown layer formed on to the surface of Fe
- Green film on surface of copper, etc...

### Reason for corrosion:-

- All metals except (Pt, Au, Ag) occurs in a combined state in nature. During extraction of metal from its ore, they are reduced to metallic compound using energy. Hence an isolated metal will be present in its excited unstable state. However, all the metals have natural tendency to go back to their combined state for its stability. As a result metal exposed to environmental factors or chemicals get converted in to its original combined state which is called corrosion.
- The corrosion process is a reversible process and is measured in units such as milli inches / year or millimeter/year.

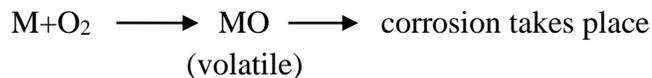
### Dis-advantages of corrosion:

1. Poor in appearance
2. The plant may be shut down due to failure.
3. Decrease in production rate and replacement of equipment is time consuming.
4. Contamination of product.
5. Decreased safety from a fire hazard or explosion or release of toxic product.
6. Health hazards from pollution due to corrosion product or due to escaping of chemical from a corroded environment.

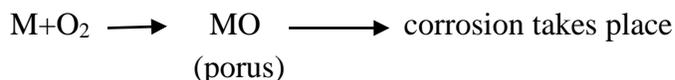
**Types corrosion:-** Based on the process how corrosion occurs, it is classified in to two types.



3. **Volatile:**-This type of metal oxide layer get continuously evaporated and hence fresh metal surface again get exposed for further corrosion leading to rapid corrosion of the metal. This type is seen in Mb (molybdenum)



4. **Porous:**- The metal oxide layer that is formed contains pores or cracks on its surface and through this pores atmospheric O<sub>2</sub> passes up to the metal surface, hence corrosion continues till the entire metal is converted to metal oxide.



S.No	Type of metal oxide	Example	Corrosion
1.	Stable	Cu, Al	Doesn't take place
2.	unstable	Pt, Au, Ag	Doesn't take place
3.	Volatile	Mb	Takes place
4.	porus	alkali &alkaline earth metals	Takes place

### Pilling – Bedworth Rule:

- The rule states that ‘an oxide is protective or non-porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed’.
- This is expressed in terms of **specific volume ratio**.

$$\text{Specific ratio} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$$

- The smaller the specific volume ratio, greater the oxide corrosion since the formed oxide film will be porous. So oxygen can diffuse and further corrosion takes place.

**Ex:** 1. Oxides formed by Alkali and Alakaline earth metals have less volume than the volume of metal, so they form porous scales and have high corrosion.

2. Metals like ‘Al’ form oxides whose volume is greater than the volume of metals, so they form non-porous scales and have low corrosion.

### **B. Corrosion By Other Gases (SO<sub>2</sub>, H<sub>2</sub>S, CO<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>) :-**

- This type of corrosion mainly depends on chemical affinity between metal & the gas involved.
- The intensity of attack depends on formation of protective or non protective films on metal surface.
- If the film is protective or non porous, the volume of metal oxide layer is greater than that of metal. So further corrosion of metal doesn't take place.

Eg: Formation of AgCl film by the attack of chlorine on Ag. The intensity of corrosion decreases due to formation AgCl non porous film on its surface which is tightly adherent on Ag.

- If the film is non- protective or porous, the volume of metal oxide layer is lesser than that of metal so further corrosion takes place.

Eg: SnCl<sub>4</sub> formed by attack of Cl<sub>2</sub> on Sn (tin) which volatiles immediately there by leaving fresh metal surface for further corrosion.

### **C. Liquid metal corrosion:-**

- This is due to chemical action of flowing liquid metal at high temperature on solid metal or alloy.
- This type of corrosion is seen in devices used for nuclear plant.
- The corrosion reaction is carried out either by dissolution of solid metal by liquid metal or internal penetration of liquid metal into solid metal. Both reactions lead to weakening of solid metal.

Eg: Na metal causes corrosion of Cd in nuclear reactor.

**2. Electrochemical / wet corrosion:-** This type of corrosion takes place when a conducting liquid is in contact with a metal or two dissimilar metals are either dipped or immersed partially in a solution.

- Usually it takes place in liquid medium.
- The electro chemical corrosion involves the following--
  1. Existence of separate anodic or cathodic parts between which current flows through conducting medium.
  2. **At anode:** Oxidation takes place at anodic part and releases electrons, forms metallic ions. Hence corrosion always occurs at anode.
$$M \longrightarrow M^{n+} + ne^{-}$$
  3. **At cathode:** Reduction reaction takes place at anode, so the released electrons from anode are accepted by non metals and forms non –metallic ions such as  $OH^{-}$  &  $O^{2-}$
  4. The metallic & non-metallic ions diffuse towards each other through conducting medium & form corrosion product.

### **Mechanism:-**

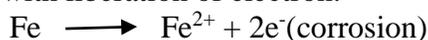
- Electro chemical corrosion involves flow of electrons between anode & cathode.
- The anodic reaction involves dissolution of metal as metal ion with liberation of electrons.



- On the other hand cathodic reactions consume electrons in two ways depending on nature of corroding environment. They are
  - a) Evolution of hydrogen
  - b) Absorption of  $O_2$

**a) Evolution of  $H_2$ :-** This type of corrosion takes place generally in acidic medium.

- For example if Fe metal is in contact with acidic medium, anodic reaction is dissolution of Fe as ferrous with liberation of electron.



- The reduced electrons from anode flow through metal to cathode where  $H^{+}$  ions are reduced to  $H_2$ .



- The overall reaction is  $Fe^{2+} + 2H^{+} \longrightarrow Fe^{2+} + H_2$
- This type of corrosion causes displacement of  $H^{+}$  ions by metal ion.
- All the metals above hydrogen in electro chemical series have a tendency to get dissolved in acidic solution with simultaneously liberation of  $H_2$  gas.

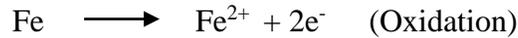
**b) Absorption of  $O_2$ :-**

- When metals are in contact with slightly alkaline or neutral solution (water) with some amount of dissolved O<sub>2</sub>, this type of corrosion takes place.

**Ex: Rusting of iron in neutral aqueous electrolyte solution in presence of atmospheric O<sub>2</sub>.**

- The surface of Fe is usually coated with thin film of FeO . However the oxide film develops cracks , which behave as anodic area & remaining metal part acts a cathode. It shows that anodes are of small area while rest of metallic part forms large area of cathode.

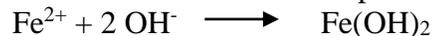
- **At anode:**- Fe dissolves in aqueous solution forms Fe<sup>2+</sup> with release of electrons.



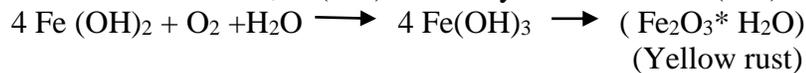
- **At cathode:**- The liberated e<sup>-</sup> flows from anode to cathode through Fe metal , these electrons are accepted by dissolved O<sub>2</sub> to form OH<sup>-</sup> ions.



- The Fe<sup>2+</sup> at anode & 2OH<sup>-</sup> at cathode react to produce Fe(OH)<sub>2</sub> precipitate



- If O<sub>2</sub> is available in excess, Fe(OH)<sub>2</sub> is easily oxidized to Fe(OH)<sub>3</sub>.



- If supply of O<sub>2</sub> is limited the corrosion product may be black anhydrous magnetite Fe<sub>3</sub>O<sub>4</sub>.

**THEORIES OF CORROSION :-**

The following theories explain about tendency & process of corrosion.

1. Direct chemical attack
2. Acid theory
3. Electro chemical theory

**1. Direct chemical attack:-**

- This theory explains about dry or chemical corrosion.
- The corrosion takes place by direct chemical attack.
- The film of a corrosive product normally formed on surface of metal, protects the metal, so further corrosion doesn't take place.

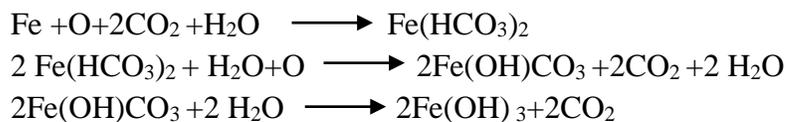


- If corrosion product is soluble, then metal is exposed to further corrosion, then metals are attacked by atmospheric O<sub>2</sub> to produce metal oxide at their respective temperatures.
- The intensity of corrosion depends on the nature of oxide deposit.
- If the formed metal oxide is non- porous, then the metal surface becomes protective and if it is porous, then O<sub>2</sub> diffuses inside the metal & thus further corrosion takes place.

Ex:Al and Cr forms extremely protective oxide layers and hence these metals are normally used for alloy formation with metals that undergo easy corrosion.

**2. Acid theory:--**

- This theory states that presence of acid is essential for corrosion.
- Rusting of Fe is well explained by this theory.
- Fe reacts with O<sub>2</sub>, CO<sub>2</sub> and moisture present in atmosphere and results in formation of a soluble Ferrous carbonate, which is further oxidized to basic ferric carbonate and finally ferric hydroxide is formed.



### 3. Electro chemical theory:-

- This theory explains about electro chemical corrosion.
- The modern electro chemical theory is based on Nernst theory. This states that all metals have tendency to pass into solution when immersed in its own salt solution (Zn – metal – immersed in ZnSO<sub>4</sub> salt). This tendency is called as electrode potential.
- If a metal having higher electrode potential comes in contact with a metal having lower electrode potential, a galvanic cell set up occurs and metal at higher electrode potential becomes anode and goes in to solution.
- If the solution is acidic then, H<sub>2</sub> gas evolves at cathode while anodic metal dissolves in it.
- The greater the difference in potential b/n anode & cathode , the greater will be corrosion and also if the anode area is smaller than cathodic area , then more severe corrosion takes place.

### Galvanic series:-

- Electrochemical series gives useful information regarding chemical reactivity of metals, however this series doesn't give sufficient information about corrosion behavior of metal in a particular set environmental conditions.
- Passivation makes effective electrode potential of some metals more passive and makes them act like cathode and exhibits noble behavior. This behavior is exactly opposite to electro chemical series.
- So a more practical series have been prepared by studying the corrosion of metals and alloys in common electrolyte called sea water using calomel electrode as reference electrode.
- Then the metals electrode potentials are arranged in increasing order towards down. This series is called **galvanic series**.
- A metal present high in series is more anodic & undergoes corrosion faster than metal below.
- This series gives real and useful information about corrosion behavior of metals and alloys in a given environment.
- Galvanic series predicts the tendency of both metals and non- metals in actual environment where as electrochemical series predicts the displacement of metals and non-metals in electrolyte.

<ol style="list-style-type: none"> <li>1. Mg</li> <li>2. Mg alloy</li> <li>3. Zn</li> <li>4. Al</li> <li>5. Al alloy</li> <li>6. Mild steel</li> <li>7. Fe</li> <li>8. High Ni cast iron</li> <li>9. Pb- Sn solder</li> <li>10. Pb</li> <li>11. Sn</li> </ol>	<p>anodic (active) ↑</p>	<ol style="list-style-type: none"> <li>14. Brass</li> <li>15. Monel</li> <li>16. Silver.</li> <li>17. Cu</li> <li>18. Ni</li> <li>19. Stainless steel</li> <li>20. 18-08 Stainless steel</li> <li>21. 18-08 MO steel</li> <li>22. Ag</li> <li>23. Ti</li> <li>24. Graphite</li> </ol>
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12. Inconel.

25. Au

13. Ni – mo – Fe alloy      cathodic (stable/ noble)

26. Pt

- Eg: Zn corrodes faster than Fe & Cu corrodes faster than Ag, Fe corrodes faster than Sn.
- However some exceptions to this generalization are known.

Eg: Ti is less reactive than Ag.

In Zn – Al couple, Zn is less corroded, while Al acts as cathode and is protected.

- These experiments clearly prove that metals like Ti & Al develop strongly adhering oxide layers on their surfaces, thereby making their effective electrode potential more +ve.

### **Galvanic corrosion or Bimetallic corrosion:** -

- When two dissimilar metals are electrically connected & exposed to electrolyte, metal higher in electrochemical series undergoes corrosion. This is called galvanic corrosion.

Eg: Zn –Cu galvanic cell:- Here Zn acts as anode where oxidation takes place , corrosion occurs & Cu act as cathode & is protected.

### **Mechanism:-**

- In acidic solution, corrosion occurs by evolution of H<sub>2</sub>, while in neutral & slightly alkaline solution absorption of O<sub>2</sub> occur.
- The e<sup>-</sup> flow from anodic metal to cathodic metal.

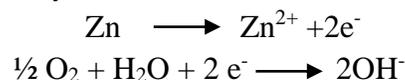


- This means corrosion occurs at anodic metal, while cathodic part is protected from attack  
eg: Steel pipe connected to copper plumbing.

### **Concentration Cell Corrosion / Differential Aeration Corrosion :-**

- This type of corrosion is due to electrochemical attack on 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.
- This occurs when one part of metal is exposed to different air concentration from other part.
- This causes a difference in potentials between differently aerated areas.
- Poorly oxygenated metallic part becomes anodic & undergoes oxidation where as well oxygenated part acts as cathode.
- Eg: When Zn metal is partially immersed in dilute neutral NaCl solution, the part above & closely adjacent to water line are well aerated. Hence become cathodic. On the other hand, part that is immersed to greater depth show a smaller oxygen concentration, thus become anodic. So a difference of potential is created which causes flow of current between two differentially aerated areas of same metal.

Zn can dissolve at anode & releases electrons which are accepted by O<sub>2</sub> at cathodic area to form hydroxyl ions.



**Factors influencing corrosion:-** The intensity and rate of corrosion depends on two types of factors

1. Nature of metal

## 2. Nature of environment

**I.Nature of metal** :- Many factors influence corrosion of metal that depend on its nature. They are--

- i. Position of in galvanic series
- ii. Over voltage
- iii. Relative areas of cathode & anode
- iv. Purity of metal
- v. Physical state of metal
- vi. Nature of surface film.
- vii. Passivity of metal.
- viii. Solubility of corrosion product
- ix. Volatility of corrosion product

1. **Position in galvanic series**:- When two metals or alloys are in contact with conducting medium the more active metal suffers corrosion. The intensity of corrosion depends on difference in their position, the faster will be corrosion of anodic metal /alloy.

2. **Over voltage**:- It is defined as difference of potential b/n practical & theoretical decomposition potentials for same solution.

Eg: Electrolysis of  $H_2SO_4$  with Pt electrode, its practical potential is about 1.70 v where as its theoretical potential is 1.229v. The diff is 0.471v which is over voltage of  $H_2SO_4$ . Reduction in over voltage of corroding metal or alloy accelerate corrosion rate.

3. **Relative areas of anode & cathode**:- Small anodic & large cathodic area causes severe corrosion when two dissimilar metals or alloys are in contact the corrosion of anode part is directly proportional to ratio of areas of cathodic & anodic part.

Eg: A small steel pipe fitted in a large copper tank.

4. **Purity of metal**:- Impurities in metal cause heterogeneity and form tiny electrochemical cells( at exposed parts ) & anodic part gets corroded.

Eg: Zn metal containing impurities Pb / Fe undergoes corrosion due to formation of local electrochemical cells.

- The rate & extent of corrosion increases with increase in exposure and extent of impurities.
- The intensity of corrosion is less when its purity is high.

5. **Physical state of metal**:- The rate of corrosion is influenced by physical state of metal such as grain size, orientation of crystals, stress etc.

- If grain size is smaller, its solubility is more and hence greater will be its corrosion.
- Moreover areas under stress, even in pure metal tend to be anodic and corrosion takes place at these areas.

6. **Nature of surface film**:- In aerated atmosphere practically all metals get covered with a thin surface film of metal oxide.

- The ratio of volume of metal oxide to metal is called specific volume ratio.
- Greater the specific volume ratio (SVR), lesser is oxidation corrosion rate

For eg: The S.V.R of Ni, Cr, W are 1.6,2.0,&3.6 respectively.

The rate of corrosion of tungsten is least even at elevated temperature.

7. **Passivity of metal**:- Passivity is a phenomenon in which metal/ alloy exhibits a much greater corrosion resistance the resulting film is highly protective but very thin & quite invisible film on surface of metal / alloy , which makes it more noble.

- Metal like Ti, Al, Cr ,Mg ,Ni &CO are passive and they exhibit much higher corrosion resistance than expected from their positions in galvanic series. Passivity of metal decrease corrosion rate.

Eg : Corrosion resistance of stainless steel is due to passive character of Cr present in steel.

8. **Solubility of corrosion product**:- In electrochemical corrosion if corrosion product is soluble in corroding medium, then corrosion proceeds at faster rate. If corrosion product is insoluble in medium or it forms another insoluble product which create physical barrier there by corrosion is suppressed.

Eg: corrosion of Pb in  $H_2SO_4$  decreases due to formation of insoluble  $PbSO_4$ .

9. **Volatility of corrosion product**:- If corrosion product has volatile nature , underlined metal is exposed further and causes severe corrosion .

Eg:  $MoO_3$  is volatile.

**II. Nature of the corroding environment**:- The following environmental factors influence intensity of corrosion.

1. Temperature.
2. Humidity of air.
3. Presence of impurities.
4. Presence of suspended particles in atmosphere.
5. Influence of  $p^H$ .
6. Nature of ions.
7. Conductance of conducting medium.
8. Formation of  $O_2$  conc cell.

1. **Temperature**:- With rise in temp. of environment, the reaction rate and also diffusion rate increases there by generally corrosion rate also increasee.

2. **Humidity of air**:- It is the deciding factor in atmospheric corrosion.

- Critical Humidity is defined as relative humidity above which the atmospheric corrosion rate of metal increases sharply.
- The value of critical humidity depends on physical characters of metal & corrosion product.
- In Humid environment the rate of corrosion is higher due to gases & vapors present in atmosphere furnish (give) water to form electrolyte, essential for setting up an electrochemical corrosion cell.
- More over the oxide film on metal surface has a property to absorb the moisture, then corrosion rate enhanced.
- The nature of moisture sources also play important role.

Eg: Rain water apart from supplying moisture for electrochemical attack, may also wash away a good part of oxide film from metal surface (unless the oxide film is exceptionally adherent).

3. **Presence of impurities in atmosphere**:-

- Presence of corrosive gases like SO<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub> etc in atmosphere increases acidity and increase electrical conductivity which causes severe corrosion.
- In marine atmosphere presence of Na & other chlorides leads to increase in conductivity there by corrosion increases.

#### **4. Presence of suspended particles in atmosphere:-**

- The suspended particles in atmosphere may be are of two types.
- **i) Chemically active:-** If suspended particles are active (NaCl , (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) they absorb moisture & act as strong electrolytes , thereby causing enhance corrosion .
- **ii) Chemically in-active:-** If suspended particles are chemically inactive, in nature (charcoal) they absorb both sulphur gas & moisture & slowly enhance corrosion rate.

#### **5. Influence of pH:-**

- Generally acidic media ( pH<7) are more corrosive than alkaline & neutral media.
- The metals are readily attacked by acid, so corrosion of metal can be reduced by increase of pH of attacking environment.  
Eg: Zn rapidly corrodes in weak acidic solution and suffers minimum corrosion at pH-11.

#### **6. Nature of ions present:-**

- Some ions increase corrosion while others decrease it.
- The presence of anions like silicate in medium leads to formation of insoluble reaction products (silica gel), which inhibit further corrosion.
- On other hand Cl<sup>-</sup> ions destroy protective & passive surface film, hence metal surface is exposed for fresh corrosion.
- Presence of NH<sub>4</sub> salts increase corrosion of Fe.
- The presence of even traces of Cu in mine water accelerates corrosion of Fe pipes, used for carrying such water.

#### **7. Conductance of conducting medium:-**

- Conductance of conducting media is important in case of underground & submerged structures.
- Conductance of dry sandy soil is lower than those of mineralized/ clayey soils.
- Stray currents (from power breakages) will cause more damage to metallic structures buried under clay & mineralized soil than those under dry sandy soils.

#### **8. Formation of O<sub>2</sub> concentration cell:-**

- As percentage of O<sub>2</sub> increases, the rate of corrosion also increases due to formation of O<sub>2</sub> conc. Cell.
- The decay of metal occurs at anodic part & cathodic part is protected.  
Anodic reaction for Fe :- Fe  $\xrightarrow{\quad} \text{Fe}^{2+} + 2 \text{e}^{-}$   
Cathodic reaction for Fe:- 2H<sub>2</sub>O + O<sub>2</sub> + 4e<sup>-</sup>  $\rightarrow$  4OH<sup>-</sup>
- Thus formation of concentration cell promotes corrosion, but it occurs where O<sub>2</sub> conc. is lower.

#### **Control of corrosion (protection against corrosion):-**

- There are several disadvantages by corrosion. Hence controlling of corrosion is essential.

- The following methods are used for corrosion control.
  1. Use of inhibitors
  2. Cathodic protection
  3. Application of protective coatings

### **1. Use of inhibitors:-**

- A corrosion inhibitor is a substance which when added in small quantities to aqueous corrosive environment, effectively decreases corrosion of metal.
- Inhibitors are of 2 types.
  1. Anodic inhibitor
  2. Cathodic inhibitor

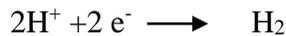
### **1. Anodic inhibitor:-**

- Chromates, phosphates, tungstates or other ions of transition elements with higher oxygen are used as anodic inhibitors.
- They are adsorbed on the metal surface forming protective coating, thereby reducing rate of corrosion forming sparingly soluble compound.
- This type of control is effective, yet may be dangerous if certain areas are left unprotected by depletion of inhibitor.

### **2. Cathodic inhibitors:-**

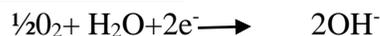
- Eg: Organic inhibitors (like amines, mercaptanes, heterocyclic nitrogenous compounds, substituted urea and thiourea, heavy metal soaps).

**In acidic environment** the corrosion reaction takes place with evolution of H<sub>2</sub>.



- Corrosion may be reduced by
  - i. Slowing down diffusion of hydrated H<sup>+</sup> ions to cathode.
  - ii. By increasing over voltage of hydrogen evolution.
- The diffusion of H<sup>+</sup> is decreased by addition of organic inhibitors.
- Sn and Arsenic oxides act as inhibitors because they deposit adherent film of metallic arsenic or antimony at cathodic areas, thereby increasing H<sub>2</sub> over voltage.

**In neutral & aqueous medium** the cathodic reaction is



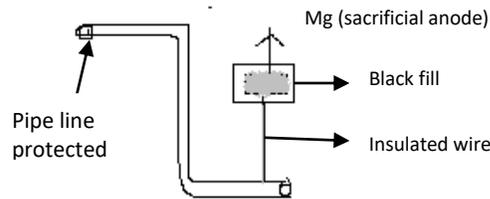
- The corrosion can be controlled by eliminating O<sub>2</sub> from conducting medium or retarding its diffusion to cathodic area.
- The former is attained by addition of Na<sub>2</sub>SO<sub>3</sub> or by de-aeration.
- Later is carried out by Mg, Zn or Ni salts which react with OH<sup>-</sup> ions (at cathode) forming corresponding insoluble hydroxides which are deposited on cathode forming more or less impermeable self barriers.

### **2. Cathodic protection:-**

- In this method of protection, a metal that acts as anode is forced to behave like cathode there by its corrosion doesn't occur.
- This is done by two methods
  1. Sacrificial anodic protection
  2. Impressed current cathodic protection

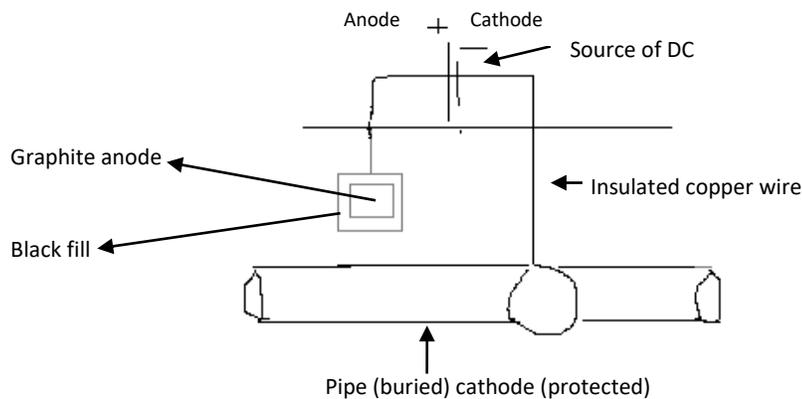
### **1. Sacrificial anodic protection: -**

- In this method of protection, metallic structure to be protected is called base metal.
- Using more active metal called sacrificial anode, base metal is protected by connecting it to sacrificial anode through a wire.
- Hence all corrosion is concentrated at sacrificial anode while base metal is protected.
- Corroded sacrificial anode block is replaced by fresh one.
- The commonly used anodic metals are Mg, Zn, Al and their alloys. Zn is used as sacrificial anode in good electrolytes as sea water. Mg is used in high resistive electrolytes due to its more –ve potential & it can provide highest current output.



## **2. Impressed current cathode protection :-**

- In this method all impressed current is applied in opposite direction to corrosion current to nullify & convert corroding metal from anode to cathode.
- Once the metal becomes cathode it is protected from corrosion.
- The impressed current is taken from battery or rectified AC line.
- The anode may be either an inert material or insoluble material such as graphite, Pt, stainless steel, high silica iron, scrap Fe etc.
- Usually sufficient DC current is passed on to insoluble anode kept in back fill composed of coke /gypsum. So as to increase electrical contact with surrounding soil.
- This protection technique is mainly used to buried structures like water tanks, water pipelines, transmission line towers, marine pipes , laid up ships etc.

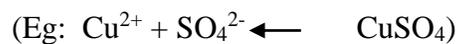


## **3. Application of protective coatings:-**

- Coating of coat metal on base metal to protect from corrosion is said to be protective coating method.
- It is oldest, traditional & best method to prevent corrosion.
- The most important coating methods are electroplating & electro-less plating.

## Electroplating:-

- It is a technique by which deposition of coat metal is done on base metal by passing direct current through electrolyte solution which contains soluble salt of coat metal.
- If base metal is having impurities like oils or greases, it should be cleaned with organic solvents like tetrachloride ethylene and if it contains surface scales, oxides are removed by applying HCl (Ni or Cu plating ) or H<sub>2</sub>SO<sub>4</sub>.
- The cleaned metal is used as cathode and anode is either an inert material of good electrical conductivity or coating metal itself.
- Electrolyte is soluble salt of coat metal.
- The anode and cathode are dipped in electrolytic solution kept in an electroplating cell or bath.
- When direct current passed through coating metal ion migrate towards cathode and deposit as thin adherent film on base metal.



**Electroplating of Ni :-** Ni plating gives hard, adherent and good wear resistant surface to base metal. After Ni plating article is finely coated with Cr.

### **Requirements: -**

Electrolyte bath: NiSO<sub>4</sub>(20 gm/L) , NiCl (450 gm/L) & boric acid (30 gm/L)

pH: 4.0 by Boric acid buffer

Operating temp: 40-70<sup>0</sup>C

Current density: 20-30 m A/cm<sup>2</sup>

Additive agent: Saccharin / Coumarin derivatives

Cathode: Metal

### **Electro-less plating / immersed plating / displacement plating :-**

- This is also widely used technique to protect base metal from corrosion.
- It is a technique in which deposition of coat metal on base metal is done by employing reducing substances (HCHO / Sodium Hypophosphate) in place of electric current.
- In this method, the base metal to be coated is immersed in noble metal salt solution used for plating.
- The noble metal ion is displaced from its salt solution by base metal ion and forms thin uniform deposit on base metal.

### **Eg: Electro-less plating of Ni :-**

- The base metal is immersed in bath containing Sodium hypophosphate & NiSO<sub>4</sub> at pH 4.5 - 5.0 and temperature is maintained at about 100<sup>0</sup> C.
- The Sodium hypophosphate reduces Ni<sup>+2</sup> ions to Ni metal and finally converts into Ni phosphate.

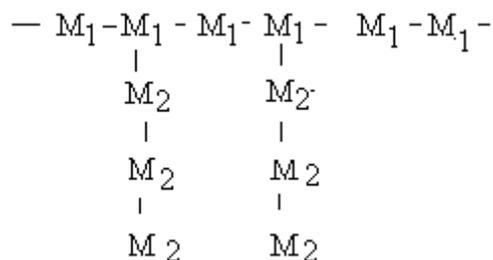
- The alloy of Ni & Ni phosphate deposited on base metal surface forms a strong adherent, non-porous coating with higher corrosion resistance.

# UNIT-III



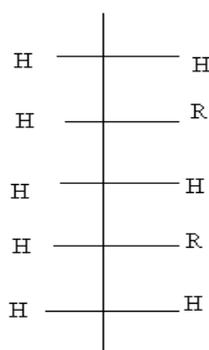


**e) Graft co-polymers:** These polymers are branched structures in which the monomer units on the branches and backbone differ.

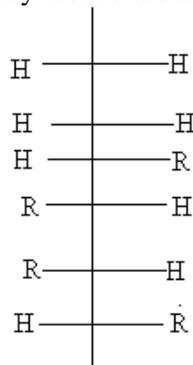


**3) Tacticity:** The orientation of functional groups in polymer is called as configuration. The difference in configuration of polymers because of the difference in arrangement of functional groups around main chain is called as Tacticity. Based on tacticity, polymers are of three types.

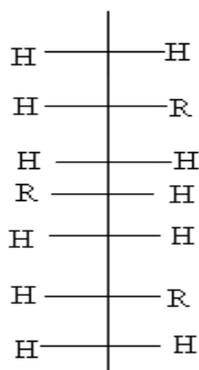
**a) Isotactic:** If all the functional groups are arranged on the same side of the chain, the polymer is called Isotactic polymer.



**b) Atactic:** If all the functional are arranged randomly around the main chain, the polymer is called Atactic polymer.



**c) Syndiotactic:** If all the functional groups are arranged alternately with respect to the main chain, the polymer is called syndiotactic polymer.



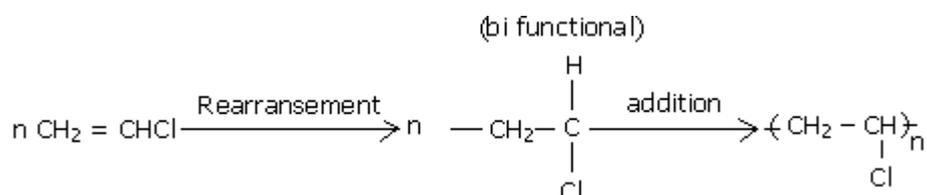
## Polymerization:

### 1) Addition Polymerization:

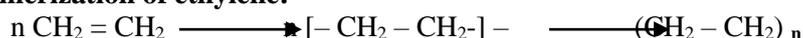
- This polymerization takes place between monomers that are bifunctional and contains double bonds in its structure.
- This can be defined as binding of several bifunctional monomers to form polymers without elimination of by products by addition reactions.
- This polymerization results in the formation of linear polymers.
- The produced polymer has same chemical composition as that of monomers.
- The molecular weight of polymer is an integral multiple of the monomer.

#### **Examples:**

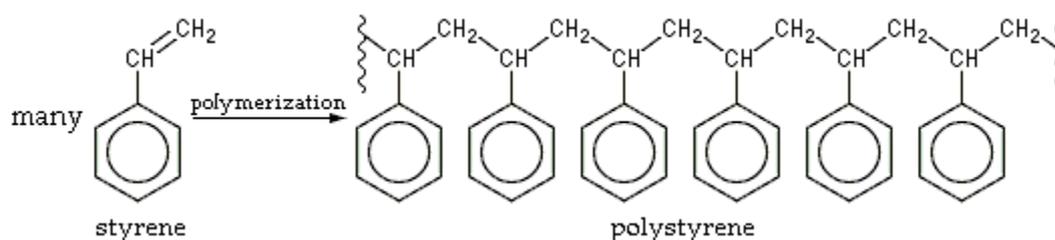
##### **1. Formation of PVC:**



##### **2. Polymerization of ethylene:**



##### **3. Polymerization of Styrene:**

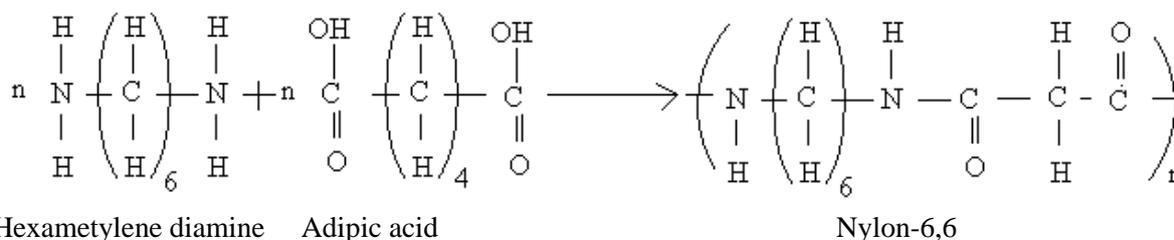


### 2) Condensation Polymerization:

- This is also called Step-wise polymerization.
- This occurs between monomers that contain polar side groups.
- A reaction occurring between the same (or) different polar groups containing monomers with elimination of small molecules like ammonia, water, HCl etc..... and forms linear (or) Cross - linked polymers is called condensation polymerization.
- The molecular weight of polymer is not an integral multiple of the mol-wt of monomer.
- The chemical composition of monomer and polymer are different.
- It results in the formation of linear or cross linked polymers.

#### **Example:**

1. **Formation of Nylon-6,6:** Formed by the condensation of Hexamethylenediamine with adipic acid (Tetra methylene dicanboxylic acid)

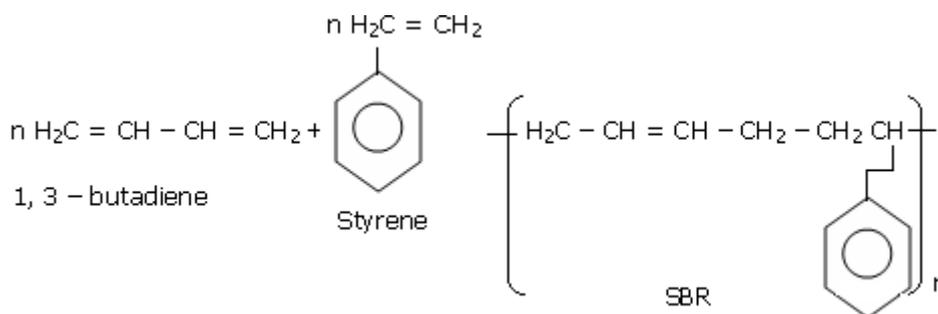


2. **Formation of Polyester:** Formed by the condensation between ethylene glycol and Terephthalic acid  
 $\text{OH-CH}_2\text{-CH}_2\text{-OH} + \text{COOH-C}_6\text{H}_4\text{-COOH} \longrightarrow \left( \text{---O-CH}_2\text{-CH}_2\text{-CO-C}_6\text{H}_4\text{-CO---} \right)_n$   
Ethylene glycol      Terephthalic acid      Polyester

### 3) Co-polymerization:

- When two (or) more different types of monomers undergo simultaneous polymerization then it is called Co-Polymerization.
- The properties of co-polymer are different from those of individual monomers.
- The copolymers may be alternating, random, block and graft polymers.

#### **Ex: Styrene butadiene rubber (SBR)**



### Plastics:

- An organic substance with high molecular weight, which can be moulded in to any desired form when subjected to heat (or) pressure in the presence of catalyst is called as plastic.
- The term plastic must be differentiated from resins.
- Resins are basic binding materials, which form a major part of the plastic and which actually undergo polymerization and condensation reactions during their preparations
- However, the term resin and plastic are considered as synonyms.

### Advantages:

Now a days, plastics play an important role in daily life because of their certain unique properties.

- Light in weight
- Transparent
- Low maintenance cost
- Chemically inert
- Corrosion resistance
- Insect resistance
- Easy transportability
- Easy workability
- Impermeable to water
- High resistance to abrasion

### Disadvantages:

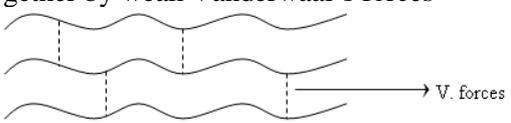
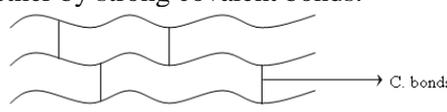
- Low heat resistance, so combustible
- High softness
- Poor ductility
- Major pollutant not degraded by soil

### Uses:

- For Making many house hold articles
- For making furniture
- For making electric goods

**Types of Plastics:** Plastics are classified in to two types

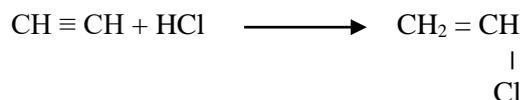
- Thermo plastics
- Thermo setting plastics.

THERMOPLASTICS	THERMO SETTING PLASTICS
<ul style="list-style-type: none"> <li>• They are formed by addition reactions. (some times formed by condensation r/n)</li> <li>• They become softened on heating &amp; hardened on cooling</li> <li>• They are soft, weak and less – brittle.</li> <li>• Adjacent polymer chains are held together by weak Vanderwaal’s forces</li> </ul>  <ul style="list-style-type: none"> <li>• They have either linear (or) branched structures</li> <li>• The chemical nature is not altered during heating &amp; cooling.</li> <li>• They can be remoulded, reshaped &amp; reused so they can be reclaimed from waste.</li> <li>• Low molecular weight thermoplastics are soluble in suitable organic solvents</li> </ul> <p><b>Ex:</b> PE, PVS, PS, Nylon Teflon etc...</p>	<ul style="list-style-type: none"> <li>• Formed by condensation reactions.</li> <li>• They become soft on initial heating and hard on cooling. On reheating they become more hard.</li> <li>• They are hard, strong and more – brittle.</li> <li>• Adjacent polymer chains are held together by strong covalent bonds.</li> </ul>  <ul style="list-style-type: none"> <li>• Due to strong bonds, they exhibit cross-linked 3D-structure.</li> <li>• Chemical changes takes place during moulding process.</li> <li>• They cannot be remoulded and reused so they cannot be reclaimed from the waste.</li> <li>• Due to strong bonds and cross links, they are not soluble in almost all organic solvents.</li> </ul> <p><b>Ex:</b> Bakelite, amino resins, poly ester resins, poly orethones epoxy resins etc.....</p>

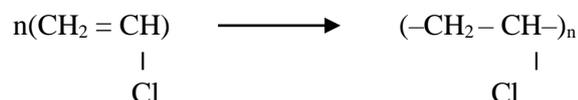
**Important plastics:** Polythene, PVC, Polystyrene, Teflon, Nylon, Bakelite

### 1. Poly Vinyl Chloride (PVC):

**Preparation:** Vinyl chloride is used as monomer for the manufacture of polyvinyl chloride. Vinyl chloride is prepared by reacting acetylene with hydrogen chloride at 100-150°C in the presence of metal salt catalyst.



PVC is prepared by heating a water- emulsion of vinyl chloride in presence of Benzoyl Peroxide in a autoclave under pressure.



#### Properties:

- PVC is colorless and odorless Powder.
- It is non-inflammable and chemically inert.
- It is soluble in chlorinated hydrocarbons like ethyl chloride, etc. and ketones.
- It has high resistance to light, inorganic acids, alkalis, and atmospheric oxygen.

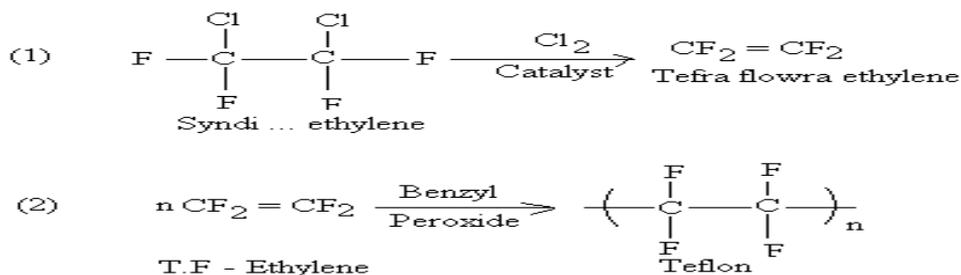
#### Uses:

- Plasticized PVC is used for making table cloths, rain coats, coatings for electric wire and cables, toilet articles, radio, T.V components, pipes, coupling valves, etc.
- Un-plasticized PVC or rigid PVC is used for making refrigerator components, cycle and motor cycle mudguards, tubes, pipes, etc.

## 2. Teflon: (Fluon / Poly Tetra Fluoro Ethylene): (-CF<sub>2</sub> - CF<sub>2</sub>-)<sub>n</sub>

Teflon is obtained by the polymerization of water emulsion of Tetra fluoro ethylene in the presence of benzoyl peroxide as catalyst. The monomer Tetra fluoro ethylene is obtained by de-chlorination of syn-dichloro tetra fluoro ethane in presence of catalyst.

### Preparation:



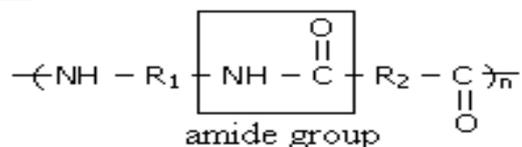
### Properties:

- It is a thermo plastic resin.
- Having high melting point – 330°C
- High density – 2.1 to 2.3 gm / CC
- Highly resin – 93 to 98%
- High chemical resistance
- Good electrical and mechanical properties
- Not soluble in any solvent

### Applications:

- For insulation of motors, generators, capacitors, transformers etc.....
- Used in making stop cocks for burettes, non-lubricating bearings, gaskets, pump parts etc.....
- Used for coating on articles like bakery trays, frying pans etc.....

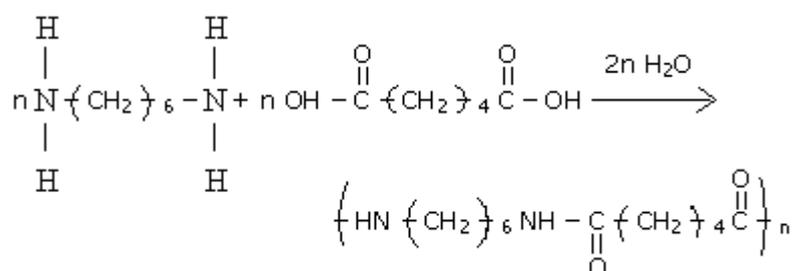
## 3. Nylon: (Poly Amid Resin)



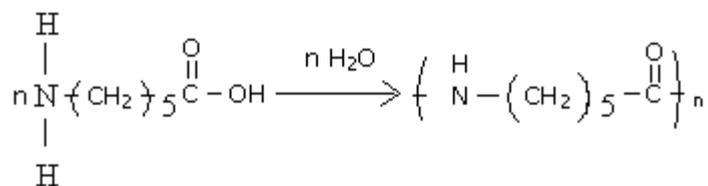
Nylon is a poly amide resin consists of amide group produced by condensation polymerization of diamine with di-acid. The Nylon has been named on the basis of the number of carbon atoms in the monomer chain.

Ex: Nylon 6:6, Nylon 6:10, Nylon 6, Nylon 11 etc..... where the first number indicates that the number of carbon atoms in diamine and the second number indicates that number of carbon atoms in diacid.

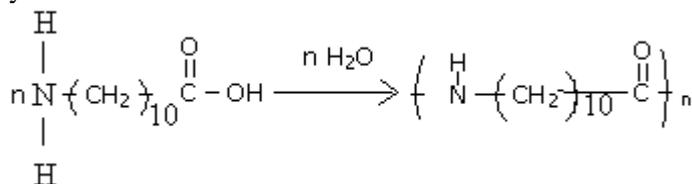
a) **Nylon 6:6:** Nylon 6:6 is produced by the condensation polymerization of hexa methylene di-amine with adipic acid.



b) **Nylon 6:** It is produced by the self condensation of α-amino caproic acid (α – amino hexanoic acid).



c) **Nylon 11:** It is made by self – condensation of w – amino uni decanoic acid.



### Properties:

- It show plastic and fibre property
- Insoluble in common solvent and soluble in pharomic acid and phenol
- Posses high strength and high melting point (160 – 264<sup>0</sup>C)
- They absorb little moisture
- Possess resistance to environmental conditions and chemicals.
- They are good electrical insulators.

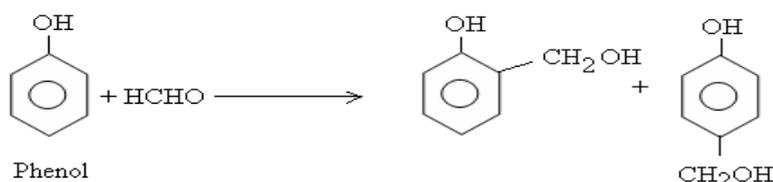
### Applications:

- Nylon 6:6 is used as fiber for making socks, dresses, lady’s hoses, carpets, under garments etc..... (i.e., Used in textile industry)
- Nylon 6 and Nylon 11 are mainly used for moulding purposes of gears and bearings etc.....
- They are also used for making filaments, films, Tire cords, bristles for tooth brushes etc.....

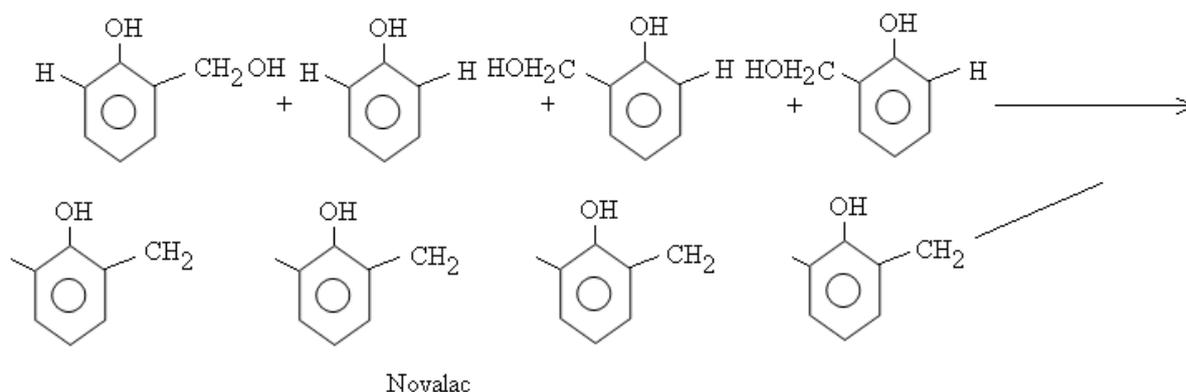
### BAKELITE: (Phenol formaldehyde resin / phenolic resin / phenoplasts)

- Bakelite is a important thermosetting resin named after the scientist Bakeland, who synthesized this resin in they year 1909.
- It is prepared by the step polymerization of phenol with formaldehyde in presence of an acid (or) Alkali as a catalyst.
- This polymerization takes place in three steps:

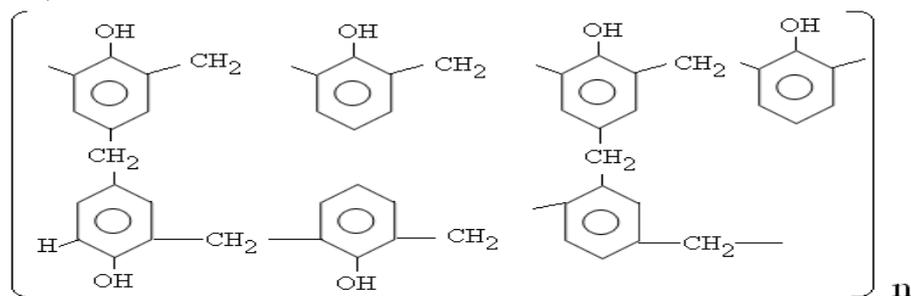
**Step I:** Phenol can condense with formaldehyde to produce O – hydroxy methyl phenol and P – hydroxy methyl phenol



**Step II:** condensation takes place between O – hydroxy methyl phenol and phenol to give linear polymer called Novalac



**Step III:** During molding, Hexa methylene tetraamine ((CH<sub>2</sub>)<sub>6</sub> N<sub>4</sub>) is added, it produces formaldehyde and ammonia. Formaldehyde converts the soluble and fusible Novalac in to a hard infusible and insoluble solid of cross – linked structure called Bakelite, whereas NH<sub>3</sub> neutralizes the acid.



### Properties:

- \* Bakelites are rigid, hard, scratch resistant, infusible, water resistant, solid substance.
- \* Resistant to acids, salts and most organic solvents but attacked by alkali due to the presence of hydroxyl groups.
- \* Good electrical insulator

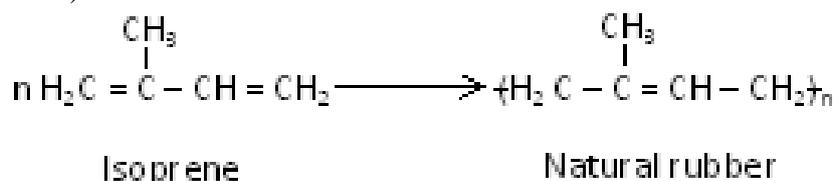
### Applications:

- \* For making electric insulator parts like switches, plugs, holders, switch boards, heater etc.....
- \* For making moulded article like telephone parts, cabinets for radio and T.V.
- \* Used in paints and varnishes
- \* as adhesives for grinding and wheels.
- \* In the product of ion exchange resin
- \* For making bearings used in propeller shops, for paper industry and Rolling mills.

### RUBBER (ELASTOMERS):

- The polymers which possess the property of elasticity are called as rubber.
- Rubbers are high polymers, which have elastic properties in excess of 300%.
- The molecular weight of raw rubber is about 1,00,000 to 1,50,000 Daltons.
- Most of the Indian production comes from kerala state.

**Natural rubber:** It is a high polymer of polyisoprene, which are arranged in Cis – Configuration (functional groups are arranged on the same side).



Natural rubber is mainly produced from the milk of the rubber tree “*Havea brasiliensis*”.

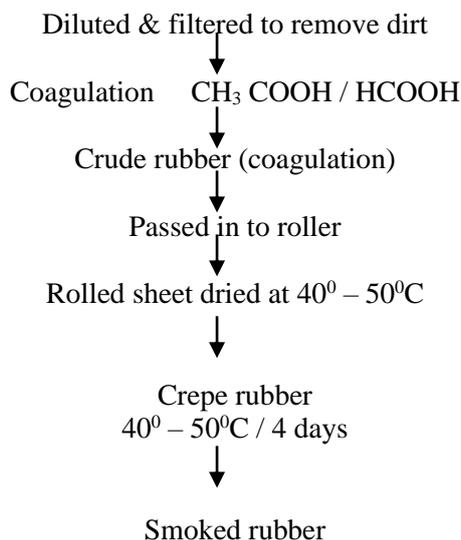
Small quantities of natural rubber is also produced from the milk of a shrub known as “guayule”.

### Processing of natural rubber:

- The milk of rubber tree is called latex.
- It is a colloidal emulsion consists a 25 – 45% of rubber and the reminder are protein and resinous materials
- The Latex was collected by cutting the bark of rubber trees.
- There after the Latex is diluted with water and filtered to eliminate dirt present in it. The Latex then coagulates by the addition of acetic acid (or) formic acid.
- The coagulated rubber is called as crude rubber. It is then made (or) rolled out in to sheets.
- The rubber sheets are dried under sunlight or mild heat and then subjected to further processing of rubber.

**a) Crepe rubber:** To the crude rubber, a small amount of sodium bi-sulphite is added to bleach the colour and passed into rollers which produce one mm or more thickness sheets which are dried in air about 40 to 50<sup>0</sup>C. The dried thin sheet of rubber are known as crepe rubber.

**b) Smoked rubber:** The crepe rubber sheets are placed inside smoke rooms maintaining a temperature 40 to 50°C for 4 days. The dried rubber sheets are called smoked rubber, which are sent to rubber factories for further processing.  
Milk of rubber latex



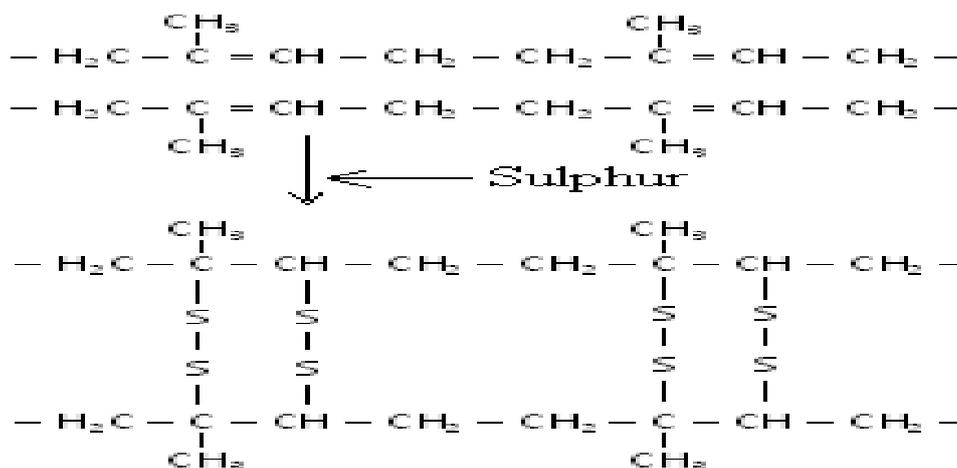
**Draw backs of crude rubber (or) raw rubber:** Crude rubber has following drawbacks.

1. Soft at high temperature and brittle at low temp.
2. It shows large water capacity
3. Shows little durability
4. Shows high elasticity
5. Attacks easily by oxidizing agents
6. Swells in organic solvents
7. Possess tackiness
8. Show low tensile strength.

The draw backs can be crude are rectified by the process of vulcanization.

### Vulcanization:

- This was discovered by “Charles Good year” in 1839.
- The process of addition of sulphur at 110-140°C to natural rubber to improve its properties is called as “Vulcanization”.
- The added sulphur combines at the double bonds of rubber chains and cross – links of the linear polymer chains, resulting in a three dimensional network structure.
- Thus the rubber loses plastic state and acquires elastic state.
- The stiffness of vulcanized rubber depends on the amount of the sulphur added.
- A flexible tyre rubber contains about 3 – 5% if sulphur whereas hard rubber contains 32% of sulphur.



### **Advantages of Vulcanization:**

Vulcanization process brings excellent changes in the properties of rubber.

A Vulcanized rubber has

- (i) Low water absorption tendency
- (ii) Higher resistance to oxidation
- (iii) High stiffness
- (iv) Slight tackiness
- (v) Good durability
- (vi) Good resistant to changing temperature
- (vii) Resistance to swelling in organic solvents etc.....

### **Compounding of rubber:**

Compounding is a process by which mixing of raw rubber with d/f substances to impart special properties to an application. The following substances are mixed with raw rubber.

**(i) Plasticizers and softners:** They give greater plasticity and flexibility and to reduce the brittleness of the products

Ex: Waxes, Stearic acid and Vegetable oils.

**(ii) Vulcanizers:** When rubber is heated with sulphur, its tensile strength, elasticity and resistance to swelling are increased. The remaining Vulcanizing agents are hydrogen peroxide ( $H_2O_2$ ), Sulphur mono – Chloride ( $S_2Cl_2$ ), Benzyl chloride, Benzyl peroxide etc...

**(iii) Anti – Oxidants:** Natural rubber has tendency for Oxidation. This Oxidation is prevented by added Anti-Oxidants like phenyl naphthyl amine and phosphates.

**(iv) Accelerators:** These shortened the time required for Vulcanization and give toughness to rubber.

Ex: z – mercaptanol and Benzothisol.

**(V) Fillers:** They give rigidity and strength to the rubber

Ex: Carbon black, Zinc oxide and  $CaCO_3$

**(vi) Coloring substances:** These substances provides pleasing colour to the rubber product.

Ex:

Titanium Oxide – White

Ferric Oxide – Red

Lead Chromate – Yellow

Antimony Oxide – Crimson

Chromic Oxide – Green

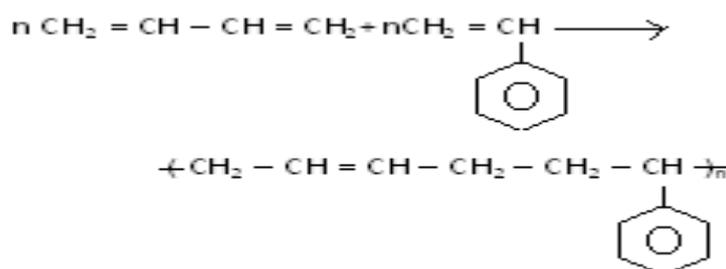
### **SYNTHETIC RUBBER: (ELASTOMERS):**

The following rubbers are considered as synthetic rubbers.

1. Buna – S - Rubber
2. Buna – N – Rubber
3. Polyurethane rubber
4. Silicone rubber

#### **1. Buna – S / Styrene / GR – S rubber:**

**Preparation:** It is prepared by copolymerization of 1, 3 – butadiene and styrene.



**Properties:**

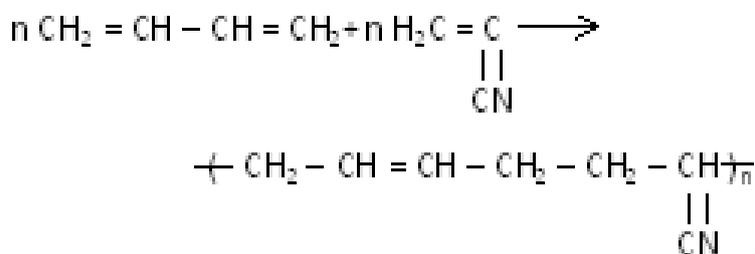
- It has high abrasion resistance and high load bearing capacity
- Easily oxidized in presence of ozone
- It swells in oils and organic solvents
- Its Vulcanization process is similar to natural rubber.

**Applications / Uses:**

- It is mainly used for manufacture of tyres.
- It is also used for floor tiles, shoe soles, gaskets, wire and cable insulations, Tank linings etc.....

**2. Buna – N / Nitrile rubber: / GR – A rubber:**

It is formed by copolymerization of 1, 3 butadiene and Acrylonitrile.

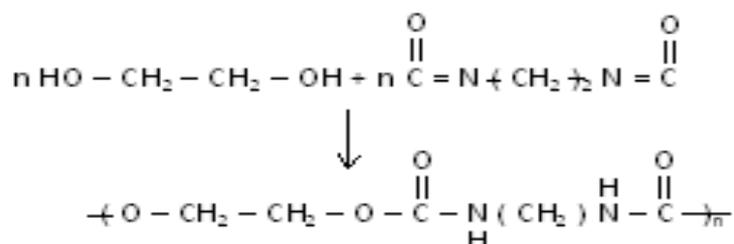
**Properties:**

- It can be vulcanized in same way as natural rubber.
- It has good oil resistance, heat resistance and abrasion resistance
- It is attacked by alkalis, due to presence of cyano groups.

**Uses:** making aircraft components, conveyor belts, tank linings, gaskets, hoses, printing rollers, automobile parts etc.

**3. Polyurethane / Isocyanate rubber:**

**Preparation:** It is obtained by polymerization of poly alcohol (ethylene glycol) with ethylene diisocyanide.

**Properties:**

- They are highly resistant to organic solvents – but are attacked by acids and alkalis
- They show good resistance to oxidation because of their saturation (single bond) character.
- Their foams are light, tough and resistant to heat, chemicals, weathering and abrasion

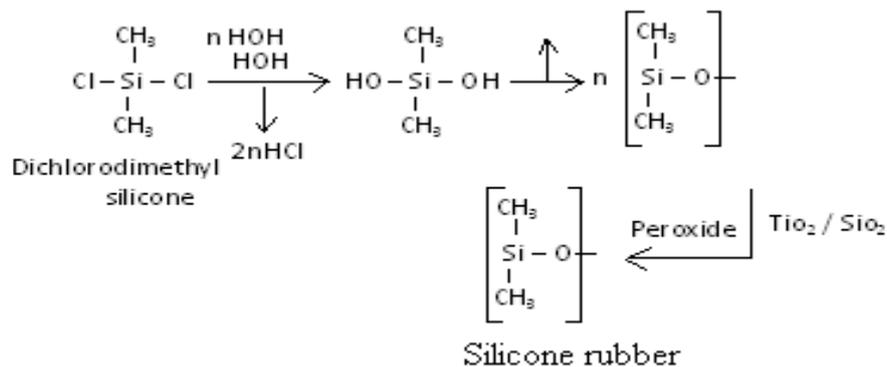
**Uses:**

- They are used for surface coatings, manufacture of foams and spandex fibers.

**4. Silicone rubber:**

**Preparation:** It is formed by the polymerization of dihydroxy dimethyl silicon, which is formed by dichlorodimethyl silicon. This step requires water molecules and HCl elimination takes place.

Dihydroxy dimethyl silicon forms an unstable silicon rubber by dehydration which yields silicon rubber in the presence of peroxide and inorganic fillers like  $\text{TiO}_2$ ,  $\text{SiO}_2$  etc. by the polymerization.



**Properties:**

- It has good resistant to Oils, dilute acids, alkalis and sunlight.
- It retains rubber properties at elevated temperatures.
- It is also resistant to air and ozone at high temperature.

**Uses:**

- It is mainly used in making lubricants, paints etc .....
- For making artificial heart valves, transfusion tubings, for special boots to be used at low temperature.

# Fuel Technology

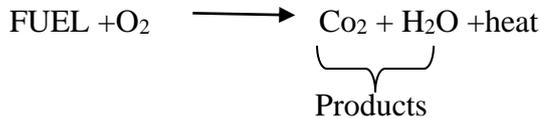
## Introduction:

With rapid growth in world population, the energy requirements have also increased. Heat energy is one of the main sources of power that is produced by burning of fuels.

**Definition:** A fuel is a combustible substance, which on proper burning gives large amount of heat that can be used economically for domestic & industrial purposes. The main elements of any fuel are C&H.

Eg: wood, petroleum, petrol, charcoal, coal, kerosene, producer gas, oil gas, natural gas, water gas.

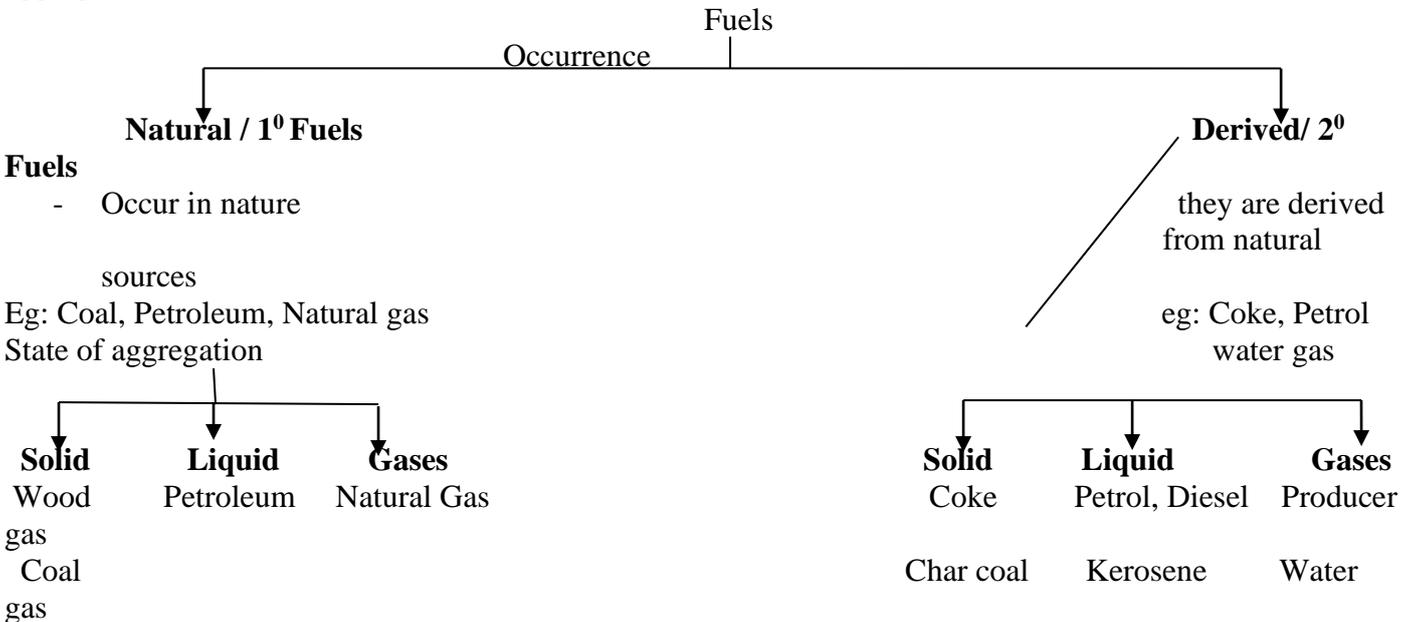
- During the process of combustion of a fuel, these elements combine with O<sub>2</sub> to produce CO<sub>2</sub> & H<sub>2</sub>O with the liberation of heat.



- The stored fuels available in earth's crust are called fossil fuels.

## Classification of FUEL:-

Fuels are classified into following types based on their occurrence, & state of aggregation.



**Characteristics of good fuel:** - A good fuel should possess the following properties for its selection for a particular purpose. .

1. High calorific value:- The total amount of heat liberated when unit quantity fuel is completely burnt is called as calorific value. A good fuel should possess high calorific value.
2. Low moisture content: A good fuel should contain low moisture content. Moisture present in the fuel reduces the heating value.
3. Moderate velocity of combustion - If the rate of combustion is low, regaining of high temp is not possible and if the rate of combustion is too high control of combustion becomes difficult.
4. Combustion products should not be harmful: - The combustion products should not pollute the atmosphere so it should not produce undesirable products or objectionable gases.
5. Low cost: - It should be cheap & readily available.

6. Easy to transport: - it must be easy to handle, store & transport at a low cost. Solid & liquid fuels can easily be transported from one place to another where as transportation of gaseous fuels is costly & can even cause fire hazards.
7. Combustion should be easily controllable: - Combustion of the fuel should be easy to start of stop when required.
8. Moderate ignition temp:-Ignition temp is the lowest temp to which the fuel must be preheated so that it starts burning smoothly. Lowest ignition temp is dangerous to store & transport of fuel since it can cause fire hazards and highest ignition Temp cause difficulty in igniting the fuel.

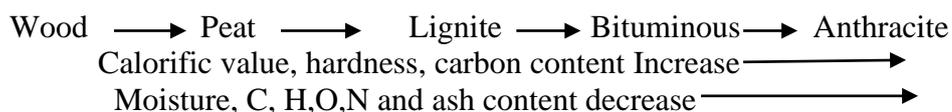
## SOLID FUELS:-

- Advantages: -
1. Easy to transport.
  2. They are convenient to store without any risk.
  3. They posses moderate ignition temp.
  4. Their cost of production is less.

- Disadvantages: -
- 1.They contains high ash content.
  2. Excess of dir is required for complete combustion.
  3. Calorific value is less compared to liquid or gaseous fuels.
  4. Can not be used as fuel internal combustion engine fuels.
  5. Combustion operation cannot be controlled easily.

Coal :- Coal is a solid fuel & lightly carbonaceous matter , which is formed from the remains of deceasing regrettable matter under the influence of heat , presence & bacterial action under health of the earth. It is composed of C,H,O,N,&S atoms besides some non- combustible in organic matter.

Classification of coal: - Various forms of coal are replenished on the basis of rank or degree of alteration or coalification from parent material wood.



Metallurgical coke :- Coke is prepared from coal by the process called carbonization. When Bituminous coal is heated strongly in the absence of air, a dense, strong and porous mass obtained called **metallurgical coke**.

Bituminous coal absence of air → coke

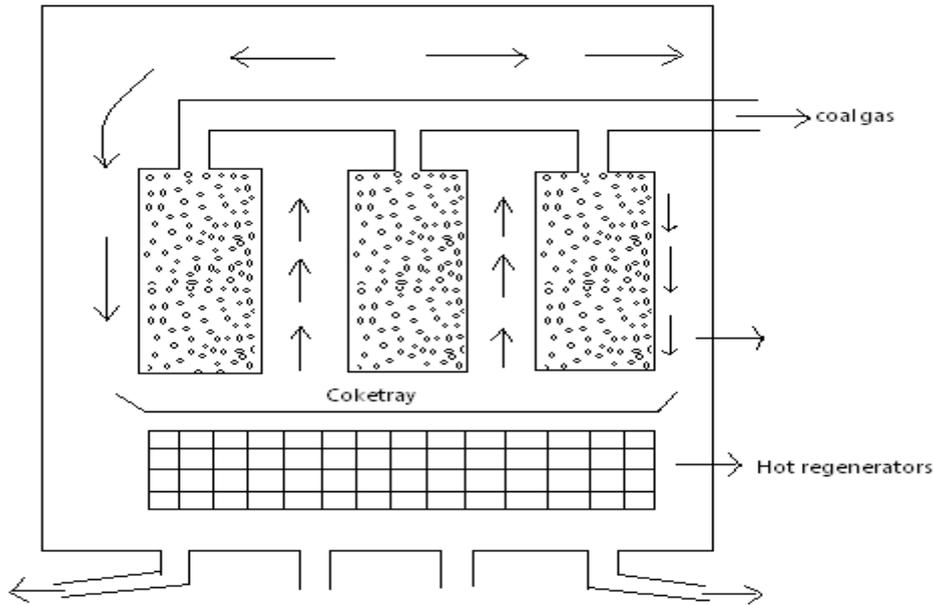
Good coke for metallurgy should have the following characteristics:-

1. Purity :- it should contain low % of moisture ,ash ,P&s  
 % of S&P moisture - heating expenses  
 Excess of ash - forms slag's  
 Excess of S&P - forms SO<sub>2</sub>,P<sub>2</sub>O<sub>3</sub>,P<sub>2</sub>O<sub>5</sub> - affect greality of metal being produced.  
 Exceed of S - makes coke brittle
2. Porosity:- It should be porous ,so that O<sub>2</sub> come in contact with the carbon of coke , there by complete combustion takes place.
3. Strength: - It should quite compact, hard strong to with stand over – burden ( ore +fuel + flux )in the Furnace.
4. Size: - It should have moderate size. i.e neither too big in size nor too small in size .  
 In case the size is too big, heating is never maintained.
5. Cost: - It should cheap & easily available.
6. Combustibility:- It should burn easily .this property mainly depends on the nature of coal, carbonization temp & reaction temp.

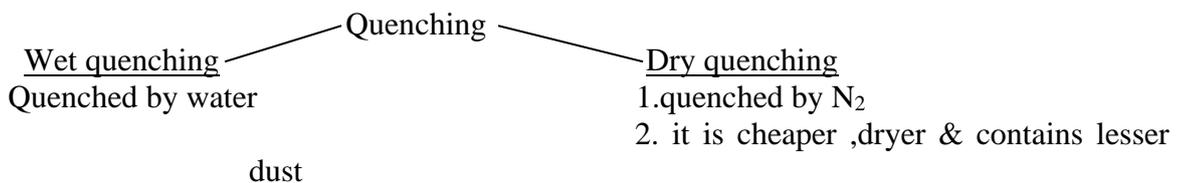
- 7. Calorific value :- It should be high .
- 8. Reactivity to steam:- The reactivity of coke should not be very high .

**Manufacture of metallurgical coke by Otto- Hoffmann By Product Recovery oven process :-**

- To increase the thermal efficiency of carbonization process & to recover the valuable by products, **Otto and Hoffmann developed a modern by-product coke oven.**



- The by-product recovery oven consists of a number of narrow silica chambers
- Each chamber is provided with a charging hole at the top, a gas off take & a refractory linked cast iron door at the base for discharging coke.
- Finely crushed coal is introduced through the charging hole at the top of chambers and they are made air tight.
- The coke oven is heated to 1200<sup>0</sup> C by burning a gaseous fuel producer gas.
- During combustion the flue gases produced ,which are passed to the regenerators having checkers brick- work ,which helps in the utilization of the heat of the flue gases so, regenerators gets heated to about 1000<sup>0</sup>C.
- The flow of heating gases is then reversed so that the hot flue gases preheat the chambers.
- The heating is continued till the evolution of volatile matter stops completely.
- The complete process takes about 11- 18 hrs.
- When carbonization is completed, a massive ram (coke pusher ) pushes the red hot coke outside, then it is subjected to quenching(sudden cooling )



**Recovery of by products :-**

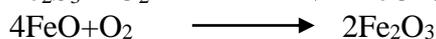
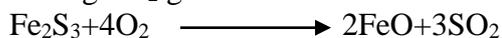
- The gas coming out from the oven is called as coke oven gas, which is composed of NH<sub>3</sub>,H<sub>2</sub>S , naphthalene, tar, benzene etc.
- 1. Recovery of tar: - The coke oven gas is passed through a tower where liquor ammonia is sprayed from the top. Dust and Tar gets collected in a tank which is heated by steam coils to recover back NH<sub>3</sub> sprayed. Hence NH<sub>3</sub> is recovered as NH<sub>4</sub> OH.
- 2. Ammonia: The gas is then passed through a tower where water is sprayed. Ammonia goes in to solution forming ammonium hydroxide.



3. Recovery of naphthalene: - The gas is then passed to a cooling tower where water is sprayed at a very temp. Condensation of some gases takes place & naphthalene is recovered.
4. Recovery of benzene: - The gas is then sprayed with petroleum. Benzene & its homologous are recovered.
5. Removal of H<sub>2</sub>S :- the gas is passed through a purities C-fennec oxide.



After some time when all Fe<sub>2</sub>O<sub>3</sub> is changed in to Fe<sub>3</sub>S<sub>3</sub>, then the purifier is exposed to air then Fe<sub>2</sub>O<sub>3</sub> is regenerated leaving SO<sub>2</sub> gas.



## Liquid fuels:

### Advantages:-

1. Liquid fuels are clean & require less amount of air for complete combustion.
2. They posses higher calorific value than solid fuels.
3. They are easy to transport through pipes.
4. They are used as internal engine fuels.
5. They burn without forming dust, ash etc.
6. Easily ignited and emission can be easily controlled.
7. Requires less amount of air for complete combustion.

### Disadvantages:-

1. Care must be taking during storage.
2. Cost is relatively higher than solid fuels.
3. They give bad odour.
4. Greater risk of fire hazards.

## Petroleum:-

- It is also called as crude oil or mineral oil.
- The name '**petroleum**' has been derived from Latin. In latin **Petra** means Rock and **Oleum** means Oil.
- It is available from earth's crust and it is dark greenish brown, viscous oil.
- It is the basic for all types of liquid fuels.
- It is mainly composed of various hydro carbons such as paraffin's, olefins (alkenes), naphthalene's & small amounts of inorganic compounds such as O, N, S.
- The average composition of petroleum:-

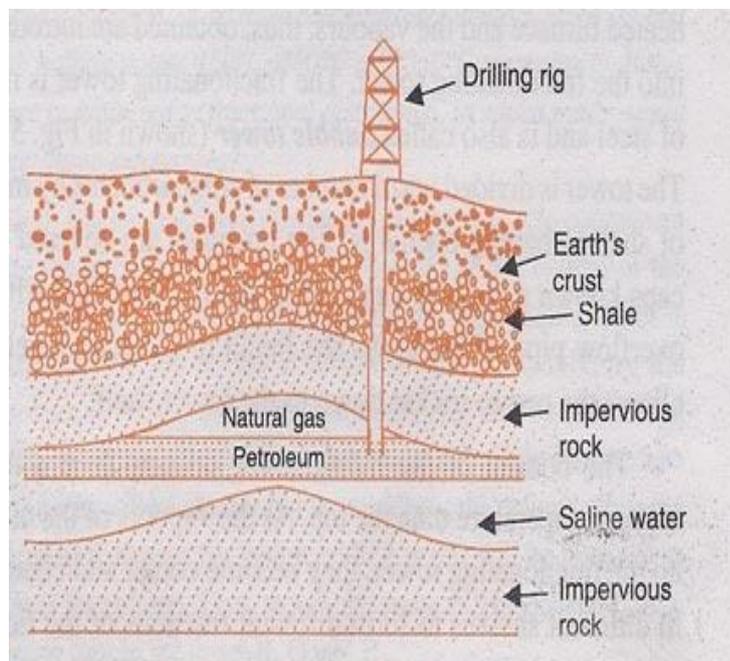
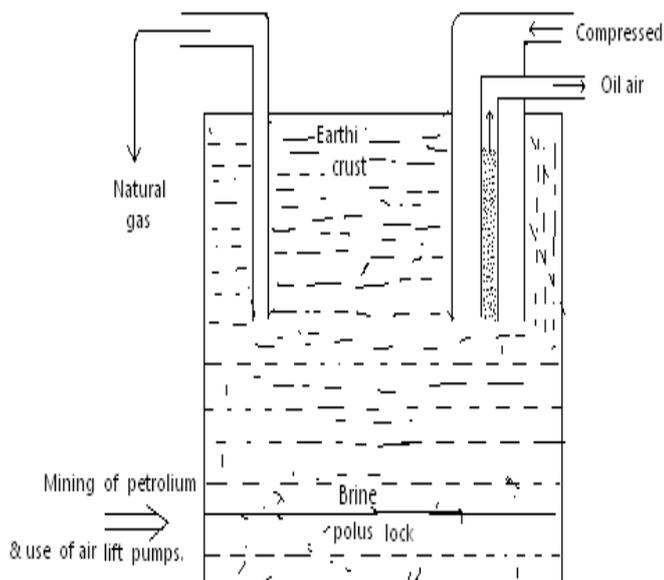


**Classification of petroleum:-** According to chemical nature , there are three types of petroleum

1. Paraffin base type crude :- Contains saturated hydro carbons up to C<sub>35</sub>H<sub>72</sub>  
The hydro carbons from C<sub>18</sub>H<sub>38</sub> to C<sub>35</sub> H<sub>72</sub>are semi solids called waxes.
2. Asphaltic base type crude: - Composed mainly of naphthalene and cyclo-paraffin's with small amount of paraffin's & aromatic hydro carbons.
3. Mixed base type crude: - Contains both paraffin and naphthalene hydro carbons and is generally rich in semi solid waxes.

### Mining of petroleum:-

- It is done by drilling holes in the earth's crust and sinking pipes up to oil bearing porous rocks.
- Oil is pushed out itself due to hydrostatic pressure of natural gas.
- When the pressure of natural gas is not sufficient, then air pressure is applied through lift pumps to force the oil out of the well.
- The co-axial pipes are lowered to the oil reservoir and compressed air is forced through the outer pipe, where oil comes out through the inner pipe which is sent to the refineries for further processing.



### **Refining of petroleum :-**

- The resulting petroleum contains unwanted impurities like  $H_2O$ ,  $Cl_2$ , S compounds.
- The process of removal of impurities from crude oil and separation into various useful fractions with different boiling ranges is called “**Refining of petroleum**”.
- The plants used for this purpose are called **oil refineries**.
- The following steps are involved in the refining.

#### **Step-1:- Separation of $H_2O$ (Cottrell’s process):-**

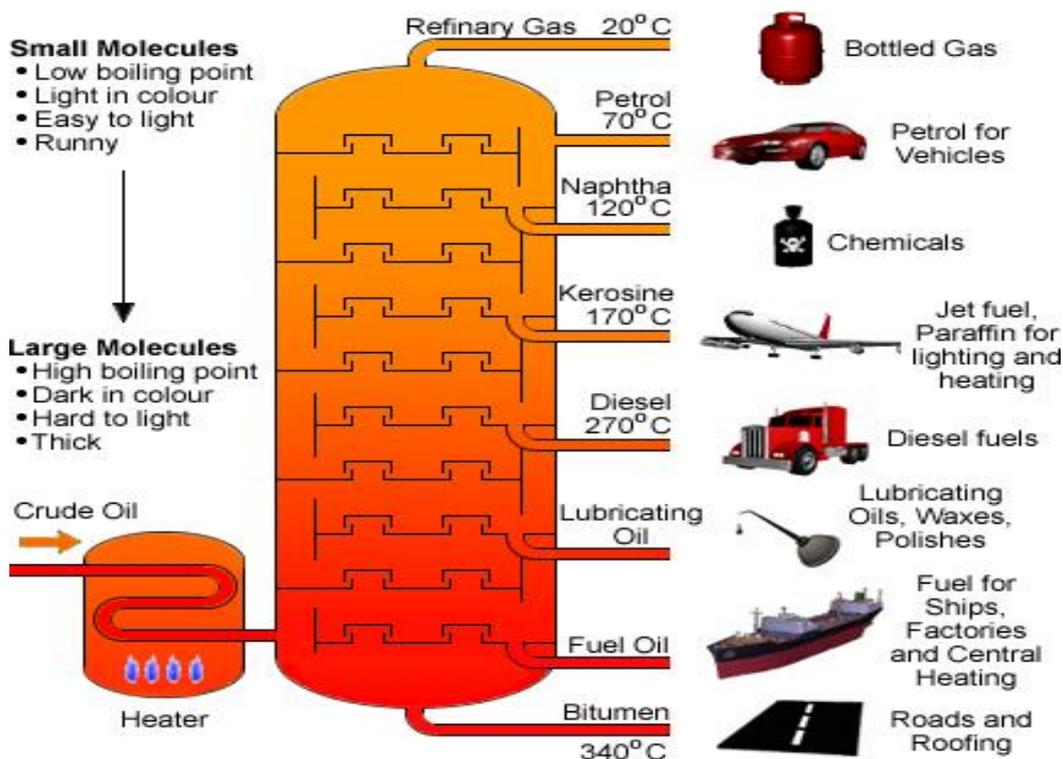
- The crude oil is an emulsion of oil and salt water.
- It is allowed to flow through two highly charged electrodes.
- The colloidal water droplets coalesce to form large drops which separate out from the oil.

#### **Step-2:- Removal of ‘S’ compounds:-**

- Sulphur compounds cause pollution.
- When crude oil is treated with copper oxide, it reacts with sulphur compounds and forms copper sulphite precipitate, which is then removed by filtration.

#### **Step-3:- Fractional distillation:-**

- The crude oil is then subjected to about  $400^{\circ}C$  temperature in an iron retort. All volatile constituents are evaporated except the residue (tar or asphalt).
- The hot vapors are then passed through a fractionating column.
- It is a tall cylindrical tower containing a number of horizontal stainless steel trays at a short distance.
- Each tray is provided with a small chimney, covered with a loose cap.
- As the vapors go up, they begin to cool and fractional condensation takes place at different heights of column.
- Higher boiling fractions condense first while lower boiling fractions condense next. Thus crude oil is fractionated into different fractions depending upon their boiling ranges.



Fraction	Boiling range	Composition	Use
1. Uncondensed gas	Below 30°C	C1 - C4	As domestic/ industrial fuel
2. Petroleum ether	30° to 70°C	C3 – C7	As a solvent
3. Gasoline / petrol	40°C- 120°C	C5- C9	As a solvent, motor fuel and in dry cleaning
4. Naphtha	120°C-180°C	C9-C10	As a solvent and dry cleaning.
5. Kerosene	180°C- 250°C	C10- C16	Fuel for stoves and aluminum
6. Diesel oil	250°C-320°C	C15 – C18	Fuel for diesel engines
7. Heavy oil	320°C- 400°C	C17- C30	For setting gasoline by cracking process
Lubricating oil			As lubricant
Petroleum jelly			Used in cosmetics & medicines
Grease			As lubricant
Paraffin wax			In candles, shoe polishes, wax paper.

## Gasoline:

### Knocking:

- In an internal combustion engine, a mixture of fuel and air is highly compressed before it is ignited in order to have maximum efficiency.
- During this process, there will be a sharp metallic sound known as '**Knocking**'. This causes more loss of energy and more engine wear.
- Knocking tendency of various hydrocarbons is

**Straight chain paraffins > Branched chain Paraffins > Olefins > Cyclo Paraffins > Aromatics.**

- Knocking can be decreased by addition of certain compounds to the fuel.
- These compounds are called **Antiknock agents**.  
Ex: Tetra Ethyl Lead (TEL) – It is a alkylated product and used as principle antiknock agent for gasoline.

### OCTANE NUMBER:

- The gasoline varies in their resistance to knocking.
- The quality of gasoline can be evaluated by measuring their knocking characteristics on **Octane Scale**.
- Octane number can be defined with reference to **n-heptane** and **iso-octane** and measured in a scale range of **0-100**.
- N-heptane produces maximum knocking, so its octane number is taken as Zero where as Iso-octane produces minimum knocking so its octane number is taken as 100.  
n-Heptane - 0  
Iso-octane - 100
- The octane number of Gasoline can be defined as the "**the % of iso-octane present in a mixture of Iso-octane and n-heptane mixture that has the same knocking characteristics as that of the gasoline under test.**"
- Higher the octane number of Gasoline, least is the tendency for knocking, but higher is its combustion characteristics.
- Ex: if the Octane number of fuel is 80 means it has the same combustion characteristics as of a mixture of 80% Iso-octane and 20% n-heptane.

### POWER ALCOHOL:

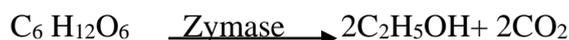
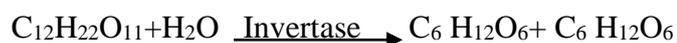
If Ethyl alcohol is added as an additive to act as a fuel for internal combustion engines, it is called **power alcohol**. Mixtures containing up to 20% alcohol with Petrol are used.

#### **Manufacture of Power Alcohol:**

The important raw materials required for manufacture of ethyl alcohol are saccharine materials such as molasses, Sugar Beets etc. or Starch materials such as Starch, Potatoes, Cereal Grains etc.

#### **Ethyl alcohol from Molasses:**

- Fermentation process is used for manufacture of ethyl alcohol from molasses.
- Molasses is a dark coloured viscous liquid left after crystallization of cane sugar from cane juice.
- It contains 20-30% of Sugar or Sucrose.
- It is converted to ethyl alcohol with the help of Yeast which gives enzymes **invertase** and **Zymase**.
- These two enzymes cause fermentation of molasses.
- Before adding Yeast, the molasses is diluted with water and pH is maintained between 4-5 by adding Sulphuric acid at 30<sup>0</sup>C.
- The process is completed with in 2-3 days.
- By using distillation process many times, the concentration of ethyl alcohol can be increased up to 97.6%.



### Advantages:

1. Addition of alcohol to petrol increases the Octane number, so power alcohol contains better anti knock properties.
2. Starting difficulties will not be there with power alcohol.
3. Air required for complete combustion is less.
4. It can be used in engines with higher compression ratio.

### Disadvantages:

1. Alcohol is easily oxidized to acids. Hence it may cause corrosion.
2. Calorific value of petrol is decreased by adding alcohol.
3. Because of high surface tension, it is difficult to atomize alcohol at low temperature. So special arrangements must be provided to start alcohol-petrol mixing in carburetor.

**Synthetic petrol:** - Petrol is synthesized from non-petroleum sources such as coal, coke etc.

The following two methods are generally used for synthesis of petrol.

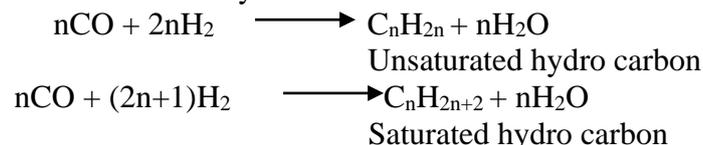
1. Fischer – Tropsch process
2. Bergius process

#### **1. Fischer – Tropsch process:-**

- Water gas is a mixture of carbon monoxide and hydrogen, produced by passing steam over red hot coke.



- Water gas is mixed with  $\text{H}_2$ .
- This gaseous mixture (water gas + Hydrogen) is purified by passing over  $\text{Fe}_2\text{O}_3$  to remove  $\text{H}_2\text{S}$  and then a mixture of  $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{CO}_3$  to remove organic sulphur compounds.
- The purified gas is compressed to 5 to 25 atm at  $200\text{--}300^\circ\text{C}$  passed through a converter containing catalyst which is a mixture of 100 parts cobalt, 5 parts thorium, 8 parts magnesium, 200 parts Kieselguhr.
- Then a mixture of saturated and unsaturated hydrocarbons is formed.



- The outgoing hot gaseous mixture is cooled in a cooler where a liquid similar to crude oil is obtained, which is then subjected to fractionation to yield gasoline and heavy oil.
- The heavy oil is reused for cracking to get more gasoline.

#### **2. Bergius process:-**

- The coal is powdered and made into a paste with heavy oil and a catalyst (Ni-Oleate and tin oleate) is mixed with it.
- This mixture is sent to a converter at  $400\text{--}500^\circ\text{C}$  and a pressure of 200-250 atm, where it meets the  $\text{H}_2$
- Hydrogenation takes place to form higher hydrocarbons. These higher hydrocarbons are further decomposed to lower hydrocarbons.
- Then these hydrocarbons are passed through a cooler, crude oil obtained.
- On fractional distillation this oil gives gasoline, middle oil, and heavy oil.
- This middle oil is subjected to hydrogenation in presence of a catalyst to produce more gasoline.
- The heavy oil is recycled to make a paste with fresh coal powder.

## Gaseous fuels:-

### Advantages:-

1. Possess higher calorific value.
2. Easily transport through pipelines .
3. They are easy to ignite.
4. Less amount of air for complete combustion
5. Burn without smoke and produce no ash.
6. They are free from solid and liquid impurities.
7. Their combustion can easily be controlled.

### Disadvantages: -

1. They are highly flammable.
2. They require very large storage take.
3. They are costlier than solid and liquid fuels.

**Important gaseous fuels: -** The most important gaseous fuels are

1. Natural gas
2. Producer gas
3. Water gas
4. Coal gas
5. Bio-gas

### **1. Natural gas:-**

- It is generally associated with petroleum deposits. It is obtained from wells dug in the oil bearing regions.
- If natural gas occurs along with petroleum in oil wells, it is called '**WET Gas**' and when it is associated with petroleum it is called '**Dry gas**'.
- Natural gas is a mixture of methane, ethane, propane, butane, pentane, CO<sub>2</sub>, N<sub>2</sub> etc.
- The approximate composition is

CH <sub>4</sub>	→	70- 90%
C <sub>6</sub> H <sub>6</sub>	→	5- 10%
H <sub>2</sub>	→	3% the rest is CO and CO <sub>2</sub> .

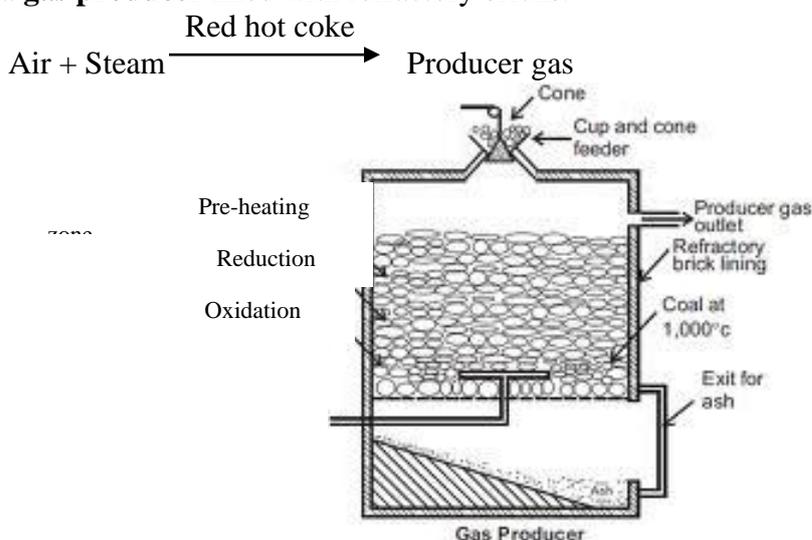
- The calorific value is 12,000-14,000 k.cal/m<sup>3</sup>

**Uses: -** 1. Used as a domestic fuel.

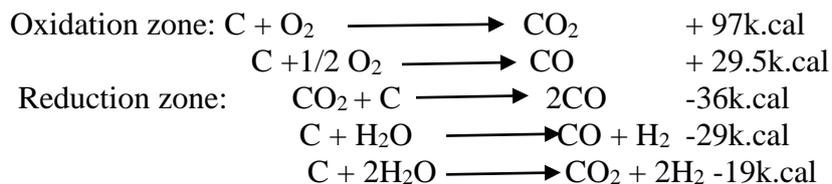
2. Raw material for manufacture of various chemicals.
3. For manufacture of H<sub>2</sub>.

### **2. Producer gas:-**

- It is a mixture of CO+N<sub>2</sub> and associated with large percentage of non combustible gases like N<sub>2</sub>, CO<sub>2</sub>.
- It is prepared by passing a mixture of air and steam over a bed of red hot coke maintained at 1100°C in a **gas producer** lined with refractory bricks.



- Reactions involved are-



- The average composition of producer gas is

CO	-	22-30%
H <sub>2</sub>	-	8-12%
N <sub>2</sub>	-	52-55%
CO <sub>2</sub>	-	3%

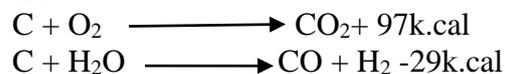
- Its calorific value is 1300 k.cal/m<sup>3</sup>.

#### Uses:-

- It is used as reducing agent in metallurgical operations.
- Used as a fuel for heating open hearth furnaces, muffle furnaces etc.

### 3. Water gas:-

- It is also known as **Blue Gas**.
- It is mixture of CO + H<sub>2</sub> and associated with non-combustible gases like N<sub>2</sub>, CO<sub>2</sub>.
- It is prepared by alternately passing air and steam over a bed of red hot coke at 900-1000<sup>0</sup>C in a reactor which is lined with refractory bricks.
- Reactions involved are-



- Average composition: CO = 4%, H<sub>2</sub> = 51%, N<sub>2</sub> = 4%, CO<sub>2</sub>=4%
- Its calorific value is 2800 k.cal.

#### Uses:-

1. It is used as source of hydrogen in the synthesis of ammonia.
2. It is used for the preparation of carbonated water gas.
3. It is used as an illuminant.
4. It is used as fuel in industries.

### 4. Coal gas:-

- It is produced by carbonization of coal at high temperature in absence of air.



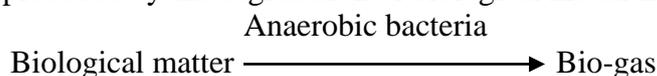
- Average composition H<sub>2</sub>= 40%, CH<sub>4</sub> = 32%, C<sub>2</sub>H<sub>2</sub>=2%, C<sub>2</sub>H<sub>4</sub>=3% CO = 7%, N<sub>2</sub> = 4%, CO<sub>2</sub>=1%, others = 4%.
- Its calorific value is 4900 k.cal/m<sup>3</sup>.

#### Uses:-

1. It is used as a fuel.
2. It is used as illuminant.
3. It is used in metallurgical operations for providing reducing atmosphere.

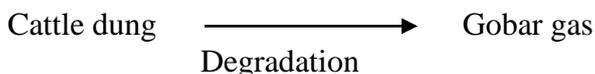
### 5. Biogas:-

- It is produced by the degradation of biological matter in the presence of anaerobic bacteria.



- Cheapest biogas is Gobar gas, which is obtained by the anaerobic degradation of cattle dung.

Anaerobic



- Composition: CH<sub>4</sub> =55%, CO<sub>2</sub> =35%, H<sub>2</sub>=7.4%, N<sub>2</sub> = 2.6% and traces of H<sub>2</sub>S.
- Calorific value: 1200k.cal/m<sup>3</sup>.

**Uses: -**

1. It is used as a domestic fuel.
2. It is used as an illuminant.

**CALORIFIC VALUE:-**

- The efficiency of fuel is expressed in terms of calorific value.
- It is defined as the total quantity of heat liberated by burning a unit mass or volume of fuel completely.
- Units of heat:-
  1. Calorie / gram.
  2. Kilo calorie /kilogram calorie.

**1. Calorie or gram calorie:-** The amount of heat required to raise the temperature of 1 gm of H<sub>2</sub>O through 1<sup>0</sup>C is called calorie.

$$1 \text{ cal} = 4.185 \text{ joules} = 4.18 \times 10^7 \text{ ergs.}$$

**2. Kilocalorie or Kilogram calorie (K.cal):-** The amount of heat required to raise the temperature of 1 kg of H<sub>2</sub>O through 1<sup>0</sup>C is called kilocalorie.

$$1 \text{ K.cal} = 1000 \text{ cal}$$

**3. British thermal unit (B.Th.U):-** The amount of heat required to raise the temperature of 1 pound (lb) of H<sub>2</sub>O through 1<sup>0</sup> F is called British thermal unit.

$$\text{B.Th.U} = 252 \text{ cal} = 1054.6 \text{ Joules} = 1054.6 \times 10^7 \text{ ergs.}$$

**4. Centigrade heat unit (C.H.U):-** The amount of heat required to raise the temperature of 1 pound of H<sub>2</sub>O through 1<sup>0</sup>C is called Centigrade heat unit.

$$1 \text{ K.cal} = 1000 \text{ cal} = 3.968 \text{ B.Th.U} = 2.2 \text{ C.H.U}$$

**Units of calorific value:-**

The calorific value for liquids and solids  $\xrightarrow{\hspace{2cm}}$  Cal/gm/ k.cal/kg/ BTH./Lb  
 For gaseous fuels  $\xrightarrow{\hspace{2cm}}$  K.cal/m<sup>3</sup> / B.Th.ft<sup>3</sup>

**1. Gross calorific value (GCV)/ Higher calorific value (HCV) :-**

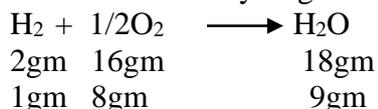
- The total amount of heat produced when a unit quantity of fuel is completely burnt and products of combustion are cooled down to room temperature (150C) is called **Gross calorific value**.
- H<sub>2</sub> that is present in almost all fuels undergo combustion to produce steam and steam is then cooled to room temperature and condensed to water.
- Latent (internal) heat that is evolved is also included in the gross calorific value.

**2. Net calorific value (NCV)/Lower calorific value (LCV):-**

- The amount of heat liberated when a unit quantity of fuel is completely burnt and combustion products are allowed to escape is called as Net calorific value.
- Generally during combustion of a fuel. The water vapours escape along with combustion products and are not condensed.

**NCV =GCV – later heat of H<sub>2</sub>O vapour formed.**

$$= \text{GCV} - \text{Mass of hydrogen} \times 9 \times \text{latent heat of steam.}$$



One part by weight of hydrogen gives 9 parts by weight of H<sub>2</sub>O.

The latent heat of steam is 587 cal/gm of 1060 B.Th.U/lb

$$\text{NCV} = \text{GCV} - 9 \times \text{H}/100 \times 587 \quad \text{where H} = \% \text{ of H}_2 \text{ in the fuel.}$$

$$\text{NCV} = \text{GCV} - 0.09 \times \text{H} \times 587$$

# UNIT-IV

## UNIT- V

# Building Materials

### Cement: -

- Cement is a dirty greenish heavy powder, used as a building material. It is a material which possesses 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 **calcareous** & Aluminium and silica are called as **argillaceous**.

### 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) Pozzolana cement: -** 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<sub>2</sub>O. 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 Ca silicates & aluminate 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.

### **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<sub>2</sub>), Alumina (Al<sub>2</sub>O<sub>3</sub>) and iron oxide is calculated by the formula

$$\frac{\text{CaO}}{2.8 \text{ SiO}_2 + 1.2 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3}$$

A good sample of Portland cement has the composition of.

Ingradient	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 <sub>3</sub>	1-1.5
7. Na <sub>2</sub> O	1
8.K <sub>2</sub> O	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

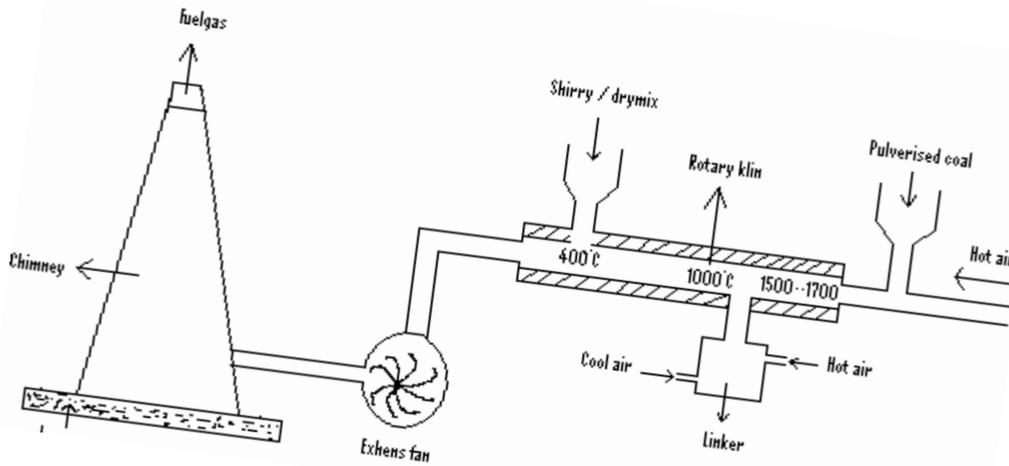
### **(1)Mixing of Raw material:-**

#### **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 introduced in to the upper end of the rotary kiln.

#### **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.



### Difference between dry & wet process:

Dry process	Wet process
<ol style="list-style-type: none"> <li>1. This process is adopted when the raw materials are quite hard.</li> <li>2. It is a slow and costly process</li> <li>3. The final consumption is low, hence smaller kiln is used.</li> <li>4. The process is not suitable if the raw material has moisture content of 15% or more.</li> </ol>	<ol style="list-style-type: none"> <li>1. This method is performed when the raw materials are soft.</li> <li>2. Comparatively cheaper and fast process.</li> <li>3. Fuel consumption is high so longer kiln is used.</li> <li>4. This process can be adopted even in wet conditions.</li> </ol>

### (2) Burning: -

- Rotary kilns are used for burning of cement.
- A Rotary kiln is an inclined steel cylinder, length is about 150—200m & 2-10m diameter and 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 pass slowly from the upper end of rotary kiln to lower end, while the burning fuel (pulverized coal, oil / natural gas) moves from lower to upper end and escape after the removal of dust.
- As the mixture or slurry gradually descends with increasing temperature the following reactions take place in rotary kiln.

#### (a) Drying zone: -

- Present in the upper part of the kiln, where the temp around 400° C
- The slurry gets dried because of hot gases.
- The clay is broken as  $Al_2O_3$ ,  $SiO_2$  &  $Fe_2O_3$ .

#### (b) Calcination zone / decarbonating zone :-

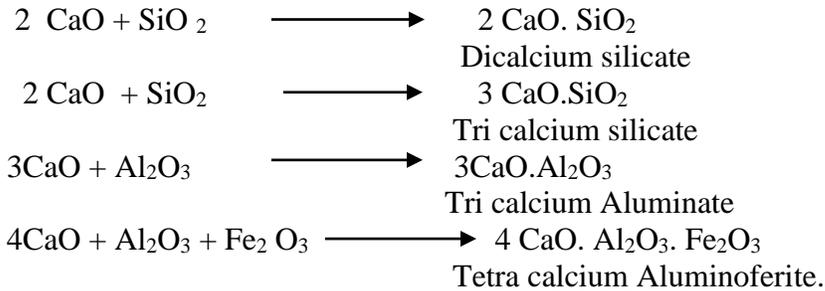
- It is present in the central part of the kiln, where the temp is around 1000°C.
- In this zone, lime stone of dry mix / slurry completely decomposed into quick lime ( $CaO$ ) &  $CO_2$ .



#### (c) Clinkering zone / Burning Zone:-

- It is present in the lower part of the rotary kiln.
- The temperature is between 1500°C to 1700°C.

- In this zone lime & clay reacts to each other forming aluminates & silicates.



- 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.

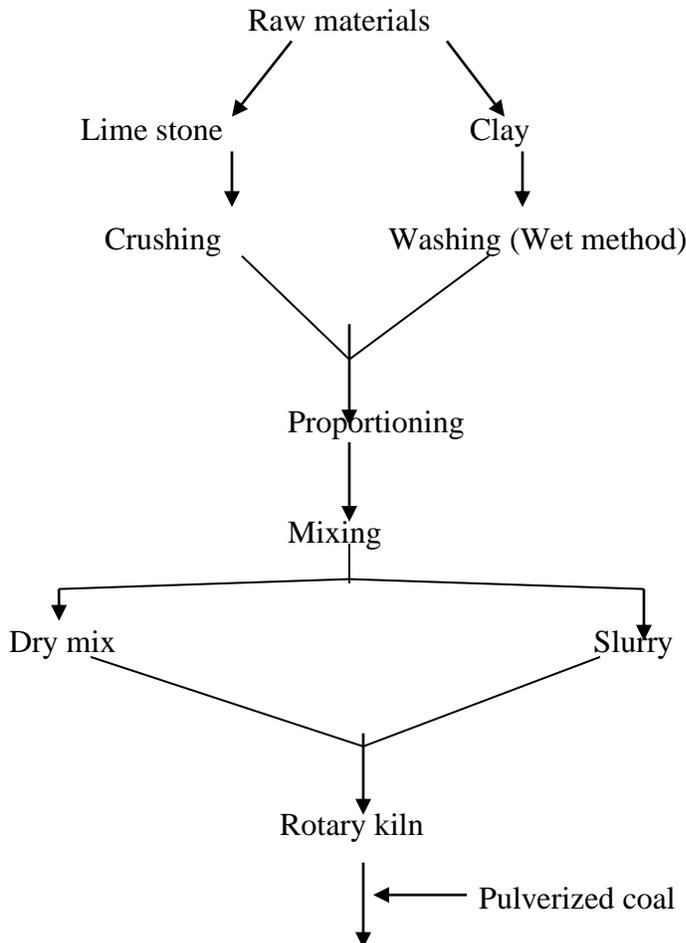
### (3) Grinding :-

- The cooled clinkers are passed to ball mills and are pulverized to form powdered mixture.
- This finely powdered clinkers set quick rapidly . So, the cement mortar will unworkable.
- Therefore its setting decreases used retarders. Commonly gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is used as retarder .
- Usually about 2-6% gypsum is mixed with clinkers in long tube mills.



- (4) Packing :-** The resulting Portland cement is stored in silos (air tight bins ) from which it is bagged or loaded for shipment.

### Flow chart of manufacture of cement:-

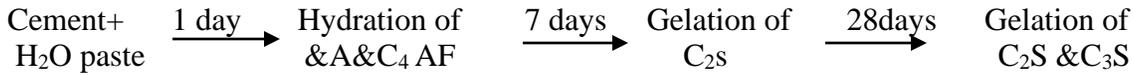




- The final setting & hardening of cement paste is due to formation of tobermonite gel and crystallization of  $\text{Ca}(\text{OH})_2$ .



### Sequence changes during setting & Hardening of cement:-



### Refractories:

An inorganic material which can withstand very high temp without softening or deformation in shape, is called as "Refractories".

Or

Any substance that is difficult to fuse / melt is a Refractory & used as constructing material.

### Characteristics: -

- They should be chemically inert to the action of Corrosive gases, molten metal's, slag's etc.
- They should have high abrasion resistance.
- Does not change their size at operating temperature.
- Expand & contract uniformly at increasing & decreasing temperature.
- They should have high load bearing capacity.

Classification: - Refractories are classified into following categories based

### I) On their chemical properties:

. Acid refractories: - These refractories consist of acidic materials such as  $\text{Al}_2\text{O}_3$ , Silica ( $\text{SiO}_2$ ). They can with stand acidic materials but easily attacked by basic materials like  $\text{CaO}$ ,  $\text{MgO}$  etc...

Eg: - Alumina, Silica & Fine clay refractories.

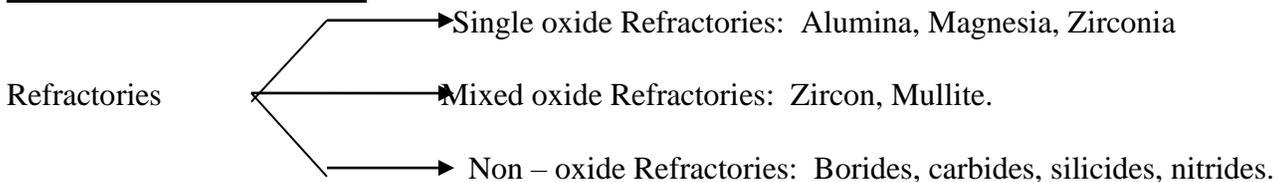
2. Basic refractories :- These refractories consists of basic materials like  $\text{CaO}$ ,  $\text{MgO}$  etc & are easily attacked by acid materials.

Eg :- Magnesite, dolomite bricks, chomo magnesite.

3. Neutral Refractories :- They made of weakly acidic / basic materials like carbon, zircon ( $\text{ZrO}_2$ ) & chromite ( $\text{FeO} \cdot \text{CrO}_2$ ). They show resistance to the action of acidic & basic materials & also show good chemical stability.

Eg: - Graphite, Zirconia & Carborundum ( $\text{SiC}$ ).

### II) On their oxide content:



### III) On the basis of fusion temperature ranges:

<u>Fusion temp</u>	<u>Example</u>
Normal Refractory	→ 1580-1780°C Eg: Fireclay
High Refractory	→ 1780-2000°C Eg: Chromite
Super Refractory	→ > 2000°C Eg: Zircon

## **Properties of Refractories:**

### **1. Refractoriness: -**

- It is the ability of a material to with stand high temp without appreciable deformation or softening under working conditions.
- It is usually measured by the softening temperature of the material.
- The material to be used as refractory, should have a softening temp much higher than the operating temperature of the furnace in which it is to be used as refractory.
- The softening temperature of the material is usually determined by the 'Pyrometric cone test' or 'Seger cone test'.

### **Measurement of Refractoriness / Pyrometric Cone Test (Seger cone) :-**

- Refractoriness is usually determined by comparing the softening behavior of test cone with that of standard cone (seger cone).
- The refractoriness is expressed in terms of pyrometric cone equivalent (PCE).
- These cones are small, pyramid shaped -38 mm high, 19 mm long sides with a triangular base.
- Test cone along with standard cones are heated under standard conditions of 10°C / minute.
- Each standard cone is made of particular refractory with a definite softening temperature and are arranged with increasing softening temperature.
- Standard cone fuses (melts) along with the test cone , the temperature at which the fusion of the test cone occurs is indicated by its apex (tip ) touching the base .
- If test cone softens earlier than one standard cone but later than the next cone , the PCE value of test cone is taken as the average value of the 2 standard cones .

Eg : - Silica bricks – PCE no –32 & softening temperature 1710°C

Magnesite bricks -- PCE no--- 38 & softening temperature 1850°C

### **2. Refractoriness Under Load / Strength: -**

- This property gives an idea of strength of refractory.
- Refractory should have high load bearing capacity under operating temperature, which can be measured by RUL test.
- This test is done in a rectangular container by applying a load of 1.75 Kg /cm<sup>2</sup> on to the refractory & heating at a constant rate of 10°C / minute.
- During this process the material will soften & its height will decrease under the load.
- This decrease in height is measured and when there is 10 % decrease to that of original height the temperature is noted.
- The RUL is then expressed as the temperature at which this 10% deformation occurs.

**3. Chemical inertness:** - The refractory selected for a specific purpose should be chemically inert and should not react with the slags, furnace gases etc. An acidic refractory should not be used in a basic furnace vice versa.

**4. Dimensional stability:** - It is defined as the resistance of material to any volume changes which may occur because of its exposure to high temperature over a prolonged period of time .These changes may be reversible/ irreversible. Further the irreversible change may result in contraction/ expansion. A good refractory should have high dimensional stability.

**5. Thermal expansion& contraction:** - The refractory tends to expand when temperature increases& contract when temperature decreases which affect the properties of the refractory. So a good refractory should have low thermal expansion& contraction.

**6. Thermal conductivity:** - The conductivity of refractory primarily depends on its chemical composition & porosity. As porosity increases thermal conductivity decreases because the entrapped air in the pores function as insulator. Depending on the type of furnaces low thermal conductivity and high thermal conductivity refractories are used.

**7. Abrasion resistance:** - A good refractory should resist the abrasion action of fuel gases, flames, slags etc...

**8. Porosity:** - Refractories usually contain pores due to manufacturing defects etc. It is the important property of a refractory, which affects many physical & chemical properties. It is the ratio of pore volume to the bulk volume.

$$P = \frac{W - D}{W - A} \times 100$$

P = porosity

W = saturated weight of specimen (with H<sub>2</sub>O)

D = Dry weight of the specimen

A = saturated weight + moisture content of specimen.

⇒ Good refractory should have low porosity.

**9. Electrical conductivity:-** In general refractories are poor conductors of electricity except graphite. However electrical conductivity of refractories increases with increasing temperature.

**10. Thermal spalling:** - It is the property of breaking, cracking / fracturing of the refractory due to rapid fluctuations in temperature causing uneven stresses & strains in the body of the refractory. A good refractory must show good resistance to thermal spalling. It is avoided by

- i. Avoiding sudden fluctuations in temp
- ii. By modification of furnace design
- iii. Low porosity & low coefficient of expansion.

### LUBRICANTS:

- All materials how smooth they are show many irregularities in the form of peaks or asperities. In all machines, when one solid surface is move over another solid surface resistance will be formed due to mutual rubbing. This resistance is called as friction.
- This friction causes lot of wear (loss of surface) and tear (roughness or brittle) of surface of moving or sliding or rolling parts which consequently requires repeated replacement.
- Friction also generates heat which dissipated thereby causing the loss of efficiency of the machine. Moreover, the moving parts gets heated up, damaged and even sometimes result in seizure (welding of two surfaces due to heat)
- These problems can be overcome or minimized by using a substance called lubricant.
- **Lubricant** is defined as a substance introduced between two moving surfaces as a thin layer with a view to reduce the frictional resistance.
- The process of reduction of frictional resistance between two moving surfaces using lubricants is called **lubrication**.
- The study of wear – tear or mechanism of friction between two surfaces and lubrication is called **tribology**.

### Functions of lubricants:

- The first and foremost imp. function is to **reduce the functional** resistance.
- It **reduces wear and tear** and surface deformation due to avoiding contact b/n two surface.
- **Act as coolant** by reducing the energy in the form of heat.
- It **prevents rust and corrosion**, thereby **reduces the maintenance and running cost** of the machines.
- It reduces expansion of metals and seizure of metals and seizure of moving surfaces by local frictional heat.
- They may also **absorb shocks** between bearings and other engine parts.
- They covers the surface of moving parts. Hence they **act as seal**.

Ex 1: Lubricant used b/n piston & Cylinder of internal combustion engine

Ex 2: Lubricant act as seal, so it avoids the leakage of gases under high pressure than the cylinder.

**CLASSIFICATION OF LUBRICANTS:** On the basis of their physical state, lubricants are classified into following types.

1. Lubricating oils / Liquid lubricants
2. Semisolid lubricants / greases
3. Solid lubricants

**1. Lubricating oils:**

- These lubricating oils provide a continuous fluid film over the moving or sliding surfaces. They act as
  1. Cooling & sealing agent
  2. Corrosion inhibitors.
- A good lubricating oils should possess
  - (i) Ideal viscosity
  - (ii) Thermo stability
  - (iii) High B.P
  - (iv) Non corrosive properties
  - (v) Low freezing point
  - (vi) High oxidation resistance
  - (vii) Stability to decomposition
- The lubricating oils are further classified into 4 types.
  - i. Animal & vegetable oils
  - ii. Mineral / petroleum oils
  - iii. Blended oils
  - iv. Synthetic oils

**1. Animal & Vegetable oils:**

- Before invention of petroleum products animal & vegetable oils are most commonly used as lubricants.
- They process good oiliness, have the property of sticking with metal surface even under increased pressure and heavy load.
- However they have the following disadvantages—
  - (1) Costly
  - (2) Undergo oxidation easily
  - (3) Forming gummy and acidic products
  - (4) Have some tendency to hydrolyze.



Ex: In Watches and scientific measurements.

<b>Animal oil</b>	<b>Source</b>	<b>Use</b>
Whale oil	Whale fish	light machines lubricants
lard oil	pig	Ordinary machines

**2. Minerals / petroleum oil:**

- They are derived from fractional distillation of petroleum at a temperature of 300°C.
- The length of the hydrocarbon chain in petroleum oils varies between about 12 to 15 carbon atoms.
- The shorter chain oils have lower viscosity than the longer chain hydro carbons.
- They are widely used lubricants, because they are

- (1) Cheap
- (2) Available in abundance
- (3) Quite stable under service conditions.

- However, they possess poor oiliness as compared to that of animal & Vegetable Oils.

Example

Used as lubricants in

- 1. Light Oil → Spindles, transformers & refrigerators
- 2. Medium Oil → Compressor, light machinery.
- 3. Heavy Oil → Internal combustion engines, gear oil, heavy machinery
- 4. Residue → Gear Oil, Steam Cylinder Oil

**3. Blended Oils:**

- No single oils serve as the most satisfactory lubricant for many of the modern machineries.
- The best properties of lubricating oils can be achieved by addition of certain chemicals called ‘additives’.
- These oils with additives are called as Blended oils.
- The following types of additives are employed.

<b>Additive</b>	<b>Function</b>	<b>Examples</b>
Oilness carriers	To improve oiliness	Vegetable, fatty acids
Viscosity index Improvers	Thinning at high temp and freezing at low temp. is prevented	Hexanol, polyisobutylene, polystyrene
Thickness	Provides high viscosity	poly styrene, polyester
Detergents	They carry away dirt particles from metal surface	Sulphonotes
Corrosion inhibitors	Reduce corrosion of bearings and other metal surfaces	Organic compound of P & Sb
Antioxidants	Resists the oxidation of lubricant	Aromatic phenolic amino compounds.
Abrasion inhibitors	Decrease abrasion	Tricresyl PO <sub>4</sub>
Emulsifiers	They promote formation of emulsion acid between oil and water	Sodium salt of sulphonic acid
Boundary lubrication Improvers	They create long wearing lubricant film	Compound containing O, S or P, castor oil

**4. Synthetic Oils:**

- Synthetic lubricating oils are used under very severe conditions when petroleum lubricants fail to work effectively.
- They are used in military jet engines, submarines, rocket motors and atomic energy plants.
- They have high thermal stability, high flash points, high viscosity index etc....

<b><u>Lubricant</u></b>	<b><u>imp-property</u></b>	<b><u>used in</u></b>
Di base acid ester	With stand high temp	Jet engine, sub marine Engines & lubricants
silicones	high Viscosity index, H <sub>2</sub> O repellent & corrosive resistance	Furnace doors, electro plating equipment under highly corrosive environment

**II. Semi – solid lubricants / Greases: (Soap + liquid lubricating oil)**

- Grease is a semi – solid consisting of a soap dispersed in a liquid lubricating oil.

- The liquid lubricant may be petroleum oil or even a synthetic oil and may contain any of the additives for specific requirements.
- Greases are prepared by saponification of fat with alkali, followed by addition of hot lubricating oil.
- At high temp, the soap dissolves in the oil, where upon an interconnected structures ceases to exist and the grease is liquified.
- Greases have high frictional resistance than oils and can support much heavier loads at lower speeds.
- Greases are used
  - (1) In bearing & gears that work at  $\uparrow$ temp.
  - (2) In situations where oil cannot remain in place, due to high load, low speed, sudden jerk etc.....
- The main function of soap is it acts as a thickening agent so that grease sticks firmly to the metal surface.
- Greases are classified in to following types on the basis of soaps used in their manufacture of
  - (1) Ca based greases
  - (2) Soda based greases
  - (3) Lithium based greases
  - (4) Axle grease.

**a) Ca based greases (CUP greases):**

- They are emulsions of petroleum oils with calcium soap. They are prepared by adding requisite amount of  $\text{Ca}(\text{OH})_2$  to the hot oil while under agitation.
 
$$\text{Ca}(\text{OH})_2 + \text{hot oil} \rightarrow \text{Ca based grease}$$
- They are cheapest, most commonly used, water resistant.
- They are used at low temp because above  $80^\circ\text{C}$ , oil & soap begin to separate out.

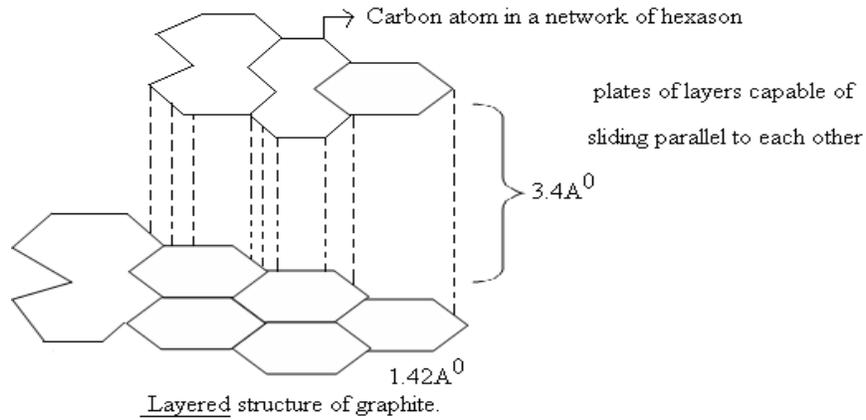
**b) Soda based:** These are petroleum oils thickened by mixing Na soap. They are not  $\text{H}_2\text{O}$  resistant, used at high temp ( $175^\circ\text{C}$ ) and suitable for use in ball bearings.

**c) Li based:** These are petroleum oils, thickened by mixing 'Li' soaps. They are  $\text{H}_2\text{O}$  resistant & suitable at low temp ( $150^\circ\text{C}$ ).

**d) Axle:** These are very cheap resin greases, prepared by adding lime to resin and fatty oils. They are  $\text{H}_2\text{O}$  resistant and suitable for less delicate equipments working under high loads and at low speeds.

**III Solid lubricants:**

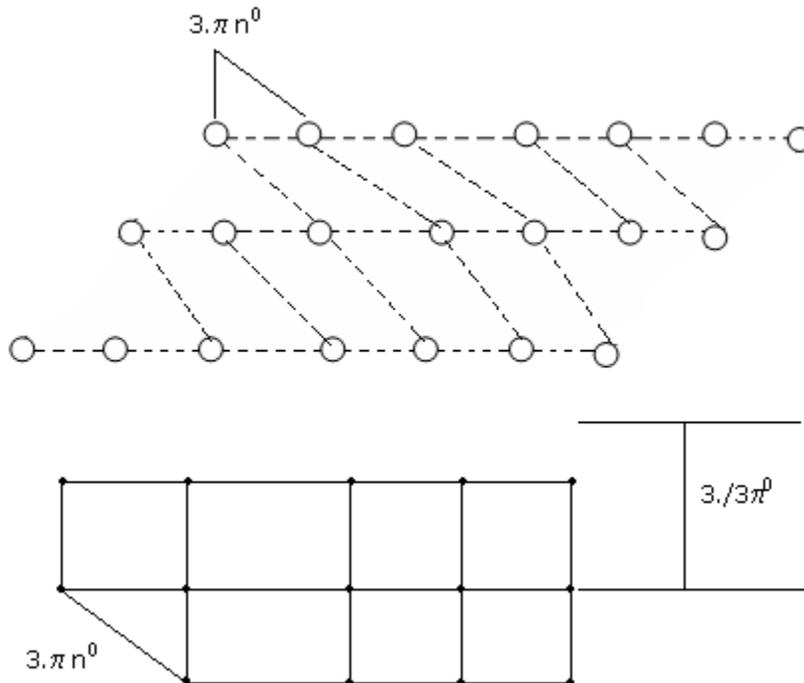
- Some of the solid substances possess strong adherence property, little shearing strength and good plastic properties.
- They are very important under high temp and heavy load.
- The most common solid lubricants are the minerals such as graphite, talc, soapstone, mica, Molebdenum disulphide and  $\text{ZnO}$ .
- The most commonly used solid lubricants are
  - (1) Graphite
  - (2) Molebdenum disulphide.



- It consists of many flat plates made up of a network hexagon in which each 'C' is in  $SP^2$  hybridization.
- The separation between the plates length is about  $3.4\text{Å}$  & little Van der Waal's forces slides the layers parallel to each other. Hence it has low coefficient of friction.
- It is very soapy to touch, non flammable & not oxidized in air below  $375^\circ\text{C}$ .
- It is used as lubricant in the form of powder or suspension in oil or water.
- The suspension of graphite in oil is termed as "Oil - dag" and used in internal combustion engines.
- Graphite is dispersed in  $\text{H}_2\text{O}$  is termed as "aqua - dag" used in food industries.
- Graphite is used as lubricant in air compressors, food stuff industries, railway track joints, open gases, machine work etc..

### MoS<sub>2</sub>:

It has a sand witch like structure in which 'Mo' atoms lie between two layers of 'S' atoms. MoS<sub>2</sub> has high specific gravity than graphite but is slightly softer.



- Commercially available as "molykotes".
- The inter laminar attraction is very weak ( $3.3/\pi\text{Å}$ )
- It has low frictional strength
- It is stable up to  $400^\circ\text{C}$
- It is used in space vehicles (70% MoS<sub>2</sub> + 7% graphite + 28% silicate)
- It can with stand extreme temp & low pressure and nuclear radiations.

## PROPERTIES

- The selection of a lubricant for a specific application is based on properties of the lubricant.
- Lubricants show following properties.

### 1. Viscosity:

- It is one of the imp-properties of lubricating oil.
- It is the property of the fluid that determines its 'resistance to flow'
- Viscosity is measured in terms of viscosity coefficient.
- Viscosity coefficient is defined as **force per unit area required to maintain a unit velocity gradient between two parallel layers.**

**Measurement:** It is measured with viscometers.

<b>Red wood Viscometer-I</b>	<b>Red wood Viscometer-II</b>
Used to determine viscosities of lubricating oils. It has a jet of base diameter 1.62 mm & length of 10 mm	Used to measure viscosities of high viscous oils like fuel oils. It has 3.8 mm & length 15mm

**Red wood viscometer:** Parts are (1) Oil cup (2) Heating bath (3) stirrer (4) Kohlrousch flask (5) spirit level & leveling screws.

#### **(1) Oil cup:**

- Is a silver plated brass cylinder (90 mm height 96.5 mm dia).
- The bottom of cylinder is opened or closed by a valve rod, which is a small silver plated brass ball fixed to a stout wire.
- Oil is filled in the cylinder up to level of pointer.
- The lid of the cup is fitted with a thermometer, which indicates oil temp.

**(2) Heating bath:** Oil cup is surrounded by a cylindrical copper bath, containing H<sub>2</sub>O.

**(3) Stirrer:** A stirrer is fitted outside the oil cylinder, it has 4 blades for stirring the H<sub>2</sub>O to maintain uniform temp. This stirrer provides a circular shield at the top, to prevent any H<sub>2</sub>O splashing into the oil cylinder.

**(4) Kolrausch flask:** A specially shaped flask, it receiver the oil from outlet. Its capacity is 50 ml.

**(5) Leveling Screws:** The lid of the cup is provided with a spirit level and the entire apparatus rest on Tripod stand with leveling screws.

### **Working Procedure:**

The oil to be tested is filled in the oil cup up to the pointer level after the ball of value rod is placed on the agate jet to close.

↓

The Kohlrousch flask is kept below jet to collect the oil.

↓

Water is filled in heating bath & heating is initiated

↓

When the oil reaches desired temp, heating is stopped & valve is removed from jet hole.

↓

Time taken to collect 50 ml of oil in to the flask is noted.

↓

The result is expressed in Red wood No.1 seconds at the definite temp.

It is observed that higher the flow of time, higher is the viscosity of the oil.

### **Viscosity index:**

- A good lubricating oil viscosity should not change with temperature.
- Generally the viscosity of liquids decreases with increase in temperature. As a result, the lubricant becomes thinner.
- Hence viscosity of good lubricating oil should not change with temperature.
- **The rate at which viscosity of an oil changes with temperature is indicated by viscosity index.**
- If viscosity index is high, it indicates that the change in viscosity with temperature is low and vice versa.

### **Measurement of Viscosity Index:**

- The viscosity index of test oil is measured with the help of two types of standard oils namely Pennsylvanian oil and Gulf oil having VI's 100 and 0 respectively.
- The Pennsylvanian oil consisting mainly of paraffin's, its a viscosity index (VI) value is considered as 100 i.e., it shows little variation in viscosity with increase in temperature.
- The other oil i.e Gulf oil Viscosity index is considered as 0 because it show high variation in its viscosity with increase in temperature. This oil is rich in naphthalene.
- VI can be calculated using the formula

$$VI = \frac{L-U \times 100}{L-H}$$

- VI=Viscosity index of the oil under test.
- L= Viscosity of gulf oil at 100<sup>0</sup> F and also having same viscosity as the oil under test at 210<sup>0</sup> F
- U= Viscosity of oil under test at 100<sup>0</sup> F
- H= Viscosity of Pennsylvanian oil at 100<sup>0</sup> F and also having the same viscosity as the oil under test 210<sup>0</sup> F.

### **(2) Flash & Fire points:**

- A good lubricating oil should not be volatile in working temp.
- Under working conditions of lubrication, if some volatilization takes place, the formed vapors should not form inflammable mixture with air. So, flash & fire points are preferred to avoid explosion.

#### **Flash Point:**

1. The lowest temp, at which the lubricant gives off enough vapors to ignite for a moment, when a tiny flame brought near it.
2. A good lubricant should have flash point above the operating temp.

#### **Fire Point:**

1. The lowest temp, at which the vapors of oil burn continuously for at least 5sec when a tiny flame brought near to it.
2. In majority cases, the fire point of oil is about 5<sup>0</sup> to 40<sup>0</sup>F higher than its flash points.

### **Determination of Flash and Fire point:** Flash fire points are determined by **Pensky Martens apparatus.**

Oil under examination is filled in the oil cup up to mark and heated by heating air bath.



The stirrer maintains the uniform heating in the oil cup.



Heat is applied to raise the temp at about 5<sup>0</sup> c per minute



At every 1<sup>0</sup> c rise of temp, test flame is introduced for a moment through opening.



The temp at which distinct flash (combination of weak sound and light) appears inside the cup – is recorded as flash point.



The heating is continued at the rate of 4 – 5° c per/min.



The temp at whom oil ignites & continues to burn for at least 5<sup>0</sup> seconds, the temp recorded as fire point of oil.

#### Cloud and Pour point:

- Petroleum oils are complex mixtures of chemical compounds & do not show a fixed C – P.
- Cloud & pour points indicate the suitability of lubricants in cold conditions.

**Cloud Point:** Cloud point is temp at which oil becomes cloudy / hazy appearance when oil is cooled slowly.

**Pour Point:** The pour point is “Temp at which oil ceases to flow or pour”

- Clud & pour points indicate the suitability of lubricants in cold conditions.

#### Determination of cloud & pour point: With Pour Point apparatus.

It has a flat bottom tube of 3cm diameter & 2cm high.



This is kept in an air jacket which is closed certainly with freezing mixture (ice + CaCl<sub>2</sub>)



The tube is half filled with oil & thermometer is introduced in the oil.



As temp proceeds slowly via air – jacket, the temp falls continuously



With every 1<sup>0</sup>C fall of temp of oil, the tube is withdrawn from jacket for a moment (about 2 – 3 sec) and examined and replaced immediately.



The temp at which cloudiness is noticed is recorded as cloud point.



The cooling is continued and the above procedure repeated.



The temp at which oil does not flow in the test tube, even when kept horizontal for 5sec, is recorded as “pour point”.

#### IV. Aniline point:

- It is defined as “The lowest equilibrium solution temperature at which equal volume of lubricating oil dissolves in equal volume of aniline.

It is determined by mixing equal volumes of aniline & Lubricating Oil in to a test tube & heating the mixture until homogeneous solution is obtained.



Then the tube is allowed to cool at a controlled rate.



The temperature at which oil and aniline separates is noted

- Aniline point gives indication of possible **deterioration of an oil in contact with rubber sealing's, packings** etc.
- Aromatic hydrocarbons have a tendency to dissolve natural rubber & certain types of synthetic rubber. **So, low aromatic content in the lubricant is desirable**
- If aromatic content is high, aniline point is low and vice versa.

- So lubricants with higher aniline point are preferred.

#### **V. Neutralisation:**

- It is also called “**acid number or value**”.
- It is defined as “The number of milli grams of KOH required to neutralize free acids in 1 gram of oil.
- A lubricating oil should possess an acid value less than 0.1.
- The acid value higher than 0.1 shows that, the oil has been oxidized, which leads to corrosion in addition to gum and sludge formation.

#### **VI. Mechanical Strength:**

- To judge the suitability of a lubricant under the condition of very high pressure, different mechanical tests are carried out.
- One of the tests is “4 balls extreme pressure lubricant test”.
- In this test the lubricant under test is placed in a machine containing 4 balls.
- Among these, lower 3 balls are stationary and the upper ball rotates.
- The load is gradually increased and the ball is drawn & examined at specific intervals for scale formation etc.....
- If the lubricant is satisfactory under given load, the ball bearings after the test come out clear / clean.
- However, when the load is progressively increased, the liberated heat causes the weld of the balls, from which the lubricant fails.
- This test is carried out to examine the maximum load that can be conducted safely with a lubricant.

**UNIT-V**

# Unit-V

## Colloids

### Introduction:

- According to the diffusing nature of substances through semi-permeable membranes, substances are divided into two kinds- crystalloids and colloids.
- The crystalline substances having tendency to diffuse rapidly in solution and can pass through the semi-permeable membrane are called crystalloids.  
Ex: Sugar, NaCl, Urea etc.
- The substances which diffuse very slowly in solution and which cannot pass through semi-permeable membrane are called colloids.  
Ex: Glue, Gelatin Gum etc.
- The word colloid is derived from Greek in which Kolla= Glue and eidos= like which means glue like substances.
- Irrespective of nature of substance, any substance can be converted into a colloid by reduction of particle to colloid size.

### Types of Solutions:

- Based on the visibility and settling nature of substances dissolved, solutions are divided into three types.

#### **1. True Solutions:**

- The solutions in which the particles are invisible and don't settle on long standing are called true solutions.
- In these solutions, the solute particles are dispersed homogeneously into the solvent as a single molecule or ions.
- The diameter of the dispersed particle ranges from  $1\text{Å}$  to  $10\text{Å}$ .
- Ex: Molecules of sugar in water.

#### **2. Suspensions:**

- The solutions in which the particles are visible and settle down on long standing and can be separated easily from the solvent are called as Suspensions.
- The solute and solvent form heterogeneous mixtures i.e. they can be seen separately through microscope or visible to the naked eye.
- The diameter of the dispersed particle ranges from  $2000\text{Å}$  to more.
- Ex: Sand in water

#### **3. Colloidal Solutions:**

- The solutions in which the particle size is between  $10\text{Å}$  to  $2000\text{Å}$ , that type of solutions are called Colloidal solutions.
- These are intermediary between True solutions and suspensions.
- They are also called as Colloidal system or colloidal dispersions or Colloids.

### **Colloidal System:**

- A Colloidal system consists of two phases namely Dispersed Phase and Dispersion Medium.
- The substance distributed as the colloidal particles is called as Dispersed phase.
- The substance in which the colloidal particles are distributed is called as Dispersion Medium.
- The dispersed phase or dispersion medium can be gas or liquid or solid.
- There are eight types of colloidal systems based on the dispersed phase or medium.

## Colloidal Solutions:

Dispersed phase	Dispersion medium	Name	Examples
Solid	Solid	Solid-sol	Ruby glass, alloys
Solid	Liquid	Sol	paint, ink
Solid	Gas	Aerosol	Smoke, haze
Liquid	Solid	Gel	Curd, cheese
Liquid	Liquid	Emulsion	Milk, Cream
Liquid	Gas	Liquid Aerosol	Cloud, mist
Gas	Solid	Solid form	Cork, pumice stone
Gas	Liquid	Foam	Froths of air

## Classification of colloidal Solutions:

- Colloidal systems in which a solid is dispersed in liquid are called as 'Sols'.
- If water is the dispersion medium, they are called as Hydrosols or aquasols, if alcohol is the dispersion medium, they are called as Alcosols and if benzene is the dispersion medium, they are called as Benzosols.
- The colloids or Sols are divided in to two types based on the affinity of colloid towards dispersion medium.
  1. Lyophilic sols (Solvent-loving)
  2. Lyophobic sols (Solvent-hating/ repellent)

## Lyophilic Solutions:

- These are the solutions in which the dispersed phase has strong affinity for the medium or solvent.
- The affinity is mainly due to the formation of hydrogen bonding between the particles and the medium.
- They are reversible in nature i.e on evaporation of medium, the residue can be reconverted in to colloidal state on addition of medium.

Ex: Starch in water  
Protein in water  
Gum in water etc.

## Lyophobic Solutions:

- These are the solutions in which the dispersed phase has no affinity for the medium or solvent.
- There is no affinity between particles and medium because there is no formation of hydrogen bonding between the particles and the medium.
- They are not stable and can be readily precipitated.

Ex: Iron in water  
Gold in water  
Sulphur in water etc.

## Preparation of Colloidal Solutions:

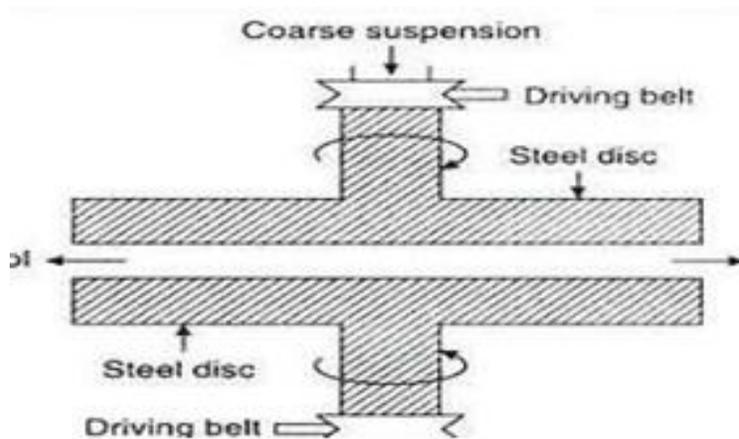
- There are two main methods for the preparation of colloidal solutions.
  1. Condensation method
  2. Dispersion or Disintegration method

## 1. Condensation Method:

- In this method, a large number of small particles are condensed to form bigger particles of colloidal dimension.
  - This can be done by following ways.
1. **By exchange of Solvent:** If the dispersed phase is insoluble in the medium, then it is first dissolved in another soluble medium and then the two mediums are mixed. Then the dispersed phase will dissolve in the insoluble medium and form colloidal solution.  
Ex: Sulphur Colloid solution in water is prepared by dissolving it first in alcohol and when mixed with water, then sulphur dissolves in water.
  2. **By changing physical state:** In this method, the dispersed phase is mixed with insoluble medium by changing its state.  
Ex: Mercury or Sulphur solution is prepared by passing their vapours through the cold water as they are insoluble in their original state.
  3. **By Chemical Methods:** There are four chemical methods by which colloids are prepared. They are
    - i. By double decomposition.
    - ii. By reduction
    - iii. By oxidation
    - iv. By hydrolysis
  4. **Dispersion or Disintegration Method:** This is a direct method in which pulverized substance is dispersed in the dispersion medium. The important dispersion methods are

### a) By mechanical Dispersion:

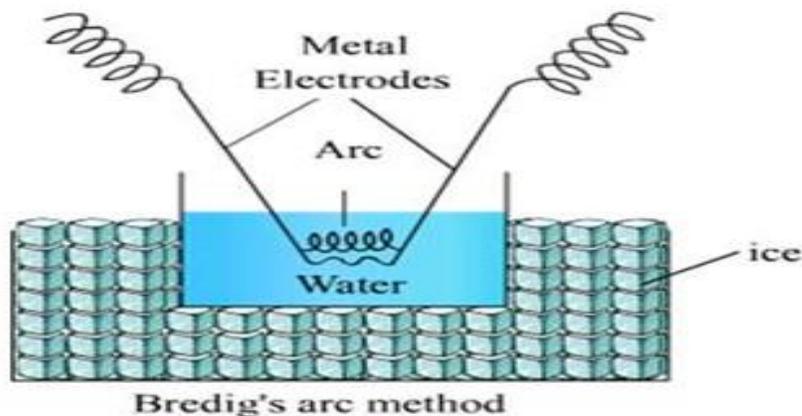
- The substance is finely ground and dispersed in a medium to form a suspension.
  - The suspension is then passed between two oppositely rotating steel discs at high speed (7000rpm) with narrow distance.
  - Then the metal discs break down the particles to colloidal size.
- Ex: Paints, Black ink, Ointments, Varnishes etc are prepared by this method.



### b) By electrical dispersion or Bredig's arc method:

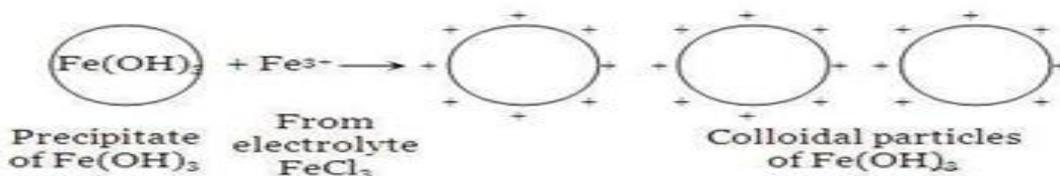
- This method is used to prepare sols of platinum, silver, copper or gold.
- The metal whose sol is to be prepared is made as two electrodes which immerse in dispersion medium such as water etc.

- The dispersion medium is kept cooled by ice.
- An electric arc is struck between the electrodes.
- The tremendous heat generated by this method gives colloidal solution.
- The colloidal solution prepared is stabilized by adding a small amount of KOH to it.



### c) By peptization method:

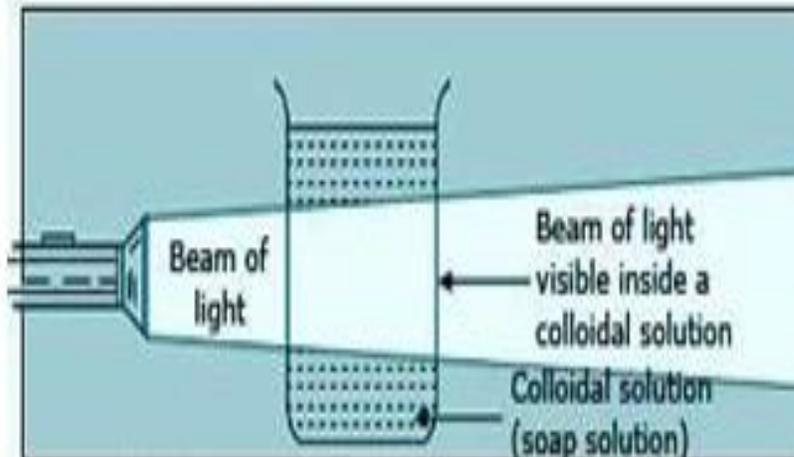
- The process of converting a freshly prepared precipitate into colloidal form by the addition of suitable electrolyte is called peptisation.
- Cause of peptisation is the adsorption of the ions of the electrolyte by the particles of the precipitate.
- The electrolyte used for this purpose is called peptizing agent or stabilizing agent.
- Important peptizing agents are sugar, gum, gelatin and electrolytes.



### Properties of Colloids:

1. **Heterogeneity:** Colloidal solutions consist of two phases dispersed phase and dispersion medium, hence they are heterogenous.
2. **Visibility of dispersed particles:** The dispersed particles present in them are not visible to the naked eye and they appear homogenous.
3. **Filterability:** The colloidal particles pass through an ordinary filter paper. However, they can be retained by animal membranes, cellophane membrane and ultrafilters.
4. **Stability:** Lyophilic sols in general and lyophobic sols in the absence of substantial concentrations of electrolytes are quite stable.
5. **Colour:** The colour of a colloidal solution depends upon the size of colloidal particles present in it. Larger particles absorb the light of longer wavelength and therefore transmit light of shorter wavelength.
6. **Tyndall Effect:**

- When an intense beam of light is passed through a colloidal solution kept in dark, the path of the beam gets illuminated with a bluish light.
- This phenomenon is called Tyndall effect and the illuminated path is known as Tyndall cone.
- The Tyndall effect is due to the scattering of light by colloidal particles.
- Tyndall effect is not exhibited by true solutions. This is because the particles present in a true solution are too small to scatter light.
- Tyndall effect can be used to distinguish a colloidal solution from a true solution. The phenomenon has also been used to devise an instrument known as ultra microscope. The instrument is used for the detection of the particles of colloidal dimensions.



#### 7. **Electrical Properties:**

- The sol particles carry an electrical charge. The most important property of colloidal dispersion is that all the suspended particles carry either positive or negative charge.
- The mutual force of repulsion between charged particles prevents them from coagulation and settling under the force of gravity.
- This gives stability to the solution.
- The particles acquire +ve or -ve charges by adsorption of +ve or -ve from the dispersion medium.

### **Applications of Colloids:**

- Colloids have very important application in our daily life starting from food products to the medicines to industries like rubber. Some of the applications of colloids are mentioned below.

#### 1. **Food and medicines:**

- Colloids have great application in food industries and food stuffs.
- Many of the food materials which we eat are of colloidal nature.
- Milk and also many milk products like cheese, cream butter etc. are colloids i.e milk is an emulsion (liquid in liquid colloidal system). In milk, butter and fat are dispersed in water.
- Bread is colloidal system in which air is dispersed in baked dough.
- Colloids also have applications in the form of medicines. Colloidal medicines are competitively more effective as they are easily absorbed by the body. That is why many medicines are emulsion.
- Some major antibiotics like penicillin and streptomycin are injected in the body in the form of colloidal sol so that they would be absorbed by the body easily.

## 2. Water Purification:

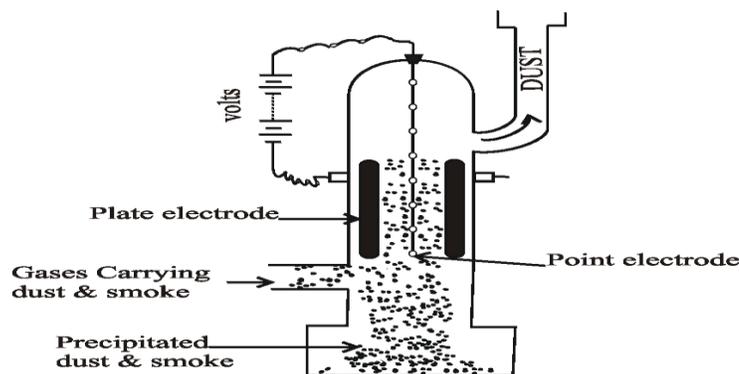
- We know that one of the very popular methods used for water purification is the addition of electrolytes like potash alum.
- Addition of these electrolytes is based on the fact because the impure water is usually a colloidal system.
- It usually contains dispersed colloidal particles which cannot be removed by filtration.
- Addition of these electrolytes results in coagulation of the impurity which can be separated by filtration then.

## 3. Sewage disposal:

- As discussed above the sewage water contains impurities like mud and dirt of colloidal size which are dispersed in the water.
- Like any other colloidal system, the colloidal particles (impurities) of sewage are also charged particles.
- These charged particles of impurities present in sewage may be removed by electrophoresis.
- For this purpose the sewage water is passed through a tunnel which is fitted with metallic electrodes and is maintained at a high potential difference.
- The charged particles of impurity present in the sewage water migrate to the oppositely charged electrodes which results in their coagulation.

## 4. Smoke precipitation:

- Smoke is also a colloidal system which mainly consists of charged particles of carbon dispersed in air.
- Smoke is a big problem for environment as it is the major source for air pollution. Removal of the dispersed colloidal particles from the air will solve the problem.
- For this, the process of electrophoresis is used.
- This is done in Cottrell precipitator. Smoke is passed through a chamber which contains a number of metal plates attached to a metal wire connected to a high potential source.
- The electrically charged colloidal particles of carbon present in air get discharged when they come in contact with the oppositely charged plates and fall down to the bottom.
- The clean hot air leaves the precipitator from an exit near the top.



Cottrell's Precipitator

## 5. Artificial rain:

- Clouds are also a colloidal system. In clouds, water vapors are present in mixture with the dust particles.

- The water molecules present in cloud have electric charge on them and are of colloidal size. So, if the charged on the molecules is neutralized somehow, they will start raining.
- Sometimes it is done by spraying some electrolytes over the clouds and the rain resulted from this is called artificial rain.

#### **6. Rubber industry:**

- Rubber is synthesized from the latex obtained from the rubber trees.
- This latex is an emulsion in which negatively charged particles of rubber are dispersed in water.
- For obtaining rubber, this latex is boiled because of which the rubber particles get coagulated.
- This coagulated mass is then vulcanized to solidify as natural rubber.

#### **7. Leather tanning:**

- Tanning is the process of treating the skins of animals to obtain the leather.
- Skin of animals is also a colloidal system in which the colloidal particles are positively charged.
- During the process, the charged particles of skin are coagulated using negatively charged material like tannin and some compounds of aluminum and chromium.

#### **8. Cleansing action of soaps:**

- As we have discussed earlier also, the soap solution is a colloidal system and it removes the oil and dirt by forming water soluble emulsions.

#### **9. Smoke screen:**

- Smoke screens are used to hide something by a layer of smoke. In generally it is used to hide the movement of troops.
- The smoke screens are also colloidal system in which the particles of titanium oxide are dispersed in air.

#### **10. Formation of delta:**

- Extensive deposits of sand and clay formed at the mouth of any river in sea at the site where the river falls into sea are called delta.
- The formation of delta is a very interesting natural phenomenon in which negatively charged colloidal particles of river are neutralized and thus coagulated by the positively charged ions of the salt present in sea.
- As it is very expected, the river water contains colloidal particles of sand and clay which are negatively charged. On the other hand the salty sea water contains a number of positive ions.
- When the water of river comes in contact with water of sea, the negative charge present on colloidal clay particles present in river water get neutralized by the positively charged ions present in sea because of which they get coagulated and deposit at the site.

## Adsorption Isotherm:

### Definition

Adsorption Isotherm is a curve that expresses the variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature.

### Freundlich Adsorption Isotherm

In 1909, German scientist Freundlich provided an empirical relationship between the amount of gas adsorbed by a unit mass of solid adsorbent and pressure at a particular temperature. It is expressed using the following equation –

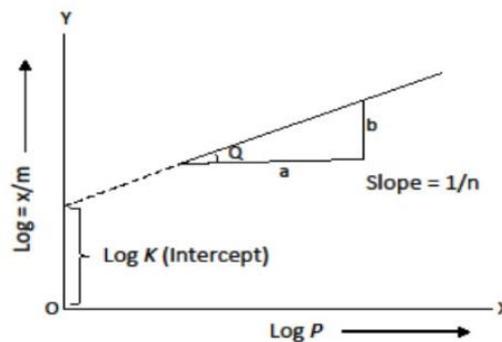
$$x/m = k.P^{1/n} \quad (n > 1)$$

where 'x' is the mass of the gas adsorbed on mass 'm' of the adsorbent at pressure 'P'. 'k' and 'n' are constants that depend on the nature of the adsorbent and the gas at a particular temperature.

The mass of the gas adsorbed per gram of the adsorbent is plotted against pressure in the form of a curve to show the relationship. Here, at a fixed pressure, physical adsorption decreases with increase in temperature. The curves reach saturation at high pressure. Now, if you take the log of the above equation –

$$\log x/m = \log k + 1/n \log P$$

To test the validity of Freundlich isotherm, we can plot  $\log x/m$  on the y-axis and  $\log P$  on the x-axis. If the plot shows a straight line, then the Freundlich isotherm is valid, otherwise, it is not. The slope of the straight line gives the value of  $1/n$ , while the intercept on the y-axis gives the value of  $\log k$ .



### Freundlich Isotherm

### **Limitations of Freundlich Isotherm:**

- Freundlich isotherm only approximately explains the behaviour of adsorption. The value of  $1/n$  can be between 0 and 1, therefore the equation holds good only over a limited range of pressure.
  - When  $1/n = 0$ ,  $x/m$  is constant, the adsorption is independent of pressure.
  - When  $1/n = 1$ ,  $x/m = k P$ , i.e.  $x/m \propto P$ , adsorption is directly proportional to pressure.
- Experimental results support both of the above mentioned conditions. At high pressure, the experimental isotherms always seem to approach saturation. Freundlich isotherm does not explain this observation and therefore, fails at high pressure.
- The Freundlich isotherm was followed by two other isotherms – Langmuir adsorption isotherm and BET adsorption isotherm. Langmuir isotherm assumed that adsorption is monolayer in nature whereas BET isotherm assumed that it is multi-layer.

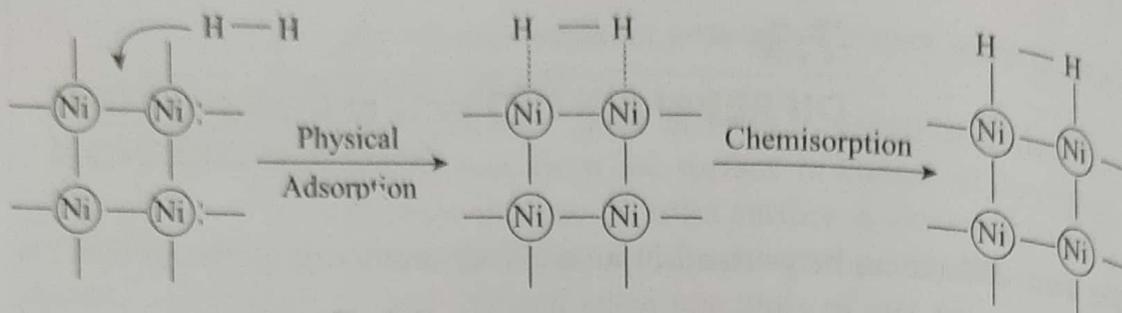


Fig. 7.3 Physisorption and chemisorption

Table 7.2 Differences between physical adsorption and chemical adsorption

Sl. No.	Physical adsorption	Chemical adsorption
1	Physisorption is due to weak van der Waals forces	Chemisorption is due to the formation of a chemical bond
2	Reversible in nature	Irreversible in nature
3	It decreases with increase in temperature	It increases with increase in temperature
4	It forms multimolecular layer on the adsorbent surface	It forms a unimolecular layer on the adsorbed surface
5	Heat of adsorption is less than 40 Kcal/mol	Heat of adsorption is in the range of 40–400 Kcal/mol
6	It does not show any specificity	It is very specific
7	The rate of adsorption increases with increase in pressure and concentration	The rate of adsorption decreases with an increase in pressure and concentration.
8	It is an instantaneous process	It may be rapid or slow.

## 7.5

### ADSORPTION OF GASES ON SOLIDS (SOLID-GAS INTERFACE)

The finely divided metals like nickel, platinum, iron, etc., and porous materials/substances like charcoal, silica gel, etc., provide a large surface area and the best solid adsorbents.

#### 7.5.1 Factors Influencing Adsorption of Gases on Solids

1. **Nature of adsorbent** Since adsorption is a surface phenomenon, it is evident that the greater the surface area, the greater is the adsorption. Due to this reason finely divided metals, charcoal and silica gel are excellent adsorbents because of their high porous structure and large surface area.
2. **Nature of gas** More easily liquefiable gases like ammonia, chlorine, etc., adsorb more readily than the permanent gases such as hydrogen, nitrogen and oxygen. The liquefaction of gases depends on its critical temperature

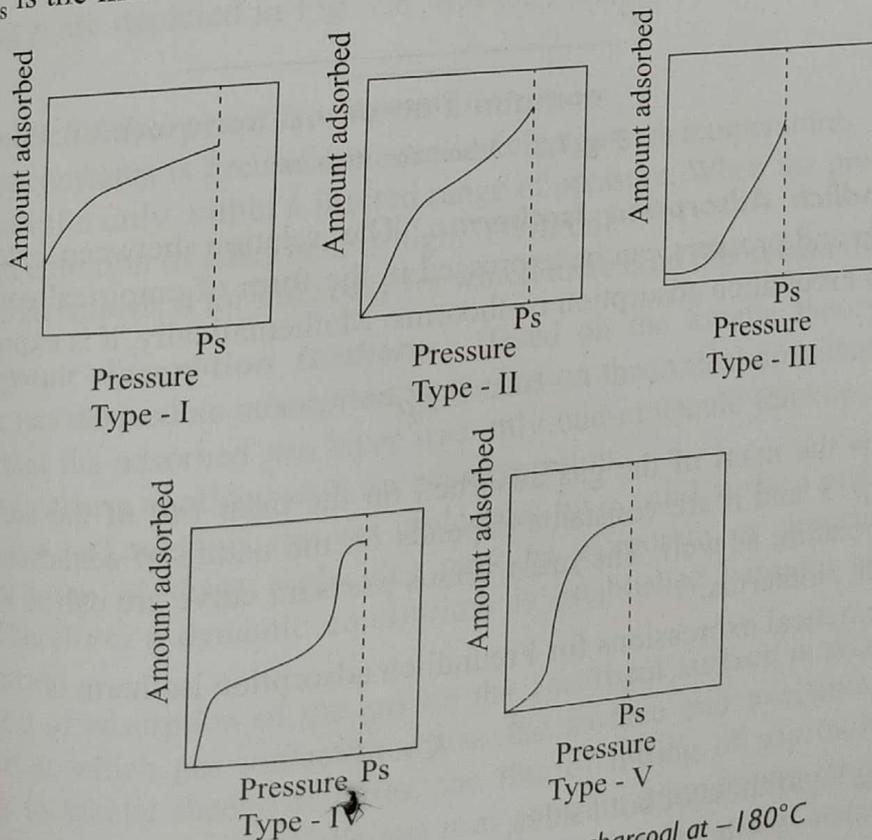
(The maximum temperature above which a gas cannot liquefy). The higher the critical temperature ( $T_c$ ), the more easily the gas liquefies and therefore more readily it is adsorbed.

3. *Effect of pressure* According to Le Chatelier's principle, the increase of pressure leads to an increase of adsorption, since dynamic equilibrium exists between the adsorbed gas and gas contact with the solid.
4. *Effect of temperature* Adsorption normally takes place with the evolution of heat. Physical adsorption increases at low temperature and decreases with the increase of temperature. Chemical adsorption increases with increase in temperature.

## 7.6

### ADSORPTION ISOTHERMS

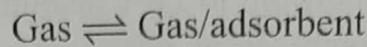
The relationship between the amount of gas adsorbed with an increase of pressure at constant temperatures is known as adsorption isotherms. Five types of isotherms have been observed in the adsorption of a gas on solids (Fig. 7.4) where  $P_s$  is the maximum adsorption occurred.



**Fig. 7.4** Type 1: Adsorption of hydrogen on charcoal at  $-180^\circ\text{C}$   
 Type 2: Adsorption of nitrogen on Pt/Fe at  $-195^\circ\text{C}$   
 Type 3: Adsorption of bromine on silica/alumina gel at  $80^\circ\text{C}$   
 Type 4: Adsorption of benzene on silica gel at  $50^\circ\text{C}$   
 Type 5: Adsorption of water vapour on activated carbon at  $100^\circ\text{C}$

### 7.6.1 Adsorption Isotherms

The phenomenon of adsorption of a gas on a solid adsorbent in a closed system is a reversible processes.



The amount of gas adsorbed on the adsorbent depends on the equilibrium temperature and pressure. At a constant temperature, the extent of adsorption will change with the variation of pressure.

Adsorption isotherm is a mathematical expression or graphical representation which shows the relationship between amount of gas adsorbed by the adsorbent under equilibrium pressure.

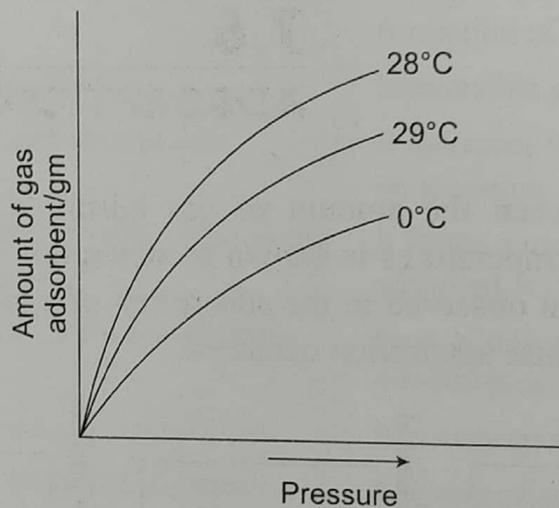


Fig. 7.5 Adsorption isotherm

(i) **Freundlich Adsorption Isotherms** The relation between intensity of adsorption and pressure can be expressed in the form of empirical equations is termed as Freundlich adsorption isotherms. Mathematically, it is expressed as

$$\frac{x}{m} = Kp^{1/n}$$

where  $x$  is the mass of the gas adsorbed on the mass ( $m$ ) of the adsorbent at pressure  $p$ .  $k$  and  $n$  are constants depends on the nature of adsorbent and gas and temperature as well. The mass versus pressure curve are called Freundlich adsorption isotherms.

Mathematical expressions for Freundlich adsorption isotherm is

$$\frac{x}{m} = K \times p^{1/n}$$

Taking logarithms of both sides,

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log p$$

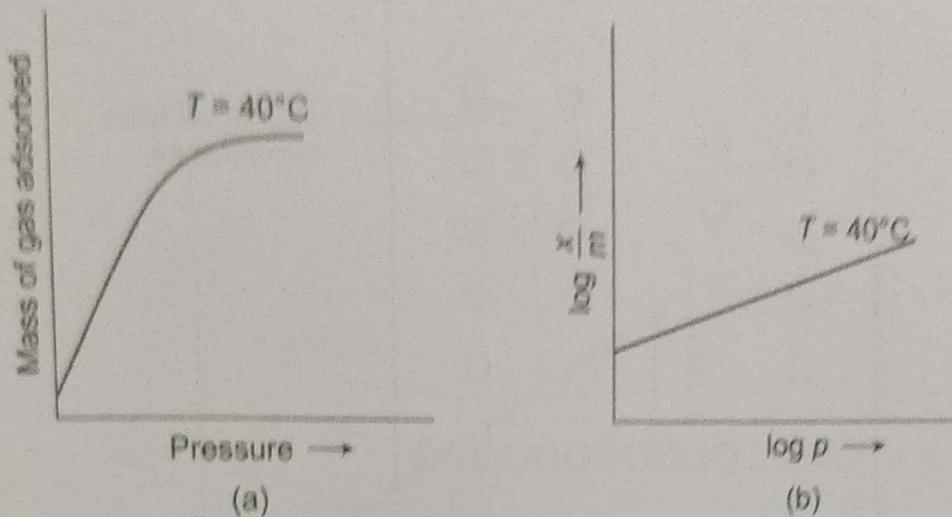


Fig. 7.6 (a) Freundlich isotherm for adsorption of ammonia over charcoal at 40°C (b) Plot of  $\log(x/m)$  vs  $\log p$  will give straight line for adsorption isotherms for ammonia on charcoal at 40°C

The above equation is a straight line. Hence, in practice, the plot of  $\log \frac{x}{m}$  vs  $\log p$  comes out to be a straight line and Freundlich isotherm stands verified. The adsorption isotherm for ammonia at 40°C and corresponding  $\log \frac{x}{m}$  versus  $\log p$  are depicted in Fig. 7.6. But the Freundlich isotherm fails at high pressure.

### (ii) Freundlich Adsorption Isotherms Limitation

- The constants in Freundlich equation change with temperature.
- It is valid only within a limited range of pressure. When the pressure and concentration of adsorbent is high, it will fail.
- It is an empirical formula only for which there is no theoretical foundation.

**(iii) Langmuir Adsorption Isotherm** Based on the kinetic theory of gas, Langmuir has derived an adsorption isotherm on theoretical consideration. He assumed that the adsorbed gas layer was only one-molecule thick. Hence, Langmuir isotherm confined well for chemisorption.

According to Langmuir, the gas molecules hit a solid surface and thus get adsorbed. Some of these molecules may be evaporate or desorbed fairly rapidly. Therefore, a dynamic equilibrium is established between adsorption and desorption.

The ratio of adsorption of the gas on the adsorbent surface is proportional to the rate at which gas molecules strike the surface and available surface. According to kinetic theory of gases, the rate of hitting of gas molecules is proportional to the pressure of the gas  $p$  at constant temperature (Fig. 7.7). If  $\theta$  is the fraction of surface covered by adsorbed molecules at any instances, the fraction uncovered surface =  $(1 - \theta)$ .

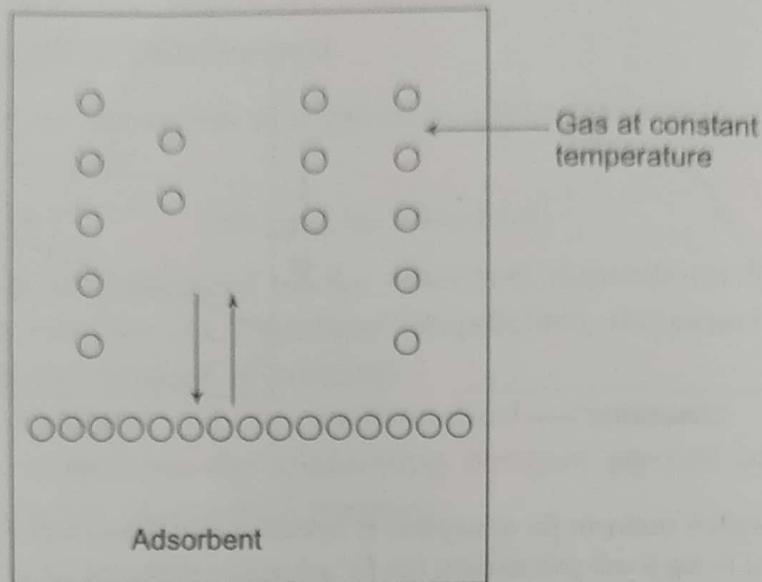


Fig. 7.7 Rate of gas molecules adsorbed is equal to rate of molecules desorbed at equilibrium

Therefore, rate of adsorption  $\propto (1 - \theta) P = K_1 (1 - \theta) P$   
where  $K$  is rate constant.

Rate of desorption  $\propto \theta = K_2 \theta$

where  $K_2$  is rate constant.

At equilibrium,

Rate of adsorption = Rate of desorption

$$\therefore K_1(1 - \theta)P = K_2\theta$$

$$K_1P - K_1P\theta = K_2\theta$$

$$\theta(K_2 + K_1P) = K_1P$$

$$\theta = \frac{K_1P}{K_2 + K_1P}$$

$$(K_2 + K_1P)$$

The mass of gas ( $x$ ) adsorbed per unit mass of adsorbent is directly proportional to fraction of surface covered ( $\theta$ ), i.e.

$x = K_3\theta$  where  $K_3$  is the proportionality constant

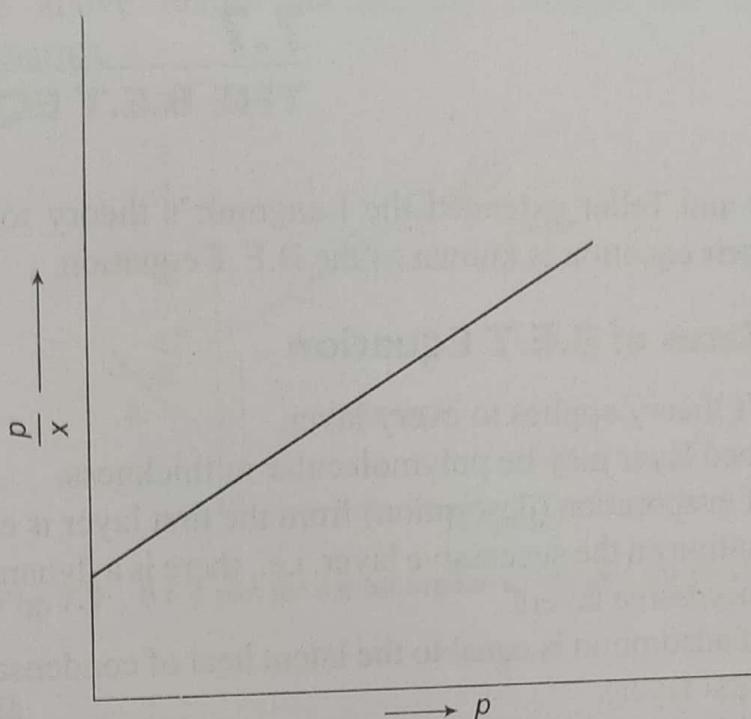
Thus,

$$x = \frac{K_1K_3}{K_1P + K_2} = \frac{\left(\frac{K_1K_3}{K_2}\right)P}{\left(\frac{K_1}{K_2}\right)P + 1} \quad \text{or} \quad x = \frac{A_p}{B_p + 1}$$

where  $A$  and  $B$  are constants. The above relation is known as Langmuir adsorption isotherm. The equation may be rewritten as

$$\frac{p}{x} = \frac{1}{A} + \left(\frac{B}{A}\right)p$$

The above equation is similar to straight line. A plot of  $p/x$  against  $p$  will be a straight line of intercept  $\frac{1}{A}$  and slope  $B/A$  (Fig. 7.8).



**Fig. 7.8** Langmuir adsorption isotherm

As stated above, the Langmuir isotherm can be written as

$$\frac{p}{x} = \frac{1}{A} + \frac{B_p}{A}$$

If pressure is very low, the factor,  $\frac{B_p}{A}$  may be ignored and the equation become

$$x = Ap$$

If  $p$  is high, this factor  $\frac{1}{A}$  may be ignore and isotherm becomes

$$x = A/B$$

Therefore, at low pressure, the amount of gas adsorbed is directly proportional to  $P$  (pressure) and at high pressure, the mass adsorbed ( $x$ ) reaches a constant value ( $A/B$ ) when the surface is completely covered with one molecules thickness layer of gas. At this, stage, adsorption is independent of pressure. Hence,

$$x = kp' \quad \text{at low pressure}$$

$$x = kp_0 \quad \text{at high pressure}$$

At intermediate pressure, we could write the expression as

$$x = kp^n$$

where  $n$  lies between 0 and 1.

### Limitations of Langmuir Theory

1. Langmuir states that a unimolecular layer of gas is adsorbed on a solid surface. But in actual practice, much thicker films have been reported.
2. Langmuir theory cannot explain all the five types of adsorption isotherms.

## 7.7

## THE B.E.T EQUATION

Brunaur, Emmet and Teller extended the Langmuir's theory to the multilayer adsorption and their equation is known as the B.E.T equation.

### 7.7.1 Postulates of B.E.T Equation

1. Langmuir's theory applies to every layer.
2. The adsorbed layer may be polymolecular in thickness.
3. The rate of evaporation (desorption) from the first layer is equal to the rate of condensation on the successive layer, i.e., there is a dynamic equilibrium between successive layers.
4. The heat of adsorption is equal to the latent heat of condensation of vapour (after the first layer).
5. Condensation forces are the main forces in adsorption.
6. The heat of adsorption in each layer is involved in each of the evaporation processes (except the first layer).

On the basis of the above postulates, B.E.T equation can be expressed as

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C_1 - 1)}{V_m C} \left( \frac{P}{P_0} \right)$$

where  $V$  is the volume of the gas adsorbed at the pressure  $P$ ,  $V_m$  is the volume of adsorbed when the surface of the solid is covered completely with a monolayer of adsorbed molecules of the gas,  $C$  is a constant depending upon the nature of the gas and is expressed as

$$C = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

where  $E_1$  = the heat of adsorption in the first layer.  
 $E_L$  = the heat of liquefaction of the gas.

### 7.7.2 Verification of B.E.T Equation

A plot of  $P/V(P_0 - P)$  against  $P/P_0$  should give a straight line

$C$  = constant for given gas.

$V_m$  = constant for the given gas-solid system.

The results obtained in the case of adsorption of nitrogen on silica gel at  $-183^\circ\text{C}$  are given in Fig. 7.9. The slope of the straight line is  $(C - 1/V_m C)$  and the intercept of the 'y' axis is  $(1/V_m C)$ .  $V_m$  and  $C$  can be evaluated from the slope and intercept. The surface area of adsorbed can be calculated by multiplying  $V_m$  with the number of molecules required to form a monomolecular layer.

Therefore, the above theory successfully explains the complex types of adsorption isotherms.

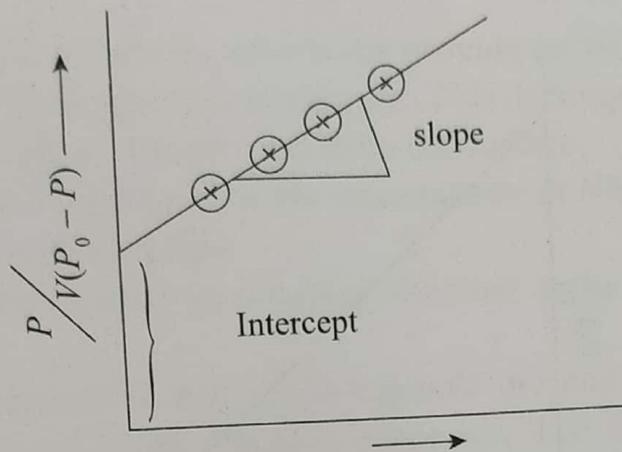


Fig. 7.9 B.E.T plot for the adsorption of nitrogen gas on silica gel

## 7.8

### ADSORPTION OF SOLUTES FROM SOLUTIONS (SOLID-LIQUID INTERFACE)

Solid substances which have porous or finely divided in nature can also adsorb tendency for dissolved substances from solutions. In this kind, activated charcoal is used to remove coloured impurities from solutions. Charcoal is also adsorb many dye stuffs. When an active acid solution is shaken with activated charcoal a portion of acetic acid is removed by the phenomenon of adsorption and resultant solution concentration is decreased.

Adsorption from solution is followed the same guiding principle of adsorption of gases by solids subjected to the following factors.

- specifically, some adsorbents have tendency to adsorb some specific solutes effectively compare to blur solutes.
- with increase of temperature, the adsorption ability decreases.
- the adsorption capacity increases with increase of surface area of adsorbents.
- solute adsorption in solutions also establish equilibrium between the amount adsorbed and concentration of solute in a solution.

The exact mechanism of adsorption from solution is not clear. But there is a limit to the adsorption with the given mass of adsorbent. So adsorption takes place when a unimolecular layer is formed on the surface of adsorbent. Freundlich isotherm taking concentration in place of pressure which is obeyed by adsorption from solution.

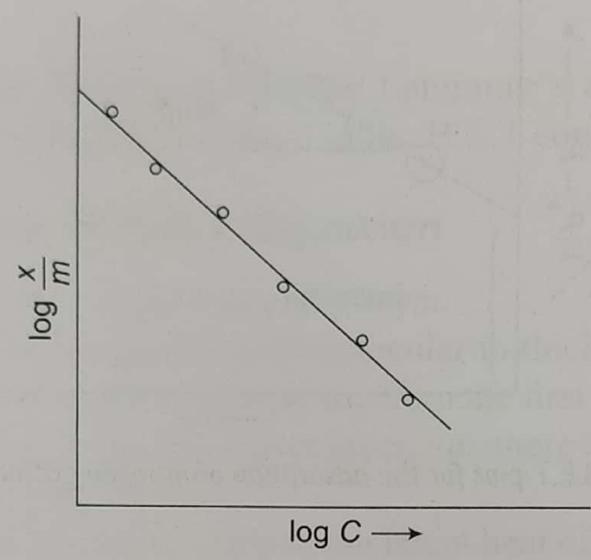
Therefore,

$$\frac{x}{m} = k \times C^{1/n}$$

where  $x$  = mass of solute adsorbed on a  $m$  mass of adsorbent

$C$  = equilibrium concentration of solution

$k, n$  = constants



**Fig. 7.10** Verification of Freundlich equation for acetic acid on charcoal at 25°C

By taking logarithm for the above expression

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

from the above equation, plot of  $\frac{x}{m}$  against  $\log C$ , should be a straight line which is a variety test for Freundlich isotherm (Fig. 7.10). Experimentally it is tested by plotting the experimented values of  $\frac{x}{m}$  and  $\log C$  with estimate for adsorption of acetic acid on charcoal at 25°C.

**Limitations**

1. It is confirmed for monolayers only. But thicker films also reported.
2. According to Langmuir, adsorption is independent of temperature. But experimentally, shows, it decreases with temperature.

**Advantages**

1. Langmuir was explained chemisorption.
2. Langmuir theory is better satisfactory than Freundlich isotherm.

**Applications of Adsorption**

Adsorption finds numerous applications in laboratory as well as industry. The main applications as follows:

1. Partially evacuated vessel connected to container having activated charcoal. If the container cooled with liquid air, the charcoal adsorb gas and created high vacuum. This processes is used in high vacuum equipment as Dewar flask for storage of liquid air or liquid hydrogen.
2. Alumina and silica gel are used as adsorbents for remove of moisture and controlling humidity of rooms

3. Most of gas masks devices provided with adsorbents such as activated charcoal. Thus adsorbents remove poisonous gases and purify the air for breathing.
4. In heterogeneous catalysis, adsorbents provide active surface for reactant molecules and form adsorption complex. This decomposes to form product molecules and which are take off from the surface.  
Finally divided iron is used in the manufacture of  $\text{NH}_3$  and Nickel is used in the hydrogenation of oils.
5. Animal charcoal is used for removal of colour in the manufacture of cane sugar.
6. For the purification of low grade sulphide ore and free from silica and earthy matters by Froth flotation processes. The stabilized air bubbles by detergent adsorbed mineral particles method with oil and raise to the surface. The impurities are stickened at the bottom.
7. Adsorption play vital role in the chromatographic analysis. Mixtures of small quantum of organic substances can be well separated using chromatography with the help of adsorption principle. Mixture of organic gases also separated by selective adsorption of gases by liquids in gas chromatography.
8. In Zeolite technique, Zeolites adsorbs hardness causing ions  $\text{Ca}^{2+}/\text{Mg}^{2+}$  from water and outlet of warming water is free from  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ions.

## NANOMATERIALS

Nano chemistry is a new discipline concerned with unique properties and associated with arrangement of atoms/molecules on a nanoscale range (between 1–10 nanometres) between that of individual building blocks. It also plays an important role in the synthesis of nano-building blocks of desired shape, composition, size and surface structure with optical target and controls self-assembly of these building blocks at different scale lengths.

The term 'nano' stands for 1 billionth of a metre in a physical scale length. Nano chemistry is defined as 'the study of synthesis and analysis of materials in nanoscale range (1–10 nanometres) including large organic molecules, inorganic cluster compounds and metallic or semiconductor particles'.

Synthesis of nanoscale inorganic and organic materials is important because small size endows these particles with unusual structural and optical properties which find numerous applications in catalysis and electro-optical devices. For example, the electronic structures of metal and semiconductor crystals differ from the isolated atoms and bulk materials. Even metals show non-metallic band gaps in 1–2 nm sized nano crystals in the case of 'Ag' clusters (band gap decreases with an increase in cluster size). In a similar way, nano sized (1–2 nm) gold metal particles exhibit unusual catalytic activity.

The synthetic way for preparation of nanomaterials that are inspired by biological processes results in the deposition of inorganic materials such as bones, teeth and shells. The deposition and growth of inorganic materials through biological processes such as bones and teeth is called 'Biomineralisation'.

The use of nanomaterials had been recognised even in the fourth century A.D. Roman glass makers fabricated coloured articles of glass, embedded with

nano particles of silver and gold. Some of the important developments in the area of nanotechnology in the chronological order are as follows:

- Fabrication of nanosized quantum wells in 1970 by thin fibres epitaxial technique.
- Synthesis of fullerenes ( $C_{60}$ ).
- Invention of Scanning Tunnelling Microscope (STM) and atomic force microscope (AFM) for viewing.
- Characterisation and manipulation of nano structures.
- Fabrication of single electron transistor.
- Synthesis of carbon nanotubes, development of photonic crystals, molecular switches and fixed effect transistors during 1990s.

Some of the examples of nanomaterials are:

- (a) nano particles of ceramic oxides, semiconductors and magnetic materials.
- (b) nano crystals and clusters of metals, quantum dots.
- (c) nano wires and rods of metals and semiconductor oxides, nitrides and sulphides.
- (d) carbon nano tubes, layered metal chalcogenides.
- (e) nano porous solids of zeolites and phosphate.
- (f) super lattices of three-dimensional structures of metals, magnetic materials and semi-conductors.

These materials have potential applications in materials technology, nanoelectronics, information technology, medicines and semiconductors.

### 7.13.1 Classification of Nanomaterials

Nanomaterials are classified into 3 types based on atoms/molecules array:

- (a) Materials with one dimension in the nano scale.  
For example, Thin films, surface coatings.
- (b) Materials that have two dimensions in nano scale.  
For example, Nanowires, nano-tubes, Biopolymers, inorganic nano tubes
- (c) Materials in 3 dimension in nano scale are quantum dots.  
For example, Tiny particles of semiconductors materials such as nanometre sized grains, fullerenes, nano particles, dendrimers.

### 7.13.2 Nanomaterial Synthesis

We can classify the synthesis routes differently for nanostructural materials. One of the classification based on the starting physical state of the material, which are solid, liquid and gas. In vapour condensation, the starting materials is gas phase. Another techniques are sol-gel, chemical and electrochemical deposition and solidification processing use liquids as the starting material. The solid material is used as starting material in ball-milling and nanolithography techniques.

The most popular way of classifying the synthesis routes is based on how the nanostructures are built and such an approach leads to two routes, namely the bottom-up and the top-down approaches. In the bottom-up approach, individual atoms and molecules are brought together (generally, starting materials are gas and liquid). In the top-down approach, macro size crystalline materials convert into nanocrystalline materials by fragmentation (Fig. 7.19).

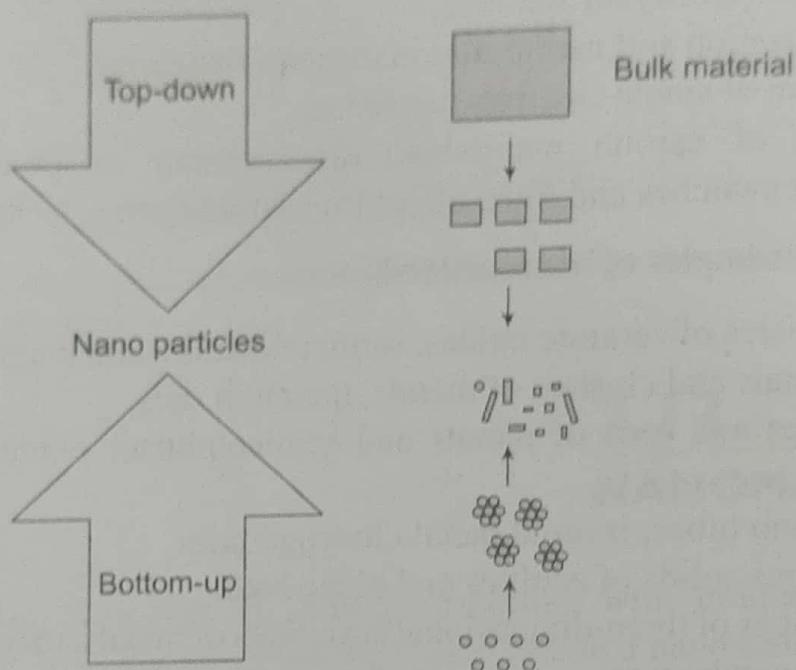
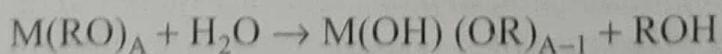


Fig. 7.19 Nanomaterial synthesis

**(i) Sol-gel Process** The sol-gel process is used for producing metal oxide and ceramic powder with high purity and homogeneity. In this process, we generate a colloidal suspension (Sol) and gelation of the sol to form a network in a continuous liquid phase (gel). In the sol-gel process, reactive metal materials involved hydrolysis, condensation and polymerisation reactions.

Organometallic compounds contain organic ligands with metal atoms. In the preparation of methoxide ( $\text{CH}_3\text{O}^\ominus \text{M}^+$ ) ethoxide ( $\text{C}_2\text{H}_5\text{O}^\ominus \text{M}^+$ ) is reacted between metal and alcohols. During the hydrolysis, the alkoxy ( $-\text{OR}$ ) ligand is replaced by the hydroxo ligand, i.e.

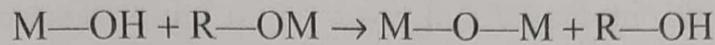
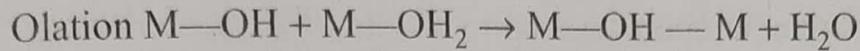


The reaction mechanism involves the addition of a hydroxyl group to the positively charged metal ion ( $\text{M}^+$ ) followed by the elimination of ( $\text{OH}^-$ ), ROH.

Some factors influence the hydrolysis reaction. These are the nature of the solvent, temperature, nature of the alkyl group, pH, and reagent content.

The condensation eliminates either alcohol or water to produce metal oxide or hydroxide linkage. Here, two mononuclear complexes of M, each comprising only one metal, can react with one another to form a polynuclear complex which consists of two metal atoms. Generally, condensation occurs in a polar group of substrates. These are metal-bonded hydroxyl represented as  $\text{M}-\text{OH}$ . Olation and oxidation lead to condensation. Olation is a reaction,

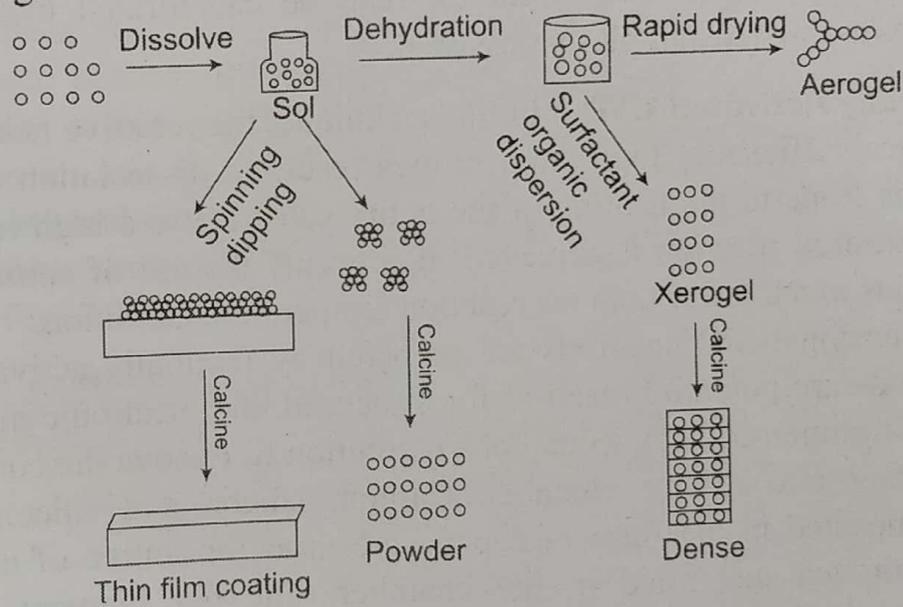
by which hydroxo or of bridge (M—OH—M) is formed between two metal cations and Oxo bridges are formed through oxidation reaction.



Under acid conditions, three-dimensional solid network consisting of extended linear M—O—M chain polymers are developed acid condensation process followed by three steps in inorganic polymers:

- (i) polymerisation of monomer units to form particles.
- (ii) growth of polymers.
- (iii) linking of particles into chains, then solid networks that extend throughout the liquid medium, thickening into a gel.

Schematic representation of sol-gel method in the synthesis of nanomaterials shown in Fig. 7.20.



**Fig. 7.20** Schematic representation of sol-gel process

1. Formation of different stable solutions of the alkoxide or solvated metal precursor.
2. In poly condensation reaction formed, an oxide or alcohol bridged network (gel).
3. Separation of liquid from gel, during which the polycondensation reaction on continue until the gel transforms into a solid mass accompanied by contraction of the gel network and expulsion of the solvent from gel pores.
4. When dry, the gel, water and other volatile liquids are removed the drying process has itself been broken into four steps
  - (i) the constant-rate period,
  - (ii) the critical point,
  - (iii) the falling rate period, and
  - (iv) the second falling rate period isolated by thermal evaporation, the solvent forms a xerogel. When the liquid the gel is removed above its critical temperature and pressure in an autoclave, the capillary pressure can be eliminated. The product thus obtained is referred to as *aerogel*.

5. During dehydration, surface-bound M—OH groups are removed, thereby stabilizing the gel against rehydration. This is achieved by calcining the monolith at temperatures up to 800°C.
6. Organic, inorganic and bio-organic molecules are doped in silica glass using sol-gel procedure. Most existing organic and bio-organic molecules cannot be entrapped in glass, because high temperature (1000°C) is required to elevate organic and bio-organic molecules removed. Ceramic materials are also prepared by using sol-gel process.

**(ii) Chemical Vapour Deposition** Chemical Vapour Deposition (CVD) is useful technique for producing nanomaterials such as metallic, ceramic and semiconducting thin films and coatings. In this process, the material is heated to form a gas then allowed to deposit as solid on surface under vacuum. Deposition by chemical reaction to form a new product which differs from the material volatilised. The CVD technique can be categorized into thermally activated, laser-assisted and plasma-assisted.

**(iii) Thermally Activated CVD** In this technique, the resistive heating of hot wall provides sufficiently high temperatures resulting dissociation of gaseous species. This leads to the heating of the entire substrate to a high temperature before the desired reaction is achieved. It prevents the use of substrates with melting points much lower than the reaction temperature condition.

One-dimensional SiC nanorods are prepared by thermally activated CVD. SiC nano rods are potential material for structural and electronic applications silicon wafer immersed in aqueous  $\text{FeNO}_3$  solution to remove the contaminates before placing into reactor chamber. Carbon, silicon and silicon dioxides powder compacted in the form of a plate are used for source of carbon and silicon. Hydrogen gas filled in the chamber. The hot filament dissociate molecular-level. Hydrogen into atomic hydrogen.

The  $\text{Fe}(\text{NO}_3)_3$  on Si water surface were reduced by high concentration of hydrogen atoms to iron nano-sized particles which act as a catalyst. The hydrocarbons and silicon mono-oxide radicals are orderly formed due to the activation by hot filaments. The nano rods are formed as diameters about 20–70 nm and 1 mm in length.

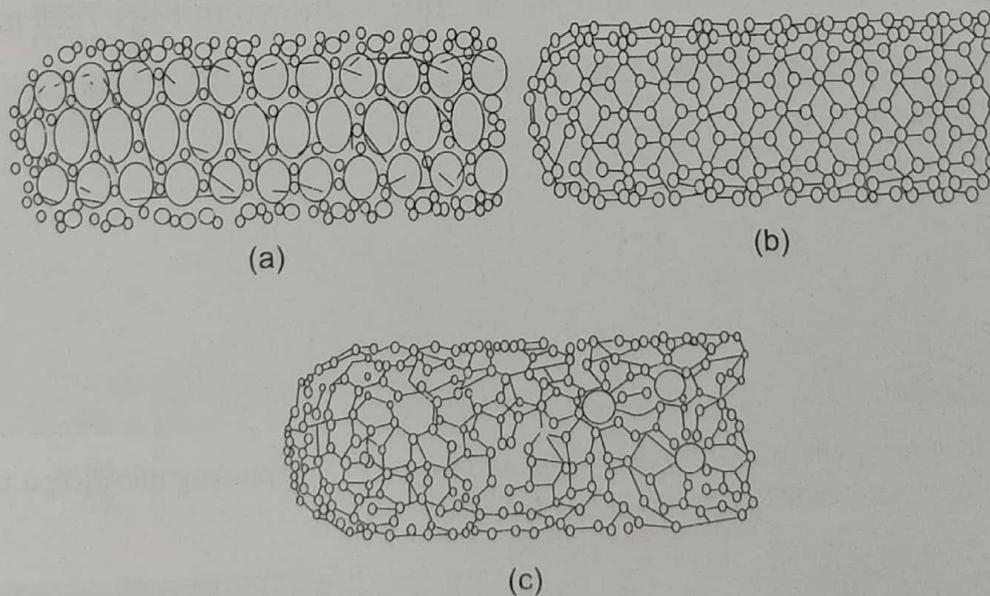
### 7.13.3 Properties of Nanomaterials

The properties of nanomaterials depend on size, crystal structure and surface characteristics. The two principal factors for the properties of nanomaterials to differ significantly from other materials are: (i) to increase relative surface area, and (ii) quantum effect. These two factors can change or enhance properties such as reactivity, strength, electrical properties and optical characteristics.

- (a) *Size*: Nano crystals have a large surface area. Colloidal particles have a large surface area and remain single crystalline and hence are named as nanocrystals. For example, Nano crystals of 10 nm size (containing about 1000 atoms) have approximately 15% of its atoms on the surface and smaller nano crystal of 1 nm size will be about 30% of its atoms on

the surface. Hence, size of crystal is important for available active surface area.

- (b) *Catalytic activity*: Catalytic activity of nano particles in the form of colloids and nano clusters have been investigated in a wide variety of reactions in homogeneous and heterogeneous phases. For example,
- (i) Rhodium hydrosols have been shown to be effective catalyst for hydrogenation of Olefins dissolved in organic phase.
  - (ii) Palladium colloids have been shown to catalyse reactions in reduction of carbon-carbon multiple bonds in presence of formic acid. It is also used in reduction of nitriles and nitroarenes.
  - (iii) Cortex catalyst, i.e., palladium metal nano particle (10 nm) on alumina support shows high catalytic activity for olefins hydrogenations.
  - (iv)  $\text{MoS}_2$  has shown catalytic activity for methanation of  $\text{CO} + \text{H}_2$  at low temp.
- (c) *Electrical properties*: Nanomaterials shows electrical properties vary between semiconducting to metallic depending upon the diameter and chirality of the molecules. For example, carbon nano tubes reveal electrical properties and act as semiconducting and metallic nature on the basis of chirality and diameter of a tube. Carbon nano tubes have been identified and show three structures, namely, arm chair, zigzag and chiral structure (see Fig. 7.21).



**Fig. 7.21** Structures of carbon nanotubes: (a) arm chair, (b) zigzag, and (c) chiral

If  $(n - m)$  is a multiple of 3, the tube is metallic, otherwise, the tube is semiconductor metallic. Nano tubes have high electrical conductivity, to be about billion amperes/cm<sup>2</sup> (much higher than copper wires).

The high electrical conductivity of nano tubes is mainly due to negligible amount of defects and hence, they possess low resistance. Nano tubes of  $\text{MoS}_2$  and  $\text{WS}_2$  have shown semiconductors at low temperature due to electrical conductivity.

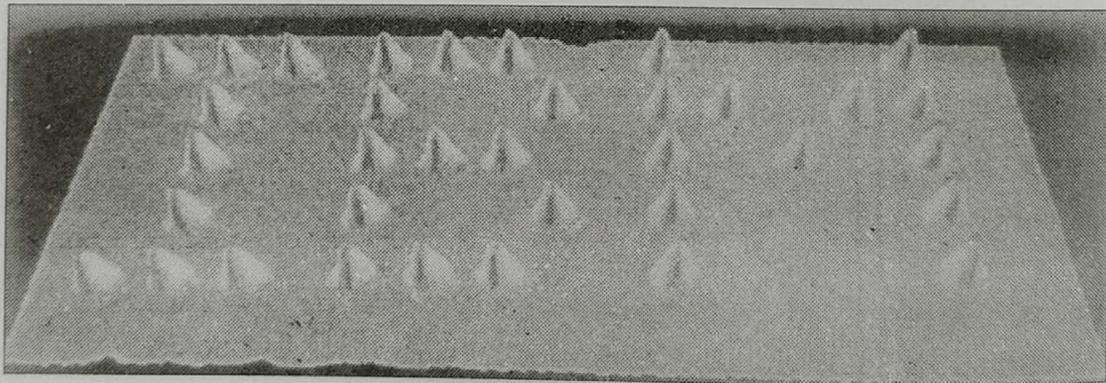
- (d) *Mechanical properties*: Nanomaterials exhibit unusual mechanical properties. For example, the tensile strength of carbon nano tube is about

604 pa (i.e. > 20 times that of steel). They are among the stiffest and strongest fibres known.

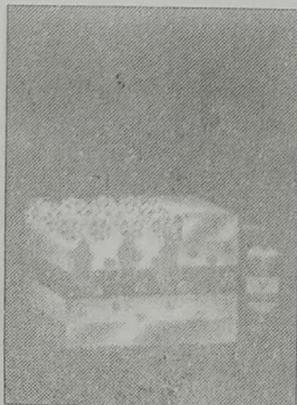
- (e) *Optical properties:* Nanomaterials that are provided large surface area exhibit better optical properties. For example, silicon nanowires show strong photoluminescence characteristics. Indium phosphide nano wire shows isotropic photoluminescence with lot of applications in constructing polarisation sensitive photodetectors. Zinc oxide nano wire exhibits room temperature ultraviolet laser action.
- (f) *Semiconductors:* Most of the nanomaterials exhibit semiconductivity properties. For example, carbon nanotubes, nanowires, some metal oxides ( $\text{MoS}_2$  and  $\text{WS}_2$ ) and inorganic nanotubes show, semiconductor properties. Semiconductor nano wires can be used as components in making field effect transistors,  $P - n$  diodes, bipolar junction transistors and complementary inverters.
- (g) *Superconductors:* There are some nanomaterials which show superconductivity properties. Nanotubes of  $\text{NbS}_2$  and  $\text{NbSe}_2$  are metallic in nature with  $\text{NbSe}_2$  becomes a superconductor at low temperature.

Some of the important nanomaterial structures and their applications are shown in Figs 7.22 to 7.25.

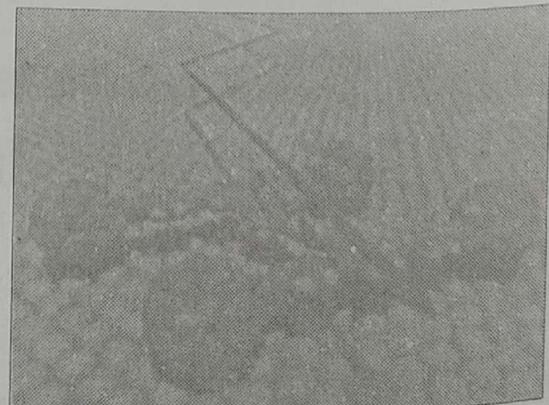
Certain statistical information on producing of nano materials and universities involved in the research as on 2003 is shown in Figs 7.26 and 7.27.



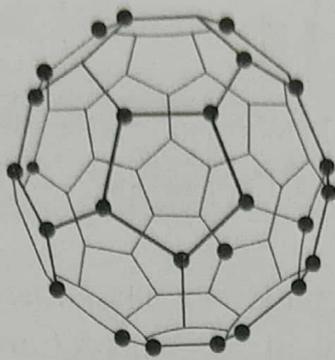
**Fig. 7.22** IBM researchers manipulating xenon atoms scanning tunnelling microscope to move 35 xenon atoms to spell out the letters "IBM"



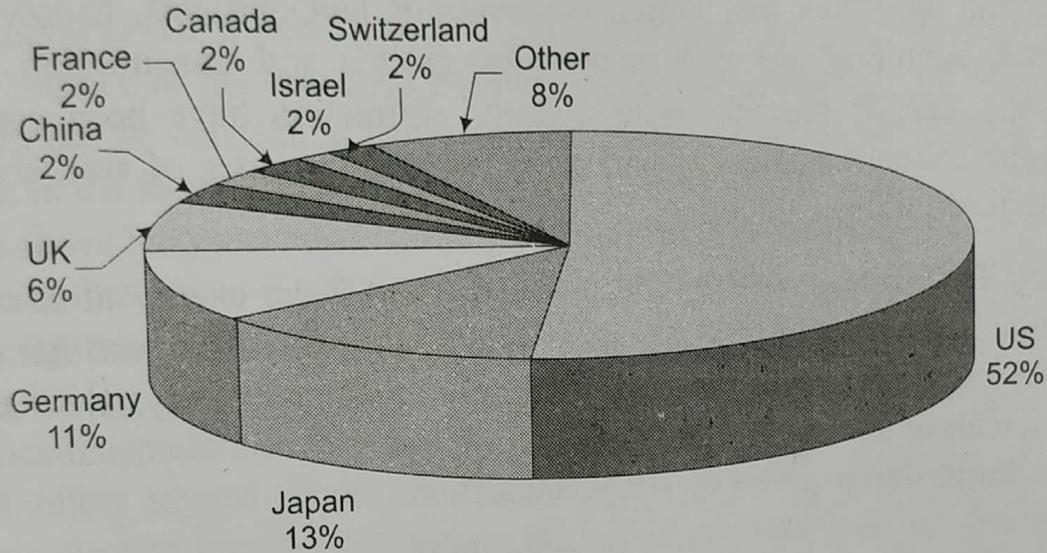
**Fig. 7.23** Graphical representation of a rotaxane useful as a molecular switch



**Fig. 7.24** Space-filing model of the nanocar on a surface, using fullerenes as wheels

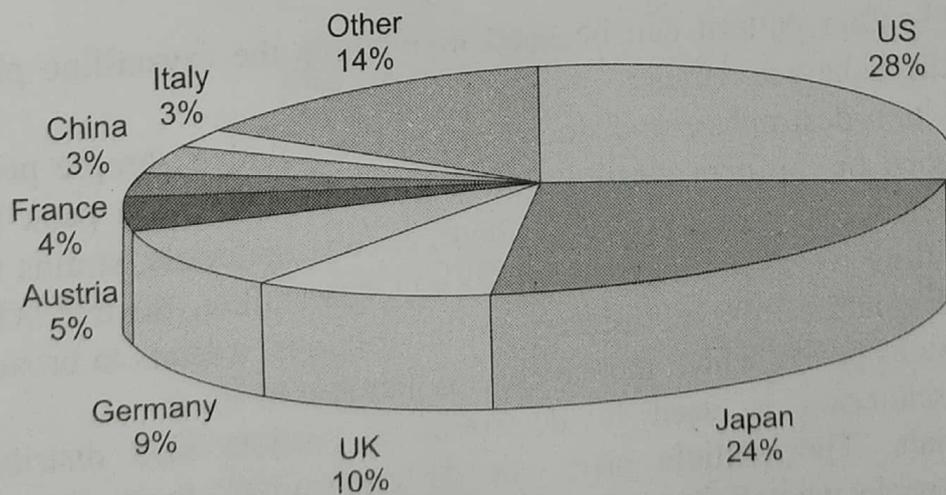


**Fig. 7.25** Structure of fullerene



**Note:** Other includes Australia, Netherlands, Taiwan, Austria, Sweden, Finland, Korea, Russia, Italy, and Spain.  
 Source: Cientifica 2003.

**Fig. 7.26** Percentage of companies producing nanomaterials by country (as of June 2003)



**Note:** Other includes Australia, Spain, Sweden, Switzerland, Belgium, Netherlands, Israel, Poland, Russia and Taiwan.  
 Source: Cientifica 2003.

**Fig. 7.27** Percentage of universities and institutions involved in nano-research by country (as of June 2003)

# CHARACTERISATION OF SURFACE BY PHYSICO-CHEMICAL METHODS

Characterisation of nanomaterials and nanostructures has been largely based on certain critical advancement in conventional characterisation methods developed for bulk materials. For example, X-ray diffraction (XRD) has been widely used for the determination of crystalline character, crystallite size, crystal structures and lattice constants of nanoparticles, nanowires and thin films. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) together with electron diffraction have been commonly used in the characterisation of nanoparticles to get an idea of size, shape and crystal defects in these materials.

**1. X-Ray Diffraction (XRD)** The fact that the wave energy of X-rays and interatomic distance in a crystal are of same order led to suggest that crystals diffract X-rays. Thus, XRD is extensively used to study the crystal structure of solids, defects and stresses.

The relationship is given by Bragg's equation.

$$n\lambda = 2d \sin \theta$$

where  $n$  = order of the diffraction

$\lambda$  = wavelength of X-ray beam

$D$  = interplanar distance

$\theta$  = diffraction angle

The diffraction pattern can be used to identify the crystalline phases and their structural characteristics.

XRD is non-destructive and does not require detailed sample preparation. Homogeneous or uniform elastic strain shifts the diffraction peak positions, without a change in peak profile. In homogeneous materials, strains may vary from crystallite to crystallite or even a single crystallite. So that XRD gives average information from all such crystallite volumes, it leads to broadening of the diffractions peaks, which increases with increase in  $\sin \theta$ .

X-ray scattering is used to determine a particle size distribution of nanomaterials. The particle size can be determined from the width of diffraction peaks using Scherrer's equation.

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where  $D$  = the average crystallite size perpendicular to the reflecting planes.

$\lambda$  = X-ray wavelength.

$\theta$  = diffraction angle.

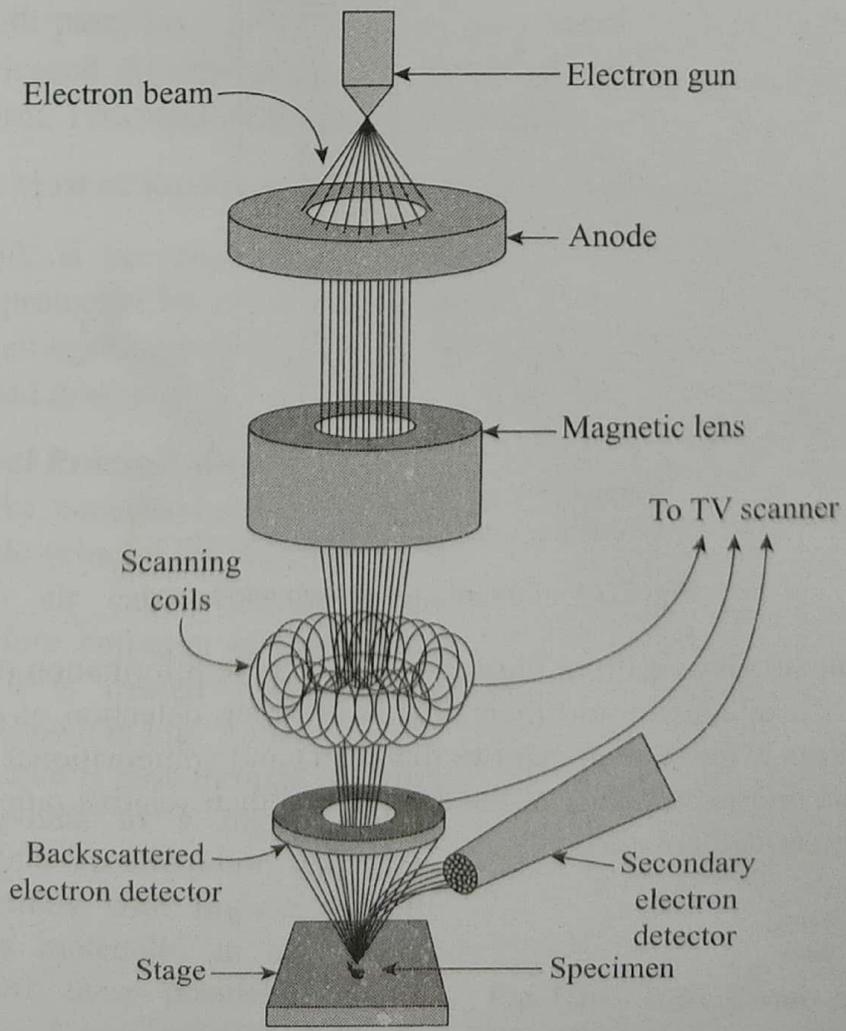
$\beta$  = the width of the peak in radians due to the finite size of the crystal.

$K$  = Scherrer's constant close to unity.

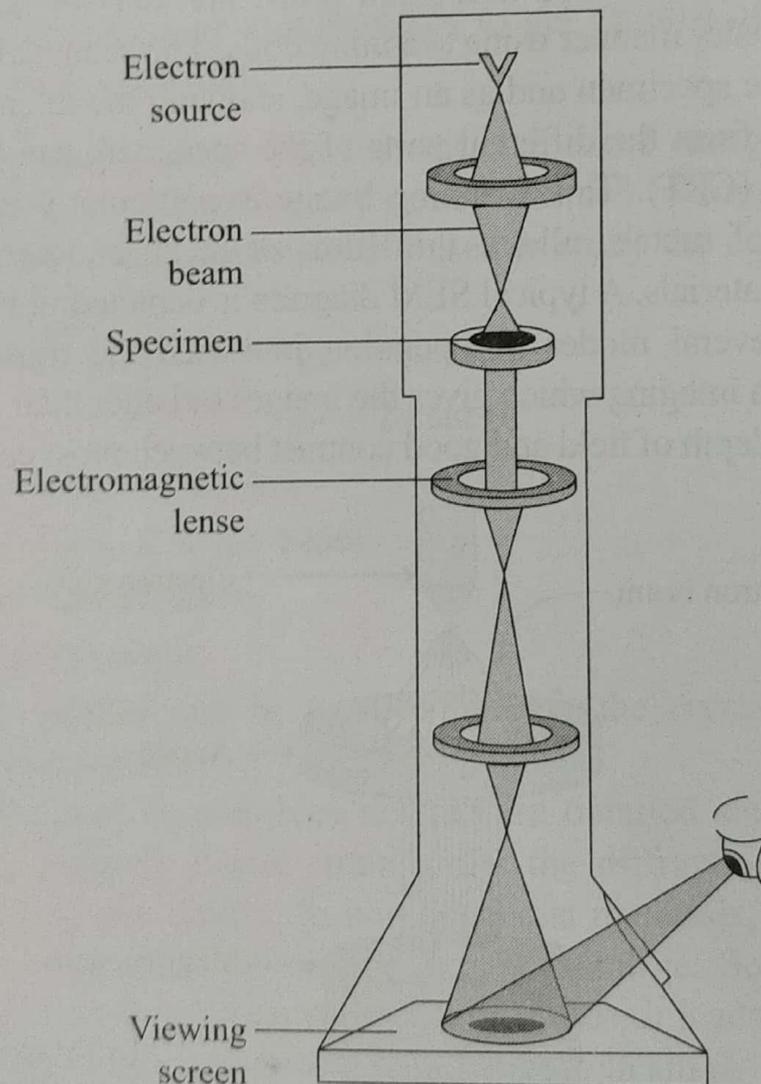
However, nanoparticles often form twinned structures and hence Scherrer's formula may not always give true particle sizes. So that X-ray diffraction provides only an average crystallite size.

**2. Scanning Electron Microscopy (SEM)** The surface morphology (shape, size and arrangement of the particles making up the object that are lying on the surface of the sample, detectable features limited to a few nanometers), homogeneity and grain size of the deposited film can be studied by SEM. It is the most versatile and commonly used instrumental technique to study the surface topology (surface features of an object, detectable features are limited to a few nanometers) and particle size. The low energy secondary electrons emitted from the surface of the specimen gives the basis for a different type of imaging. The beam can be concentrated to a small probe that may be detected across the specimen in the faster manner using scanning coils. The secondary electron can be detected above the specimen and as an image, showing the intensity of secondary electrons emitted from the different parts of the specimen, can be displayed in a cathode ray tube (CRT). This scanning image is particularly useful to examine the morphology of metals, alloys, thin films of metal and semiconductors and nanocrystalline materials. A typical SEM diagram is depicted in Fig. 7.28.

SEM offers several modes of operation in which the most widely used is secondary electron imaging which gives the images of better than 100 Å resolutions almost unlimited depth of field and good contrast between most cell components.



**3. Transmission Electron Microscopy (TEM)** In TEM, an electron beam with energy of 10 Kev or more (up to 3 MeV) is allowed to go through a thin specimen. Scattering occurs when the electron beam interacts with matter. Scattering may be of no energy change (elastic) or energy change (inelastic). Elastic scattering can be in the form of rings in the case of polycrystalline materials. High-resolution TEM (HRTEM) is one of the most powerful tools of nanoscience. Interaction of electron with the sample produces elastic or/and inelastic scattering. Most of the studies are done with the elastically scattered electrons which form the bright image. Electrons emerging from the sample, after a series of interactions with the atoms of the target material or transferred to the viewing screen to form an image, either diffraction patterns or particle images, as shown in Fig. 7.29.



**Fig. 7.29** Transmission electron microscope

TEM analysis gives morphology, crystallographic information (arrangement of atoms in the specimen and their degree of order, detection of atomic-scale defects in areas a few nanometers in diameter) and compositional information (the elements and compounds of the sample and their relative ratios, in areas a few nanometers in diameter).

## 7.15.1 Applications of Colloids

Colloids play an important vital role in our daily life and industry. To understand some of natural phenomena happening around us, knowledge on colloidal chemistry is essential. A few applications of colloids are described below:

**(i) Mediums** As colloidal medium is finely divided, an effectively and easily absorbed in having systems. Many ointments for skin application consists of medicinal compound dissolved in gel and made into an emulsion with water. Antibiotics such as penicillin and streptomycin are produced in the form of colloids suitable for injections. Trivalent  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  colloids are employed in blood coagulation.

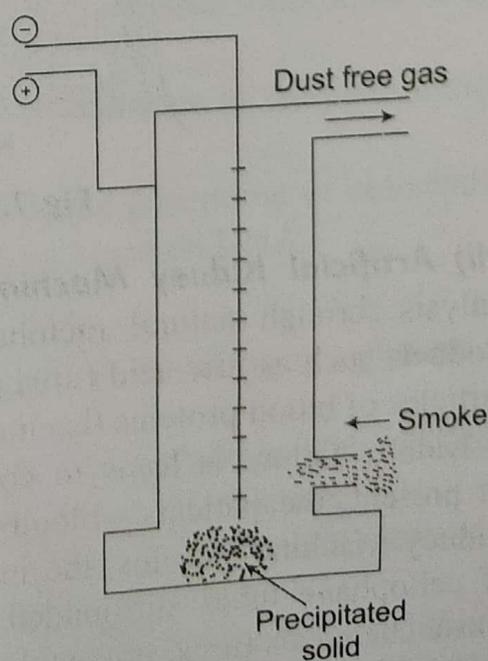
**(ii) Thixotropic or Non-drip Paints** All the paints are colloidal dispersion of pigment in a liquid medium. Modern thixotropic paints containing long chain polymers. At rest polymer molecules are coiled and entrap much dispersion medium. The resultant paint is a semi-solid gel structure. When shear stress is applied with paint brush, the coiled molecules straighten and the entrapped medium is released. As soon as brush is removed, the liquid paint reverts back to semi-solid form. This renders the paint as non-drip.

**(iii) Foods** Most of food materials are colloidal in nature.

**Example** Milk is an emulsion of butter fat in water protected by a protein called casein, fruit jellies, whipped cream, gelatin dessert and salad dressing.

**(iv) Electrical Precipitation of Smoke** Most of smoke emissions from industries and automobile vehicles are colloidal form, dispersion in air causes environmental pollution. Before emission of smoke into atmosphere, it is treated with Cottrell precipitator (shown in Fig. 7.30).

Let this smoke pass through a source it changed points to a high potential (~20,000–70,000 V). The points discharge negative electrons with highest velocity which ionize molecules in air. Smoke particles adsorb these positive ions and

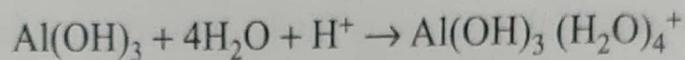
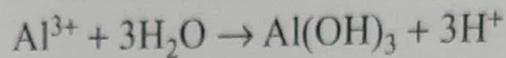


**Fig. 7.30** Cottrell || smoke precipitator

become charged. The charged particles are trapped by opposite charged electrodes and get discharged, precipitated. The gas leave from cottrell precipitator is free from smoke.

Ex. Arsenic is recovered from smelter smoke.

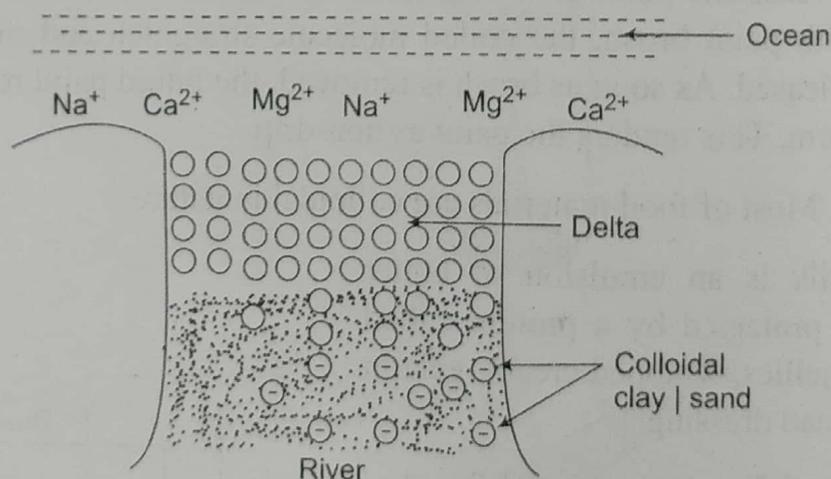
**(v) Classification of Municipal Water** Municipal feed water from natural resources contains oftenly colloidal particles. The process of coagulation is used to settle these colloidal particle from water. The colloidal particles carry negative charge. When alum ( $\text{Al}_2(\text{SO}_4)_3$ ) is added to water a gelatinous precipitates of hydrated aluminium hydroxide (floc) is formed.



The positively charged floc attract negative sol particles which are taped (or) coagulated. The floc along with suspended matter settle down leaving clear water.

**(vi) Formation of Delta**

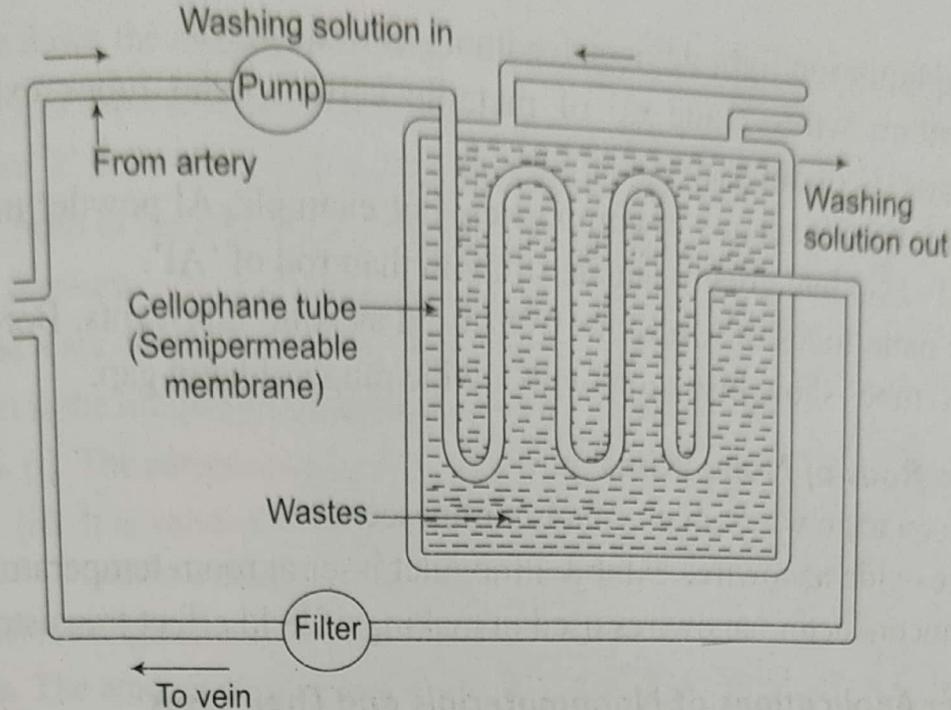
River water contains rich of colloidal particles of clay, sand which carry negative charge. On the other hand sea water contains positive ions such as  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ . At this end of river journey, meet sea water, these ions discharges clay or sand particles which are precipitated as delta (Fig 7.31).



**Fig. 7.31** Formation of delta

**(vii) Artificial Kidney Machine** The human kidney purify the blood by dialysis through natural membranes. During purification, the toxic wastes products such as uric acid (urea pass through the membrane and colloidal size particles of blood proteins (haemoglobin) are retained.

Kidney failure is leads to contamination of blood with poisonous waste. At present, the patients's blood can be cleaned with providing of 'Artificial Kidney Machine'. In this, the impure blood is made to pass through a series of cellophane tubes surrounded by a washing solution in water. The toxic waste chemicals (urea, uric acid) diffuse across the tube walls into the washing solution (Fig 7.32).



**Fig. 7.32** Artificial kidney machine from purification of blood by dialysis

The purified blood is transfer to the patient. It is one of the main application of artificial kidney machine to save the life of humans across the world.

**(viii) In the medical field** If a person is suffering from acidity, a suitable medicine containing an anion exchanger can neutralise it.

### 7.15.2 Applications of Nanomaterials

Nanomaterials show potential applications because of their unusual and unique properties. Nano particles, nano tubes, nano rods and nano wires show the following applications:

#### (i) Nano Particle

- These are used as important catalyst in hydrogenation and catalysis.
- As zero-dimensional quantum dots, one-dimensional quantum wires and in planar arrays of ordered structures, they have been used in the design of new super computers.
- Magnetic nano particles have potential applications in magneto optical storage and magnetic drug transport.
- Nano particles are potential components in the generation of biometallic nanostructures and nanomechanical devices based on DNA.

#### (ii) Carbon Nano Tubes (CNT)

- Nano tube field emission transistors for use as switching components in computers.
- Protective shield against electromagnetic radiation due to high electrical conductivity and poor transmitters of electromagnetic radiation.
- They act as sensors of gases such as  $\text{NO}_2$  and  $\text{NH}_3$  on the basis of increase in electrical conductivity when  $\text{NO}_2$  was allowed to flow over CNTs.
- They act as storage device in lithium batteries. This is due to every lithium atom stored for every six carbon atoms of CNT and hence, it can be used to store the charge carrier, lithium in lithium batteries.

- (e) Field emission light devices for fluorescent displays.
- (f) Quantum wires made up of metallic carbon nano tubes exhibit high electrical conductivity.
- (g) Reinforced elements in composites. For example, Al powder mixed with CNT (5%) had greater tensile strength than rod of 'Al'.
- (h) The nano tubes of  $\text{MoS}_2$  and  $\text{WS}_2$  used as solid lubricants. Boron nitride nano tubes show insulators with a wide range of band gap.

**(iii) Nano Rods of Nano Wires**

- (a) Silicon nano wires shows photoluminescence.
- (b) Zinc oxide nanowires exhibit ultraviolet laser at room temperature.
- (c) Semiconductor nanowires used in making of field effect transistor.

**(iv) Other Applications of Nanomaterials and Their Uses**

- (a) Sunscreens, cosmetics, coating on surfaces, hard cutting tools.
- (b) Fuel cells, displays, batteries, catalysts.
- (c) Magnetic materials, lubricants, machinable ceramics, military bottle suits.