# ANNAMALAI UNIVERSITY
# FACULTY OF ENGINEERING AND TECHNOLOGY
# CHEMISTRY SECTION
# APPLIED CHEMISTRY

## UNIT - I

## WATER TREATMENT

**CONTENTS :** Water – Hardness of water – softening of water by ion-exchange process and zeolite process – boiler feed water – specifications – boiler troubles (Sludge and scale formation, priming and foaming, caustic embrittlement and boiler corrosion) –removal of dissolved $CO_2$, $O_2$ and acids – internal treatment of boiler feed water (colloidal, carbonate, phosphate, calgon and EDTA conditioning) – disinfection of water – break point chlorination – desalination of brackish water by reverse osmosis method - Determination of total hardness by EDTA method.

# HARDNESS OF WATER

**Hard water is formed when water passes through or over limestone or chalk areas and calcium and magnesium ions dissolve into the water. The hardness is made up of two parts: temporary (carbonate) and permanent (non carbonate) hardness. When water is boiled, calcium carbonate scale can form, which can deposit on things like kettle elements. The scale will not stick to kettles that have a plastic polypropylene lining but will float on the surface. The permanent hardness that comprises calcium and magnesium sulphate does not go on to form scale when heated or boiled.**

**The presence of dissolved mineral matter in water causes hardness and alkalinity. Hardness of water is commonly defined as its soap consuming capacity. Soaps containing sodium and potassium salt of higher fatty acid such as oleic acid, palmitic acid and stearic acid. Consumption of soap by water mainly due to the presence of dissolved calcium and magnesium ions.**

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

**Soap (soluble in water)** **(Calcium soap insoluble)**

**Both calcium and magnesium produces insoluble scams with soaps and reduces the cleaning action.**

**Generally hardness of water is taken as a measure of its calcium and magnesium ions content in the soluble state.**

## TEMPORARY HARDNESS (OR) CARBONATE HARDNESS

**It is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals.**

**Temporary hardness mostly destroyed by boiling the water. On boiling bicarbonates are decomposes and yielding insoluble carbonates or hydroxides.**

△

¾

$Ca(HCO_3)_2$ Heat¾¾® $CaCO_3\downarrow + H_2O + CO_2\uparrow$

**Calcium Bicarbonate**

△

¾

$Mg(HCO_3)_2$ Heat¾¾® $Mg(OH)_2\downarrow + 2CO_2\uparrow$

**Magnesium Bicarbonate**

## PERMANENT HARDNESS (OR) NON- CARBONATE HARDNESS

**It is due to the presence of chlorides and sulphates of calcium, magnesium and other heavy metals. It is not destroyed on boiling.**

**Disadvantages of Hardness**

**In domestic use:**

**It is not used washing because it does not give lather with soap.**

- **Cleaning quality of soap depressed, so bathing also not advisable.**
- **It causes bad effect on our digestive system**

**In industrial uses:**

- **Because of the presence of calcium and magnesium salts, it is not advisable to use in textile industry. Sugar industry, dyeing and paper industries.**

- **In steam generation in boilers it generates many problems.**

  I. **Scale and sludge formation**
  II. **Corrosion**
  III. **Priming and foaming**
  IV. **Caustic embitterment**

**UNITS OF HARDNESS**

**Hardness caused by different salts can be expressed in terms of equivalent hardness of single salt ($CaCO_3$).**

**(i) Parts per million (ppm)**

**The part of calcium carbonate equivalent hardness per $10^6$ part of water.**

**(ii) Milligrams per litre (mg/l)**

**It is the number of milligrams of $CaCO_3$ equivalent hardness present per litre of water.**

**1 mg/L = 1 mg of $CaCO_3$ eq. hardness of 1L of water**
**but 1 litre of water =1 kg = 1000g =1000x1000=$10^6$ mg.**
**1 mg /L = 1 mg of $CaCO_3$ per $10^6$ mg of water = $10^6$ ppm.**

**Molecular weight of $CaCO_3$ is 100, its equivalents.**

**100 g $CaCO_3$ ≡111 g of $CaCl_2$ ≡ 136 g of $CaSO_4$ ≡ 95 g of $MgCl_2$**
**≡ 120 g of $MgSO_4$ ≡ 162 g of $Ca(HCO_3)$ ≡ 146 g of $Mg(HCO_3)_2$**
**≡ 164 g of Ca $(NO_3)_2$ ≡ 44 g of $CO_2$**

It means 111g of $CaCl_2$ react with same amount of soap as 100g of $CaCO_3$. If 'x' g of $CaCl_2$ to convert in to $CaCO_3$ equivalent by 'X' x 100/111

### (iii) Equivalent per million (epm)

One equivalent per million is a unit chemical equivalent weight of solution per $10^6$ weight units of solution.

In titrimetry 1 epm is conventionally taken as equal to 1 ml of 1N solution per litre.

1 epm of $CaCO_3$ = 50mg/L (or) 50 ppm of $CaCO_3$ .

### (iv) grains per imperial gallon (gpg)

In English hardness is expressed in terms of grains

(grains = 1/70,000 Ib) per gallon (10 Ibs) . i.e. parts per 70,000 parts grains per gallon is also called as degree cleric.

1ppm =1mg/L = 0.1° French =0.07° clark =0.07 grains per impressed gallon.

### (v) Degree French:

Degree French is the parts of $CaCO_3$ equivalent hardness per $10^5$ parts of water.

### Problems

1. Calculate the temporary and permanent hardness of a sample of water containing the following impurities.

$Mg(HCO_3)_2$ =73 mg/L ; $Ca(HCO_3)_2$ =162 mg/L; $CaSO_4$=136 mg/L

$MgCl_2$=95 mg/L; $CaCl_2$ =111 mg/L NaCl =100 mg/L $SiO_2$ = 100 mg/L

Solution:

The concentration of the impurities has to be converted to $CaCO_3$ equivalent of hardness.

| Salt | Conversion Factor | $CaCO_3$ equivalent |
|---|---|---|
| $Mg(HCO_3)_2$ = | 73x100/146 = | 50 mg/L = 50 ppm |
| $Ca(HCO_3)_2$ = | 162x 100/162 = | 100 mg/L = 100 ppm |

**$CaSO_4$ = 136x100/136= 100 mg/L = 100 ppm**

**$MgCl_2$ = 95x100/95 = 100 mg/L = 100 ppm**

**$CaCl_2$ = 111x100/111= 100 mg/L = 100 ppm**

**NaCl and $SiO_2$ do not contribute to hardness and hence they are omitted from calculation of hardness.**

**Temporary hardness = Hardness of $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$**
**= 50+100 = 150 ppm**

**Permanent hardness = Hardness due to $CuSO_4$ +$MgCl_2$ +$CaCl_2$**
**= 100+100+100=300 ppm**

**Total hardness = Temporary hardness +permanent hardness**
**= 150+300 = 450 ppm.**

**2. Calculate the temporary hardness and permanent hardness of a sample of water containing $Mg(HCO_3)_2$ =7.3 mg/L , $Ca(HCO_3)_2$ = 16.2 mg/L ; $MgCl_2$ = 9.5 mg/L ; $CaSO_4$ =13.6 mg/L.**

| **Constituent** | **conversion factor** | **$CaCO_3$ equivalent** |
|---|---|---|
| **$Mg(HCO_3)_2$ =7.3 mg/L** | **100/146** | $7.3\text{x}\frac{100}{146} = 5mg/L$ |
| **$Ca(HCO_3)_2$ =16.2 mg/L** | **100/162** | $16.2\text{x}\frac{100}{162} = 10mg/L$ |
| **$MgCl_2$ = 9.5 mg/L** | **100/95** | $9.5\text{x}\frac{100}{95} = 10mg/L$ |
| **$CaSO_4$ = 13.6 mg /L** | **100/136** | $13.6\text{x}\frac{100}{136} = 10mg/L$ |

**Temporary hardness due to magnesium and calcium bicarbonates**
**= (5+10)mg/L = 15mg/L (or) 15 ppm**

**Permanent hardness due to $MgCl_2$ and $CaSO_4$**
**= (10+10)mg/L = 20mg/L (or) 20ppm.**

**3. Sample A,B,C, having following salt contents I.Sample 'A' contain 168mg of Mg $CO_3$ per litre**
**II.Sample 'B' contain 820mg of $Ca(NO_3)_2$ per litre**
**III.Sample 'C' contain 2g of $CaCO_3$ per 500ml.**

**Determine hardness of all of the above three sample in ppm and in grains per gallon.**

| **Sample** | **constituent** | **$CaCo_3$ equivalent** |
|---|---|---|

| | | |
|---|---|---|
| **A** | **$MgCO_3$ =168 mg/L** | **168x** $\frac{100}{84} = 200 mg/L$ |
| **B** | **$Ca(NO_3)_2$ = 820 mg/L** | **20x** $\frac{100}{164} = 500 mg/L$ |
| **C** | **$CaCO_3$ = 2 g /500ml or 4000mg/L** | **4000x** $\frac{100}{100} = 4000 mg/L$ |

**Hardness of samples**

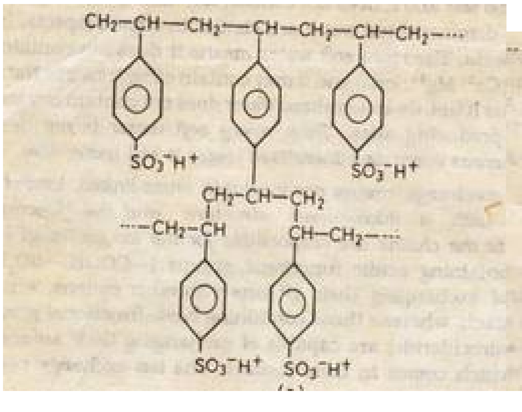
| | | | | | | |
|---|---|---|---|---|---|---|
| **A** | **= 200ppm** | **=** | **200x0.07** | **=** | **14grains /gallon** |
| **B** | **= 500ppm** | **=** | **500x0.07** | **=** | **35grains /gallon** |
| **C** | **= 4000ppm** | **=** | **4000x0.07** | **=** | **280grains /gallon** |

## Ion - exchange process:

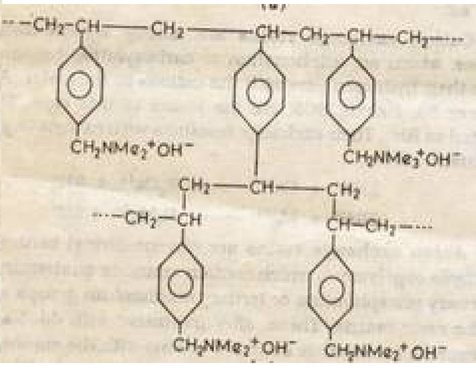
**The external treatment of water is carried out before its entry into the boiler. The external treatment can be done by the Ion Exchange or Deionization or Demineralization process**

**In this process, cations like $Ca^{2+}$, $Mg^{2+}$ and anions like $Cl^-$, $SO_4^{2-}$, which are responsible for hardness are removed respectively by cation exchange resins and anion exchange resins.**

**Ion exchange resins are insoluble, cross linked, long chain organic polymers with a micro porous structure. The functional groups attached to the chains are responsible for the ion exchanging properties. Resins containing acidic groups (-COOH, $-SO_3H$) are capable or exchanging their $H^+$ ions with cations of hard water. Resins containing basic groups ($-NH_2$, - OH) are capable of exchanging their anions with the anions of hard water.**



**Acid resin**



**Basic resin**

**Process: Water is passed through a tank having cation exchanger which absorbs all the cations present in water.**

$$2RH^{+} + Ca^{2+} \rightarrow R_2Ca^{2+} + 2H^{+}$$

$$2RH^{+} + Mg^{2+} \rightarrow R_2Mg^{2+} + 2H^{+}$$

**The cation free water is now passed through another tank having anion exchanger which absorbs all the anions present in the water.**

$$R'OH^{-} + Cl^{-} \rightarrow R'Cl + OH^{-}$$

$$2R'OH^{-} + SO_4^{2-} \rightarrow R'SO_4^{2-} + 2OH^{-}$$

**The water coming out of the anion exchanger is completely free from cations and anions responsible for hardness. It is known as deionised water or demineralised water. It is as pure as distilled water.**

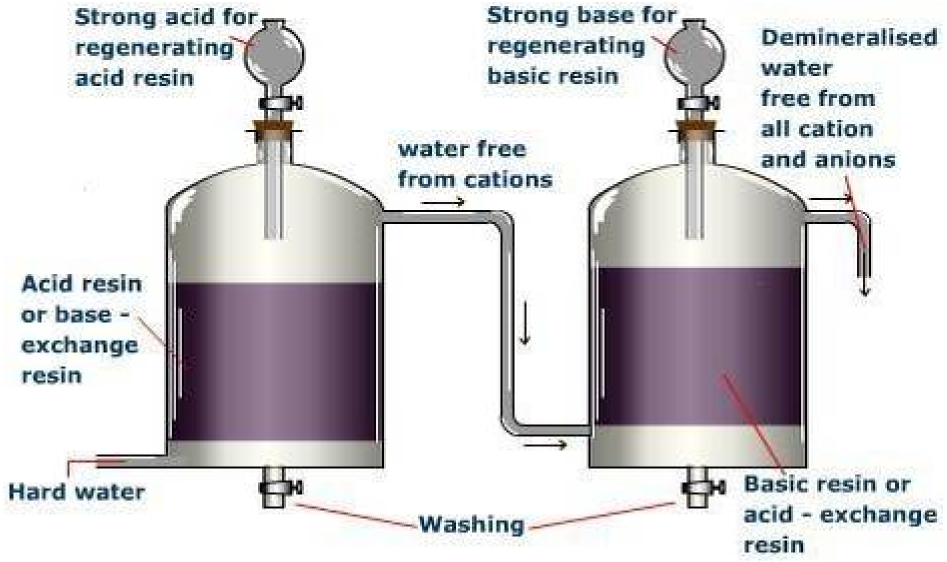
***Regeneration:*** **Cation exchange resins (acid resin) are regenerated by passing a dilute solution of hydrochloric acid through them.**

$$R_2Ca^{2+} + 2H^{+} \rightarrow 2RH^{+} + Ca^{2+}$$

**Similarly, the anion exchange resins (basic resin) are regenerated by passing a dilute solution of sodium hydroxide through them.**

$$R_2SO_4^{2-} + 2OH^{-} \rightarrow 2ROH^{-} + SO_4^{2-}$$

**A typical deionizer:**



**Deioniser**

**Advantages of ion exchange process are as follows.**

**(a) Highly acidic or alkaline water can be treated by this process.**
**(b) This produces water of very low hardness (nearly 2 ppm)**

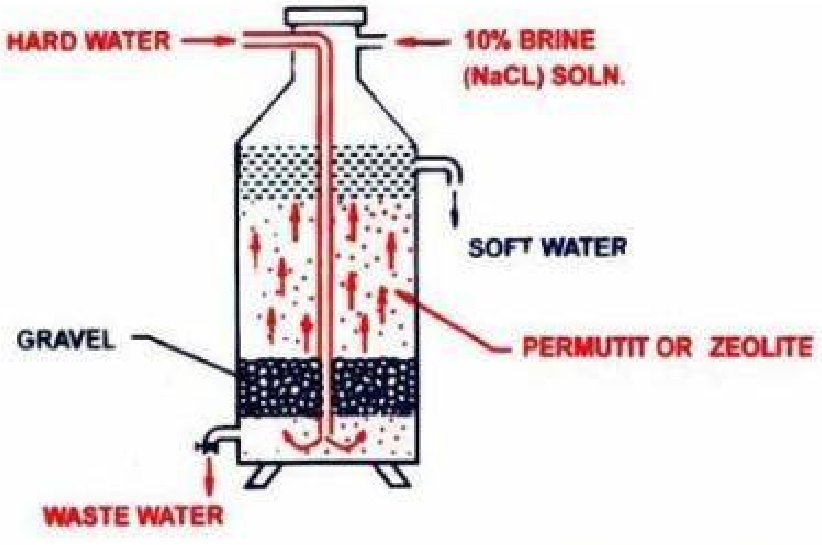
**The demineralization process has the following disadvantages.**

**(a) The equipment is costly and more expensive chemicals are needed.**
**(b) If water contains turbidity, then the output of the process is reduced.**

## *Ion Exchange Process (zeolite (or) Permutit Process)*

**Permutit or sodium aluminium silicate is a complex chemical compound, which occurs as a natural mineral called Zeolite. Permutit or zeolites are insoluble in water and have the property of exchanging ions present in them with the ions present in the solution.**

**Permutit or zeolites are packed in a suitable container and a slow stream of hard water is passed through this material. As a result, calcium and magnesium ions present in hard water are exchanged with sodium ions in the permutit ($Na^+$Al-Silicate). The outgoing water contains sodium salts, which do not cause hardness.**



**PERMUTIT'S PROCESS OF SOFTENING OF HARD WATER**

$$\underset{\text{in hard water}}{CaCl_2} + \underset{\text{permutit}}{2Na^+(\text{Al-Silicate}^-)} \longrightarrow Ca(\text{Al-Silicate})_2 + 2NaCl$$

$$\underset{\text{in hard water}}{MgSO_4} + \underset{\text{permutit}}{2Na^+(\text{Al-Silicate}^-)} \longrightarrow Mg(\text{Al-Silicate})_2 + Na_2SO_4$$

**This is the basic concept of ion exchange and hardness removal.**

**Regeneration**

**As the process continues, sodium zeolites gets exhausted due to its conversion into calcium and magnesium zeolites. Hence it must be regenerated. This is done by percolating a 10% brine solution(NaCl solution)through the exhausted zeolite. This operation converts calcium and magnesium zeolites back into sodium zeolite, as shown below,**

$CaZ + 2NaCl \rightarrow Na_2Z + CaCl_2$

$MgZ + 2NaCl \rightarrow Na_2Z + MgCl_2$

**Advantages:**

1. **Water obtained by this process will have a residual hardness between 7 and 15 ppm.**
2. **The method is cheap, because the regenerated zeolite can be used again.**
3. **The plant is compact and occupies a small space.**

**Limitations:**

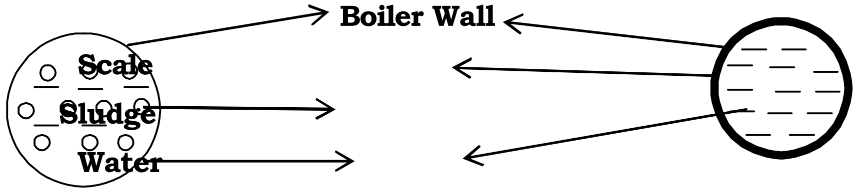
1. **The process exchanges only $Ca^{2+}$ and $Mg^{2+}$ions with $2Na^+$ ions. It does not remove the acidic ions like $HCO_3^-$,$CO_2^{2-}$.**
2. **Water containing such ions is not much suitable for boilers as it may cause corrosion of boilers.**
3. **The water containing turbidity and suspended impurities cannot be treated by this method because turbidity clogs the pores of the zeolite bed.**

## BOILER TROUBLES

**Boilers are used for stream generation in industries and power houses. If hard water, without prior treatment, is directly fed into the boilers, the following problems may arise.**

### (1) Scale and Sludge Formation

**As water evaporates continuously in boilers, the concentration of dissolved salt increases. When their saturation points are reached, the salts are precipitated on the inner walls of the boilers. If the precipitate formed is soft, loose and slimy, it is called sludge.**



**If the precipitate, on the other hand, is hard and adhering on the inner walls, it is called scale.**

**Sludges are formed by substances like $MgCl_2$, $MgCO_3$, $MgSO_4$, and $CaCl_2$ which have greater solubilities in hot water than in cold water. Sludges are generally formed at the colder parts of the boilers and get collected at places where the flow rate is slow they can be easily removed by scraping off with wire be brush. Sludges are poor conductors of heat and also cause choking of pipes. Sludge formation can be prevented by using softened water and can be removed by 'blow down operation', which consists of drawal of portion of concentrated water from the boiler and replacing it with fresh water.**

**Scales are the firmly sticking hard substances which cannot be removed mechanically by abrasion. It is the main source of boiler problems and may be formed due to following reasons inside the boiler.**

**(i) Decomposition of calcium bicarbonate $Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$**

**(ii)Solubility of $CaSO_4$ decreases with increasing temperature. Due to this reason, when hard water containing $CaSO_4$ is heated in boilers calcium sulphate gets precipitated as hard scale on the hotter parts of the boiler. This type of scale causes troubles mainly in high pressure boilers.**

**(iii) Dissolved magnesium salts get hydrolysed under high temperature conditions inside the boiler giving rise to soft $Mg(OH)_2$ scales. $MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2\,HCl$**

**(iv) Even if a small quantity of silica is present $CaSiO_3$ and $MgSiO_3$ scales are deposited and they adhere very firmly to the boiler walls which are difficult to remove.**

**Since scales are poor thermal conductors, they act as partial heat insulators and the transfer of heat from inner boiler surface to water inside is greatly reduced. This results in wastage of fuels, and to maintain steady supply of steam, the scale coated boiler has to be over heated. When thick scales crack due to uneven expansion, water comes suddenly in contact with over heated**

**portion and large quantity of steam is formed instantaneously producing very high pressure which may cause explosion of boiler.**

**Brittle scales may be removed by giving thermal shocks. Loosely sticking scales can be removed by scraping. The above are the mechanical methods of removal of scales. Alternatively, firmly sticking scales can be removed by chemical reactions. For example, calcium carbonate scales being basic in nature can be dissolved by 5% hydrochloric acid solution. Calcium sulphate and silica scales can be removed by dissolving them with EDTA solution, since Ca-EDTA complex is highly soluble in water.**

### Prevention of Scale Formation:-

**The scale formation can be prevented of minimized by subjecting boiler feed water to certain chemical treatments. Treatment of water before feeding the boiler is known as external treatment. Treating the raw water inside the boiler is known as internal treatment internal conditioning or sequestration.**

### Caustic Embitterment

**This type of corrosion in boiler is caused by use of highly alkaline water and found in high pressure boilers. If water is externally treated by soda lime the $Na_2CO_3$ present in water decomposes to give NaOH and $CO_2$**

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2 \uparrow$$

**NaOH produced makes the water alkaline and this caustic water flows into the minute cracks present in the inner walls of the boiler. On evaporation, the concentration of NaOH increases which converts the boiler walls into sodium ferrate. This causes embrittlement of the boiler walls in parts like rivets, joints and bends which are under constant stress.**

**(i) By keeping the pH at 8 – 9, caustic embrittlement can be prevented. Also (ii) sodium phosphate can be used instead of $Na_2CO_3$ in external treatment of boiler water and (iii) Tannin or $Na_2SO_4$ can be added to water which blocks the hairline cracks in the boiler walls thus preventing the infiltration of NaOH into these areas.**

### (3) Boiler Corrosion

**Boiler corrosion is the decay or disintegration of boiler body material either due to chemical or electrochemical reaction with its environment. The presence of acidic materials, dissolved oxygen and dissolved carbondi-oxide are the main factors causing boiler corrosion.**

**$MgCl_2$ prevent in water is hydrolysed to give hydrochloric acid.**

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$

**Hydrochloric acid reacts with iron of boiler material giving**

$$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2\downarrow + 2HCl$$

**These reactions are chainlike in producing hydrochloric acid. This is prevented by adding alkali to neutralize the acid formed.**

**The carbon di-oxide reacts with water to give carbonic acid. This acid like other acids causes corrosion of the boiler material. The insoluble bicarbonates in water also release $CO_2$ according to the following reaction.**

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

$$CO_2 + H_2O \rightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$$

**$CO_2$ can be removed by appropriate mechanical aeration or by adding ammonium hydroxide.**

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

**At room temperature, generally water contains approximately 8 ppm of dissolved oxygen. At higher temperature inside the boiler, oxygen corrodes the boiler material.**

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2\downarrow$$

$$4Fe(OH)_2 + O_2 \rightarrow \underset{\text{Rust}}{2Fe_2O_3.2H_2O}$$

**Dissolved $O_2$ can be removed by adding a reducing agent hydrazine, sodium sulphite or sodium sulphide.**

$$\underset{\text{Hydrazine}}{N_2H_4} + O_2 \rightarrow N_2 + 2H_2O$$

$$\underset{\text{Sodium sulphite}}{2Na_2SO_3} + O_2 \rightarrow 2Na_2SO_4$$

$$\underset{\text{Sodium sulphide}}{Na_2S} + 2O_2 \rightarrow Na_2SO_4$$

**By adding sodium sulphite or sodium sulphide increase the concentration of sodium sulphate, which under high pressure may decompose to give out $SO_2$ which reacts with $H_2O$ and forms sulphurous acid, which is corrosive. The dissolved $O_2$ can be removed by mechanical deaeration.**

**(4) Priming and Foaming**

**When steam is produced rapidly in the boilers some droplets of water are carried along with the steam. The formation of 'wetsteam' is called priming. The presence of dissolved solids, sudden boiling, high steam velocity and improper designing of boiler are the main factors for priming. Efficient softening of boiler feed water, controlling rapid change in steam velocity, fitting mechanical steam purifiers and proper designing of boiler will be helpful in preventing priming.**

**'Foaming' is caused by oily substances, which reduce the surface tension of water. These foams are unbreakable. Both priming and foaming occur together. This is disadvantageous in boilers, as the salts carried by them are deposited in blades of turbine, and other mechanical parts thereby decreasing their lives. Foaming can be minimized either by adding substances such as sodium aluminate etc. to remove the oil from water or by using antifoaming agents like castor oil.**

## INTERNAL TREATMENT OF BOILER FEED WATER

**(i) Carbonate conditioning: In low pressure boilers scale forming salt like $CaSO_4$ can be precipitated in the form of insoluble calcium carbonate by adding $Na_2CO_3$**

$$CaSO_4 + Na_2CO_3 \rightarrow \underset{\text{Sludge}}{CaCO_3} + Na_2SO_4$$

**This loose sludge of $CaCO_3$ formed can be removed by blow down operation.**

**(ii) Colloidal conditioning**

**Scale formation can be avoided in low pressure boilers by adding substances like tannin, agaragar and kerosene. These substances get absorbed over the scale forming solids preventing aggregation into hard substances. These loose deposits formed can be easily removed by blow down operation.**

**(iii) Treatment with Sodium Aluminate**

**When sodium aluminate is added to the boiler feed water, it gets hydrolysed**

$$Na_2AlO_2 + 2H_2O \rightarrow Al(OH)_2 \downarrow + 2NaOH$$

**Both Al $(OH)_3$ and $Mg(OH)_2$ are flocculant precipitates and they easily absorb any finely suspended and colloidal impurities such as silica and oil. These loose precipitates can be removed by blow down operation.**

### (iv) Phosphate conditioning

**This is suitable for high pressure boilers. Scale formation in this can be prevented by adding sodium phosphate in the form of $NaH_2PO_4$, $Na_2HPO_4$ and $Na_3PO_4$. The phosphate ion reacts with magnesium and calcium salts and gives non-adherent soft sludge of calcium or magnesium phosphates which can be removed by blow down operation.**

$$3MCl_2 + 2Na_3PO_4 \rightarrow M_3(PO_4)_2 \downarrow + 6\,NaCl$$

$$M = Ca^{2+}, Mg^{2+}$$

**Calcium can be properly precipitated only at pH 9.5 or above. The phosphate chosen should adjust the pH to an optimum of 9.5 to 10.5. If pH is high due to alkalinity, monosodium phosphate is used, which is acidic in nature. If the alkalinity is adequate in boiler water, disodium phosphate is used. If the alkalinity of boiler water is low, in order to raise the pH value to 9.5-10.5 sodium phosphate ($Na_3PO_4$) which is highly alkaline in nature is added.**

### (v) Calgon Conditioning

**Sodium hexametaphosphate $(NaPO_3)_6$ otherwise known as Calgon, is extremely used in internal treatment. This prevents the scale and sludge formation by converting the scale forming impurity like $CaSO_4$ to a highly soluble complex. Thus,**

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

$$2CaSO_4 + Na_2[Na_4P_6O_{18}] \rightleftharpoons 2Na_2SO_4 + Na_2[Ca_2P_6O_{18}] \text{ soluble complex.}$$

### (vi) Electrical Conditioning

**Sealed glass bulbs containing mercury are connected to a battery and the bulbs are placed in the boiler water and kept rotating. Mercury bulbs produce electrical discharges which prevent the coalescence of scale forming solids and effectively control the formation of hard scales.**

### (vii) EDTA conditioning

**Di-Sodium salt of Elthylene Diamine Tetra Acetic acid is used as the permanent complexing agent with the $Ca^{2+}$ and $Mg^{2+}$ ions of hard water in the EDTA method, the sodium - salt of EDTA forms stable complex with water containing $Ca^{2+}$ and $Mg^{2+}$ ions replacing the unstable complex.**

## DESINFECTION OR STERILIZATION OF WATER

**Water used, particularly for drinking purposes must be freed from disease causing bacteria. Disinfection or sterilization is a process of destroying the disease causing bacteria, micro organisms etc., from water. The chemicals used for killing the bacteria are known as disinfectants. The disinfectants generally used for sterilizing water are (a) bleaching powder (b) chlorine(c) UV light and (d) ozone and (e) chloramines.**

**(a) Disinfection by chlorine or bleaching powder*:* Chlorine is most widely used as element or as hypochlorite's (bleaching powder). It is used either directly as gas or concentrated solution.**

**When bleaching powder is added to water, HOCl which is a powerful germicide is produced. It is believed that HOCl reacts with bacteria and inactivate the enzymes responsible for the metabolic activities of bacteria. Since these enzymes are inactivated, all the bacteria's are killed and the water is sterilized.**

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

$$\underset{\text{(hypochlorous acid)}}{HOCl} + \text{bacteria} \longrightarrow \text{bacteria is killed}$$

**Break- point chlorination**

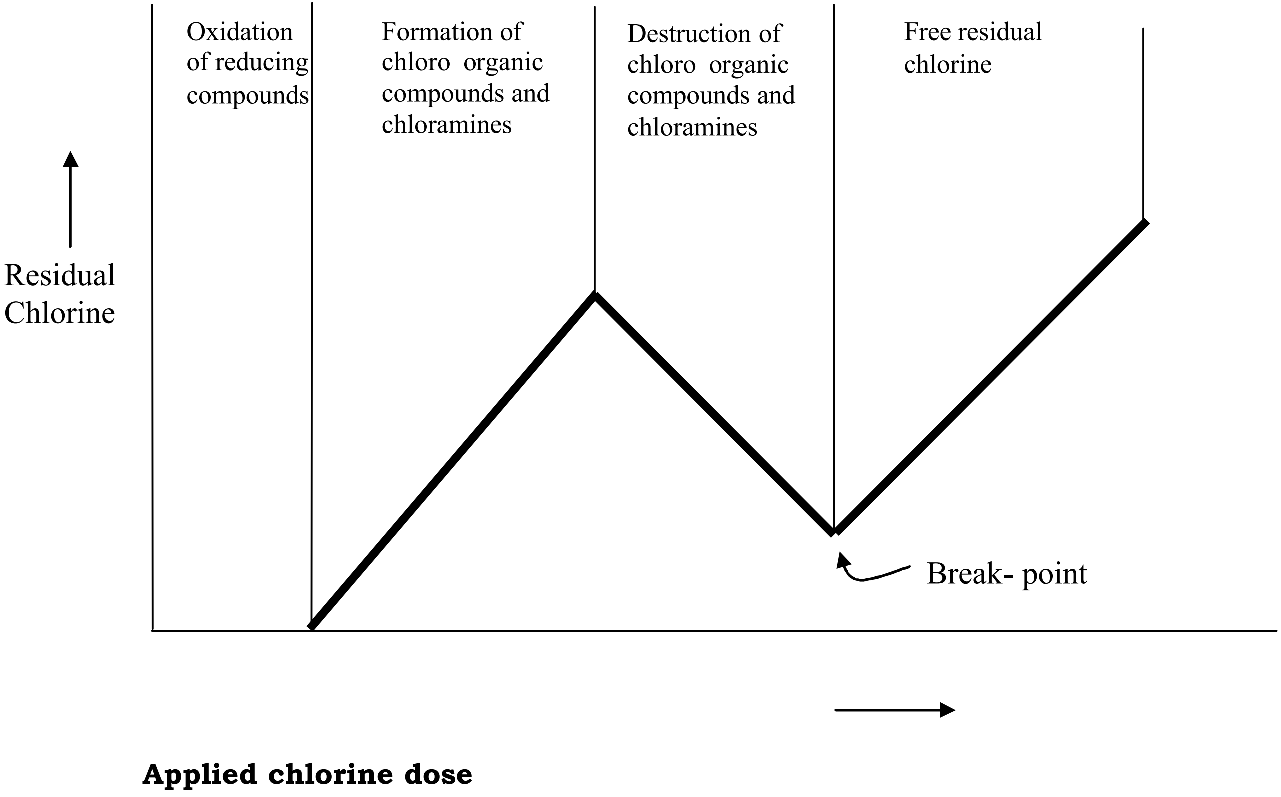
**In Break-point chlorination sufficient amount of chlorine is added to oxidize (a) organic matter, (b) reducing substances($Fe^{2+}$. $H_2S$), (c) free ammonia in raw water leaving behind mainly free chlorine which destroys pathogenic bacteria.**

**When chlorine is added to water, initially it reacts with ammonia resulting in the formation of chloramines.**

$$NH_3 + Cl_2 \longrightarrow NH_2Cl + HCl$$

$$NH_2Cl + Cl_2 \longrightarrow NHCl_2 + HCl$$

$$NHCl_2 + Cl_2 \longrightarrow NCl_3 + HCl$$



**Break- point chlorination curve**

**The amount of combined residual chlorine(chloramines) increases with increasing dosage. Then oxidation of chloramines and other impurities starts and there is fall in the combined chlorine content. Thus combined residual chlorine reaches a minimum point called break-point at which oxidation of chloramines and other organic compounds are complete. Break-point chlorination eliminates bad taste and odour. Further chlorination increases the free residual chlorine. Hence to use chlorine as a disinfectant, the chlorine dosage has to be more effective than the break-point.**

***(b) Disinfection by Ultraviolet radiations:*****Ultraviolet radiations from mercury vapour lamps are capable of sterilizing water. This process is particularly useful for sterilizing the swimming pool water.**

***(c) Disinfection by ozone:*****Ozone is a powerful disinfectant. It is highly unstable and liberates nascent oxygen which kills the micro organism and oxidizes the organic matter present in water. Excess ozone does not impart any odour to the water.**

$$O_3 \longrightarrow O_2 + (O)$$

$$(O) + \text{germs} \longrightarrow \text{Dead germs}$$

***(d)* Disinfection by chloramines:**

**Chloramine is prepared by mixing chlorine and ammonia in the ratio 2:1 by volume.**

$$NH_3 + Cl_2 \longrightarrow \underset{\text{(chloramine)}}{NH_2Cl} + HCl$$

$$NH_2Cl + H_2O \longrightarrow \underset{\text{(kills germs)}}{HOCl} + NH_3$$

**Chloramine is much more lasting than chlorine and consequently it imparts a good taste to the treated water.**

## Desalination of brackish water by reverse osmosis

**Depending upon the quantity of dissolved solids, water is graded as**

**(a) Fresh water - has < 1000 ppm of dissolved solids**
**(b) Brackish water - has > 1000 ppm but < 35, 000 ppm of dissolved solids**
**(c) Sea water - has > 35, 000 ppm of dissolved solids.**

**The water containing dissolved salts with a peculiar salty (or) brackish taste is called brackish water. Sea water containing about 3.5% salts comes under this category. It is totally unfit for drinking purposes. Sea water and brackish water can be made available for drinking purpose by desalination process. The process of removing extra common salt (sodium chloride) from the water is known as de-salination. In most of the coastal towns and harbours water for drinking purposes is to be brought from long distance and in oil areas such as Kuwait, Saudi Arabia etc. there is no alternative left except to desalinate sea water.**

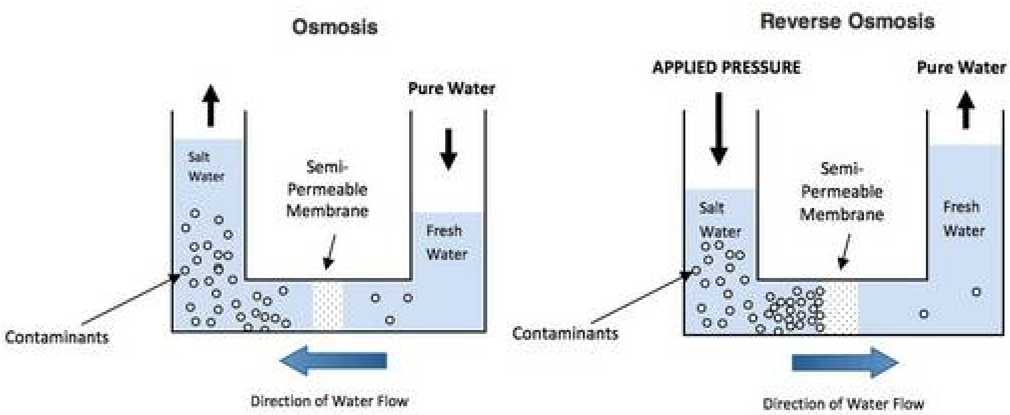
**Some of the commonly used methods for the desalination of brackish water are:**

**(1) Distillation, (2) Electrodialysis, (3) Reverse Osmosis**
**(4) Freezing.**

### Reverse Osmosis

**When two solutions of unequal concentrations are separated by a semipermeable membrane (which selectively does not permit the passage of dissolved solute particles ie. molecules, ions etc) flow of solvent takes place from dilute to concentrated sides, due to osmosis. The osmotic flow depends on the concentration gradient and the osmotic pressure existing across the membrane. If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverses. ie., solvent is forced to move from**

**concentrated side to dilute side across the membrane. This is the principle of reverse osmosis. In reverse osmosis, pure solvent (water) is separated from its contaminants. This membrane filtration is also called <u>super filtration</u> or <u>hyper – filtration.</u>**



**Reverse osmosis**

**In this process, pressure of the order 15 to 40 $kgcm^{-2}$ is applied to the sea water to force its pure water out through the semi-permeable membrane leaving behind the dissolved solids (both ionic and non-ionic) (fig 23) The membrane consists of very thin films of cellulose acetate affixed to either side of a perforated tube. Recently membranes having superior properties have come into use ie. polymethacrylate, polysulphone and polyamide polymers.**

**In reverse osmosis method not only ionic, non-ionic substances but also clloidal and high molecular weight organic matters are removed. Also the lifetime of the membrane is quite high, about two years and the membrane can be replaced within a few minutes. Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is preferred for converting sea water into drinking water.**

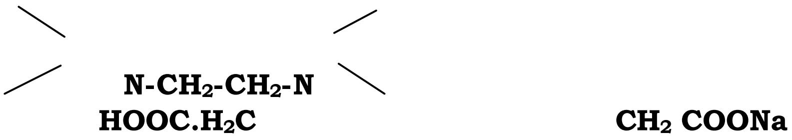
## ESTIMATION OF HARDNESS

### Estimation of hardness by EDATA method

**Di-Sodium salt of Elthylene Diamine Tetra Acetic acid is used as the permanent complexing agent with the $Ca^{2+}$ and $Mg^{2+}$ ions of hard water in the EDTA method**

**The structure of EDT A (sodium salt) is given below**

**$NaOOCH_2C$ $CH_2COOH$**



**Before starting the titration, to the hard water ammonia buffer (to maintain pH 9-10) and Eriochrome black-T indicator are added which forms an unstable complex of wine red colour.**

Ca $^{2+}$Eriochrome black - T

CaMg$_{22++}$+ Eriochrome black -T ¾pH¾/9-¾10® Mg $^{2+}$

UnstableComplex Complex

Wine red Colour

**After the titration, the sodium - salt of EDTA forms stable complex with water containing $Ca^{2+}$ and $Mg^{2+}$ ions replacing the unstable complex.**

**The completion of the complex formation is indicated by Eriochrome Black -T indicator at a pH range 9-10 givingj a steel blue colour**

Ca $^{2+}$Ca $^{2+}$Eriochrome black - T

ComplexEriochrome black - T+ EDTA ¾¾®

2+ EDTA complex+ (in alkaline medium

Mg

Mg2+ Stable ComplexSteel Blue Colour)

**Experiment**

1. **Preparation of EDTA solution: Dissolve 4 g of pure sodium salt of EDTA crystals in 1 litre of distilled water**
2. **Preparation of standard hard water: Dissolve 1.0 g pure dry $CaCO_3$ in small quantity of dilute hydrochloric acid and then evaporate the solution to dryness. Dissolve the residue in distilled water to make 1 litre solution. 1 ml of this solution contains 1 mg of $CaCO_3$ equivalent hardness.**
3. **Preparation of buffer solution: Add 67.5g of $NH_4Cl$ to 570ml of concentrated ammonia solution and dilute the solution with distilled water to 1 litre.**

**4. Preparation of indicator: Dissolve 0.5g of Eriochrome black– T in 100 ml of alchohol.**

**5. Standardisation of EDTA solution: The burette is filled with the EDTA solution 50ml of standard hard water is pipetted out into a clean conical flask. Add 10-15ml of buffer solution and few drops of Eriochrome blackT indicator. The wine red solution present in the conical flask is titrated against the EDTA solution till the wine red colour changes to steel blue colour. Let the volume of EDTA consumed be $V_1$ ml.**

**6. Estimation of total hardness: Pipette out 50 ml of sample hard water into the conical flask. Add the ammonia buffer and indicator and titrate it against the same EDTA solution to get the end point Let $V_2$ be the volume of EDTA consumed**

**7. Estimation of permanent hardness: The water sample of 250ml is taken in a beaker and1 evaporate nearly to 50ml. The temporary hard salts settle down. Filter and wash thoroughly and make up the solution again to 250ml. Pipette out 50ml of the made up solution into a clean conical flask and titrate it against the (EDTA), burette solution to get the end point. Let the volume of EDTA consumed be $V_3$ml.**

**Calculations:**

**$V_1$ml of EDTA is consumed by 50ml Std hard water.**

**$V_1$ml of EDTA = 50 mg of $CaCO_3$**

**\ 1 ml of EDTA = $50/V_1$ mg of $CaCO_3$**

**($V_2$ ml of EDTA is consumed by 50 ml sample hardwater)**

**1 ml of EDTA is consumed by $50/V_1$ mg of $CaCO_3$**

**\ $V_2$ml of EDTA = $50/V_1$ X $V_2$ mg of $CaCO_3$**

**50 ml sample hard water contain = $50/V_1$ x $V_2$ mg $CaCO_3$**

**\ 1000 ml sample hardwater = $50/V_1$ x $V_2/50$ x 1000 mg/lt.**

**\ Total hardness = $V_1/V_2$ x 1000 mg of $CaCO_3$ (equivalents) Permanent**

**hardness:**

**50 ml of sample hardwater after removing temporary hardness consumes $V_3$ ml EDTA**

**1 ml of EDTA = $50/V_1$ mg of $CaCO_3$ equivalents**

**\ $V_3$ ml of EDTA = $50/V_1$ x $V_3$ mg $CaCO_3$ equivalents**

**50 ml of sample hardwater**

**after boiling contain = $50/V_1$ x $V_3$ mg $CaCO_3$ equivalents**

**\ 1000 ml of sample hardwater = $50/V_1$ x $V_3/50$ x 1000 mg/lt**

**= $V_3/V_1$ x 1000 mg of $CaCO_3$ (equivalents)**

**Temporary hardness**

**Temporary hardness = Total hardness – permanent hardness**

**= [$V_2/V_1$ x 1000] - [$V_3/V_1$ x 1000]**

**= 1000 x [$V_2/V_1$] - [$V_3/V_1$] ppm**

**= 1000 x [$V_2 – V_3$ / $V_1$] ppm**

**QUESTIONS**

1. **Calculate the temporary hardness and permanent hardness of a sample of water containing Mg $(HCO_3)_2$ =73 mg/L ; $Ca(HCO_3)_2$ =40.5 mg/L**
    1. **$MgSO_4$ = 34 mg/L ; $CaSO_4$= 34 mg/L ; $CaCl_2$= 27.5 mg/L**
    2. **[Answer: 75 ppm; 100 ppm]**
2. **Calculate the temporary hardness, permanent hardness and total hardness of a sample of water containing Mg $(HCO_3)_2$ = 146 mg/L ; Ca $(HCO_3)_2$ = 81 mg/L**
3. **$MgSO_4$ = 162 mg/L ; $CaSO_4$ = 68 mg/L ; $MgCl_2$= 95 mg/L; NaCl= 68 mg/L**
    1. **[Answer: 150 ppm; 250 ppm; 400 ppm]**
4. **Explain Ion-exchange process of demineralization of hardwater any one method.**
5. **What are boiler troubles? Explain them.**
6. **Explain the internal treatment of boiler feed water.**
7. **Write short notes on**
    1. **Scales and sludges ii. Caustic Embrittlement iii. Calgon conditioning**
8. **Discuss the desalination of brackish water by 'reverse osmosis'.**
9. **Discuss the various methods of disinfection.**
10. **Write a brief note on break-point chlorination.**

## Unit 1 SURFACE CHEMSITRY

Surfacechemistry – Definition – types of adsorption – characteristics of adsorption – adsorption isotherms – Freundlich's adsorption isotherms and Langmuir's adsorption isotherms – applications of adsorption..

**2.**

.

**3.**

**4.**

**5.**
**6.**

**7. ADSORPTION**

**The process of accumulation of a substance on the surface of a solid or liquid is called adsorption.**

**8. Adsorbent**

**The substance surface in which adsorption occurs is called adsorbent.**

**Adsorbate**

**The substance which is taken up on the surface of a substrate (adsorbent) is known as adsorbate.**

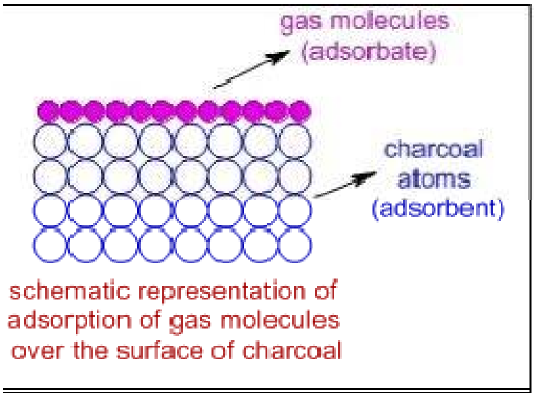
**Example**

**i. Ammonia is adsorbed by charcoal.**

**In this case, charcoal is the adsorbent and ammonia is the adsorbate**

**ii. Adsorption of water vapour (adsorbate) on silica gel (adsorbent).**

**Adsorption is a surface phenomenon. The large the surface area, greater will be the magnitude of adsorption.**



schematic representation of adsorption of gas molecules over the surface of charcoal

## 9. ABSORPTION

**Absorption is the phenomenon in which the substance is not only retained in the surface but distributed uniformly throughout the body of solid or liquid.**

**Example**

**Water vapour is absorbed by anhydrous calcium chloride.**

## 10. SORPTION

**Sometimes the adsorbed substance may be diffused into the body of the adsorbent. This phenomenon of adsorption followed by absorption is called sorption.**

**Example**

i. **When hydrogen gas is brought in contact with charcoal, it first concentrates on the surface. This is adsorption. After sometime, the gas is diffused into the body of charcoal forming solid solution. This is absorption.**

ii. **Taking up of gas by zeolites. iii. Dyeing of cotton**

**fabrics.**

### 11. Types of adsorption

**There are two types of absorption depending upon the nature of force holding the gas molecules on the solid.**

1. **Physical adsorption or physisorption**
2. **Chemical adsorption or chemisorption**

### 12. Physical adsorption

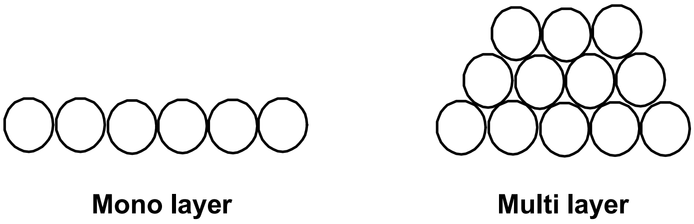
i. **It is a physical process in which the gas molecules are held on the surface of the solid by weak van der Waal's forces.**

ii. **Since the forces involved are very weak, a small rise in temperature will cause desorption.**

iii. **The week forces of attraction are balanced by forces of repulsion that rapidly grow over short distances. Hence, physical adsorption is a reversible process.**

iv. **It is characterized by low heat of adsorption.**

v. **It may involve mono or multiplayer formation.**



**Example**

a) **Adsorption of gases on charcoal**

b) Adsorption of $N_2$ on mica

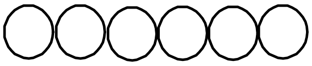
### 13. Chemical adsorption

i. It is a chemical process in which the gas molecules interact with the surface of the solid to form a chemical compound.

ii. Since the forces involved are very strong, chemisorption is irreversible in nature and desorption takes place only at elevated temperatures.

iii. It is characterized by high heat of adsorption.

iv. It involves only monolayer formation.



Mono layer

Example

a) adsorption of $O_2$ on metals

b) adsorption of $H_2$ on nickel

### 14. Difference between physisorption and chemisorption

| S. No | Physisorption | Chemisorption |
|---|---|---|
| 1. | The gas molecules are held on the surface of solid by weak van der walls force of attraction | The gas molecules are held on the surface of solid by strong chemical bonds |
| 2. | Involves low heat of adsorption (< 40 KJ) | Involves high heat of formation (40 – 400 KJ) |
| 3. | Occurs at ordinary temperature | Occurs at high temperature |
| 4. | No compound formation | Involves compound formation |
| 5. | No appreciable activation energy | Involves compound formation |
| 6. | Reversible and the gas are desorbed by slight heating | Irreversible and the gas can be desorbed only at high temperature |
| 7. | Non-specific. Any gas would be adsorbed on any solid | Highly specific. A gas is adsorbed only on those solids with which it can react |
| 8. | Mono or multiplayer formation | Only a monolayer formation |

|  |  |  |
|---|---|---|
| 9. | The magnitude of adsorption increases continuously with pressure | The magnitude of adsorption increases with pressure and reaches a limiting value |
| 10. | The magnitude of adsorption decreases continuously with temperature | The magnitude of adsorption first increases and then decreases with temperature |

## 15. Adsorption of gases

The adsorption of gases by solid adsorbents has certain characteristic features.

### 1. Adsorption and surface area

Adsorption being a surface phenomenon, the extent of adsorption depends on the surface area. The larger the surface area, greater will be the magnitude of adsorption.

Thus finely divided metals (nickel, platinum) and porous substances (charcoal, silica gel) provide a large surface area and are best solid adsorbents.

### 2. Nature of gas

The amount of gas adsorbed by a solid depends on the nature of the gas. In general, more easily liquefiable a gas is (that is higher its critical temperature), the more readily will it be adsorbed.

Thus 1 g of activated charcoala adsorbs 380 ml of sulphur of oxide (critical temperature 157qC).

### 3. Heats of adsorption

Heat of adsorption is defined as the energy liberated when 1 g mole of a gas is adsorbed on the solid surface. Thus, adsorption like condensation is an exothermic process.

Since the attraction between the gas molecules and solid surface are due to relatively weak Vanderwaal's forces, heat of adsorptions are small (about 5k cal mol$^{-1}$).

**4. Reversible character**

**Physical adsorption is a reversible process. The gas adsorbed on to a solid can be removed (desorbed) under reversed conditions of temperature and pressure. Thus**

$$\text{Gas} \longleftarrow \text{Gas/Solid + heat}$$

**Chemisorption is not reversible because a surface compound is formed.**

**5. Effect of temperature**

**Physical adsorption occurs rapidly at low temperature and decreases with increasing temperature (Le Chatelier Principle).**

**Chemical adsorption, like most chemical changes, generally increases with temperature. Thus a rise in temperature can often cause physical adsorption to change to chemical adsorption.**

**Example: Nitrogen is physically adsorbed on iron at 190° C but chemisorbed to form nitride at 500°C.**

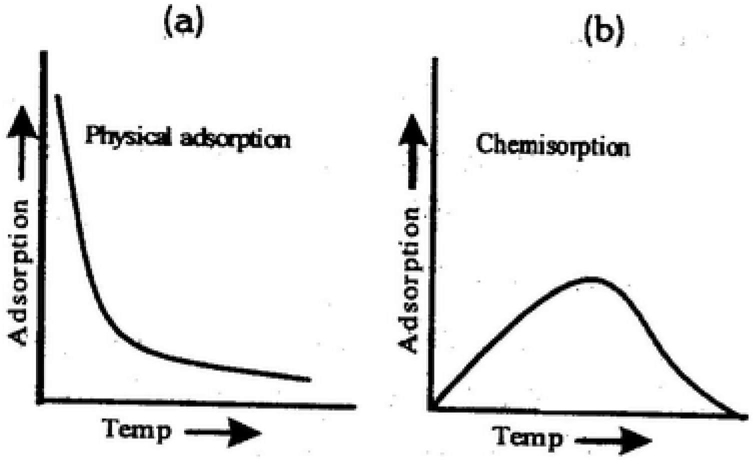


**Fig. 1 (a) Physical adsorption Vs temperature**

**(b) Chemical adsorption Vs temperature**

**6. Effect of pressure**

**A dynamic equilibrium exists between the adsorbed gas and the gas in contact with the solid. It has been found that increase of**

**pressure leads to increase of adsorption and decrease of pressure causes desorption.**

### 7. Thickness of adsorbed layer of gas

**Langmuir showed that at low pressure the physically adsorbed gas forms only one molecular thick layer. However, above a certain pressure multi molecular thick layer is formed.**

## 16. Adsorption isotherms

**The adsorption of a gas on a solid adsorbent in a closed container is a reversible process.**

$$\textbf{Free gas} \rightleftharpoons \textbf{Gas absorbed on solid}$$

**If x is the mass of gas adsorbed and m is the mass of the solid adsorbent, x/m represents the magnitude of adsorption.**

### Definition

**A mathematical expression or a graphical plot which represents the variation of adsorption with pressure at constant temperature is called an adsorption isotherm.**

**On the basis of experimental results, five different types of adsorption isotherms have been recognized.**

**Type I : Represents monolayer physical adsorption on porous materials**

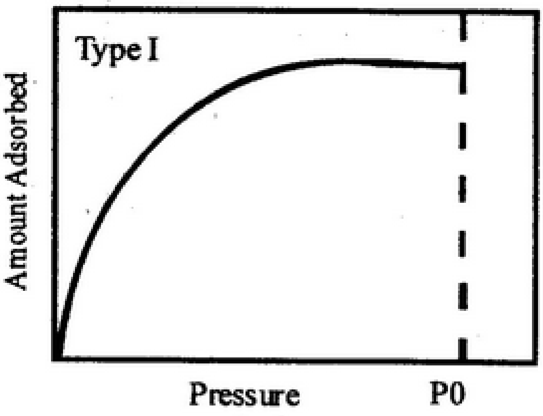


**Fig. 2. Type I adsorption isotherm**

**Example**

**Adsorption of $N_2$ on charcoal at - 195qC.**

**Type II**

**Represent a case of multilayer physical adsorption on nonporous materials.**

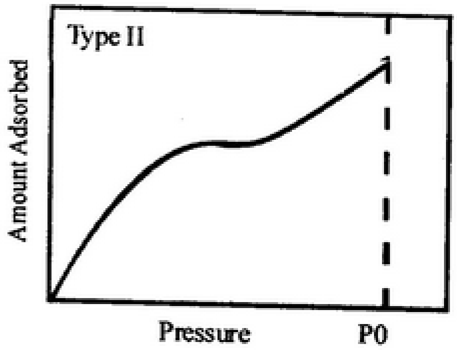


**Fig. 3. Type II adsorption isotherm**

**Example**

**Adsorption of $N_2$ on silica get a 195qC.**

**Type III**

**Represent the case of multilayer physical adsorption on nonporous materials.**

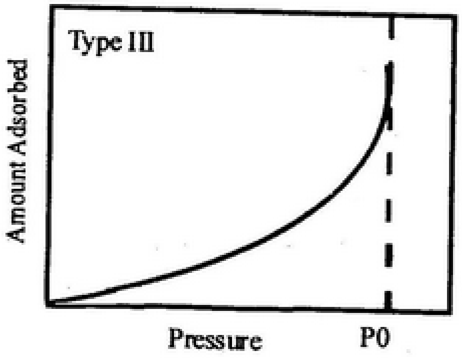


**Fig. 4. Type III adsorption isotherm**

**Example**

**Adsorption of $Br_2$ vapours on silica gel at 79qC**

**Type IV**

**Represent the case of multilayer physical adsorption on porous materials.**

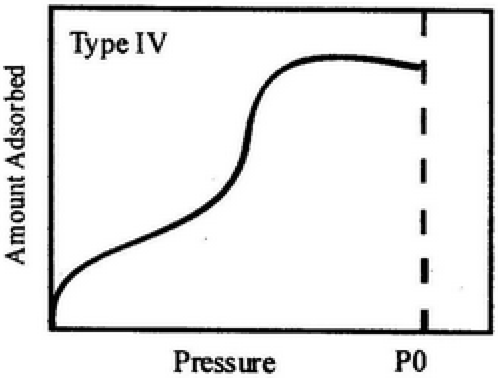


**Fig. 5. Type VI adsorption isotherm**

Example: **Adsorption of water vapour on charcoal at 100qC**.

**Type V**

**Represent the case of multilayer physical adsorption on non-porous materials.**

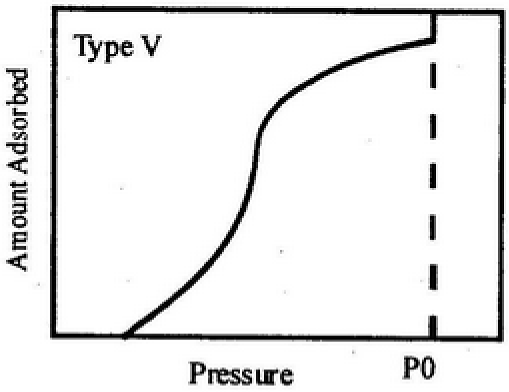


**Fig. 6. Type V adsorption isotherm Example**

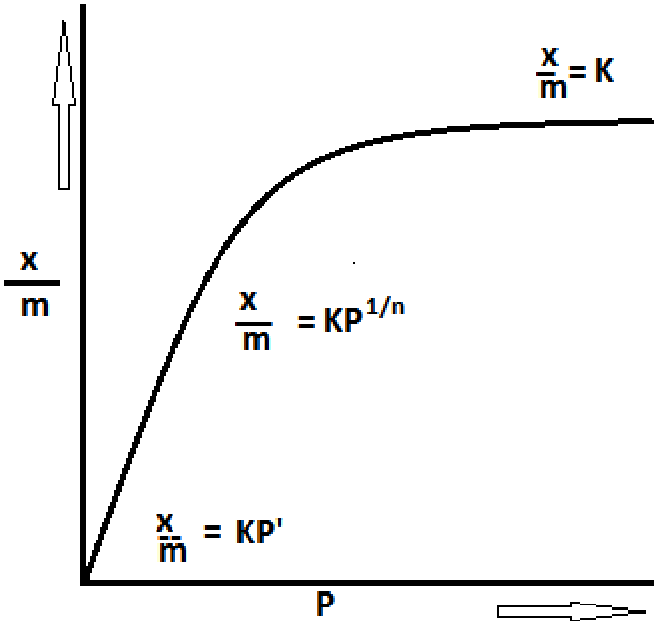
**Adsorption of benzene on ferric oxide gel at 50qC.**

### 17. Freundlich adsorption isotherm

**Freundlich proposed an empirical relationship between the quantity of gas adsorbed per unit mass of a solid absorbent $\left(\frac{x}{m}\right)$ and pressure (p) of the gas at a fixed temperature (T) in the form of a mathematical equation. This is Freundlich adsorption isotherm.**

$$\left(\frac{x}{m}\right) K p^{1/n}$$

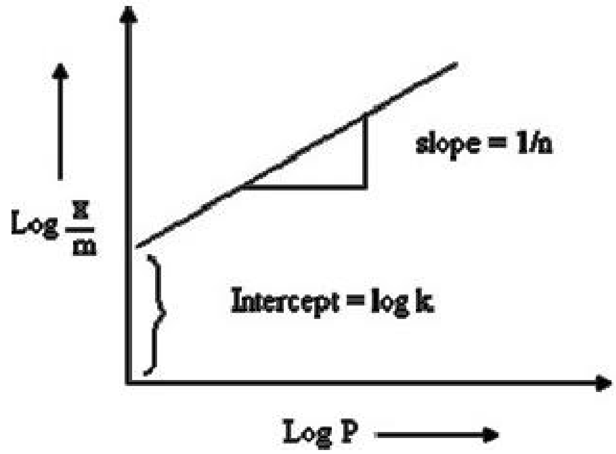
**Where, x = mass of gas adsorbed m = mass of the solid adsorbent p = pressure of the gas K and n = constants**



Taking log on both sides

**Log x/m = log K + 1/n log P**

The plot of log x/m vs. log P is straight line with slop 1/n and intercept log K.



### 18. Limitations of Freundlich isotherm

§ *x*·

1. **It has been found that the plots of log ¨ —¸against log p are straight ©*m*¹ lines only at low pressure. The plot shows a slight curvature at higher pressures. Thus, it is applicable for small ranges of pressure only.**

2. **Freundlich equation is purely empirical. It has no theoretical basis.**

3. **The constants k and n are not temperature independent. They vary with temperature.**

### 19. Langmuir adsorption isotherm

**The experimental isotherms of adsorption of gases on solids reveal that**

i. **Adsorption tends to approach saturation or limiting valve at high pressure.**

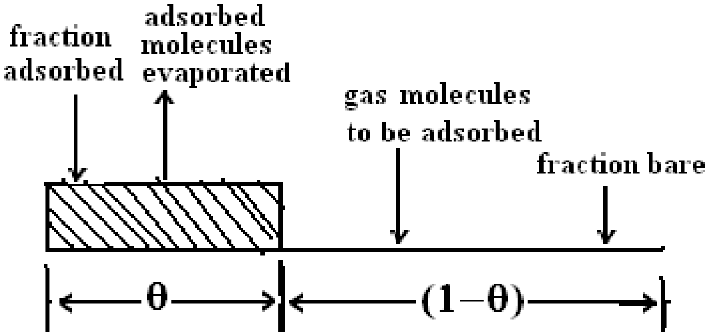
ii. **Adsorption of gases on solid surfaces is either zero order or fractional order reaction.**

**The first satisfactory interpretation of these experimental observations was given by Irving Langmuir based on the following assumptions:**

1. **The solid surface contains a fixed number of adsorption sites and each site can hold one and only one molecular species of the absorbate.**

2. **The bond between the gas molecule and the adsorbent site maybe physical or chemical.**

3. **The molecular species adsorbed on different sites do not interact with each other.**
4. **The adsorbed gas is uni-molecular in thickness.**
5. **The heat of adsorption is the same for all the sites and is independent of the fraction of the adsorbent surface covered.**
6. **There exists a dynamic equilibrium between the rate of condensation of gas molecules on the vacant sites of the adsorbent (adsorption) and the rate of evaporation of gas molecules from the occupied sites of the adsorbent (absorption).**



**DERIVATION:**

Based on the above postulates, the rate of adsorption depends on the pressure (P) and the number of vacant sites on the surface (1 - ş) (uncovered surface), where ş is the fraction of surface occupied by adsorbed gas molecules.

Now, since the rate of adsorption is proportional to the pressure (P) of the gas as well as uncovered surface (1 - ş) of the adsorbent available for adsorption.

Rate of Adsorption **Ĵ** P (1 - ş)

= **$k_1$ P (1 - ş)** ---➩ (Eq.1) Where k1 is a proportionality constant.

Rate of Desorption **Ĵ**ş

= **$k_2$ş** ---➩(Eq.2) Where $k_2$ is a proportionality constant. **At Equilibrium: Rate of adsorption = Rate of desorption** $k_1$ P (1 - ş) = $k_2$ ş ; $k_1$ P - $k_1$ P ş = $k_2$ş ;

$k_1$ P = $k_2$ş + $k_1$ P ş ; $k_1$ P = ş ($k_2$ + $k_1$ P) ş = $k_1$ P/ ($k_2$ + $k_1$ P) ş =

$k_1$/ $k_2$ P/ (1+ $k_1$/ $k_2$ P) $k_1$/ $k_2$ = K, which is another constant.

**ş** = K P/ (1 + KP) ---➩ (Eq.3)

Since the adsorbed molecules form uni-molecular layer, the amount of gas adsorbed per unit area or per unit mass of adsorbent must be proportional to the fraction of the surface covered,

i.e. x **Ĵ**ş ---➩ (Eq.4) on comparing equation (3) and (4), it becomes

$x$ Ĵ $K P/ (1 + KP)$

$x = K' K P/ (1 + KP)$ --➩ (eq. 5) where
$K'$ = new constant.

The equation (5) gives the relation between the amount of gas absorbed to the pressure of the gas at constant temperature is known as Langmuir adsorption isotherm.

The above equation (5) may be we-written as

$1+KP = K'KP/x$

$1/KK' + KP/K'K = P/x$ -➩ (Eq. 6)

The equation (6) is similar to an equation for a straight line. If the graph is plotted between P/x Vs P, we should get a straight line with slope $K/K'K$ and the intercept $1/K'K$

This equation is found valid in all cases.

Case (1) At low pressure: if the pressure (P) is very low $KP/K'K$ term is negligible,

i.e., $1/K'K >> KP/K'K$

hence equation 6 becomes

$1/K'K = P/x$ (or) $x = PK'K$ (or) $x$ Ĵ $P$

i.e., amount of adsorption per unit weight of adsorbent is directly proportional to the P at low pressure.

Case (2) At high pressure: if the pressure is high $1/KK'$ term is negligible,

i.e., $KP/KK' >> 1/KK'$

hence equation 6 becomes $KP/KK' = P/x$ (or) $x = K'$ (constant)

ie., extent of adsorption is independent of pressure of the gas, because the surface becomes completely covered at high pressure.

Case (3) At normal pressure: if the pressure P is normal the equation becomes

$X = K'P^n$

Where, n lies between 0 and 1, it is called Freundlich's adsorption isotherm.

## 20. Applications of adsorption

### 1. Industrial applications *i. Chemical industries*

**Solid catalysts are immensely used in chemical industries. Most of the chemical reactions take place through adsorption of reactants on the surface of solid catalysts.**

| **Process** | **Catalyst used** |
|---|---|
| **Synthesis of ammonia** | **Iron** |
| **Hydrogenation of oils** | **Nickel** |
| **Manufacture of $H_2SO_4$** | **Pt or $V_2O_5$** |

***ii. Sugar industry***

**Animal charcoal is used in decolouring sugar solutions. The colouring impurities are adsorbed by charcoal and removed.**

***iii. Dyeing industry***

**Dyeing of fabrics involves adsorption of the colouring matter by the mordant.**

***iv. Metallurgy***

**Concentration of ores by froth floatation process using pine oil is based on adsorption.**

## 21. General applications

### i. Purification of air

**The adsorption principle is used to design gas masks. These are devices containing activated charcoal which can adsorb harmful gases present in atmospheric air. Thus, air is purified for inhalation.**

**ii. Creating vacuum**

Activated charcoal has been used in creating high vacuum in Dewar vessels which are used for storing liquid air and liquid hydrogen. The charcoal will absorb air of the vessel.

**iii. Removal of moisture**

Silica gel and alumina are used to remove moisture from delicate instruments before they are stored of shipped and for controlling the humidity of rooms.

**iv. Softening of hard water**

Hard water is softened using zeolities (Permutit process) and synthetic resins (Ion exchange process). They act as adsorbents for the ions present in hard water.

**v. Surface active agents**

Soaps and detergents are used as surface active agents to remove dirt from cloths by adsorption.

**vi. Curing diseases**

Most of the drugs are adsorbed on disease producing germs and kill them.

**22. Analytical applications**

**i. Chromatography**

Biological substances like vitamins, alkaloids etc., can be separated and purified by chromatography. This technique works on the principle of selective adsorption.

**ii. Adsorption indicators**

Substances like fluorescein, cosin etc., as their sodium salts have been used as indicators in precipitation titrations. They give a characteristic colour change on the surface of the precipitate at the end point. These are called adsorption indicators.

The action of adsorption indicators can be explained by taking titration of NaCl against $AgNO_3$ using sodium salt of fluorescein as follows:

**When $AgNO_3$ is added to NaCl, a while precipitate of AgCl is formed. In the beginning, the chloride ions are adsorbed on the surface of the precipitate followed by $Na^+$ ions. Thus, chloride ions are held in the primary adsorption layer and $Na^+$ ions are held by secondary adsorption layer. The primary adsorption layer can not hold rosy-red fluorescein anions due to electrostatic repulsion.**

**As soon as the end-point is reached, all the $Cl^-$ ions are precipitated as AgCl and $Ag^+$ ions which are present in excess will be adsorbed through primary adsorption and acquires +ve charge. Now, fluorescein anions are adsorbed through secondary adsorption. Thus, the white precipitate turns rosy-red.**

### 23. Ion-exchange adsorption

**In recent years, synthetic resins are used as ion-exchange resins or ion-exchangers. Ion-exchangers have one ion adsorbed on it. These ion – exchangers release this ion and adsorb another like ion. The process is called ion-exchange adsorption.**

**Example**

**Demineralization of rwate by ion – exchange method.**

UNIT II

## ELECTROCHEMISTRTY [9 HOURS]

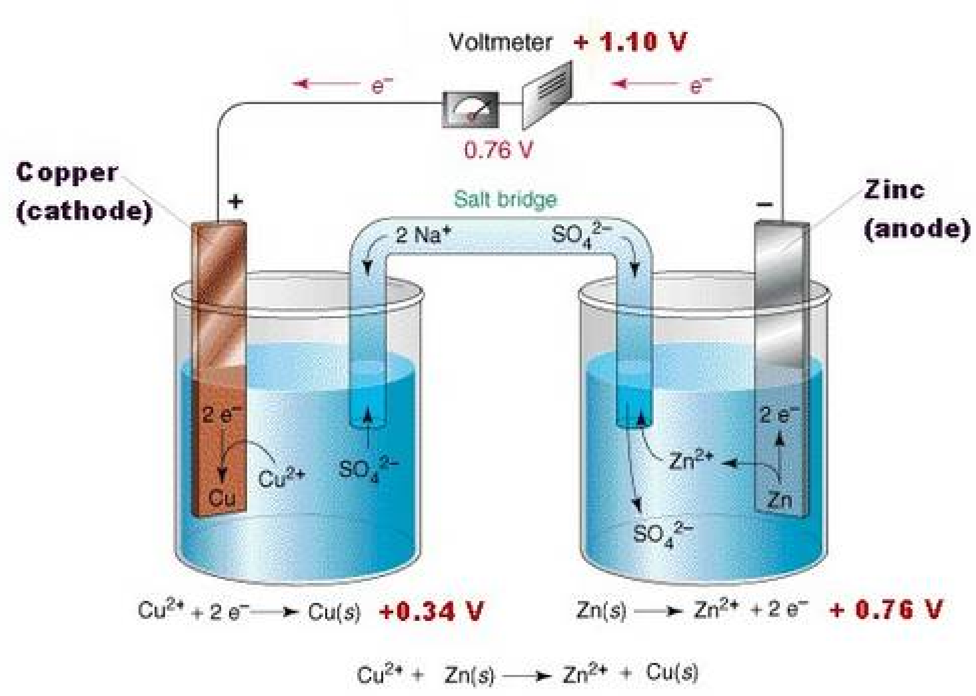
Electrochemical cells – EMF – determination of EMF of electrochemical cells – single electrode potential – standard electrode potential – Nernst equation – reference electrodes – standard hydrogen electrode, calomel electrode, glass electrode – electrochemical series – concentration cells.

### 24. Electrochemical cell

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

**commonly referred as voltaic cell or galvanic cell, in which oxidation occurs at anode and reduction occurs at cathode.**

**Daniel cell: The practical application of an electrochemical cell is a Daniel cell(Fig 1).It consists of zinc electrode, dipping in $ZnSO_4$ solution( where oxidation takes place) and a copper electrode dipping in solution of $CuSO_4$ (where reduction takes place). Each electrode may be regarded as a half-cell. The two solutions are connected together by a salt-bridge.The solutions seep through the salt bridge and come in contact with each other.**



1

**25.** **Daniel cell**

**The electrode reactions are: (half-cell reactions)**

**At anode (-ve electrode) :** $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

**(oxidation)**

**At cathode (+ve electrode):** $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu$

**(reduction)**

**Cell reaction:** $Zn_{(s)} + Cu^{2+}_{(aq)} \dashrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

**The emf of the cell is 1.1 V.**

**EMF :The difference of potential, which causes flow of electrons from the electrode of higher potential to the electrode of lower potential, is called electromotive force (EMF). The emf of galvanic cell is calculated from the reduction half-cell potentials using the following relation.**

**E(cell) = E(right) – E(left)**

**Where**

**E(cell) = e.m.f of cell**

**E(right) = reduction potential of right hand side electrode**

**E(left) = reduction potential of left hand side electrode Applications of EMF measurement:**

1. **Potentiometer titrations can be carried out.**
2. **Transport number of the ions can be determined.**
3. **Measurement of pH using hydrogen, quinhydrone and glass electrode.**
4. **From the EMF data the free energy changes, equilibrium constant of a reaction can be found out.**
5. **Hydrolysis constant can be determined.**
6. **Solubility of a sparingly soluble salt can be found out.**

**Single electrode potential: The presence of two half cells reactions and the EMF of a cell gives only the difference in the driving forces of the electrodes.**

**Ecell = Reduction potential of reduced species – Reduction potential of oxidized species**

**Ecell = Reduction potential of reduced species + Oxidational potential of oxidized species**

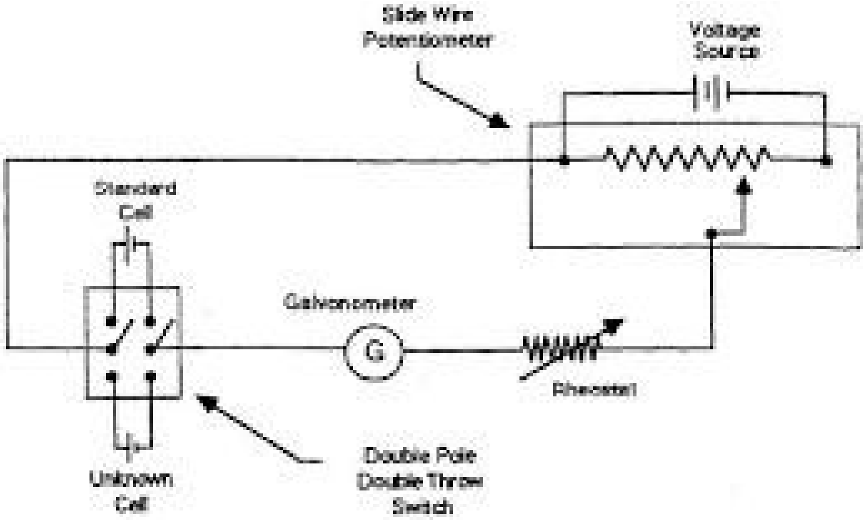
**Here prefix standard implies experimental conditions where the half cell potential or single electrode potential.**

**By knowing the standard electrode potential of one electrode it is possible to determine electrode potentials of all the other electrodes by suitable coupling and measuring the cell voltage.**

**Significance:**

1. **When elements are arranged in increasing order of their standard electrode potential a series called electro chemical series is obtained.**
2. **If the concentration of solution (Mn+) is increased, the electrode potential increases and vice-versa.**
3. **If temperature is increased the electrode potential increases and viceversa.**

### Emf of an unknown cell using a potentiometer (Poggendorff's method)



**In this experiment, the potentiometer consists of a long uniform wire with a constant current in it and a method**

for inserting, sequentially, a standard cell for calibration and the unknown cell for measurement. The resistance of the wire is uniform and, therefore, any particular length, L, will have a resistance proportional to that length. Since, from Ohms Law, voltage is proportional to the resistance (assuming constant current), the voltage across the length, L, is proportional to L and V = kL, where V is the voltage in volts, L is the variable length of wire in meters and k is the proportionality constant in volts per meter. If a parallel circuit is connected to the wire with a sliding contact, galvanometer, and standard voltage source (see diagram below), the sliding contact may be adjusted to a length of wire in which the voltage drop is just equal to that of the standard cell. At this point, there is no net current in the parallel circuit and

$$Emf=kL. \quad \text{(eq 1)}$$

Since the Emf and L are known, k can be calculated. Substitution of an unknown cell through a similar procedure will enable one to determine the Emf of that unknown cell. PROCEDURE:

1. Connect the circuit as shown in Figure I. Voltage supply is set at its appropriate value, so the current is fairly small. This is to protect the galvanometer.

2. Close the DPDT switch to the standard cell side and calibrate the potentiometer by finding what length of wire corresponds to the voltage of the standard cell. This is done by finding the location of the sliding contact where the galvanometer does not deflect when the key switch is closed.

3. Calculate the constant, k, using the emf of the standard cell and the length, L measured to the sliding contact - use Eq. 1.

S

4. Throw the DPDT switch to connect the unknown battery in the circuit and move the sliding contact until the galvanometer indicates zero current as in Step 2. (Do not adjust R since this will change the voltage t across the potentiometer wire and upset your calibration). Read the length L , measured to the sliding contact. u

5. Calculate the emf of the unknown battery. emf = $k L_U$

**6. Now measure the voltage of the unknown battery with the voltmeter.**

**Explain the difference.**

**Nernst equation**

**Potential difference is developed between the metal ions from metal to the solution (or) from solution to the metal. At equilibrium the potential difference remains constant, this is known as electrode potential of metal. The electrode potential of a metal is defined as the direct measure of its tendency to get reduced is called reduction potential, its value is +x volts. Similarly the tendency of an electrode to lose electrons is a measure of its tendency to get oxidized is called oxidation potential, its value is –x volts.**

**Expression for electrode potential: Consider the following redox reaction**

**$Mn+ + ne-$ ṇ M**

**For such a redox reversible reaction, the free energy change (¨G) and its equilibrium constant (K) are related as; ¨G = -RT ln k + RT ln [product]/ [Reactant]**

**¨$G_0$ + RT ln [product] /[Reactant] .........Eq- (1) Where ¨$G_0$ = standard free energy change**

**The above equation is known as Van't Hoff Isotherm.**

**The decrease in free energy in the reversible reaction will produce electrical energy i.e. ¨G = nEF and**

**¨$G_0$ = -nE0F ...............Eq-(2)**

**Where E = Electrode potential**

**$E_0$ = Standard electrode potential F = Faraday (96,500 coulombs)**

$$-nEF = -nE_0F + RT \ln[M]/[M^{n+}]$$

$$= -nE_0F + Rt \ln 1/[M^{n+}]$$

**Where, concentration of the metal is unity or**

$$-nEF = -nE_0F - RT \ln [M^{n+}]$$

**Dividing the equation by –nF**

$$E= E_0 + RT \ln[M^{n+}]/nF$$

$$E= E_0 + 2.303RT \log [Mn+]/nF$$

$$E= E_0 + 0.0591 \log [Mn+]/n \text{ ..............Eq-(3)}$$

**This equation-3 is known as "Nernst Equation" for electrode potential. Applications of Nernst Equation:**

**1. One of the major application of Nernst equation is in determining ion concentration**

**2. It is also used to calculate the potential of an ion of charge "z" across a membrane.**

**3. It is used in oxygen and the aquatic environment.**

**4. It is also used in solubility products and potentio-metric titrations.**

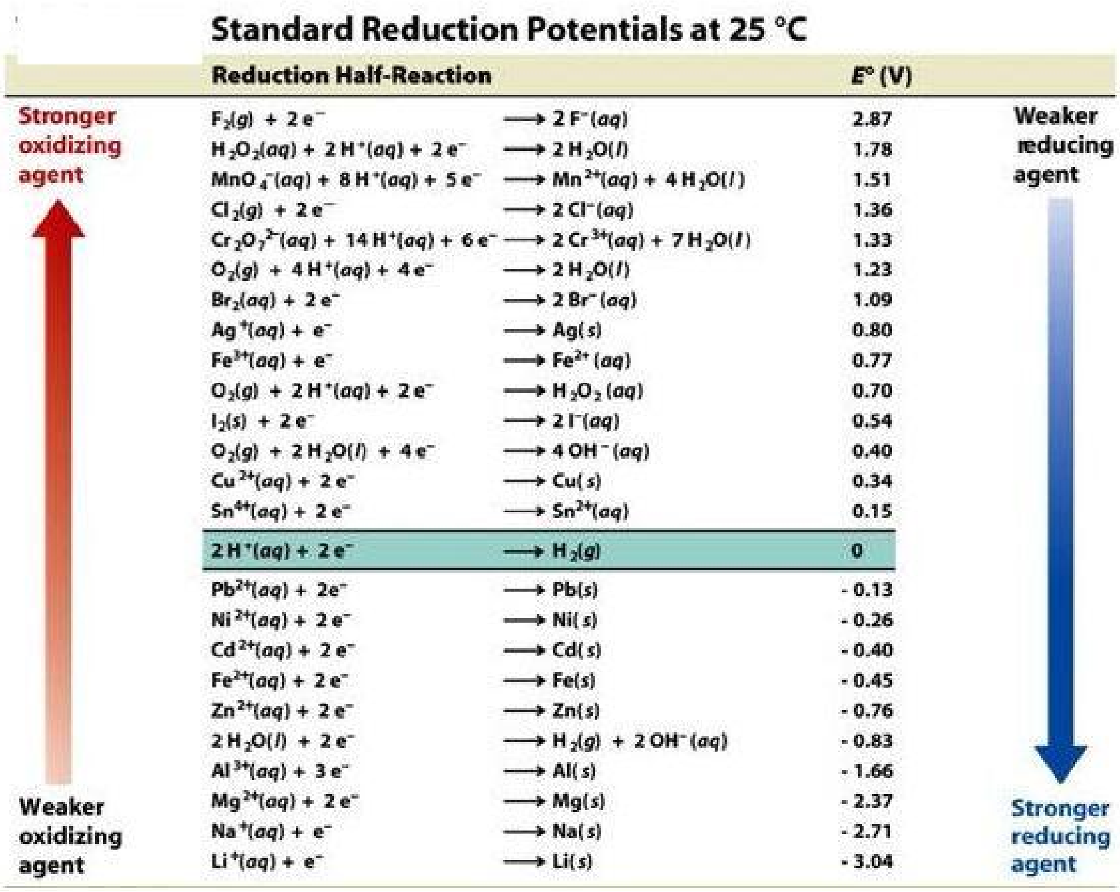
**5. It is also used in pH measurements.**

## Electrochemical series

**In an electrochemical series the various electrodes are arranged in the order of their increasing values of standard reduction potentials on the hydrogen scale.**

**The standard electrode potentials(reduction potentials) of a few electrodes are given in the Table1. These values are said to be on hydrogen scale since in these determinations, the potential of standard hydrogen electrode used as the reference electrode has been taken as zero.**

**Table 1. Electrochemical series**



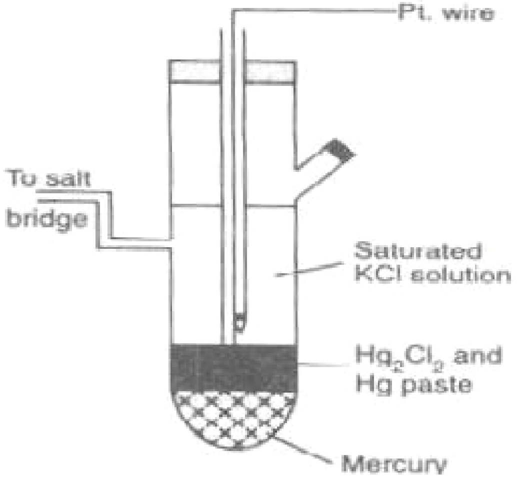
Standard Reduction Potentials at 25 °C

| Reduction Half-Reaction | | $E^\circ$ (V) |
|---|---|---|
| $F_2(g) + 2e^-$ | $\longrightarrow 2F^-(aq)$ | 2.87 |
| $H_2O_2(aq) + 2H^+(aq) + 2e^-$ | $\longrightarrow 2H_2O(l)$ | 1.78 |
| $MnO_4^-(aq) + 8H^+(aq) + 5e^-$ | $\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$ | 1.51 |
| $Cl_2(g) + 2e^-$ | $\longrightarrow 2Cl^-(aq)$ | 1.36 |
| $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$ | $\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ | 1.33 |
| $O_2(g) + 4H^+(aq) + 4e^-$ | $\longrightarrow 2H_2O(l)$ | 1.23 |
| $Br_2(aq) + 2e^-$ | $\longrightarrow 2Br^-(aq)$ | 1.09 |
| $Ag^+(aq) + e^-$ | $\longrightarrow Ag(s)$ | 0.80 |
| $Fe^{3+}(aq) + e^-$ | $\longrightarrow Fe^{2+}(aq)$ | 0.77 |
| $O_2(g) + 2H^+(aq) + 2e^-$ | $\longrightarrow H_2O_2(aq)$ | 0.70 |
| $I_2(s) + 2e^-$ | $\longrightarrow 2I^-(aq)$ | 0.54 |
| $O_2(g) + 2H_2O(l) + 4e^-$ | $\longrightarrow 4OH^-(aq)$ | 0.40 |
| $Cu^{2+}(aq) + 2e^-$ | $\longrightarrow Cu(s)$ | 0.34 |
| $Sn^{4+}(aq) + 2e^-$ | $\longrightarrow Sn^{2+}(aq)$ | 0.15 |
| $2H^+(aq) + 2e^-$ | $\longrightarrow H_2(g)$ | 0 |
| $Pb^{2+}(aq) + 2e^-$ | $\longrightarrow Pb(s)$ | - 0.13 |
| $Ni^{2+}(aq) + 2e^-$ | $\longrightarrow Ni(s)$ | - 0.26 |
| $Cd^{2+}(aq) + 2e^-$ | $\longrightarrow Cd(s)$ | - 0.40 |
| $Fe^{2+}(aq) + 2e^-$ | $\longrightarrow Fe(s)$ | - 0.45 |
| $Zn^{2+}(aq) + 2e^-$ | $\longrightarrow Zn(s)$ | - 0.76 |
| $2H_2O(l) + 2e^-$ | $\longrightarrow H_2(g) + 2OH^-(aq)$ | - 0.83 |
| $Al^{3+}(aq) + 3e^-$ | $\longrightarrow Al(s)$ | - 1.66 |
| $Mg^{2+}(aq) + 2e^-$ | $\longrightarrow Mg(s)$ | - 2.37 |
| $Na^+(aq) + e^-$ | $\longrightarrow Na(s)$ | - 2.71 |
| $Li^+(aq) + e^-$ | $\longrightarrow Li(s)$ | - 3.04 |

**Standard Calomel Electrode – SCE**

**Calomel electrode is particularly very simple to construct, free from surface sensitivity and accurate to use even in a very normal laboratory. The calomel electrode consists of an inner glass tube and an outer jacket. In the inner glass tube a platinum wire is dipped into mercury which rests on a paste of mercurous chloride, $Hg_2Cl_2$ (commercially known as calomel) and mercury. This paste is in contact with KCl present in the outer jacket, through the glass frit plug fixed at the bottom of inner glass tube. The calomel electrode comes in contact with the experimental solution through a frit arranged to the outer jacket. The potential of this electrode depends on the concentration of KCl taken in the outer jacket. Some of the most popularly used concentrations of KCl and corresponding single electrode (reduction) potentials on the hydrogen scale at 250C are given below; 0.1M KCl | $Hg_2Cl_2$ (s) | Hg, pt 0.3338 V**

1.0M KCl | $Hg_2Cl_2$ (s) | Hg, pt 0.2800 V
Saturated KCl | $Hg_2Cl_2$ (s) | Hg, pt 0.2415V
The corresponding electrode reaction is;
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$ [red]
And corresponding Nernst's expression is;
$E_{Hg2Cl2 | Cl^-} = E^0_{Hg2Cl2 | Cl^-} - \frac{2.303}{F} \log [Cl]^2$



### Glass Electrode:

Most often used pH electrodes are called glass electrodes and belong to the family of ISEs. They are sensitive only to H+ ions. Typical glass electrode is made of glass tube engaged with small glass bubble sensitive to protons. Inside of the electrode is usually filled with buffered solution of chlorides in which silver wire covered with silver chloride is immersed. pH of internal solution varies- for example it can be 1.0(0.1M HCl) or 7.0

Active part of the electrode is the glass bubble. While tube has strong and thick walls, bubble is made to be as thin as possible. Surface of the glass is protonated by both internal and external solution till equilibrium is achieved. Both sides of the glass are charged by the adsorbed protons, this charge is responsible for potential difference. This potential in turn is described by the Nernst equation and is directly proportional to the pH difference between solutions on both sides of the glass.

The majority of pH electrodes available now a day are combination electrodes that have both glass $H^+$ ion sensitive electrode and reference electrode compartments, conveniently placed in one housing.

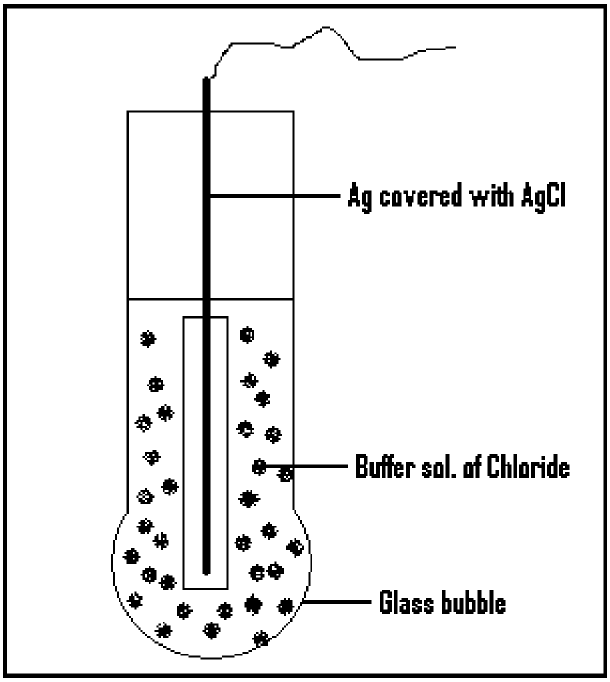
### Range of a pH glass electrode

The pH range at a constant concentration can be divided into 3 parts Useful Working Range: Dependence of potential on pH has linear behavior and within which such electrode really works as ion-selective electrode for pH and obeys Nernst equation.

Alkali error range: At very low concentration of hydrogen-ions (high values of pH) metal ions interfere. In this situation dependence of the potential on pH become non-linear.

Acidic error range: At very high concentration of hydrogen-ions (low values of pH) the anions plays a big role as interfering ions, in addition to destruction of the glass matrix used for making glass bulb.

Almost all commonly used glass electrodes have a working pH range from pH = 1 till pH = 12. So specially designed electrodes should be used only for working in aggressive conditions.



Representation Ag, HCl(1M)/Glass $E_G$= $E^0_G$ – 0.059pH (at 25ÝC)

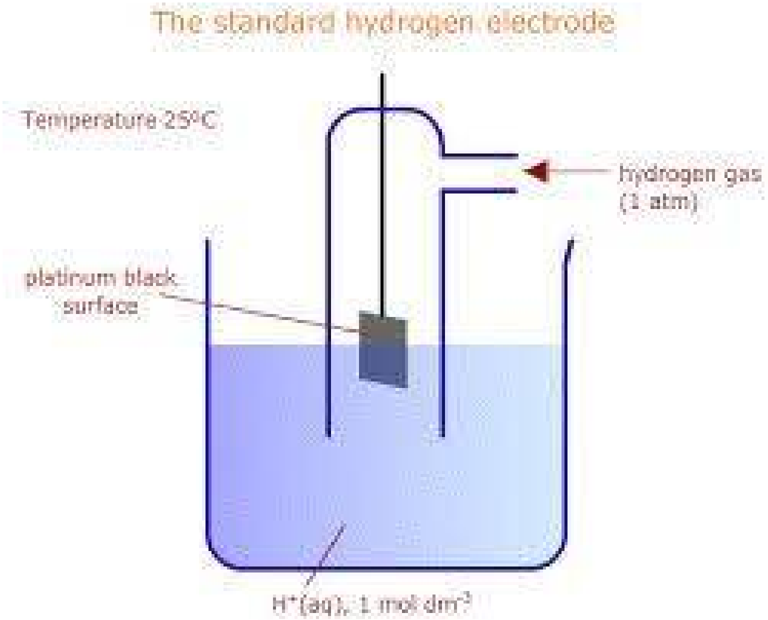
## The Standard Hydrogen Electrode

**This is an apparatus setup that is used to compare the electrode potentials of metal and other electrode systems. It comprises hydrogen gas at atmospheric pressure brought into contact with a platinum black electrode in 1molar (mol dm$^{-3}$) acid solution. The hydrogen ions from the acid solution set up an equilibrium with the hydrogen gas.**

$$2H^+ + 2e \rightleftharpoons H_2$$

**If the other half cell connected to the standard hydrogen electrode releases electrons then it can be said to be relatively negative with respect to the standard hydrogen electrode (which is assigned a value of 0 volts)**

**For example, metals that are more reactive than hydrogen gas preferentially release electrons (forcing the SHE to accept the electrons) and have standard electrode potentials with negative values.**



**Pt/$H_2$ (1 atm)/$H^+$ (1M) ; $E_0$ = 0 V**

## Concentration Cell

It is an electrochemical cell which produces electrical energy by the transfer of material from a system of higher concentration to a system of lower concentration. The difference in concentration may be due to difference in concentration of the electrodes or electrolyes.

Electrode concentration cell- In this cell, two electrodes of same metal with different concentrations are dipped in the same solution of electrolyte, eg., amalgam concentration cell.

Electrolyte concentration cell- In this cell, two electrodes of same matel are dipped in the solutions containing their ions at different concentrations(Fig 2).The electrode dipped in the solution of lower concentration is anode and the electrode dipped in the solution of higher concentration is cathode. The overall reaction involves the transfer of material from higher concentration to lower concentration. The two solutions are connected together by a salt-bridge.

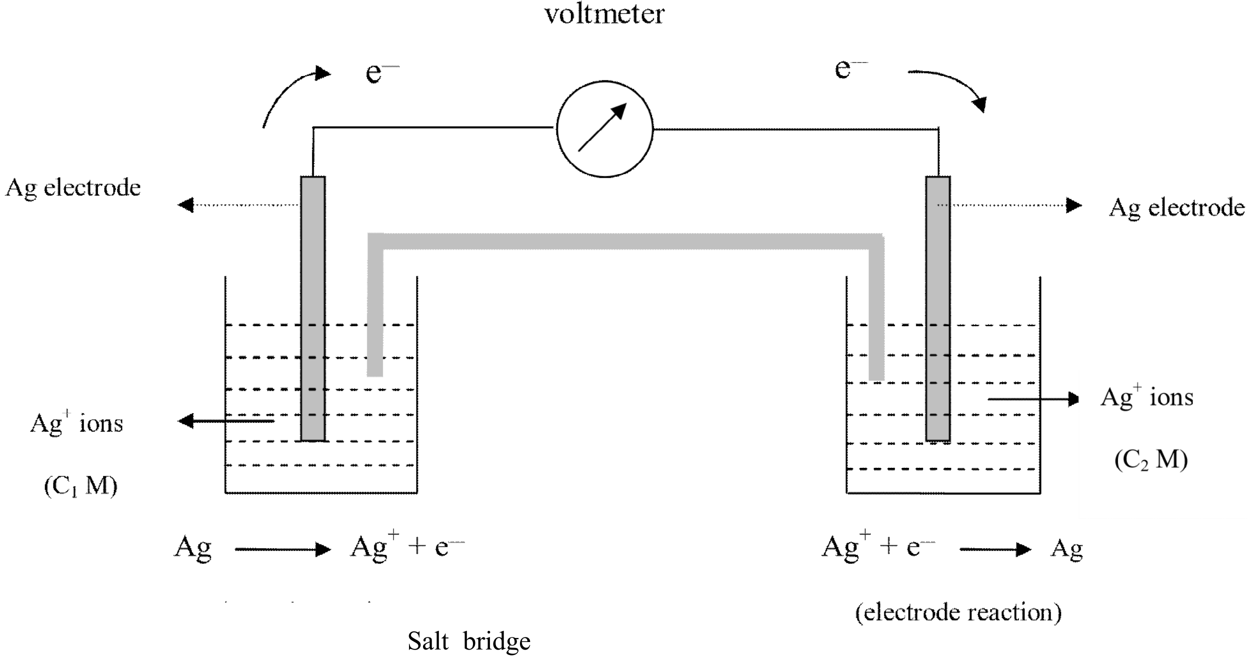
At anode: Ag $Ag^{+}(C_1)$ $\underset{>}{+}$ $e^{-}$ At

cathode: $Ag^{+}(C_2)$ + $e^{-}$ ______Ag >

The cell reaction is $Ag^{+}(C_1)$ > $Ag^{+}(C_2)$

The emf of the cell = ______ 0.0591 log

$[C_1/C_2]n$



$C_2 > C_1$

**Concentration Cell**

## Unit 2 CORROSION AND PREVENTION

Corrosion: Dry and wet corrosion – Pilling-Bedworth rule – mechanism of wet corrosion – types of wet corrosion – galvanic corrosion – differential aeration corrosion – factors affecting corrosions. Corrosion control methods – design and material selection – cathodic protections – sacrificial anode and impressed current method –

---

### Corrosion

Corrosion is defined as the deterioration of a material, usually a metal, because of a reaction with its environment and which requires the presence of an anode, a cathode, an electrolyte, and an electrical circuit.

DRY OR CHEMICAL CORROSION

Dry corrosion occurs through the direct chemical action of environment / atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid with metal surfaces in immediate proximity.

1. Oxidation corrosion is brought about by the direct action of oxygen at low or high temperatures on metals, usually, in the absence of moisture. The reactions in the oxidation corrosion are:

$$2\,M \longrightarrow \underset{\text{Metal ions}}{2\,M^{n+}} + 2\,ne^-$$

$$n\,O_2 + 2\,n\,e^- \longrightarrow \underset{\text{Oxide ions}}{2\,n\,O^{2-}}$$

$$\text{or}\quad 2\,M + n\,O_2 \longrightarrow \underset{\text{Metal ions}}{2\,M^{n+}} + \underset{\text{Oxide ions}}{2\,n\,O^{2-}}$$

**Metal oxide**

Mechanism: Oxidation occurs first at the surface of the metal and the resulting metal oxide scale forms a barrier, that tends to restrict further oxidation. For oxidation to continue either the metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale to the underlying metal. Both transfers occur, but the outward diffusion of metal is, generally, much more rapid than the inward diffusion of oxygen, since the metal ion is appreciably smaller than the oxygen ion and consequently, of much higher mobility.

**Mechanism:** At the surface of metal oxidation occurs and the resulting metal oxide scale forms a barrier whichrestricts further oxidation. For oxidation to continue either the metal must diffused outwardsthrough the scale to the surface or the oxygen must defuse inwards through the scale to the underlyingmetal. Both the cases are possible. But the outward diffusion of metal is generally more rapid than inwarddiffusion of oxygen since metal ion is appreciably smaller than the oxygen ion and hence more mobile.

**Metal + Oxygen →Metal oxide**

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decidesfurther action. If the film is,a)Stable, it behaves has a protective coating in nature e.g., the oxide films on Al, Pb, Cu,Pt etc., are stable and therefore further oxidation corrosion of prohibited.

b) Unstable that is the oxide layer formed decomposes back into metal and oxygen. So, Oxidation Corrosion is notpossible.

**Metal oxide →Metal + Oxygen**

e.g., Ag, Au and Pt do not undergo oxidation Corrosion.

c) Volatile that is oxide layer volatilizes after formation and as such leaves the underlying metal surface exposed furtherattack. This causes continuous which is excessive. e.g. Molybdenum oxide ($MoO_3$)

d) Porous that is the oxide layer formed having pores or cracks. In this case the Atmospheric oxygen passesthrough the pores or cracks of the underlying metal surface. This causes continuous corrosion till complete conversionof metal into its oxide.

**Pilling-Bedworth rule:** According to it "an oxide is protective or non-porous, if thevolume of the oxide is atleast as great as the volume of the metal from which it is formed". On theother hand, "if the volume of the oxide is less than the volume of metal, the oxide layer is porous (ornon-continuous) and hence, non-protective, because it cannot prevent the access of oxygen to thefresh metal surface below".Thus, alkali and alkaline earth metals (like Li, K, Na, Mg) form oxides of volume less than thevolume of metals. Consequently, the oxide layer faces stress and strains, thereby developing cracksand pores in its structure. Porous oxide scale permits free access of oxygen to the underlying metalsurface (through cracks and pores) for fresh action and thus, corrosion continues non-stop.Metals like Aluminium forms oxide, whose volume is greater than the volume of metal.Consequently, an extremely tightly-adhering non-porous layer is formed. Due to the absence ofany pores or cracks in the oxide film, the rate of oxidation rapidly decreases to zero.

**Wet Corrosion (or) Electro-chemical (or) Immersed Corrosion.-**

This type of Corrosion occurs where a conducting liquid is in contact with the metal or when two dissimilar metals or alloysare dipped partially in a solution. This corrosion occurs due to the existence of separate anodic and cathodic parts,between which current flows through the conducting solution. At anodic area, oxidation reaction occurs there bydestroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

**At Anode: $M \rightarrow M^{n+} + ne^-$**

Dissolution

$M^{n+}$<Formation of compound

At cathodic part, reduction reaction (electro nation) occurs. It does not affect the cathode, since most metalscannot be further reduced. At cathodic part, the dissolved constituents in the conducting medium accept the electronsforming ions ($OH^-$, $O^{2-}$). The metallic ions formed at anodic part and the ions formed at cathodic part diffuse towardseach other through conducting medium and form a corrosion product somewhere between anode and cathode.

**Mechanism:**

Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reactioninvolves dissolution of metal liberating free electrons.

**$M \rightarrow M^{n+} + ne^-$**

The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygenwhich depends on the nature of corrosive environment.

**Evolution of hydrogen:** This type of corrosion occurs in acidic medium e.g., considering the metalFe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.

**$Fe \rightarrow Fe^{2+} + 2e^-$( Oxidation)**

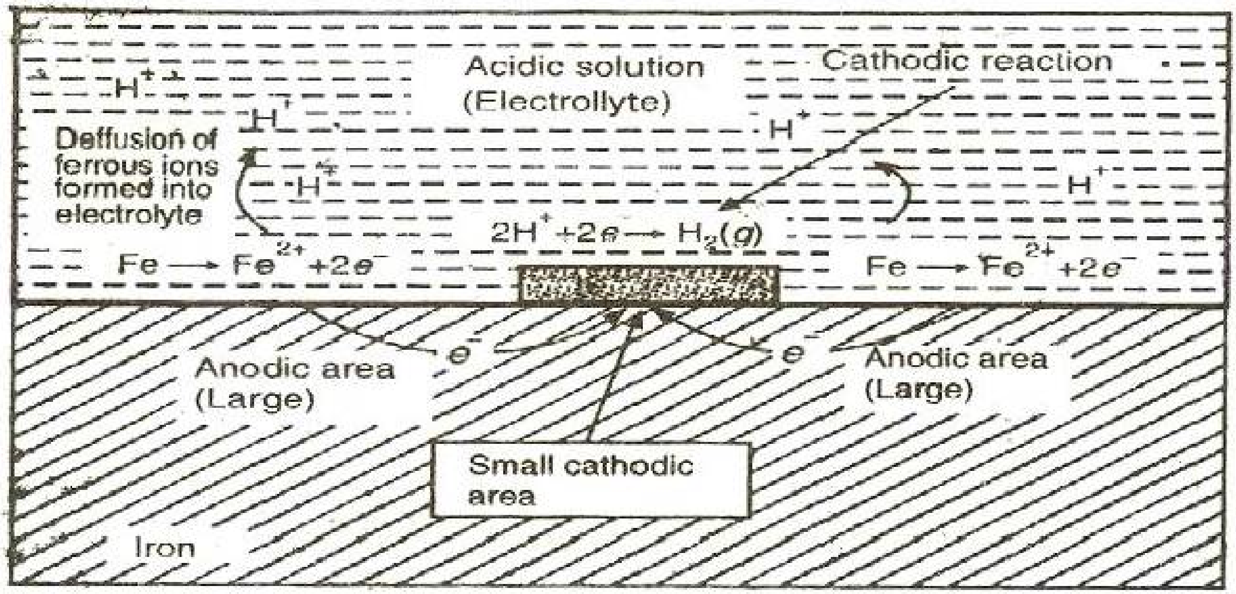
The electrons released flow through the metal fromanode to cathode, whereas H+ ions of acidic solutionare eliminated as hydrogen gas.

**$2H^+ + 2e^- \rightarrow H_2$**

The overall reaction is

$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$

This type of corrosion causes displacement ofhydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendencyto get dissolved in acidic solution with simultaneous evolution of $H_2$ gas. The anodes are large areas, whereascathodes are small areas.



**Absorption of oxygen: -** For example, rusting of iron in neutral aqueous solution of electrolytes inpresence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the filmdevelops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It

**At anode:** $Fe \rightarrow Fe^{2+} + 2e^-$ (Oxidation)

**At cathode:**

The released electrons flow from anode to cathodethrough iron metal.

**$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$**

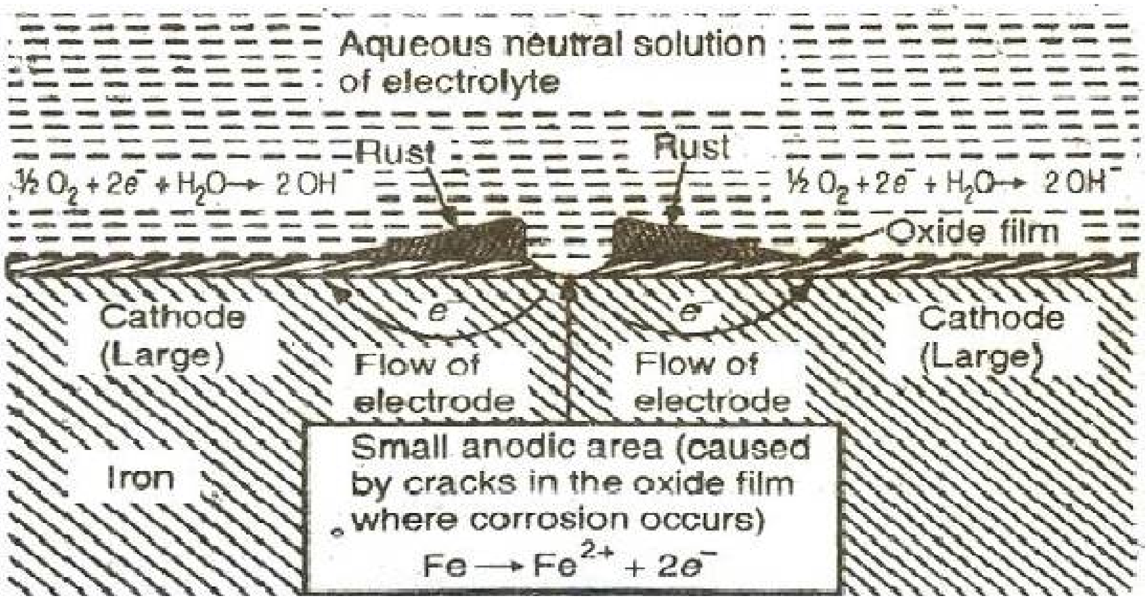
**(Reduction)**

**$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$**

If oxygen is in excess, ferrous hydroxide is easilyoxidized to ferric hydroxide.

**$4Fe^{2+}(OH)^-_2 + O_2 + 2H_2O \rightarrow 4Fe\ (OH)_3$**

The product called yellow rust corresponds to $Fe_2O_3$. $xH_2O$.



**TYPES OF ELECTROCHEMICAL CORROSION**

The electrochemical corrosion is classified into the following two types:

(i) Galvanic (or Bimetallic) Corrosion

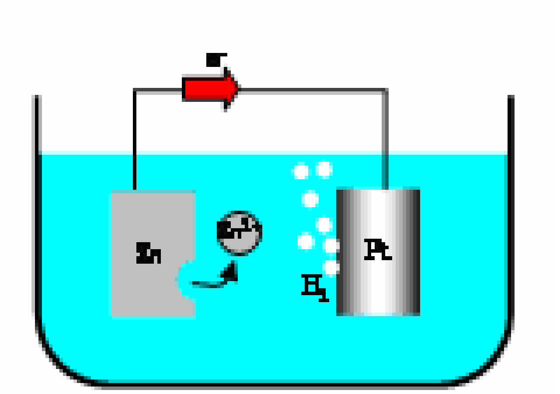
(ii) Differential aeration or concentration cell corrosion.

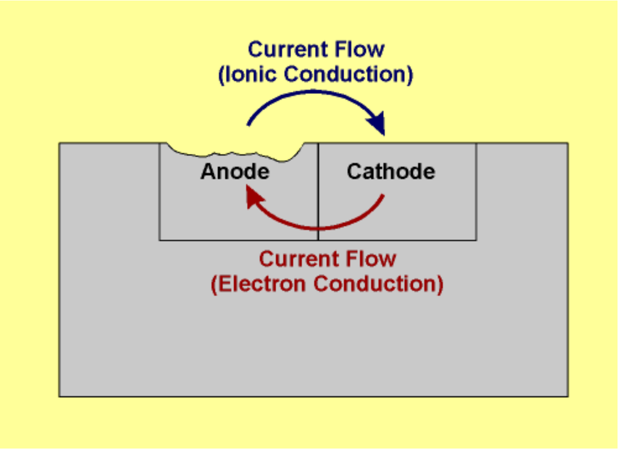
**Galvanic Corrosion:**

When two dissimilar metals (eg., zinc and copper) are electrically connected and exposed toan electrolyte, the metal higher in electrochemical series undergoes corrosion. In this process, themore active metal (with more negative electrode potential) acts as a anode while the less activemetal (with less negative electrode potential) acts as cathode.In the above example, zinc (higher in electrochemical series) forms the anode and is attackedand gets dissolved; whereas copper (lower in electrochemical series or more noble)acts as cathode.Mechanism: In acidic solution, the corrosion occurs by the hydrogen evolution process;while in neutral or slightly alkaline solution, oxygen absorption occurs. The electron-current flowsfrom the anode metal, zinc to the cathode metal, copper.

$Zn \rightarrow Zn^{2+} + 2e^-$ (Oxidation)

Thus it is evident that the corrosion occurs at the anode metal; while the cathodic part isprotected from the attack.Example: (i) Steel screws in a brass marine hardware (ii)Lead-antimony solder aroundcopper wise; (iii) a steel propeller shaft in bronze bearing (iv Steel pipe connected to copperplumbing.

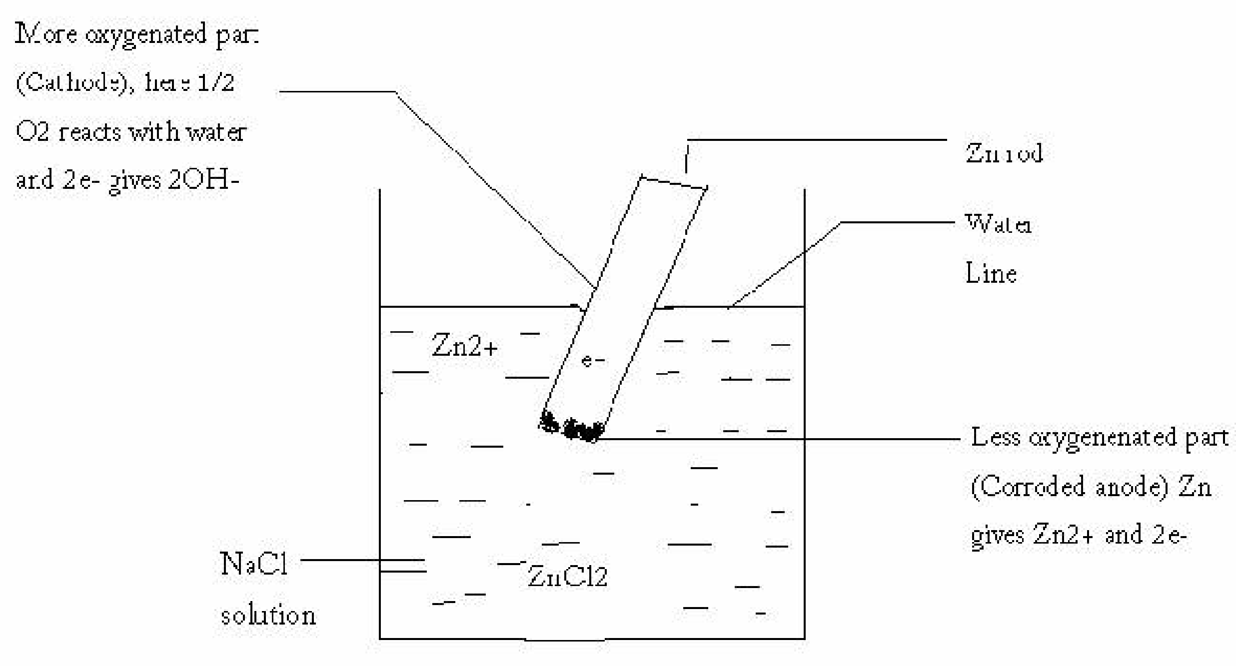




**Concentration Cell Corrosion:**

It is due to electrochemical attack on the metal surface, exposed to an electrolyte of varyingconcentrations or of varying aeration.It occurs when one part of metal is exposed to a different air concentration from the otherpart. This causes a difference in potential between differently aerated areas. It has been foundexperimentally that poor-oxygenated parts are anodic.Examples: i) The metal part immersed in water or in a conducting liquid is called water linecorrosion.ii) The metal part partially buried in soil.

Explanation: If a metal is partially immersed in a conducting solution the metal part above thesolution is more aerated and becomes cathodic. The metal part inside the solution is less aerated andthus becomes anodic and suffers corrosion.

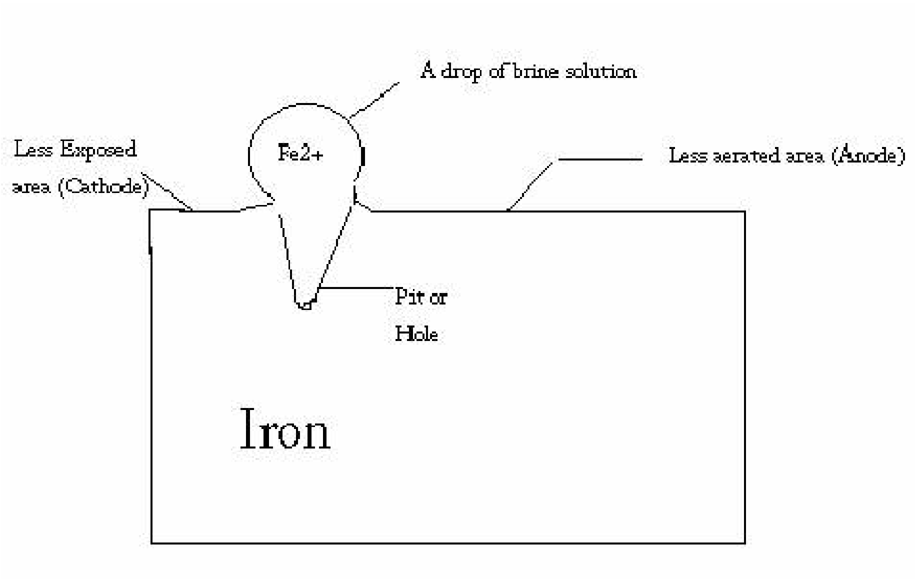


At anode: Corrosion occurs (less aerated) $M \rightarrow M^{2+} + 2e^-$
At cathode: OH- ions are produced (more aerated) $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH$

Examplesfor this type of corrosion are
1) Pitting or localized corrosion
2) Crevice corrosion
3) Pipeline corrosion
4) Corrosion on wire fence

**Pitting Corrosion:**

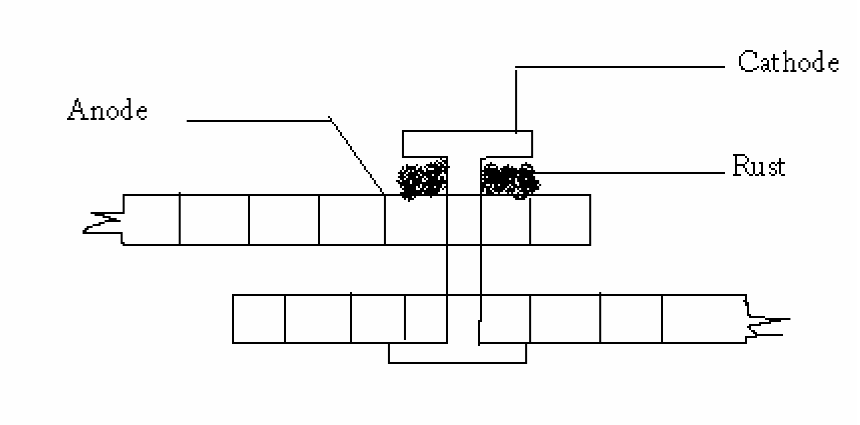
Pitting is a localized attack, which results in the formation of a hole around which the metal isrelatively unattacked.The mechanism of this corrosion involves setting up of differential aeration or concentrationcell.Metal area covered by a drop of water, dust, sand, scale etc. is the aeration or concentrationcell.Pitting corrosion is explained by considering a drop of water or brine solution (aqueoussolution of NaCl) on a metal surface, (especially iron).The area covered by the drop of salt solution as less oxygen and acts as anode. This areasuffers corrosion, the uncovered area acts as cathode due to high oxygen content.It has been found that the rate of corrosion will be more when the area of cathode is largerand the area of the anode is smaller. Hence there is more material around the small anodic arearesults in the formation hole or pit.



At anode: Corrosion occurs (less aerated) M $\rightarrow M^{2+} + 2e^-$
At cathode: OH- ions are produced (more aerated) $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH$

The net reaction is
$Fe + 2OH^- \rightarrow Fe(OH)_2$
The above mechanisms can be confirmed by using ferroxyl indicator (a mixture containingphenolphthalein and potassium ferricyanide). Since OH- ions are formed at the cathode, this area
imparts pink colour with phenolphthalein indicator. At the anode, iron is oxidized to $Fe^{2+}$ which
combines with ferricyanide and shows blue colour.

**Crevice corrosion:**
If a crevice ( a crack forming a narrow opening) between metallic and non-metallic material is
in contact with a liquid, the crevice becomes anodic region and undergoes corrosion. Hence,oxygen supply to the crevice is less. The exposed area has high oxygen supply and acts as cathode.Bolts, nuts, rivets, joints are examples for this type of corrosion.



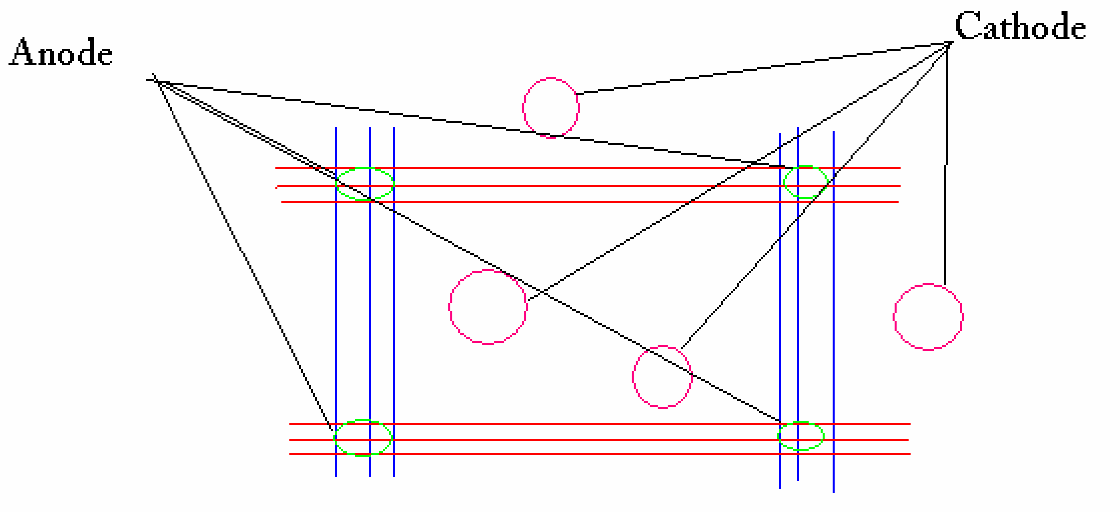
Crevice Corrosion

**Pipeline corrosion:**

Buried pipelines or cables passing from one type of soil (clay less aerated) to another soil(sand more aerated) may get corroded due to differential aeration.

**Corrosion in wire fence:**

A wire fence is one in which the areas where the wires cross (anodic ) are less aerated thanthe rest of the fence (cathodic). Hence corrosion takes place at the wire crossing.Corrosion occurring under metal washers and lead pipeline passing through clay tocinders(ash) are other examples.



Corrosion in wire fence

## FACTORS AFFECTING CORROSION

The rate and extent of corrosion depends on the following factors.

1. Nature of the metal
2. Nature of the environment

## 1. Nature of the metal

### a. Position in galvanic series

The metal higher up in the galvanic series suffers corrosion. The metal higher up in galvanic series becomes anode. If the metals are apart in the galvanic series, the difference in their oxidation potential will be greater. This results in a faster corrosion of the anode metal.

### b. Over voltage

The reduction in over voltage increases corrosion. If pure zinc is placed in $H_2SO_4$, the rate of corrosion is slow because of high over voltage of 0.70 V. When a drop of $CuSO_4$ is added the hydrogen over voltage is 0.33V.There is an increase in corrosion. If a drop of platonic chloride is added, the over voltage is 0.2 V. The corrosion is faster and thus the reduction in over voltage increases corrosion.

### c. Relative areas of the anode and cathode

Corrosion of the anode is directly proportional to the area of the cathode. If the anode area is smaller, the current density at the smaller anode is greater. There is a great demand for electrons by the large cathode area. It is met by the smaller anode only by undergoing corrosion.

### d. Purity of metal

Impurities in a metal are heterogeneous. They form minute electrochemical cells with the rest of the metal under appropriate environment and the anode parts gets corroded.

### e. Physical state of the metal

If the grain size of the metal is small, the solubility will be high. The orientation of the crystals at the metal surface and the areas under stress influence the corrosion.

### f. Nature of surface film

Metal surfaces come into contact with atmospheric gases like oxygen, halogens, hydrogen sulphide, sulphur dioxide and nitrogen. A film of the corrosion product is formed on the surface of the metal. Metals like Mg, Ca, Li, Na, K and Ba form oxides. The specific volume of the oxides is less than that of metal atom. The oxide film will be porous and though this more oxygen can diffuse to bring about further corrosion. Metals like Al, Cr, Ni, and W form oxides. The specific volume of oxides is greater than that of the metal atom. The oxide film so formed is non porous and it protects the metal from further oxidation.

### g. Solubility of corrosion products

The corrosion product is formed between anode and cathode. The corrosion reaction goes on without any change of the corrosion product goes into the solution. Some of the corrosion products are insoluble compounds. This may reduce the rate of subsequent corrosion.

## 2. Nature of the environment

### a. Temperature

The rate of chemical reactions and the rate of diffusion increase with temperature. Thus a passive metal may become active at a higher temperature.

### b. Humidity

Humidity of air is an important factor in the atmospheric corrosion. Corrosion of iron is slow in dry air but increases rapidly in the presence of moisture.

### c. Impurities

The air in industrial areas contains corrosive gases and fumes. These gases increase the acidity of the liquid that comes into contact with metal surfaces. The electrical conductivity increased and this results in an increase of corrosion.

### d. Effect of pH

The hydrogen ion concentration is an important factor in the corrosion of metallic surfaces. Corrosion can be reduced by increasing the pH of the solution

### e. Ions

Presence of anions may form an insoluble reaction product. The reaction product inhibits corrosion. On the other hand, chloride ions destroy the surface film and corrode the metals and alloys.

### f. Conductance of the medium

It is important in the case of underground structures. Conductance of dry soil is lower than those of clay soils. Hence stray currents will damage the metal structures buried under clay or mineralized soils then those under dry sandy soils.

**g. Formation of oxygen concentration cell**

Differential aeration promotes corrosion by the formation of concentration cells. The region where oxygen concentration is less becomes anode and suffers corrosion.

**h. Flow velocity of process stream**

When the corrosion is diffusion controlled velocity can have considerable effect. When metals that do not passivity are under diffusion control, and increase in velocity reduces the difficulty in diffusion and increases the rate of corrosion.

## CORROSION CONTROL (PROTECTION AGAINST CORROSION)

### 1. PROPER DESIGNING

The design of the material should be such that "corrosion, even if it occurs, is ***uniform*** and does not result in the intense and localized corrosion". Important design principle are:

i. "Avoid the contact of dissimilar metals in the presence of a corroding solution. If this principle is not followed, then corrosion is localized on the more active (in the immediate vicinity of contact); while the less active metal remains protected.

ii. When two dissimilar metals are to be in contact, the ***anodic material should have as large area*** as possible; whereas the cathodic metal should have as much smaller area as possible.

iii. If two dissimilar metals in contact have to be used, ***they should beas close as possible to each other in the electrochemical series***.

iv. Whenever the direct joining of dissimilar metals, is unavoidable, an ***insulating fitting***may be applied in between them to avoid direct metal-metal electrical corrosion.

v. ***The anodic metal should not be painted or coated***, whenever in contact with a dissimilar cathodic metal, because any break in coating would lead to rapid localized corrosion.

vi. ***Prevent the occurrence of inhomogeneities,*** both in the metal and in the corrosive environment. Thus, a proper design should avoid the presence of crevices between adjacent parts of the structure, even in the case of the same metal, since crevices permit concentration differences. Bolts and reverts are undesirable for this reason and these should preferably be replaced by a butt-weld (Fig. 1). When it is impractical to avoid crevices in a given design, their harmful effects can be minimized, if the corroding medium is denied access to crevices with an impervious material or by painting.

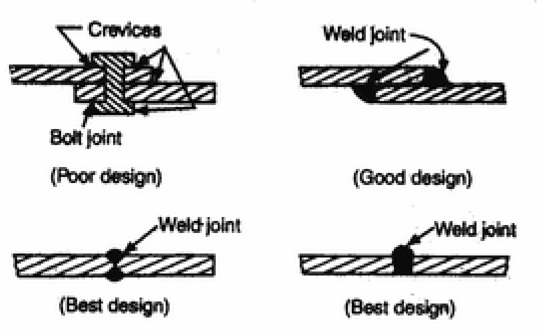


**Fig. 1. Different types of joints**

vii. It is desirable that the design allows for adequate cleaning and flushing of the critical parts (i.e., susceptible to dirt, deposition, etc.) of the equipment. ***Sharp concerns and recesses should be avoided,*** because they favour the formation of stagnant areas and accumulation of solids, etc. (Fig. 2).

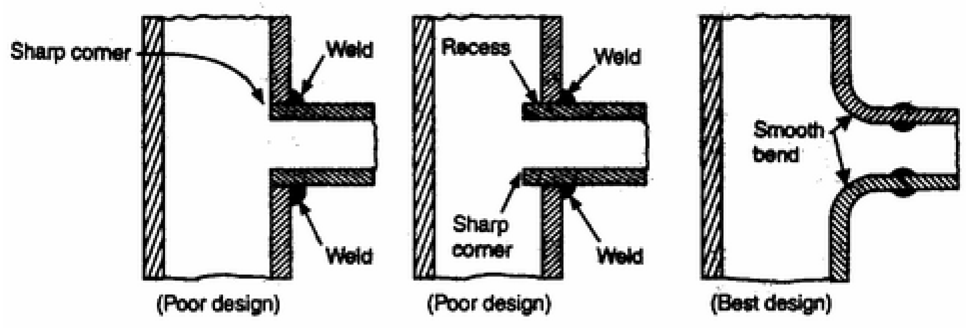


**Fig. 2. Prevention of corrosion by design-elimination of sharp corners and stresses**

viii. Whenever possible, the equipment should be supported on legs to allow free circulation of air and prevent the formation of stagnant pools or damp areas (Fig. 3).

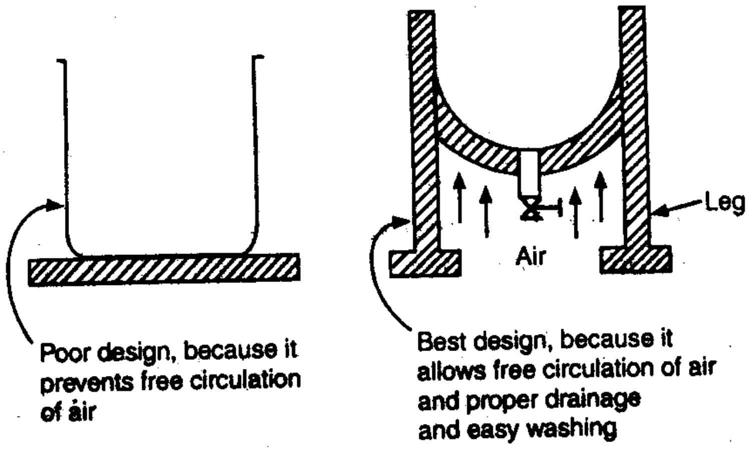


**Fig. 3. Prevention of corrosion by design**

ix. Uniform flow of a corrosion liquid is desirable, since both stagnant areas and highly turbulent flow and high velocities can cause accelerated corrosion. So, highly impingement conditions of flowing liquid should be avoided as much as practically possible.

x. A proper design should prevent condition subjecting some areas of structure to stress (cold-worked part). Such an area could set up a galvanic couple with a non-stressed (not worked) areas of the metal (Fig. 3).

## 2. USING PURE METAL

Impurities in a metal cause ***heterogeneity,*** which decreases corrosion-resistance of the metal. Thus, the corrosion-resistance of a given metal may be improved by ***increasing*** its purity. Purification of metals like Al, Mg, etc., provides a coherent and impervious protective oxide film on their surfaces, when exposed to environment. However, corrosion-resistance of a purified metal depends on the ***nature*** of corrosive environment.

## 3. USING METAL ALLOYS

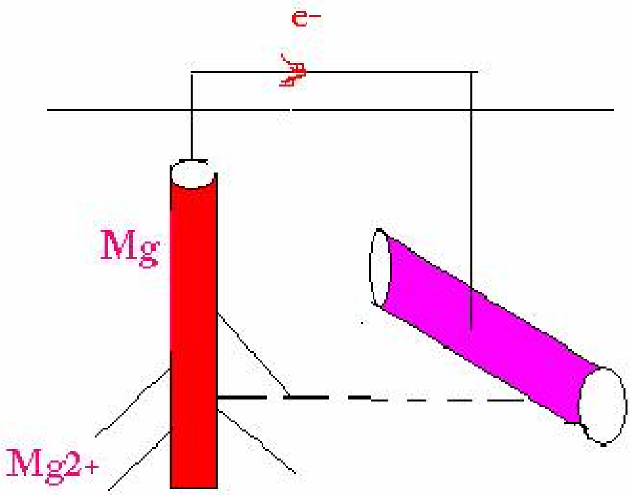
Noble, but precious metals such as platinum and gold are corrosion-resistant. Corrosion-resistance of most metals is best increased by alloying them with suitable elements, but for maximum corrosion-resistance ***alloyshould be completely homogenous.*** Chromium is the best suitable alloying metal for iron or steel. Its film is self-healing.

## 4. CATHODIC PROTECTION

The principle involved in this method is to force the metal to be protected to behave like a ***cathode,*** thereby corrosion does not occur. There are two types of cathodic protections.

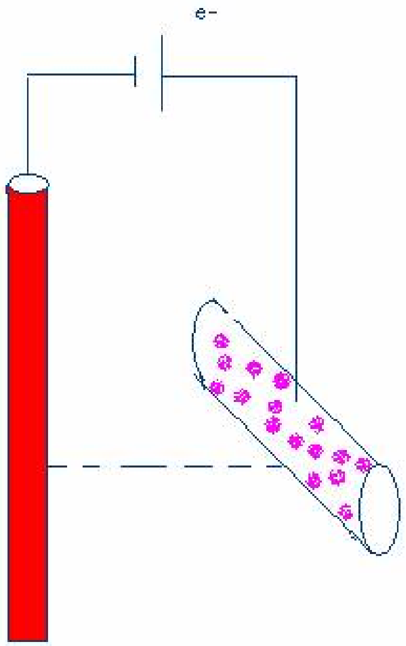
### *i. Sacrificial anodic protection method*

In this protection method, the metallic structure (to be protected) is connected by a wire to a ***more anodic metal,*** so that all the corrosion is concentrated at this more active metal. The more active metal itself gets ***corroded slowly;*** while the parent structure (cathodic) is protected. The more active metal so-employed is called “sacrificial anode”. The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminium and their alloys. Important applications of sacrificial anodic method include protection of buried pipelines, underground cables, marine structures, ship-hulls, water-tanks, piers etc. (Fig. 4).



In cathodic protection, an anode of a more strongly reducing metal is sacrificed to maintain the integrity of the protected object (eg., a pipeline, bridge, ship hull or boat).

### *ii. Impressed current cathodic protection*



In Impressed-current cathodic protection, electrons are supplied from an external cell so that the object itself becomes cathodic and is not oxidized.

## UNIT III

Classification of fuels – calorific value – HCV and LCV – Analysis of coal – proximate and ultimate analysis – **carbonization of coal** (HTC and LTC) – Manufacture of coke – properties of coke – flue gas analysis by Orsat's apparatus. Petroleum – Refining – Synthetic petrol – Fischer – Tropsch and **Bergius process** – cracking – polymerization process – **knocking in petrol and diesel engines** – **octane number and cetane number** – **properties of straight run, cracked and polymer gasoline.**

## INTRODUCTION

Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purposes. During the process of combustion of a fuel (like coal), the atoms of carbon, hydrogen, etc. combine with oxygen with the simultaneous liberation of heat at a rapid rate. This energy is liberated due to the "rearrangement of valency elections" in these atoms, resulting in the formation of new compounds (like $CO_2$, $H_2O$, etc.). These new compounds have less energy (or heat content) in them and therefore, the energy (or heat) released during the combustion process is the difference in the energy of the reactants (C, H and O, etc. of fuel) and that of the products formed.

$$\underset{\text{More heat energy content}}{\text{FUEL} + O_2} \longrightarrow \underset{\text{Lesser heat energy content}}{\text{PRODUCTS}} + \text{HEAT}$$

## CLASSIFICATION OF FUELS

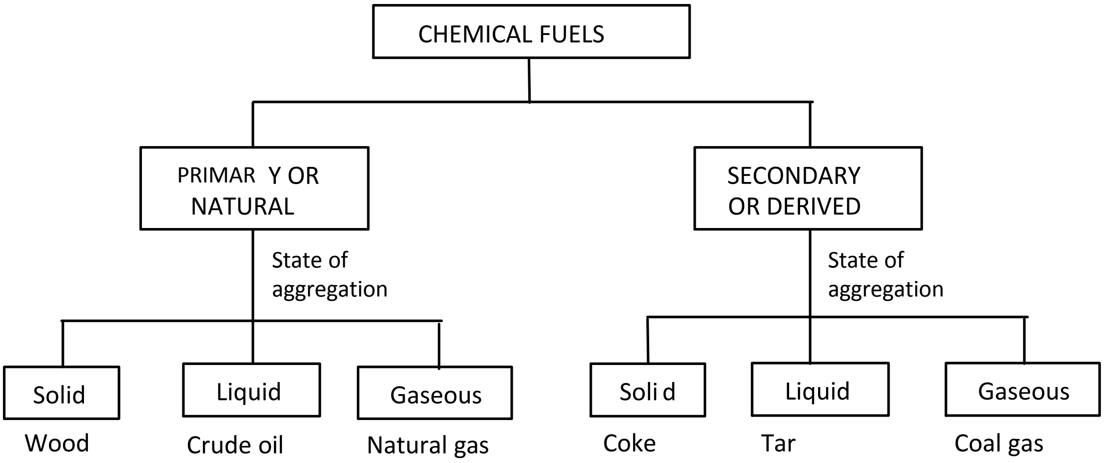
The fossil fuels have been classified according to their: (1) occurrence (and preparation) and (2) the state of aggregation. According to the first classification, we have: (a) natural or primary fuels, which are found in nature as such, e.g., wood, peat, coal, petroleum, natural gas, etc. ; (b) artificial or secondary fuels are those which are prepared form the primary fuels. For example, charcoal, coke, kerosene oil, diesel oil, petrol, coal gas, oil gas, producer gas, blast furnace gas, etc.

Peat Lignite
Coal
Dung

Charcoal
Petroleum
coke Coal
briquette

Kerosene
Diesel
Petrol
Fuel oil
Synthetic
Gasoline L.P.G.

Water gas
Oil gas
Biogas
Blast furnace
Gas
Coke oven gas



The second classification is based upon their state of aggregation like: (a) solid fuels; (b) liquid fuels and (c) gaseous fuels.

## 26. CALORIFIC VALUE

Calorific value of a fuel is 'the total quantity of heat liberated, when a unit mass (or volume) of the fuel is burnt completely".

1. **Calorie:** It is the amount of heat required to increase the temperature of 1 gram of water through one degree centigrade.

2. **Kilocalorie:** This is the unit of heat in metric system, and is defined as the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade.

**1k.cal=1000cal**

**1k.cal=3.968B.Th.U**

3. **British thermal unit (B.Th.U):** This is the unit of heat in English system, it is defined as "the quantity of heat required to increase the temperature of one pound of water through of one degree of Fahrenheit.

**1B.Th.U=252cal=0.252k.cal**

4. **Centigrade heat unit (C.H.U):** It is the quantity of heat required to raise the temperature of one pound of water through one degree centigrade.

**1k.cal=3.968B.Th.U=2.2C.H.U**

**Inter conversion of various units of heat:**

On the basis that **1kg=2.2lband1$^0$C=1.8$^0$Fwehave**

**1k.cal=1000cals=3.968B.Th.U=2.2C.H.U1**
**B.Th.U=252cals**Units of

**calorific value:**

**Forsolidorliquidfuels:cal/gork.cal/kg,B.Th.U/lbForgaseousfuels:k.cal/cubicmeterork.cal/m$^3$B.Th.U/ft$^3$orB.Th.U/cubicfeet**

**Relation between various units:**

**1k.cal/kg=1.8B.Th.U/lb=1cal/g1k.cal/m$^3$=**
**0.1077B.Th.U/ft$^3$**
**1B.Th.U/ft$^3$=9.3k.cal/m$^3$**

**Higher or gross calorific value:** “The total amount of heat produced, when unit mass / volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature” (i.e., 15qC or 60qF).]

**Lower or net calorific value:** “The net heat produced, when unit mass/volume of the fuel is burnt completely and the products are permitted to escape”. Alternatively, net or lower calorific value (LCV).

= HCV – Latent heat of water vapour formed

= HCV – Mass of hydrogen u 9 u Latent heat of steam

because 1 part by mass of hydrogen produces 9 parts by mass of water. The latent heat of team is 587 kcal/kg.

Net calorific value = Gross calorific value – 9 x H x 587 100

= Gross calorific value – 52.83 x %H Where % H =

percentage of hydrogen.
The gross and net calorific values of coal can be calculated by bomb calorimeter.

## 27. ANALYSIS OF COAL

In order to assess the quality of coal, the following two type of analysis are made:

**(A) Proximate analysis involves in the following determinations:**

(1) **Moisture:** About 1 g of finely powered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105q - 110qC. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture

Loss in weight

Percentage of moisture = ______________ u100

Wt. of coal taken

(2) **Volatile matter:** The dried sample of coal left in the crucible is covered with a lid and placed in an electric furnace (muffle furnace), maintained at 925qr 20qC. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside a desiccator and weighed again.

Loss in weight due to removal of volatile matter

Percentage of volatile matter =

______________

u100 Wt. of coal sample taken

(3) **Ash:** The residual coal in the crucible in (2) is then heated without lid in a muffle furnace at 700 r 50qC for ½ hour. The crucible is then taken out, cooled and weighed.

Wt. of ash left percentage

of ash = ______________ u100

Wt. of coal taken

(4) **Fixed carbon:** Percentage of fixed carbon

= 100 - % of (moisture + volatile matter + ash)

**Importance of proximate analysis:** Proximate analysis provides following valuable informations in assessing the quality of coal:

(1) **Moisture** in coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal. Moreover, it quenches the fire in the furnace. Hence, lesser the moisture content, better the quality of coal as a fuel. However, presence of moisture, upto 10%, produces a more uniform fuel-bed and less of “fly-ash”.

(2) **Volatile matter:** A high volatile matter content means that a high proportion of fuel will distill over as gas or vapour, a large proportion of which escapes unburnt, So, higher volatile content in coal is undesirable. A high volatile matter containing coal burns with a long flame, high smoke and has low calorific

value. Hence, lesser the volatile matter, better the rank of the coal. The volatile matter affects the furnace volume and arrangement of heating space.

Thus, high-volatile matter containing coals (usually of low rank) do not cake well, whereas medium-volatile matter content coals (containing 26-30% volatile matter) are capable of yielding hard and strong coke on carbonization. On the other hand, lowvolatile matter containing coals do not cake at all and consequently, they are totally unsuitable for coke making.

(3) **Ash** is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby clinkers (i.e., fused ash lumps), which block the interspaces of the grate, on which coal is being burnt. This in-turn causes obstruction to air supply, thereby the burning of coal becomes irregular. Hence, lower the ash content, better the quality of coal. The presence of ash (similar to moisture) also increases transporting, handling and storage costs. It also involves additional coast in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

(4) **Fixed carbon:** Higher the percentage of fixed carbon, greater is its calorific and better the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon (in coal) that can be burnt by a primary current of air drawn through the hot bed of a fuel. Hence, high percentage of fixed carbon is desirable. The percentage of fixed carbon helps in designing the furnace and the shape of the fire-box, because it is the fixed carbon that burns in the solid state.

**(B) Ultimate analysis involves in the following determinations:**

**(1) Carbon and hydrogen:** About 1-2 g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into $CO_2$ and $H_2O$ respectively. The gaseous products of combustion are absorbed respectively in KOH and $CaCl_2$ tubes of known weights. The increase in weights of these are then determined.

$C + O_2 \longrightarrow$ $CO_2 : H_2 + \underline{1}O_2 \longrightarrow H_2O$

2

$\underline{1244} \longrightarrow$ 2 18

$2\,KOH + \longrightarrow CO_2K_2CO + H_2O$

$CaCl_2 + 7\,H_2OCaCl_27\,H_2O$ ·

?Percentage of C = ———————— Increase in

weight of KOH tube u 12 u 100Weight of coal

sample taken u 44

$$\text{Percentage of H} = \frac{\text{Increase in weight of CaCl}^{2}\text{ tube u 2 u 100 and}}{\text{Weight of coal sample taken u 18}}$$

(2) **Nitrogen:** About 1 g of accurately weighed powdered coal is heated with concentrated $H_2SO_4$(catalyst) in a long-necked flask (called Kjeldahl's flask). After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows:

$$\text{Percentage of N} = \frac{\text{Volume of acid used u Normalit u 1.4}}{\text{Weight of coal taken}}$$

(3) **Sulphur** is determined from the washings obtained from the known mass of coal, used in a bomb calorimeter for determination of a calorific value. During this determination, S is converted into sulphate. The washings are treated with barium chloride solution, when barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$= \frac{\text{Weight of BaSO}^{4}\text{ obtained u32 u 100 u100}}{\text{Weight of coal sample taken in bomb u 233}}$$

(4) **Ash** determination is carried out as in proximate analysis.

(5) **Oxygen:** It is obtained by difference.

Percentage of O = 100 – Percentage of (C + H + S + N + ash)

**Importance of ultimate analysis: (1) Carbon and hydrogen:** Greater the percentage of carbon and hydrogen, better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile matter and hence, it affects the use to which the coal is put.

**Note:**Also higher percentage of carbon in coal reduces the size of combustion chamber required. The amount of carbon, the major combustible constituent of coal, depends on the type of coal and its percentage increases with rank from lignites to anthracites. Thus, percentage of carbon forms the basis of classification of coal.

(2) **Nitrogen** has no calorific value and hence, its presence in coal is undesirable. Thus, a good quality coal should have very little nitrogen content.

**(3)** **Sulphur,** although contributes to the heating value of coal, yet on combustion produces acids ($SO_2$ and $SO_3$), which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 3.0% and derived from ores like iron pyrites, gypsum, etc., mines along-with the coal.

Presence of sulphur is highly undesirable in coal to be used for making coke for iron industry, since it is transferred to the iron metal and badly affects the quality and properties of steel. Moreover, oxides of sulphur (formed as combustion products) pollute the atmosphere and leads to corrosion.

**(4)** **Oxygen** content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value and coking power. Moreover, oxygen is in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1.7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

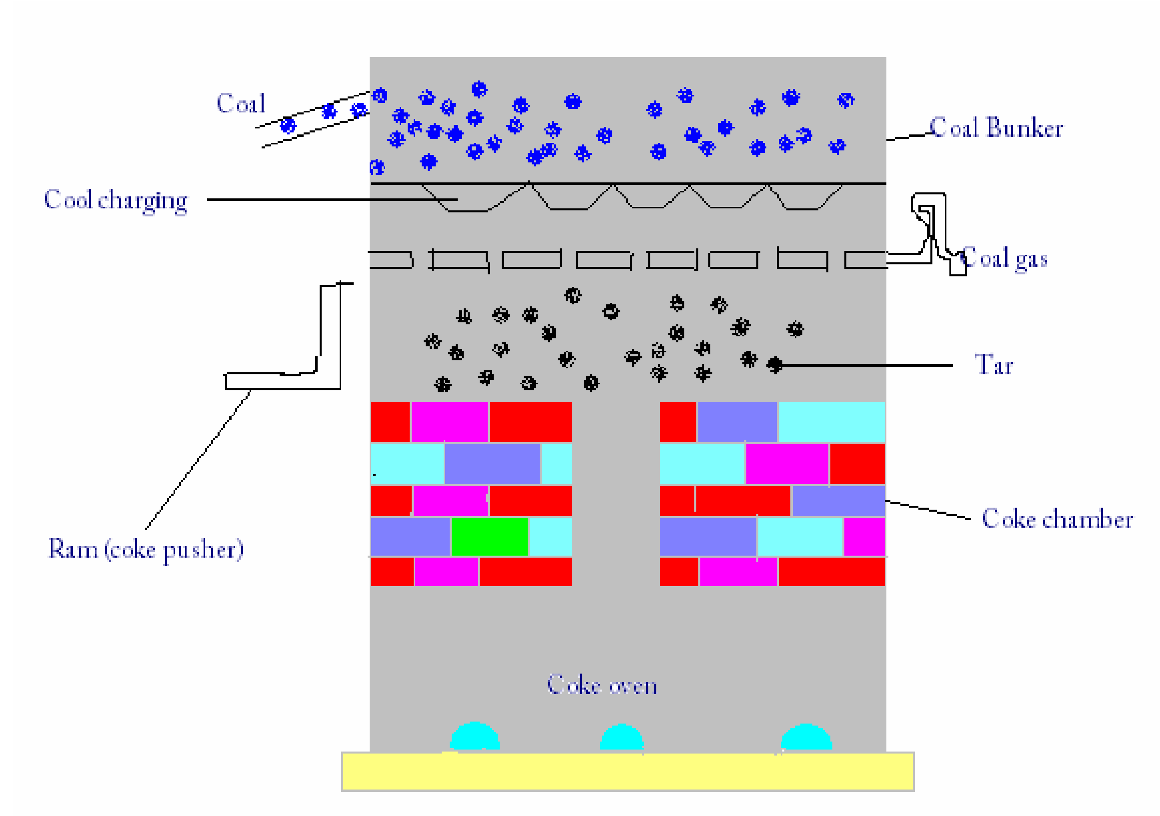
## Manufacture of coke

The cokemaking process involves carbonization of coal to high temperatures (1100°C) in an oxygen deficient atmosphere in order to concentrate the carbon. The commercial cokemaking process can be broken down into two categories: a) By-product Cokemaking and b) Non-Recovery/Heat Recovery Cokemaking. A brief description of each coking process is presented here.

### Manufacture of Metallurgical coke by Otto Hoffmann's method:

In order to (i) save the fuel for heating purpose and (ii) recover valuable by-products like coal gas, ammonia, benzol oil, tar etc. Otto Hoffmann developed a modern by-product coke oven. Here, the heating is done externally by a portion of coal gas produced during the process itself. It also utilizes the waste flue gases for heating the checker work bricks. The oven consists of a number of narrow silica chambers, each about 10-12 m long,

3-4 m tall and 0.4-0.45 m wide, erected side by side with vertical flues between them to form a sort of battery. Each chamber has a hole at the top to introduce the charge, a gas off take and a refractory lined cast iron door at each end for coke discharge. The oven works on heat regenerative principle ie. the waste gas produced during carbonization is utilized for heating. The ovens are charged from the top and closed to restrict the entry of air.



Finely powdered, crushed coal is introduced through the charging hole at the top of the chambers which are then tightly closed at both ends to cut off the supply of air. The ovens are heated to 1200° deg C by burning producer gas. The air required for the combustion of the fuel is preheated in regenerators flanking the retorts, while the flue gases leave their acquired heat to one generator; the other generator is used for preheating the incoming air. The cycle goes on and the heating is continued until all the volatile matter has escaped. It takes nearly 18 hours for carbonization of a charge. The heating of air-alone is required if the fuel gas is coal gas which has a high calorific value. If the fuel is producer gas or blast furnace gas, both air and fuel need to be preheated as they have low calorific value. When the carbonization is over, the red hot coke is pushed out into truck by a massive ram. It is then quenched by spraying water (wet quenching). Alternatively, the red hot coke may be placed in a chamber and cooled by sending in inert gases from boilers. The inert gases are then circulated to boilers where they generate steam. This method is known as dry quenching. The dry quenched coke is cleaner, drier and stronger and contains lesser dust than the wet quenched. The yield is about 70 %.

**Recovery of by-products:**

The gas coming out of the retort is known as coke oven gas. This consist of tar, ammonia, moisture, aromatic hydrocarbons (naphthalene, benzene), H2S etc. It can be used as a fuel after removing coal tar and ammonia.

i) Recovery of tar: The coke oven gas is first passed through a tower in which liquid ammonia is sprayed. Tar and dust get collected in a tank below, which is heated by a steam coil to recover back the ammonia sprayed.

ii) Recovery of ammonia: The coke oven gas is passed through another tower in which water is sprayed. Gaseous ammonia goes into solution as NH4OH. iii) Recovery of naphthalene: After recovering ammonia, the remaining gases are led through another tower where water is sprayed at low temperature when naphthalene gets condensed. iv) Recovery of benzene: The resultant gas from the previous step is sprayed with petroleum whereby benzene and its homologues can be recovered.

v) Recovery of H2S: The gases are then passed through a purifier, packed with moist Fe2O3. Hydrogen sulphide is retained here.

Fe2O3 + 3 H2S Fe2S3 + 3 H2O

When all the Fe2O3 is converted into Fe2S3, the purifier on exposure to the atmosphere, regenerates Fe2O3 in the following manner.

Fe2S3 + 4 O2 2 FeO + 3 SO2

4 FeO + O2 2 Fe2O3

## REFINING OF CRUDE OIL or PETROLEUM

It is separated into various useful fractions by fractional distillation and finally converted into desired specific products. Impurities are also removed. The whole process is called “Refining of crude oil” and the plants setup for the purpose are called “Refineries”.

### Step 1:

### Separation of water (Cottrell’s process):

The crude oil from the oil well is an extremely stable emulsion of oil and salt water. In the process to free the oil from water, the crude oil is allowed to flow between two highly charged electrodes. The colloidal water-droplets condense to form large drops which separate out from the oil.

Step 2:

### Removal of harmful Sulphur Compound:

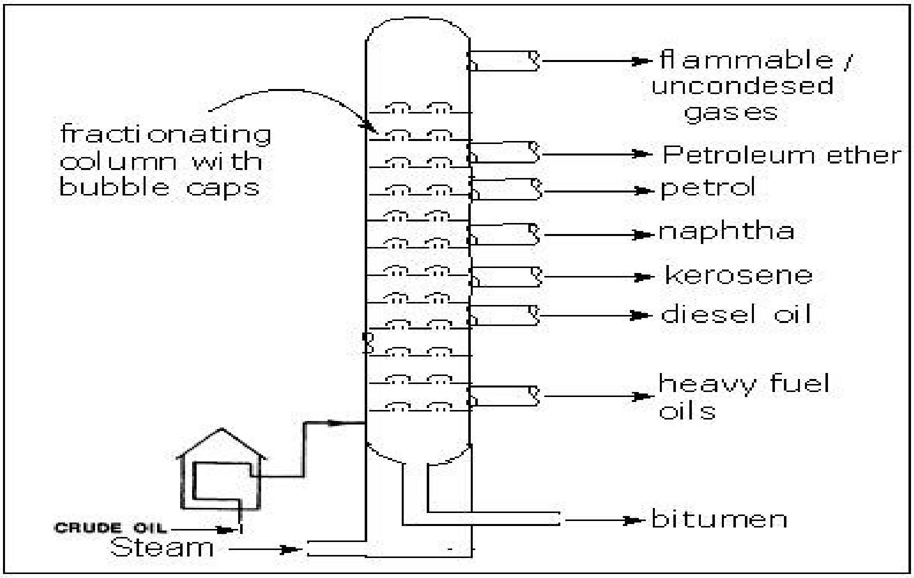
It involves treating oil with Copper oxide. It forms copper sulphide with sulphur compounds which is removed by filtrations.

Step 3:

### *Fractional distillation:*

The crude oil is then heated to about $400^{o}$C in an iron retort. All volatile constituents other than residue are evaporated. The hot vapours are then passed up to a “fractionating column”, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney, which is covered with a loose cap.

As the vapours go up, they gradually become water and fractional condensation takes place at different heights of the column. Higher boiling fraction condenses first followed by lower boiling fractions. Low boiling fractions are used after purification and reforming. High boiling fractions are subjected to cracking operation to get more useful lower-boiling fractions.



**Fractions obtained by distillation of crude:**

| Name of the fraction | Boiling range | Approx. composition in terms of hydrocarbons containing C atoms | Uses |
|---|---|---|---|
| 1.Uncondensed gases | Below 30° C | $C_1$ to $C_4$ (Such as ethane, propane, isobutene) | As domestic or industrial fuel under the name L.P.G (Liquefied petroleum gases). |
| 2.Petroleum ether | 30 – 70° C | $C_5$- $C_7$ | As a solvent |
| 3. Gasoline or petrol or motor spirit. | 40 – 120° C | $C_5$ – $C_9$ (Calorific value=11,250 kcal/kg) | As motor fuel, solvent and in dry cleaning. |
| 4.Naptha or solvent spirit | 120 – 180° C | $C_9$ – $C_{10}$ | As solvent and in dry cleaning. |
| 5.Kerosene oil | 180 – 250° C | $C_{10}$ – $C_{16}$ (Calorific value=11,000 kcal/kg) | As an illuminant, jet engine fuel and for preparing laboratory gas. |

| | | | |
|---|---|---|---|
| 6.Diesel oil or fuel oil or gas oil | 250 – 320° C | $C_{10} – C_{16}$<br>(Calorific value=11,000 kcal/kg) | As Diesel engine fuel. |
| 7. Heavy oil. This on refractionation gives: a)Lubricating oils<br>b)Petroleum jelly | 320 – 400° C<br>---<br>--- | $C_{17} – C_{90}$<br>---<br>--- | For getting gasoline by cracking process.<br>As lubricant As lubricant and in cosmetics and |
| c)Grease<br>d)Paraffin wax | ---<br>--- | ---<br>--- | medicine As lubricant In candles, boot polishes, wax paper, tarpaulin cloth, etc. |
| 8. Residue.<br>May be either<br>a)Asphalt<br>or<br>b)Petroleum cake | Above 400° C<br>---<br>--- | $C_3$ and above<br>---<br>--- | Water proofing of roofs and road making.<br>As a fuel and in moulding arc light rods. |

Three most important liquid fuels derived from petroleum are,

**i) Gasoline or Petrol:**

It is a fraction obtained between 40 -120°C and is a mixture of hydrocarbons such as $C_5H_{12}$ (Pentane) to $C_8H_{18}$ (Octane). Its approximate composition is C=84%; H=15%; N+S+O=1%. Its calorific value is about 11,250 kcal/kg. It is highly volatile, inflammable and used as fuel for internal combustion engines of automobiles and aeroplanes.

**ii) Kerosene Oil:**

It is a fraction obtained between 180-250°C and is a mixture of hydrocarbons such as $C_{10}H_{22}$ (decane) to $C_{16}H_{34}$ (hexadecane). Its approximate composition is C=84%; H=16% with less than 1%S. Its specific gravity is 0.75 – 0.85. Its calorific value is 11,000 kcal/kg. Due to high boiling point range, kerosene does not vaporize easily. It is used as domestic fuel and for making oil gas.

**iii) Diesel Oil:**

It is a fraction obtained between 250 – 320$^oC$ and is a mixture C15H32 to C18H38 hydrocarbons. Its density is 0.86 to 0.95. Its calorific value is about 11,000 kcal/kg. It is used as a diesel engine fuel.

## CRACKING

Cracking is defined as “the decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of lower molecular weight”.

Eg,

Cracking

$$C_{10}H_{32} \longrightarrow C_5H_{12} + C_5H_{10}$$

Decane (n-pentane) (pentene)

B.P. = 36$^oC$

Of all the fractions obtained by fractionation of petroleum, gasoline has the largest demand as a motor fuel, but the yield of this fraction is only 20% of the crude. Also the quality of so-called ‘straight-run’ gasoline is not high. It has to be properly blended. Moreover, there is a surplus of heavier petroleum fractions. To overcome these difficulties, the middle and heavy fractions are cracked to get petrol. The petrol made by cracking has four better characteristics than ‘straight-run’ petrol. Petrol from cracking methods now contributes to about half of the total petrol used.

**There are two methods of cracking in use:**

### 1. Thermal cracking:

In this method, the heavy oils are subjected to high temperature and pressure, when the bigger hydrocarbon molecules break down to give smaller molecules of the paraffin, olefins, plus some hydrogen. However, some of the smaller fragments may even undergo polymerization to give molecules larger than those originally present. This process may be carried out either in ‘liquid phase’ or ‘vapour phase’.

a) Liquid-phase thermal cracking:

In this method, the heavy oil or gas oil stock is cracked at suitable temperature of 475 – 530$^oC$ and under pressure of 100 kg/cm$^2$. The cracked products are then separated in a fractionating column. The yield is 50 – 60% and octane rating of the petrol produced is 65 – 70.

b) Vapour-phase thermal cracking:

In this method, the cracking oil is first vaporized and the cracked at about 600 – 650$^oC$ and under a low pressure of 10 – 20 kg/cm$^2$. This type of process is suitable only for those oils which may be readily vaporized. This method requires less time than the liquid-phase method. Petrol obtained from vapour phase cracking has better anti-knock properties, but poorer stability than petrol from liquid phase cracking.

## 2. Catalytic cracking:

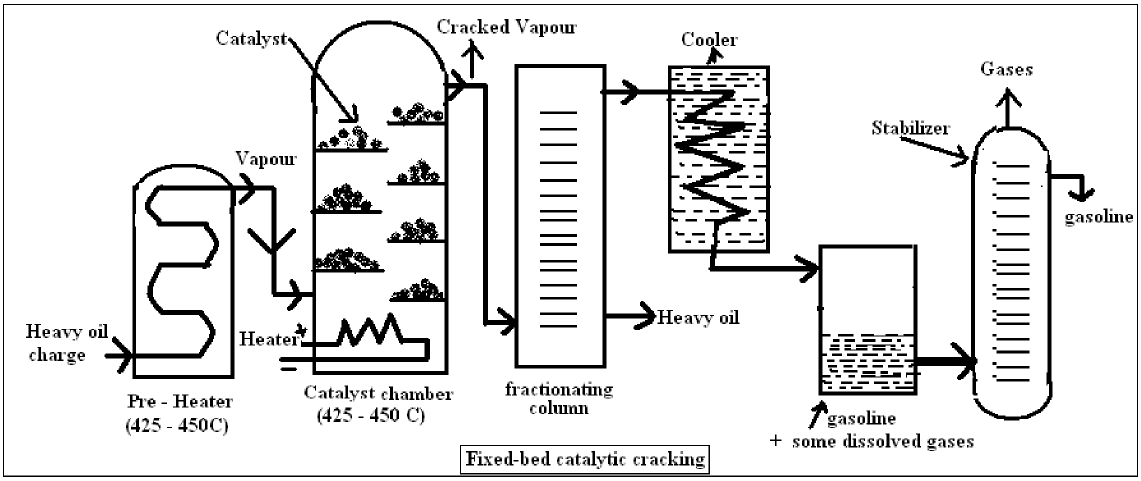
The quality and yield of gasoline produced by cracking can be greatly improved by using a suitable catalyst like aluminium silicate $Al_2(SiO_3)_3$ or alumina $Al_2O_3$. The catalytic cracking possesses the following advantages over the thermal cracking method.

1. The yield of petrol is higher.
2. The quality of petrol produced is better.
3. No external fuel is necessary for cracking. The heat required for cracking is derived from the coal, embedded in the catalyst.
4. A much lower pressure is needed in catalytic cracking.
5. The cracking process can easily be controlled, so the desired products can be obtained.
6. The evolution of by-product gases can be minimized, thereby the yield of desired petrol is higher.
7. The product of cracking contains a higher amount of aromatic and hence, it possesses better anti-knock characteristics.
8. Isomerisation to branched-chain compounds occur, thereby better petrol is produced.
9. The product contains very little amount of undesirable S, because a major portion of it escapes out as $H_2S$ gas, during cracking.
10. The percentage of gum or gum-forming compounds is very low.
11. Catalysts are selective in their action and therefore, they permit cracking of only the high-boiling hydrocarbons.
12. In presence of catalyst, cracking is more of naphthenic materials than paraffinic. So the products of catalytic cracking are more paraffinic.
13. Decomposition of aromatics removes only the side chains, but no ring itself is broken.

### a) Fixed-bed catalytic cracking:

In this, the oil vapours are heated in a pre-heater to cracking temperatures (425 450°C) and then forced through a catalytic chamber maintained at 425-450°C and 1.5 kg/cm$^2$ pressure. During their passage through the tower, about 40% of the charge is converted into gasoline and about 2 – 4% carbon is formed. The latter gets adsorbed on the catalyst bed. The vapours are then led through a cooler, where some of the gases are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a stabilizer, where the dissolved gases are removed and pure gasoline is obtained.

The catalyst, after 8 to 10 hours stops functioning due to the deposit of black layer of carbon, formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activation interval, the vapours are diverted through another catalyst chamber.

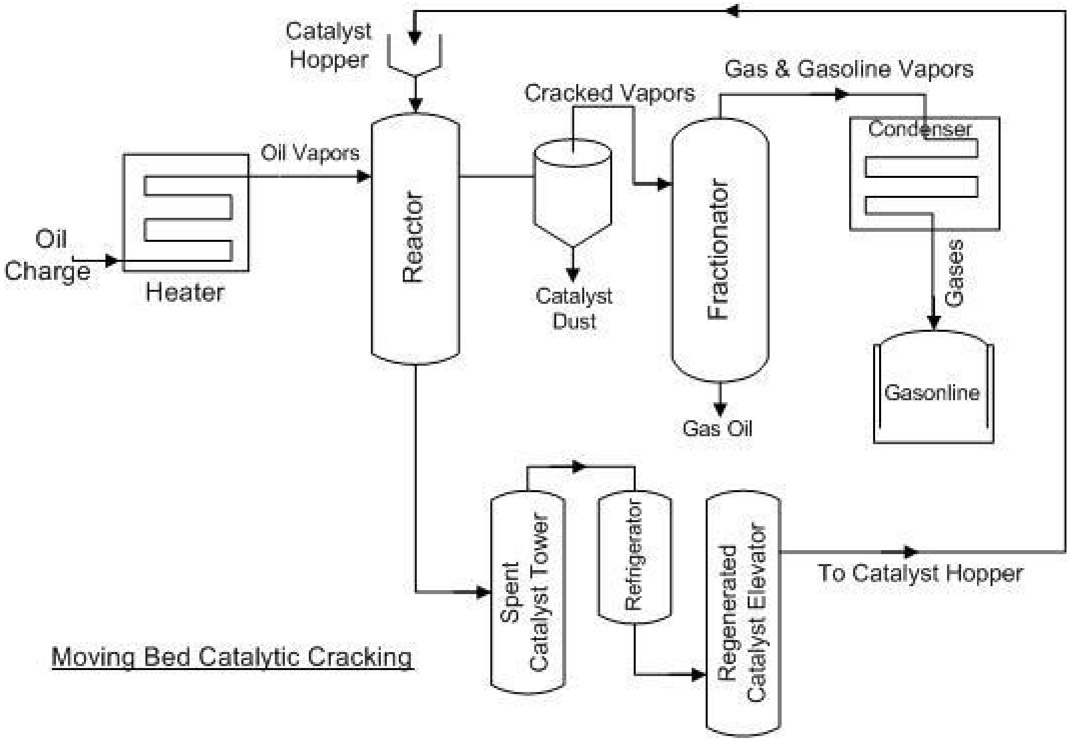


Fixed-bed catalytic cracking

b) Moving bed catalytic cracking:

In this process, the solid catalyst is very finely powdered so that it behaves almost as a fluid, which can be circulated in gas stream. The vapours of cracking stock mixed with fluidized catalyst is forced up into a large reactor where the mixture forms a floating turbulent ‘bed’ in which cracking of the heavier into lighter molecules occurs. Near the top of the reactor, there is a centrifugal separator, which allows only the cracked oil vapours to pass on to the fractionating column, but retains all the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier due to coating with carbon, and it settles to the bottom, from where it is forced by an air blast to regenerator.

In regenerator, carbon is burnt and the regenerated catalyst the flows through a stand-pipe for mixing with fresh batch of incoming cracking oil. At the top of the regenerator, there is a separator which permits only gases to pass out, but holds back catalyst powder.



Moving Bed Catalytic Cracking

## KNOCKING

A mixture of gasoline vapour and air is used as afuel in an internal combustion engine. The combustion reaction is initiated by a spark in the cylinder. The flame should spread rapidly and smoothly through the gaseous mixture. Therfore the expanding gas drives the piston down the cylinder.

The ratio of the gaseous volume in the cylinder at the end of the sution-stroke to the volume at the end of compression stroke of the piston is known as the ‘compression ratio’.

The efficiency of an internal combustion engine increases with the compression ratio. Combustion ratio is depending upon the nature of the constituents present in the gasoline used.

In certain circumstances, due to the presence of some constituents in the gasoline used, the rate of oxidation becomes so great that the last portion of the fuel-air mixture gets ignited instantaneously, producing an explosive violence, known as ‘Knocking’. The knocking results in the loss of efficiency, since this ultimately decreases the compression ratio.

## Chemical Structure and Knocking:

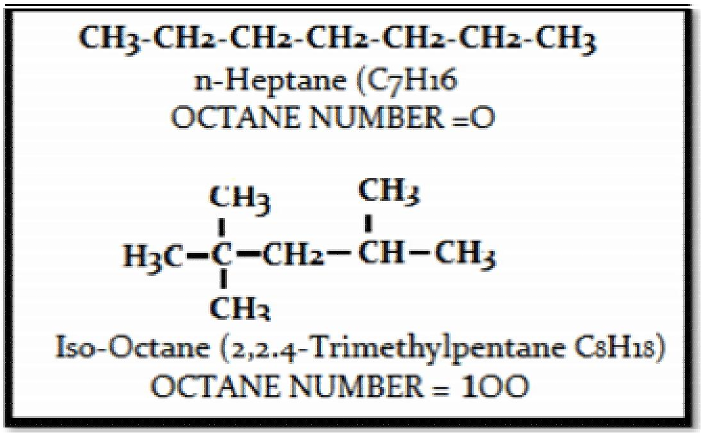
The tendency of fuel constituents to knock is in the following order.

Straight-chain paraffins > branched-chain paraffins(i.e., iso paraffins) >olefins > cyclo paraffins (i.e., naphthalene) > aromatics.

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

## OCTANE RATING

The most common way of expressing the knocking characteristics of a combustion engine fuel is by “octane number”. N-heptane knocks very badly and hence, its anti-knock value has arbitrarily been given zero.



$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

n-Heptane ($C_7H_{16}$

OCTANE NUMBER =0

$$\begin{array}{ccccc} & CH_3 & & CH_3 & \\ & | & & | & \\ H_3C- & C & -CH_2- & CH & -CH_3 \\ & | & & & \\ & CH_3 & & & \end{array}$$

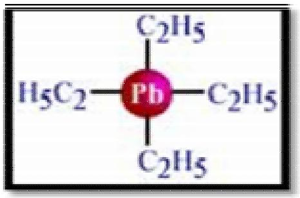
Iso-Octane (2,2,4-Trimethylpentane $C_8H_{18}$)

OCTANE NUMBER = 100

Octane number of a gasoline is the percentage of iso-octane in a mixture of iso-octane and n-heptane, which matches the fuel under test in knocking characteristics.

An iso-octane fuel is one which has the same combustion characteristics as an 80:20 mixture of iso-octane and n-heptane. Now today’s gasoline with octane rating as high as 135 and even more have been produced and they are used for aviation purposes. **<u>Improvement of anti-knock characteristics of a fuel</u>**

The octane number of many poor fuels can be raised by the addition of such extremely poisonous materials as tetra ethyl lead $(C_2H_5)_4Pb$ or TEL and diethyl telluride $(C_2H_5)_2Te$. In motor spirit about 0.5 ml and in aviation fuels about 1 to 1.5 ml of TEL is added per litre of petrol.



TEL is converted in to a cloud of finely divided lead oxide particles in the cylinder and these particles react with any hydrocarbon peroxide molecules formed thereby slowing down the chain oxidation reaction and thus decreasing the chances of any early detonation. Deposit of lead oxide is harmful to the engine life. Consequently in order to help the simultaneous elimination of lead oxide formed from the engine, a small amount of ethylene dibromide is also added to petrol. The added ethylene dibromide removes lead oxide as volatile lead bromide along with the exhaust gases. The presence of sulphur compounds in petrol reduces the effectiveness of the TEL. TEL is more effective on saturated hydrocarbons than on unsaturated ones.

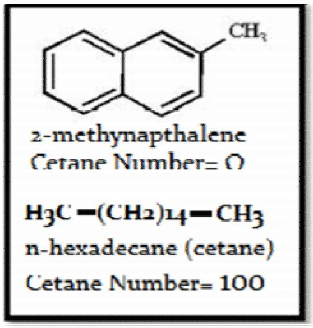
**CETANENUMBER:** The knocking tendency of a diesel fuel is expressed in terms of cetane number. Diesel engines works on the principle of compression ignition.

Cetane (n-cetane) or hexadecane [CH3-(CH2)14-CH3] is a saturated hydrocarbon, its cetane number is arbitrarily fixed as 100. Ɉ-Methyl naphthalene is an aromatic hydrocarbon, its cetane number is arbitrarily fixed as zero.

***<u>Definition:</u>Cetanenumberisdefinedasthepercentageofhexadecane(n-cetane) presentinamixtureofhexadecaneand2-methylnaphthalene, whichhasthesameignitioncharacteristicofdieselfuelintest.*** Generally diesel fuels with cetane numbers of 70-80 are used. **Note:**

(1) Hydrocarbons which are poor gasoline fuels are good diesel fuels.

(2) The cetane number of diesel fuel can be raised by the addition of small quantity of certain pre-ignition dopes like ethyl nitrite, isoamyl nitrite, acetone peroxide, etc.



**SYNTHETIC PETROL**

Petrol is synthesised by any of the following method:

**<u>1. Polymerisation</u>**

The gases obtained as a by-product from cracking of heavy oils contain olefin (like ethylene, propene and butanes) and alkanes (such as methane, ethane, propane and butane). When these gas mixtures are subjected to high pressure and high temperature with or without the presence of catalyst, they polymerise to form higher hydrocarbons, resembling gasoline.

Pressure, heat and/or catalyst

$$CH_3.CH=CH_2+CH_3CH_2CH=CH_2 \longrightarrow CH_2=CH.CH_2CH\ (CH_3)_2$$

(Propene) (Butene-1) (5-Methyl hexane-1)

The polymerization is of two types:

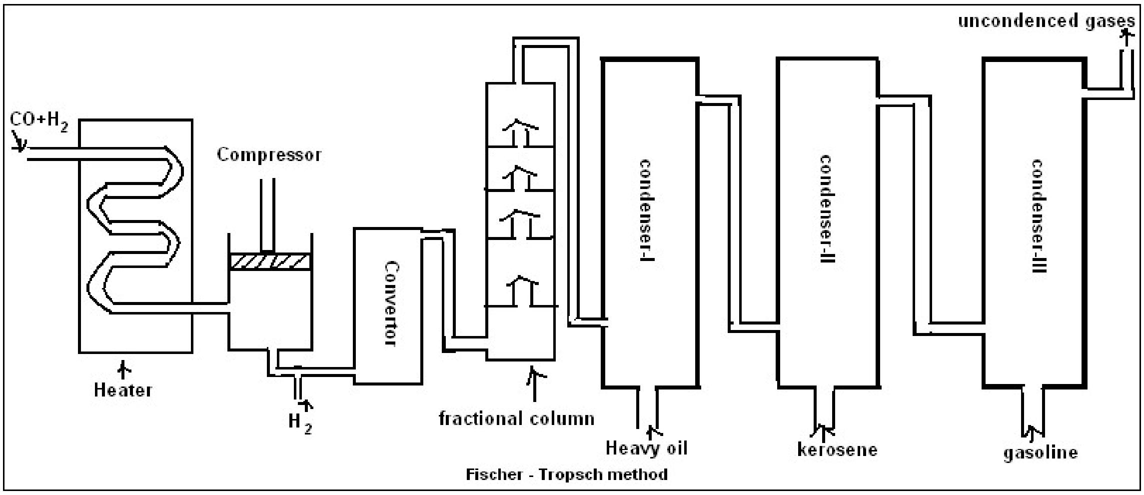
i) **Thermal polymerization is one in which polymerization of cracked gases is carried out at 500 - 600°C and 70 - 350 kg/cm$_2$ pressure. The product is gasoline and gas oil mixture, from which they are separated by fractionation.**

ii) **Catalytic polymerization is carried out in presence of a catalyst like phosphoric acid. In this case, lower temperature of 150 – 200°C is employed. Products are gasoline and unpolymerised gas. The latter is separated and recycled for polymerization.**

**2. Fischer-Tropsch method**

**Water gas ($CO+H_2$) which is produced by passing steam over heated coke, is mixed with hydrogen. The gas is purified by passing through $Fe_2O_3$ (to remove $H_2S$) and then into a mixture of $Fe_2O_3.Na_2CO_3$ and to remove organic sulphur compounds. The purified gas is compressed to 5 to 25 atmospheres. The compressed gas is then led through a converter (containing a catalyst, consisting of a mixture of 100 parts cobalt, 5 parts thoria, 8 parts magnesia and 200 parts keiselgular-earth) maintained at about 200 – 300°C. A mixture of saturated and unsaturated hydrocarbons results :**

**$n\ CO + 2n\ H_2 \longrightarrow C_nH_{2n} + n\ H_2O$ $n\ CO +$**
**$(2n+1)H_2$ $C_nH_{2n+2} \longrightarrow + n\ H_2O$**

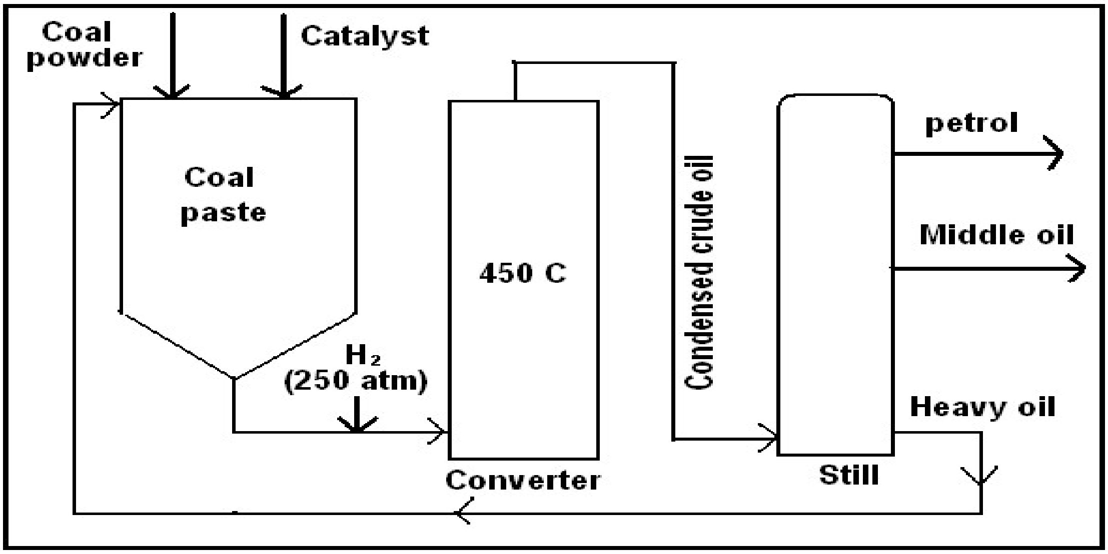


Fischer - Tropsch method

The reaction is exothermic. So out coming hot gaseous mixture is led to a cooler, Where a liquid resembling crude oil is obtained. The crude oil thus obtained is then fractionated to yield:
(i) gasoline, (ii) high-boiling heavy oil. The heavy oil is reused for cracking to get more gasoline.

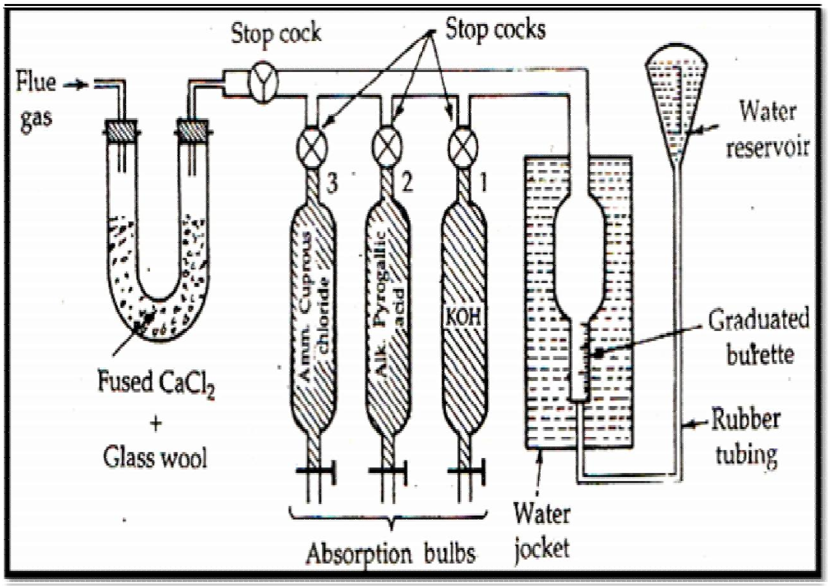
### 3. Bergius process

In this, low ash coal(which is largely a mixture of solid hydrocarbons) is finely powdered and made into paste with heavy oil and then a catalyst (composed of tin or nickel oleate) is added. The whole mixture is heated with hydrogen at $450^{o}$C and under a pressure of 200 – 250 atmospheres for about 1.5 hours. There, hydrogen combines with coal to form saturated hydrocarbons, which decompose at prevailing high temperature and pressure to yield low-boiling liquid hydrocarbons. The gases from the reaction vessel are led to condenser, where a liquid resembling crude oil is obtained. This crude oil is then fractionated to get: (i) gasoline, (ii) middle oil, and (iii) heavy oil. The latter is used again for making paste with fresh coal dust. The middle oil is hydrogenated in vapourphase in presence of a solid catalyst to yield more gasoline. The yield of gasoline in about 60% of the coal dust used.



**Description of orsat's apparatus**

It consists of a horizontal tube. At one end of this tube, U-tube containing fused $CaCl_2$ is connected through 3-way stop cock. The other end of this tube is connected with a graduated burette. The burette is surrounded by a water-jacket to keep the temperature of gas constant. The lower end of the burette connected to a water reservoir by means of a rubber tube. The level of water in the burette can be raised or lowered by raising or lowering the reservoir



The horizontal tube is also connected with three different absorption bulbs I, II, and III for absorbing $CO_2$, $O_2$ and CO.

**I-bulb:** It contains 'potassium hydroxide' solution, and it absorbs only $CO_2$.

**H-bulb:** It contains 'alkaline pyrogallol' solution, and it absorbs $CO_2$ and $O_2$.

**IH-bulb:** It contains 'ammoniacal cuprous chloride solution' and it absorbs $CO_2$, $O_2$ and CO.

### Working

The 3-way stop-cock is opened to the atmosphere and the reservoir is raised, till the burette is completely filled with water and air is excluded from the burette. The 3-way stop-cock is now connected to the flue gas supply and the flue gas is sucked into the burette and the volume of flue gas is adjusted to 100 cc by raising and lowering the reservoir. Then the 3-way stop cock is closed.

### (a) Absorption of $CO_2$

The stopper of the absorption bulb-I, containing KOH solution, is opened and all the gas is passed into the bulb-I by raising the level of water in the burette. The gas enters into the bulb-I, where $CO_2$ present in the flue gas is absorbed by KOH.

The gas is again sent to the burette. This process is repeated several times to ensure complete absorption of $CO_2$. The decrease in volume of the flue gas in the burette indicates the volume of $C0_2$ in 100 cc of the flue gas.

### (b) Absorption of $O_2$

Stop-cock of bulb-I is closed and stop cock of bulb-II is opened. The gas is again sent into the absorption bulb-II, where $0_2$ present in the flue gas is absorbed by alkaline pyrogallol. The decrease in volume of the flue gas in the burette indicates the volume of $O_2$.

### (c) Absorption of CO

Now stop-cock of bulb-II is closed and stop-cock of bulb-III is opened. The remaining gas is sent into the absorption bulb-III, where CO present in the flue gas is absorbed by ammoniacal cuprous chloride. The decrease in volume of the flue gas in the burette indicates the volume of CO. The remaining gas in the burette after the absorption of $CO_2$, $O_2$& CO is taken as nitrogen.

### Significance or uses of flue gas analysis

1. Flue gas analysis gives an idea about the complete incomplete combustion process.
2. If the flue gases contain considerable amount of CO, it indicates that incomplete combustion is occurring and it also indicates that the short supply of $O_2$.
3. If the flue gases contain considerable amount of $0_9$, it indicates that complete combustion is occurring and also it indicates that the excess of $O_2$ is supplied.

### Properties of straight run, cracked and polymer gasoline

| Straight run gasoline | Cracked gasoline | Polymer gasoline |
|---|---|---|
| It is obtained by straight distillation of crude petroleum | It is obtained from heavy oil. | It is obtained from low molecular weight components. |
| It is physically separated from crude oil | It is chemical process | Low molecular weight fractions are polymerized in to higher molecular weight so it is chemical process |
| It have low octane number | It have higher octane number | It have highest octane |
| It contain only normal alkanes | It containing more aromatic, naphthalene and branched chain hydrocarbons | It containing more number of branched hydrocarbons |
| Composition range is wide C5 – C9 | Composition range is C6 – C8 | Composition range is very narrow C7 – C8 |

## Unit 3 ENERGY STORAGE DEVICES

Introduction – Definition – Types of battery – commercial voltaic cells – primary battery – secondary storage cells – lead – acid cells, nickel-cadmium cells, lithium battery – fuel cells – hydrogen-oxygen fuel cell – **photovoltaic cell – principle, working and applications.**

**Batteries:**

When two or more electrochemical cells are electrically interconnected, each of which containing two electrodesand an electrolyte is called a Battery. In everyday usage, "battery" is also used to refer to a single cell. No one batterydesign is perfect for every application. There are many parameters like cost, voltage, duty cycle, dimension, stabilitywith time and temperature, shelf life, etc., on which a battery is selected for a particular operation. It is important toprioritize our list of requirements before choosing one and requires compromise. Here duty cycle refers to conditionsthe battery experiences during use like, type of discharge and current drain, e.g. continuous, intermittent, continuouswith pulses, etc.

**Primary and secondary cells**

Batteries are classified into two categories depending on their recharging capabilities.

a. Primary batteries
b. Secondary Batteries

**Primary batteries:**

These are non-rechargeable and are meant for a single use and meant to be discarded after use.Primary batteries are non-rechargeable and are less expensive and are often used in ordinary gadgets liketorch lights, watches and toys. Commercially many kinds of primary batteries are available but our discussion only onLeclanche cell, Alkaline cell and Lithium cell.

**Secondary batteries:**

Secondary batteries are rechargeable and are meant for a multi cycle use. After every use the electrochemicalreaction could be reversed by external application of voltage. The cycle is reversed till the capacity fades or lost dueto leakage or internal short circuit.

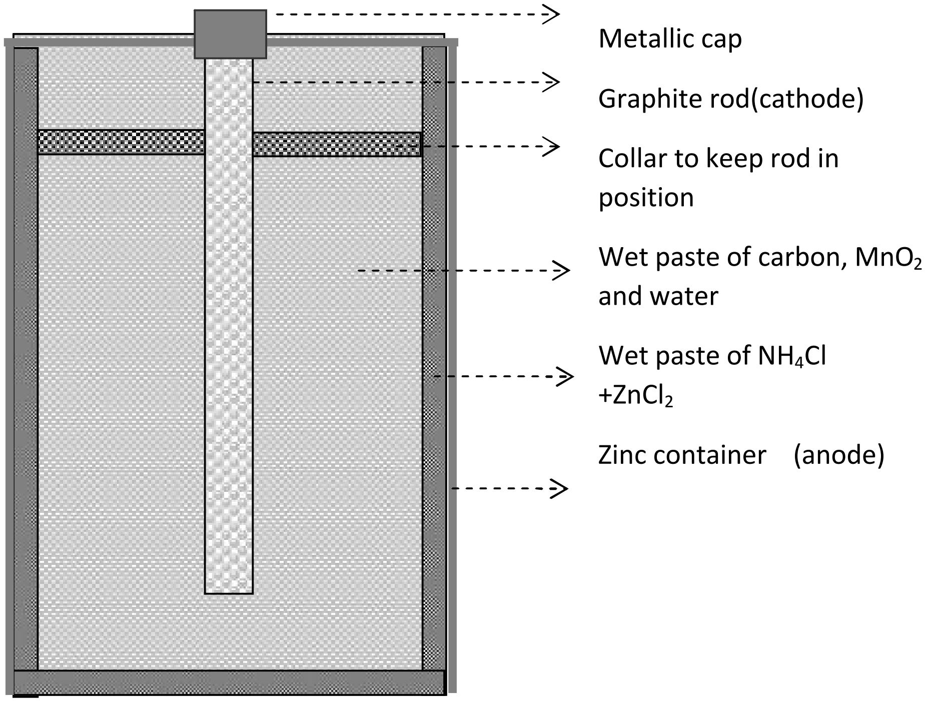
These cells are rechargeable and reusable. A combination of all reversible electrochemical cells givessecondary batteries. Many kinds of secondary batteries are available in the market but we are restricting ourdiscussion to Lead-acid cell, Ni/Cd cells, Ni-Metal hydride cell and Lithium ion cells.

| **S.No.** | **PRIMARY CELLS** | **SECONDARY CELLS** |
|---|---|---|
| 1 | Secondary batteries are rechargeable and are meant for a multi cycle use | These are non-rechargeable and are meant for a single use and meant to be discarded after use. |
| 2 | Cell reaction is not reversible | Cell reaction can be reversed |
| 3 | Cannot be rechargeable | Can be rechargeable |
| 4 | Less expensive | Expensive |
| 5 | Can be used as long as the materials are active in their composition | Can be used again and again by recharging the cell |
| 5 | Example: Leclanche cell, Lithium cells | Lead acid cell, Nickel-cadmium cell |

**Dry cell**

Dry cell is a primary cell. It is cheap to make and gives a voltage of about 1.5V. It finds applications in flash-lights, calculators, transistor radios etc.

Dry cell is a cell without fluid component in which the zinc container acts as anode and a graphite rod, surrounded by a paste of ground carbon, $MnO_2$ and water placed in muslin cloth serves as cathode. The electrolyte consists of $NH_4Cl$ and $ZnCl_2$ to which starch is added to make it as thick paste.



At the negative electrode (anode) the following reaction takes place

$Zn\ (s) \rightarrow Zn^{2}\ (aq.) + 2e^{-}$

Ammonia then combines with zinc ions to form complex

$Zn^{2+} + 4\ NH_3 \rightarrow [Zn\ (NH_3)]^{2+}$ (aq.)

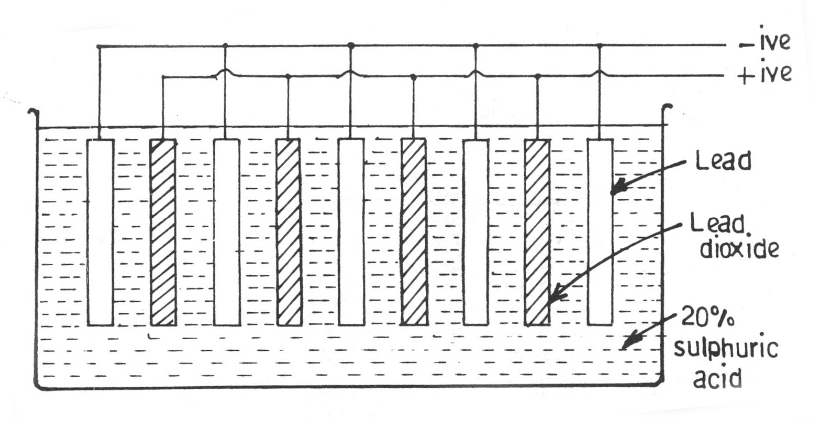
At the positive electrode (cathode) the following reaction take place.

$2MnO_2\ (2) + 2\ NH_4^{+}\ (aq)\ 2e^{-} \rightarrow Mn_2O_3\ (s) + H_2O + 2NH_3\ (aq.)$

The ammonia produced combines with $Zn^{2+}$ to form $[Zn\ (NH_3)_4]^{2+}$ ions at the zinc reactivity of $NH_4$ Cl paste with zinc container.

Dry cell is used places where small amounts of current are required for a short time eg. transistors, tape recorder, quartz, watches, electronic wall clocks, torches etc.

**Lead - acid storage cell**



Lead acid storage cell

The storage cell acts both as voltaic cell as well as electrolytic cell.

On giving electrical energy, the storage cell acts as a voltaic cell. After this on recharging, the cell acts as an electrolytic cell. Thus the storage cell can be recharged to produce electrical energy.

In the lead-acid storage cell a number of lead plates (-ve plates) are connected in parallel and a number of lead dioxide (pressed into grids) plates (five plates) are also connected in parallel. The lead plates are placed in between the lead dioxide plates. The plates are separated from one another by rubber or glass fibre.

The entire electrodes are immersed the 20% dilute sulphuric acid.

**Discharging :** The lead plate (anode) dipped in dilute sulphuric acid acts as voltaic cell. The lead loses electrons thereby oxidation of lead takes place at anode. The electrons released from lead plates flow through the wire in the form of electric current. Later the electrons enter the cathode plates ($PbO_2$). At anode the following reactions take place.

$Pb \rightarrow Pb^{2+} + 2e^-$ (anode)

Then the lead ion combines with sulphate ions to produce lead sulphate.

$PbO_2 + 4H^+ + 2e^- \rightarrow Pb\ So_4 \downarrow$

At cathode the following reactions take place.

$PbO2 + 4H^+ + 2e^- \rightarrow Pb^2 + 2\ H_2O$ (cathode)

$$\begin{array}{c} Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \downarrow \\ \hline PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O + \text{energy} \end{array}$$

The voltage of the lead storage cell is 2.0 volts.

**Recharging**

For recharging the lead storage cell, and external emf greater than 2 volts from an electrical source is passed through the electrodes. The reactions already taken place are reversed.

The following is the reaction taking place at cathode.

$PbSO_4 + 2^{e-} \rightarrow Pb + Pb + SO_4^{2-}$

The following is the electron taking place at the anode (five electrode).

$2PbSO_4 + 2H_2O + \text{energy} \rightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$

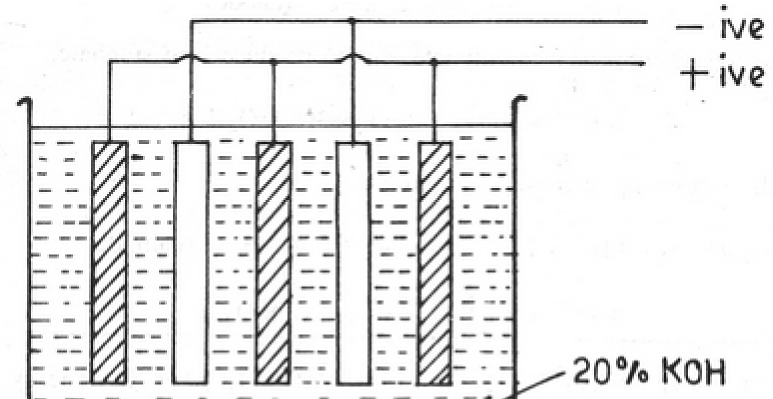
On recharging the electrodes of cell are restored to their original conditions (Lead plates and $PbO_2$ plates)

The lead storage cells are used for many purpose. In automobiles a combination of six lead storage cells in series to form a battery producing in e.m.f. of 12 volts is generally made use of. The lead storage cells are also used in telephone exchanges, mines, laboratories, hospitals, broad casting stations, gas engine ignition etc.

**Nickel - Cadmium cell**

The Nickel - Cadmium cell constitutes the positive plates of nickel oxide and hydroxide with flakes of graphite or metallic nickel. The negative plates of the cell ismade of spongy cadmium. The electrodes are dipped inside an electrolyte of 20% solution of caustic potash (KOH) with a small amount of lithium hydroxide (LiOH).

The nickel compound plates are connected in parallel and constitute the positive terminal. Similarly the spongy cadmium plates connected in parallel constitute the negative terminal.



## Nickel cadmium cell

The following are the chemical reaction taking place at cathode (+ive) and anode (-ive) during discharging process.

(1) $Cd (s) + 2OH^-(aq) \rightarrow Cd (OH)_2 (s) + 2^{e-}$ (anode - ive)

(2) $NiO_2 (s) + 2H_2 O (1) + 2e^- \rightarrow Ni (OH)_2 (s) + 2OH^-(aq)$ (cathode + ive)

The following are the reactions taking place at cathode (-ive) and anode (+ive) during recharging process.

(1) $Ni (OH)_2 + 2OH^-(aq) \rightarrow Ni O_2(s) + 2H_2O + 2^{e-}$ (anode + ive)

(2) $NiO_2 (s) + 2H_2 O (1) + 2e^- \rightarrow Ni (OH)_2 (s) + 2OH^-(aq)$ (cathode + ive)

The discharging and recharging reactions can be depicted by a single reversible cell reaction.

$$2NiO_2(s) + Cd(s) + 2H_2O(1) \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2Ni (OH)_2(s) + Cd (OH)_2(s)$$

The Nickel - Cadmium cell has a voltage of 1.2 V and considerably longer life since the products of reaction stick to the electrodes without affecting it. The cell has long life with low maintenance cost.

The nickel-cadmium cells are used in locomotives, railway car lighting and air conditioning, industries etc

**Lithium cell:**

Lithium cell consists of lithium anode and either solid electrolyte or liquid electrolyte and solid or liquidcathode. A thin protective insulating film is formed on the lithium anode protecting the anode against corrosion as itis conductive to lithium ions but not electrons. Water and alcohol do not form such a protective film and hencecannot be used as solvents. Organic solvents such as dioxane, tetrahydrofuran, propylene carbonate ether, etc., andelectrolyte salts of lithium such as perchlorate, tetrafluoroborate or hexafluorophospahate are used.

Lithium-iodide solid cathode cell consists of iodine-PVP (polyvinyl pyrrolidone) cathode with voltage of 3V. ithas low current densities but is highly stable and dependable and hence used in medical source for electronic flashguns of cameras.Lithium-sulphur dioxide cell consists of a liquid cathode of a mixture of acetonitrile or propylene carbonate withsulphur dioxide. Instead of the solvents acetonitrile or propylene carbonate, thionyl chloride has been found to bebetter as it generates a potential of 3.5 V and has high energy density.

**Lithium ion Cells:**
**Anode:** Carbon compound, Graphite
**Cathode:** Lithium oxide
**Applications:** Laptops, cellular phones, electrical vehicles.

Lithium metal batteries have some safety disadvantages, Lithium ion batteries overcomes that problem.Cathodes consists of a layered crystal (graphite) into which the lithium is intercalated. Experimental cellshave also used lithiated metal oxides such as $LiCoO_2$, $NiNi_{0.3}Co_{0.7}O_2$, $LiNiO_2$, $LiV_2O_5$, $LiV_6O_{13}$, $LiMn_4O_9$, $LiMn_2O_4$,$LiNiO_{0.2}CoO_2$.

Electrolytes are usually $LiPF_6$, although this has a problem with aluminum corrosion, and so alternatives arebeing sought. One such is $LiBF_4$. The electrolyte in current production batteries is a patented liquid, and uses anorganic solvent.Membranes are necessary to separate the electrons from the ions. Currently the batteries in wide use have microporouspolyethylene membranes.Intercalation keeps the small ions such as Lithium, sodium and other alkali metals, into the interstitial spacesin a graphite crystal. This makes the graphite is conductive, dilutes the Lithium for safety, is reasonably cheap, anddoes not allow dendrites or other unwanted crystal structures of Li to form.

## FUEL CELLS

Fuel cells are cells producing electrical energy from chemical energy produced out of the chemical reactions of different fuels. Fuel cells are a kind of voltaic cells only.

### Hydrogen oxygen fuel cells

One of the earliest fuel cell is the hydrogen oxygen fuel cell. This fuel cell make use of the fuel hydrogen and the oxidiser-oxygen in the presence of a liquid electrolyte.

The reaction between hydrogen and oxygen to produce water and the excess electron produced by the net reaction produces the electric current.

$H_2 \rightarrow 2H$

$2H + 2OH^- \rightarrow 2H_2O + 2^{e-}$

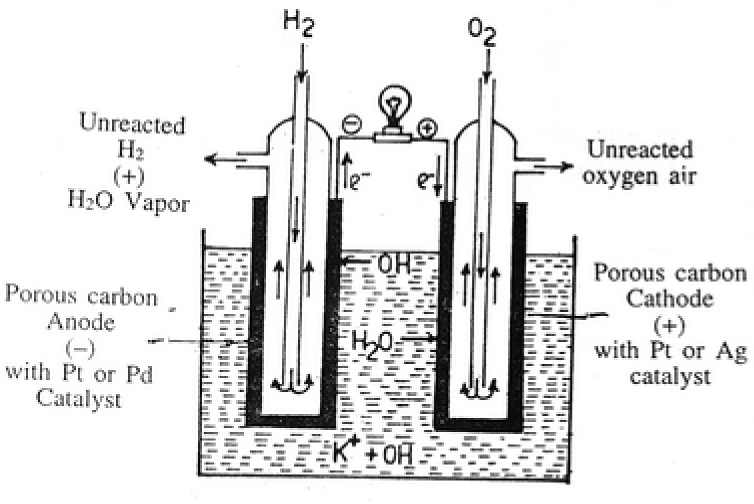
Net anode reaction $H_2 + 2OH^- \rightarrow 2H_2O + 2^{e-}$

Cathode reaction $O_2 + 2H_2O + 4^{e-}$

In the hydrogen - oxygen fuel cell at the anode hydrogen gas is diffused through a porous carbon electrode, the surface of which are embedded with finely divided Pt or Pd. The cathode of the cell is also a porous carbon rod inpregrated with cobalt oxide or platinum or silver catalyst. The two electrodes are 'kept in an electrolyte like potassium hydroxide.

The electrons produced at the anode pass through the external conductor to the cathode-where it reacts with the diffused water molecules and oxygen to produce hydroxyl ions.

The hydroxyl ions produced migrates from cathode to anode carrying the excess negative charge (electrons). Thus the electrolyte constitution will be undisturbed with the passage of electron producing the electric circuit.



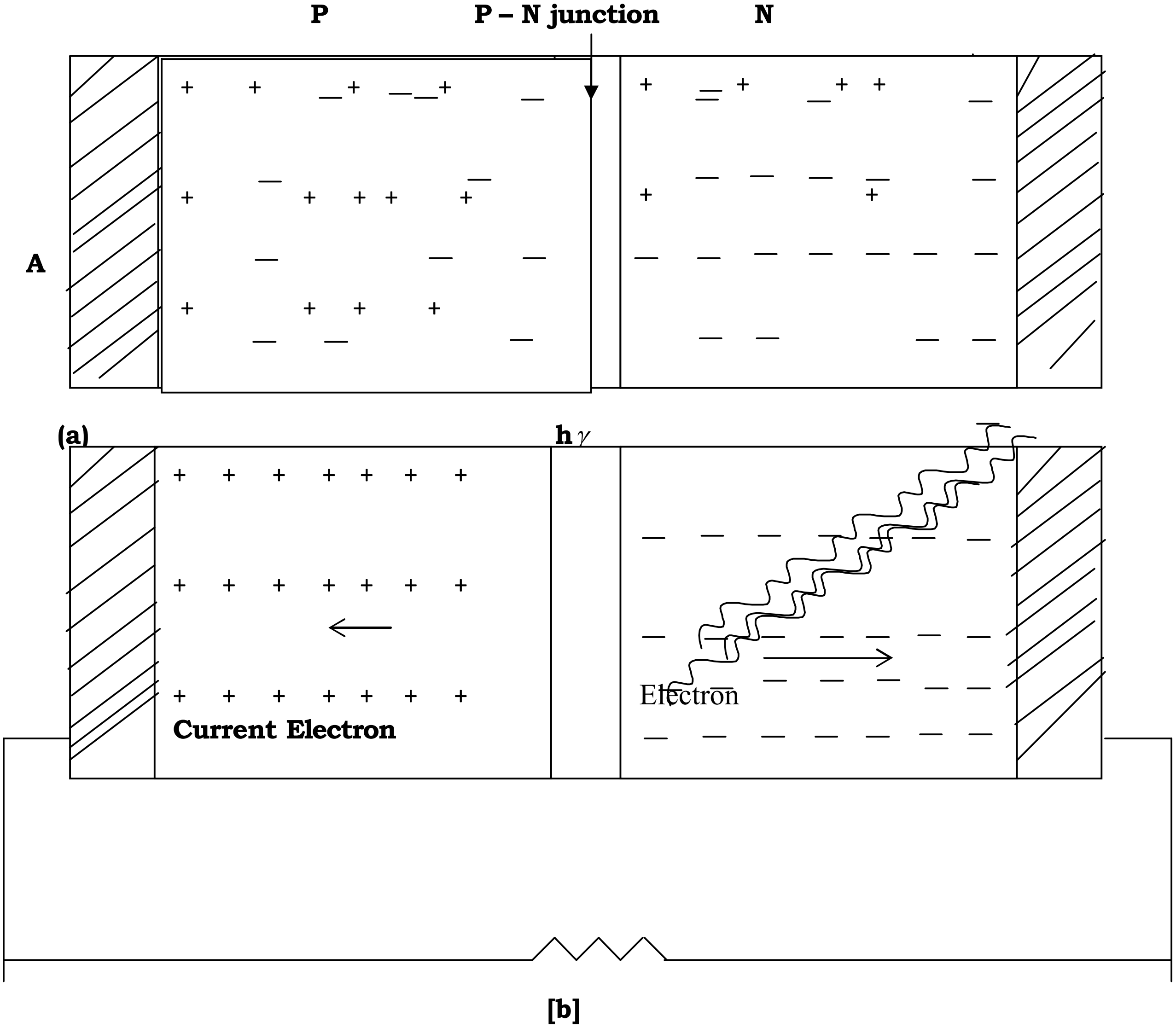
**Hydrogen – Oxygen fuel cell**

Anodic reaction $2H_2 + 4OH^- \rightarrow 4H_2O + 4^{e-}$

Cathodic reaction $O_2 + 2H_2O + 4^{e-} \rightarrow 4OH^-$

Net reaction $O_2 + 2H_2 \rightarrow 2H_2O$

**Photovoltaic (PV) cells** : Also known as solar cells. A photovoltaic cell is made of thin wafers of two slightly different types of silicon, which is a semiconductor. One, doped with tiny quantities of boron, is called P-type (P-for positive) and contains positively charged holes which are missing electrons (Electrons are negatively charged particles that orbit the nuclei of atoms). The other type of silicon is doped with small amounts of phosphorus and is called N-type (N for negative). It contains extra electrons. Putting these two thin P and N materials together produces a junction fig (a) which, when exposed to light, will produced a movement of electrons and that constitutes an electric current. Photovoltaic (PV) cells thus convert light energy into electrical energy, which can be transmitted by placing metal contacts on the top and bottom.

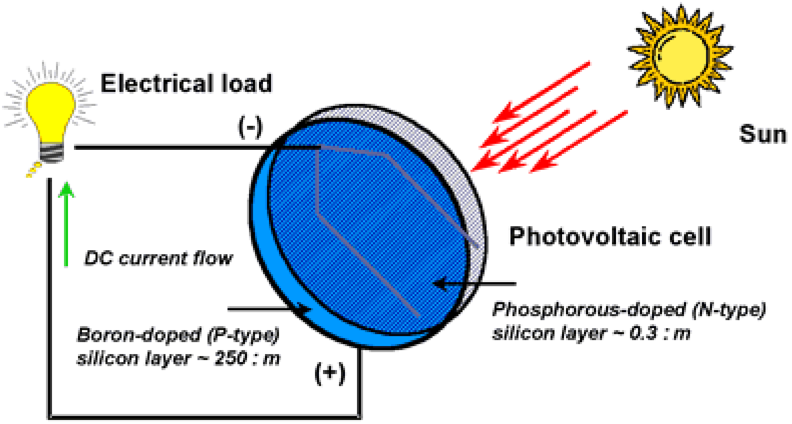


**[b]**

**Fig : Use of semiconductors as solar cells of the PV cell, we can draw that current to use externally**

**Since the P-N junction is a barrier to both types of charge carriers, concentration of holes builds up on the N-side of the junction. When these concentrations exceed the equilibrium concentration of the carriers in the corresponding parts of a semiconductor a drift of holes towards A and a drift of electrons towards B**

**takes place. Therefore if A and B are connected with a conductor, there occurs a flow of current from A to B and flow of electrons from B to A (fig.b).**



### Advantages of Solar Energy

Solar energy is a universal, decentralized, non-polluting energy

(a) Solar energy is essential for every kind of living organisms
(b) Solar energy has more of the disadvantages found in the combustion of fossil fuels such as coal, oil or gas.
(c) Solar energy is bound to achieve great economic importance in future because of depletion trend of conventional energy sources.

### Applications of Photovotaic (PV) Systems

Lighting using PV has always been a popular application for remote, unelectrified rural areas. Such lighting is in the form of street lighting, domestic lighting and portable lanterns. PV systems are used for powering microwave repeater stations located at hill tops. In general, PV systems caters to vast number of communication loads.

### Environmental implications of Solar Energy

(i) Solar energy installation of large size have to be made without reducing the forest cover.
(ii) Cadmium used in thin film solar cells is both poisonous and a possible carcinogen.
(iii) Carbon dioxide produced when silicon is obtained from silica increases the atmospheric temperature.
(iv) Silicon dust is an important occupational hazard.

## 28.

## 29. UNIT 4

**Unit 4** **POLYMERS**

High polymers: plastics – Thermoplastics and thermosetting resins. Addition polymerization and condensation polymerization – Important engineering plastics – polyethylene, PVC, Teflon, Polystyrenes, Nylon 6,6, Bakelite, Polyurethane .

---

## POLYMERS

Polymers (Greek poly-many;' mers-units or parts) are macromolecules (gaint molecules of high molecular mass) made by linking together a large number of small molecules called monomers. The simplest example is the polymer polyethylene which is formed by the linking together a large number of ethylene ($C_2H_4$) molecules.

$$n\ CH_2 = CH_2 \xrightarrow[\text{Catalyst}]{\text{Heat/pressure}} (-CH_2-CH_2-)_n$$

**Ethylene** **Catalyst** **Polyethylene**

Thus, small molecules which combine with each other to form polymer molecules are formed *monomers* and the reaction by which monomers combine to form polymers is termed polymerization. The number of repeating units (n) in chain formed in a polymer, is known as *degree of polymerization* (DP). The n value for most of the polymers fall into the 5000-200,000 molecular weight range.

### 30. Nomenclature

Polymer made out of identical monomer units are know as *homopolymers* and that are made out of different kind of monomers are known as *copolymers.*

$$\ldots\ -M-M-M-M-M-\ \ldots$$

Hompolymer

$. - M_1 - M_2 - M_1 - M_2 - M_1 -$

Co-polymer

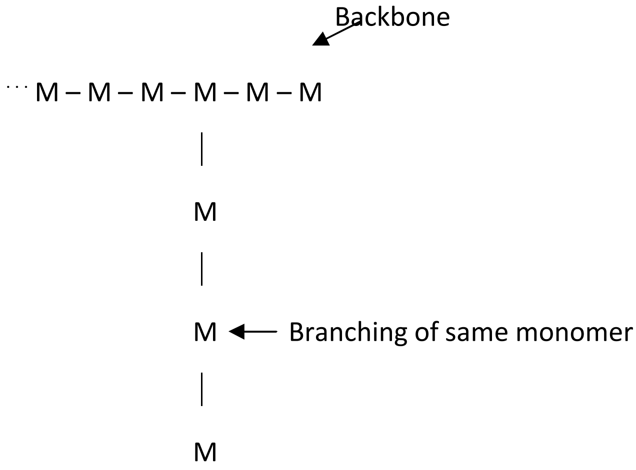
The momomeric unit is a polymer may be present in *linear, branched* or cross-lined (three-dimentional) structure.

$\cdots - M - M - M - M - M - M - \cdots$

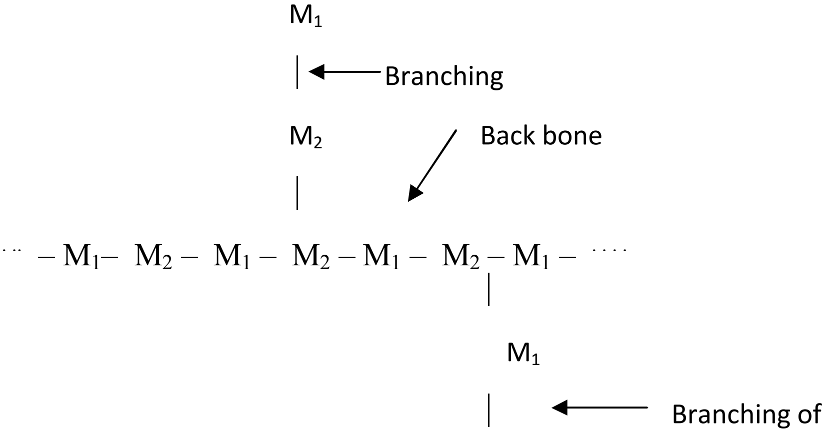
Liner homopolymer

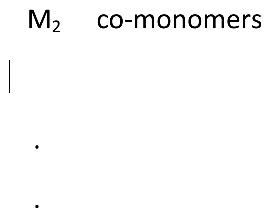
$\cdots - M_1 - M_2 - M_1 - M_2 - M_1 - M_2 - \cdots$

Linear copolymer

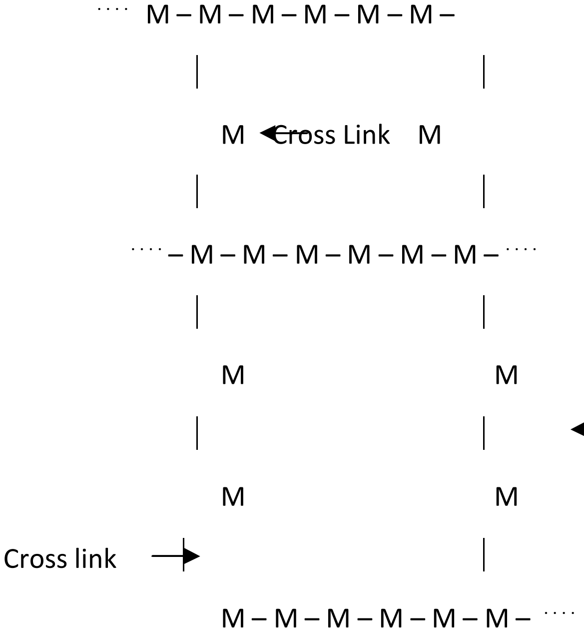


Branched Chain homopolymer





Branched copolymer



Cross-linked homopolymer

If the chain is made up of same species of atoms, the polymer is called homochain polymer, and if the main chain is made up of different atoms, then it is called *"heterochain polymer"*. Thus,

– C – C – C – C – C – C –

Main chain Homochain polymer

- C – C – C – O – C – C – O – C – C – O –

Main chain Heterochain polymer

In copolymer molecules, the monome units may be arranged in the chain at random or regularly.

$\cdots - M_1 - M_2 - M_1 - M_2 - M_1 - M_2 - M_1 - M_2 - \cdots$

$\cdots - M_1 - M_1 - M_2 - M_2 - M_1 - M_1 - M_2 - M_2 - \cdots$

$\cdots M_1 - M_1 - M_1 - M_2 - M_1 - M_1 - M_1 - M_2 - \cdots$

Regular copolymers

$- M_1 - M_2 - M_1 - M_2 - M_2 - M_1 - M_1 - M_2 - \cdots$

Irregular or random copolymers

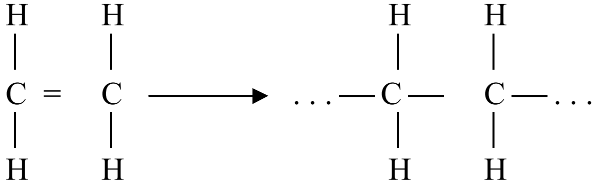
$\cdots M_1 - M_2 - M_1 - M_2 - M_1 - M_2 - M_1 - \cdots$

Alternating copolymers.

**31.**

### 32. Functionality

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



$$\overset{H}{\underset{H}{C}} = \overset{H}{\underset{H}{C}} \longrightarrow \ldots - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \ldots$$

Thus ethylene is considered as bifunctional. Other reactive groups are hydroxyl, acid, amino acid, di - or – polyalohols, diamino acids, di acids etc.

Depending upon the functionality of monomeric units it is possible to obtain different types of structures. Bifunctional monomers mainly form linear polymers. Mixtures of bifunctional and trifunctional polymers form branched polymers as well as cross-linked polymers.

## TYPES OF POLYMERIZATION

**Addition or Chain polymerization** is a reaction that yields a product, which is an exact multiple of the original monomeric molecule. Such a monomeric molecule, usually, contains one or more double bonds, which by intermolecular rearrangement, may make the molecule bifunctional. The addition polymerization reaction does not occur simple by placing monomers close to one another, but it must be instigated by the application of light, pressure or a catalyst for breaking down the double covalent bonds of monomers. Thus:

$$n[CH_2{=}CH_2] \text{ ----->-[ } -CH_2 - CH_2 - \text{]-}_n$$

Ethylene Polyethylene

**2) Condensation or step-polymeryzation** may be defined as “a reaction occurring between simple polar group containing monomers with the formation of polymer and elimination of small molecules like water, HCl, etc. For example:

$$nNH_2\text{-}(CH)_6\text{-}NH_2 \ +nHOOC\text{-}(CH)_4\text{-}COOH\text{-------->} \text{ --}HN\text{-}(CH)_6\text{-}NH\text{-}CO\text{-}(CH)_4\text{-}CO\text{--}$$

$$-2nH_2O$$

**3) Copolymerization** is the joint polymerization of two or more monioner species. High molecular weight compounds obtained by copolymerization, are called copolymers. For example, butadiene and styrene copolymerize to yield GR-S rubber.

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

nCH2 = CH – CH = CH2 + n CH2 = CH –Ph ------>-(-H2C -CH = CH –CH --CH2 –CH – Ph-)n-

Copolymerization has found extensive practical usage, because it enables us to vary of the properties of high molecular weight compounds over a wide range. For instance, the copolymer of acrylonitrille ($CH_2{=}CHCN$) and vinyl choloride ($CH_2{=}CHCl$).

is readily soluble in acetone: whereas polyacrylonitrile (PAN) and polyvinyl chloride (PVC) are soluble only in high-boiling and difficulty available solvents.

## PLASTICS

Plastics are high molecular weight materials which can be moulded or formed into stable shapes by the application of heat and pressure.

### Compounding of plastics

Compounding of plastics is a process by which the high polymer resins are mixed with other substances like fillers, plasticizers, colorants, etc. to remove the quality are of fabrication and to impart certain specific properties.

Plastic may contain a number of constituents such as (1) binders, (2) fillers, (3) dyes and pigments, (4) plasticizers, (5) lubricants and (6) catalysts.

(1) *Binders:* The main purpose of a binder to a hold the other constituents of the plastic together. The binder used may be natural or synthetic resins. Two types of resins used are (a) thermoplastic resins, (b) thermosetting resins. On the basis of the type of resin use din its preparation, the plastic itself if called thermoplastic or thermosetting plastic.

(2) *Fillers:* Fillers are added for two purposes (a) to reduce the cost and (b) to impart special property on the product. For example, quarts and mica are used to improve hardness; asbestos is added to improve heat resistance.

(3) *Dyes and pigments:* These materials provide pleasing colours to the plastic. They are inorganic colouring pigments as well as organic colouring dyes.

**Table 1. Dyes and pigments**

| **Name of the pigment/dye/inorganic substance** | Colour |
|---|---|
| Carbon black | Black |
| Zinc oxide | White |
| Chromium trioxide | Green |
| Phthalocyanin dye | Blue |

(4) *Plasticizers:* The important functions of a plasticizer in plastics are to improve plasticity and flexibility so as to reduce the temperature and pressure required for moulding, *e.g.* dioctylphthalate. These molecules distribute themselves between the polymer chains thereby decreasing the attractive forces between them. This results in increased plasticity and flexibility.

(5) *Lubricants:* They help in easy moulding and also prevent the plastic material from sticking to the fabrication equipment, *e.g.* oils, waxes, etc.

(6) *Catalysts:* They are use din case of thermosetting plastics to accelerate the condensation polymerization to form the cross-linked products, *e.g.* peroxides.

**Table 2. Differences between thermoplastics and thermosetting plastics**

| Thermoplastics | **Thermosetting plastics** |
|---|---|
| 1. They are formed by addition polymerization | They are formed by condensation polymerization |
| 2. Adjacent polymer chains are held together by weak van der Waals forces | Adjacent polymer chains are held together by strong covalent bonds called cross-links |
| 3. They soften on heating and stiffen on cooling | They do not soften on heating |
| 4. They can be remoulded | They cannot be remoulded because once set, they are permanently set. |
| 5. They are weak, soft and less brittle | They are strong, hard and more brittle |
| 6. They are soluble in organic solvents | They are insoluble in organic solvents |
| 7. They have very low molecular weights | They have high molecular weights |

**Some important thermoplastics**

***1. Polyethylene:*** it is obtained from ethylene which is a byproduct in petroleum industries

$$n\text{-}CH_2{=}CH_2 \xrightarrow{\text{Polymerisation}} \left[ -CH_2-CH_2- \right]_n$$

There are two kinds of polyethylene, namely, (i) low density polyethylene (LDPE) and (ii) high density polyethylene (HDPE).

(i) **LDPE:** LDPE is obtained by polymerization of ethylene using $O_2$ as the initiator with the pressure of 1500 atmospheres and at the temperature range of 180-250°C. This can be prepared by solution by solution polymerization or bulk polymerization.

*Properties:* The melting point of LDPE is 110-125°C and 40 per cent crystalline. The density is around 0.91-0.92 g/ml. It is insoluble in any solvent at room temperature. At high temperature it is soluble in $CCl_4$, toluene and xylene.

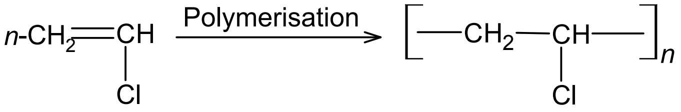
*Uses:* It is used for making films, table cloth, packing materials, etc.

(ii) **HDPE:** HDPE is produced by coordination polymerization using Ziegler-Natta catalyst and the polymerization reaction is carried out at low pressure.

*Properties:* The melting point of HDPE is 144-150°C. It has a higher density (0.965 g/ml). It is a near crystalline polymer (90 per cent). It is chemically more resistant than LDPE.

*Uses:* It is used for making toys, detergent bottles, pipes, etc.

***2. Polyvinyl chloride*:** It is prepared by the polymerization of vinyl chloride in presence of benzoyl peroxide.

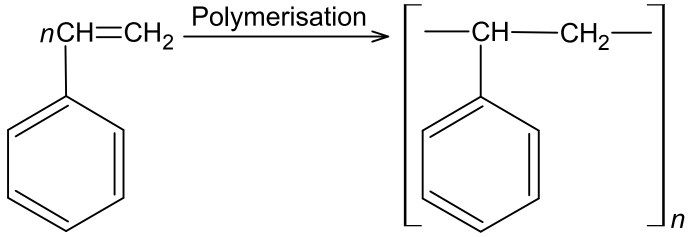


$$n\text{-}CH_2{=}\underset{\displaystyle Cl}{\underset{|}{CH}} \xrightarrow{\text{Polymerisation}} \left[-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-\right]_n$$

*Properties:* It is hard and stiff amorphous plastic. It is characterized by excellent flame resistance and low cost. It has outstanding strength, lightness and chemical resistance.

*Uses:* It is used for the production of pipes, cable insulations, table-covers, safety helmets, rain-coats, etc.

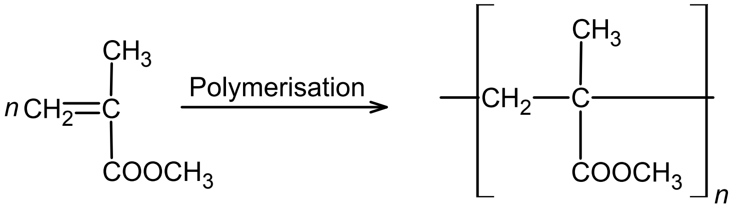
***3. Polystyrene*:** It is prepared by polymerization of styrene in presence of a peroxide.



*Properties:* It is chemically insert. Acids, alkalis and oxidizing agents have little effect on it.

*Uses:* It is used in the manufacture of jars, bottles, toys, etc.

***4. Polymethylmethacrylate(PMMA)or Plexiglass or Lucite*:** It is obtained by polymerization of methylmethacrylate in presence of acetyl peroxide.



$$n\,\mathrm{CH_2{=}}\underset{\mathrm{COOCH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} \xrightarrow{\text{Polymerisation}} \left[ -\mathrm{CH_2}-\underset{\mathrm{COOCH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}- \right]_n$$

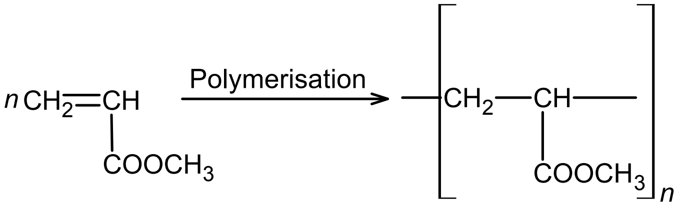
It is used to make sign boards, durable lenses for automobile lighting. The sheets are used in buildings for decorative purposes. It is also used in paints, adhesives, etc.

***5. Polytetrafluoroethylene (PTFE) or Tefton*:** It is prepared by polymerization of tetrafluoroethylene at higher pressures in presence of benzoyl peroxide.

$$n\,\mathrm{CF_2{=}CF_2} \xrightarrow{\text{Polymerisation}} \left[ -\mathrm{CF_2}-\mathrm{CF_2}- \right]_n$$

Teflon is used as an electrical insulator even at elevated temperatures. It is also used as non-strick coating on frying pans, solid lubricants, etc.

***6. Polyvinyl acetate (PVA)*:** It is prepared from vinyl acetate by heating in presence of a small quantity of peroxide.



$$n\,\mathrm{CH_2{=}}\underset{\mathrm{COOCH_3}}{\mathrm{CH}} \xrightarrow{\text{Polymerisation}} \left[ -\mathrm{CH_2}-\underset{\mathrm{COOCH_3}}{\mathrm{CH}}- \right]_n$$

It is used for the manufacture of polyvinyl alcohol. It is used in making emulsion paints, adhesives, LP records, etc. It is also used for making chewing gums.

**Some important thermosetting plastics**

***1. Nylon:*** It is obtained by heating adipic acid and hexamethylenediamine. Nylon 6,6 derives its name from its starting materials adipic acid and hexamethylenediamine both the which have six carbons.

$$\underset{\text{adipic acid}}{HOOC-(CH_2)_4-COOH} + \underset{\text{hexamethylenediamine}}{H_2N-(CH_2)_6-NH_2} \longrightarrow$$

$$HOOC-(CH_2)_4-CO-NH-(CH_2)_6-NH_2 + H_2O$$

$$\downarrow$$

$$-\!\!\left[CO-(CH_2)_4-CO-NH-(CH_2)_6-NH\right]\!\!-$$

Nylon 6,6

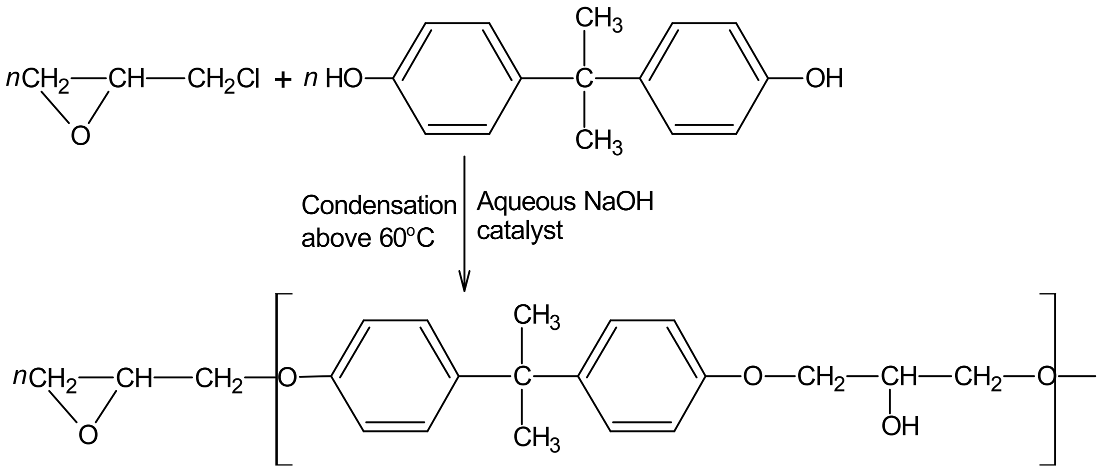
*Properties:*Nylon is tough, strong and easily mouldable. It has good chemical resistance and low coefficient of friction.

*Uses:*

1. Nylon is used to make textile fibres for use in dresses, socks, undergarments, carpets, etc.
2. It is also used for making filaments for ropes, bristles for tooth brush, etc.
3. It is used as a good substitute for metal in gears and bearings

4. It is also used in making tyres, watch straps, etc.

***2. Epoxy resins*:** The most commonly used epoxy resin is prepared by the condensation of epichlorohydrin with bis-phenol A. An excess of epichlorohydrin is used so that the linear polymer chain can be terminated at each end by epoxy grouping.



Epoxy resin

By controlling the degree of polymerization, the physical state of the resin produced can vary from solid to fully liquid.

*Properties:* Epoxy resins have remarkable chemical resistance, excellent toughness and good adhesion.

*Uses:*

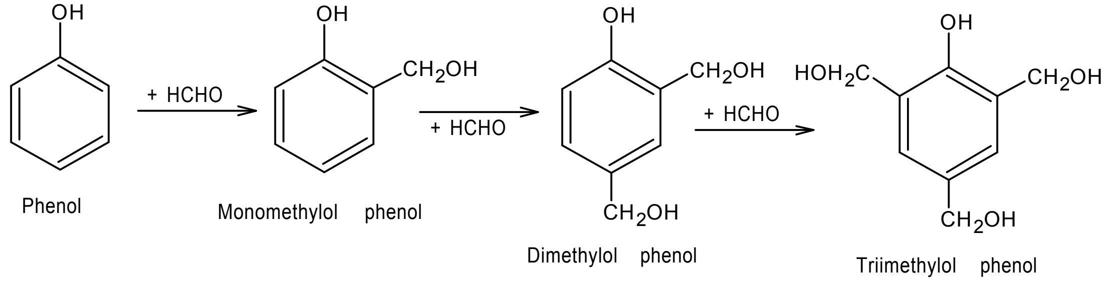
1. They are mainly used as surface coating materials.
2. They are also used in industrial floorings.

3. They are used as good adhesives
4. They are used in glass fibre reinforced plastics.

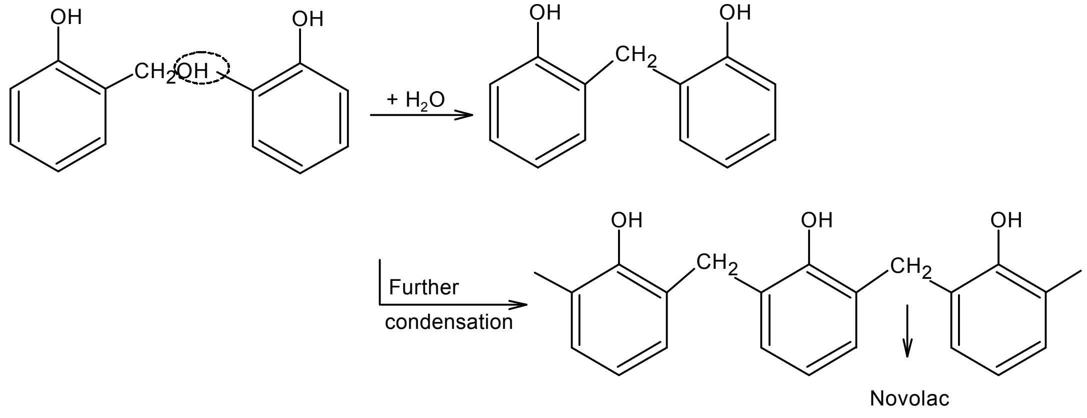
***3.*** **Bakelite:** It is obtained by the condensation reacting of phenol and formaldehyde.

The nature of the product depends upon the proportion of the reactants and the nature of the catalyst, *i.e.* acidic or basic. If the mole ratio of phenol to formaldehyde is greater than 1, the reaction proceeds in a linear fashion. On the other hand, if the mole ratio of phenol to formaldehyde is less than 1 and if an alkaline catalyst is used, three-dimensional network structure would be produced.

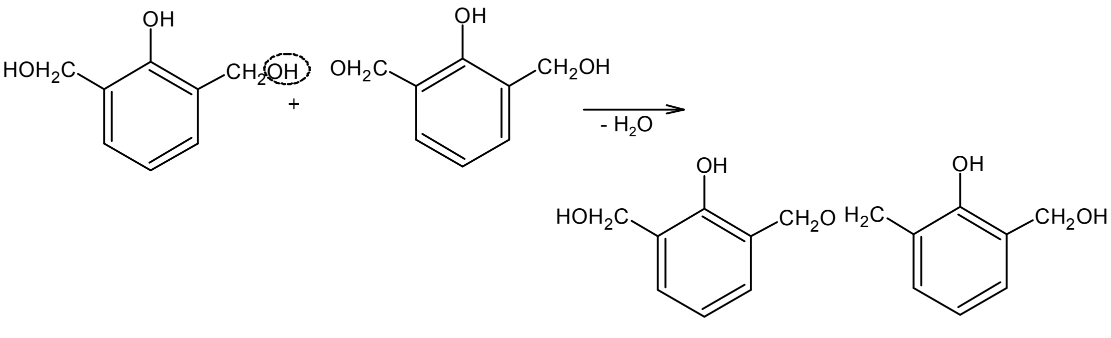
**(a) Methylolation:** The first step is the reaction between phenol and formaldehyde and formation of addition compound known as methylol derivatives. These products may be considered as the monomers for subsequent polymerization.



**(b) Novolac formation:** In the presence of acid catalysts and with excess of phenol, the methylol derivatives condense with phenol to form dihydroxy-diphenylmethane. On further condensation, linear low polymers called novolacs are formed.

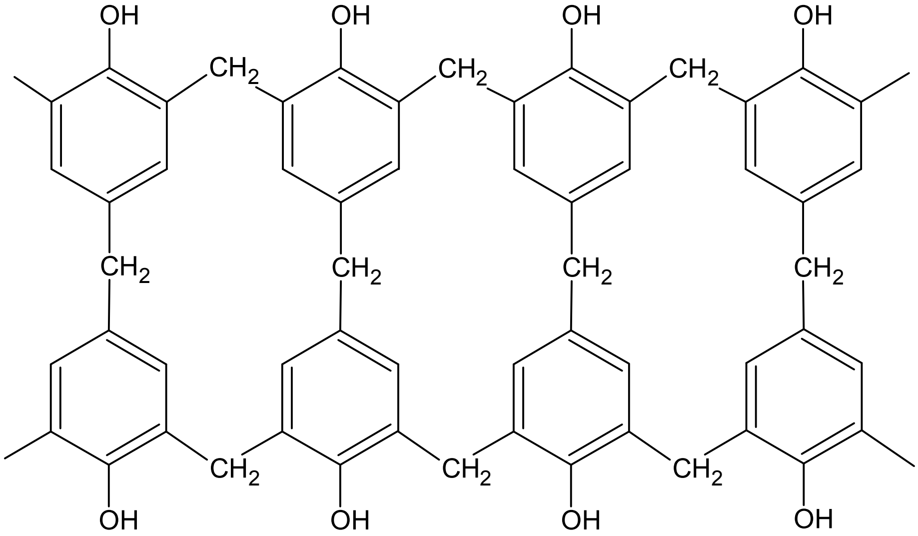


**(c) Resole formation:** In the presence of alkaline catalyst and with excess of formaldehyde, the methylol phenols can condense through ether linkages to form resoles.



Resole

*Production of bakelite:* Further heating of novolac or resole or both in the presence of curing agent (hexamethylenetetramine) produces excessive cross-links. The final product is a hard, rigid and infusible solid called bakelite.



Bakelite

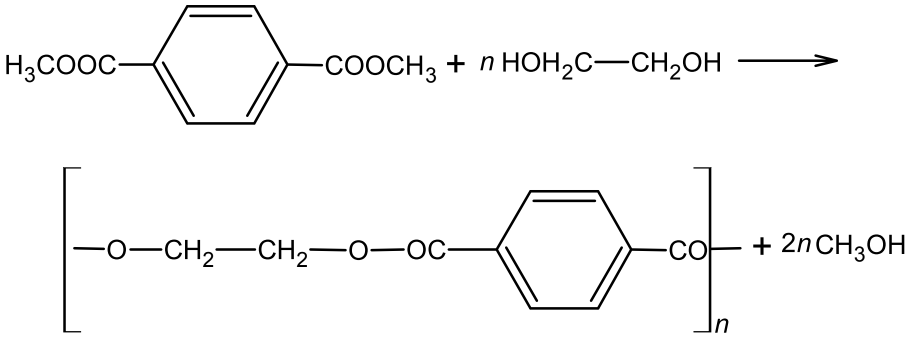
*Properties:*

1. Phenolic resin or bakelite is resistant to acids, salts and many organic solvents.
2. It possesses excellent electrical insulating character.

*Uses:*

1. It is used as a bonding adhesive in plywood
2. It is used for making electrical insulator parts like switches, plugs, switch boards, heater handles, etc.

***4. Polyethylene terephthalate (PET):*** It is prepared by heating dimethyl terephthalate with excess of ethylene glycol at 140-220°C in presence of a catalyst (manganese acetate). Methanol is removed as a by-product.



*Properties:* Its chemical and solvent resistant are good.

*Uses:* The major use of this plastics is in the development of blown bottles for soft-drink use.

## Nano Materials:

### Introduction to Nano materials:-

Nanomaterials are defined as materials with at least one external dimension in the size range from approximately 1-100 nanometers. Nanoparticles are objects with all three external dimensions at the nanoscale. Nanoparticles that are naturally occurring (e.g., volcanic ash, soot from forest fires) or are the incidental byproducts of combustion processes (e.g., welding, diesel engines) are usually physically and chemically heterogeneous and often termed ultrafine particles. Engineered nanoparticles are intentionally produced and designed with very specific properties related to shape, size, surface properties and chemistry. These properties are reflected in aerosols, colloids, or powders. Often, the behavior of nanomaterials may depend more on surface area than particle composition itself. Relative-surface area is one of the principal factors that enhance its reactivity, strength and electrical properties.

Engineered nanoparticles may be bought from commercial vendors or generated via experimental procedures by researchers in the laboratory (e.g., CNTs can be produced by laser ablation, HiPCO (high-pressure carbon monoxide, arc discharge, and chemical vapor deposition (CVD)). Examples of engineered nanomaterials include: carbon buckeyballs or fullerenes; carbon nanotubes; metal or metal oxide nanoparticles (e.g., gold, titanium dioxide); quantum dots, among many others.

Particles at the nanoscale are below the wavelength of visible light, and therefore cannot be seen. Consequently, they can impart new properties while being invisible themselves Fluorescent nanoparticles, or quantum dots (mentioned earlier) have a whole range of possible applications. They are invisible until 'lit up' by ultraviolet light, and can even be made to exhibit a range of colours, depending on their composition and size.

Nanoparticles can seem to be quite strange as they have new and unusual properties that are not obvious in the corresponding bulk material. This is because a nanoparticle has a large surface area in relation to its size, and is consequently highly reactive. This is exemplified by the fine grained materials that we use in our daily lives, such as flour, which can become explosive in some circumstances. Applications of nanoparticles include nanoparticulate titanium dioxide for sunscreens, and it also acts as a photocatalytic agent in coatings that can be applied to stay-clean windows, causing the dirt to be oxidized and easily washed away by rain.

**Brief outline of SOL-GEL processes:-**

A sol is a dispersion of the solid particles (~ 0.1-1 μm) in a liquid where only the Brownian motions suspend the particles. A gel is a state where both liquid and solid are dispersed in each other, which presents a solid network containing liquid components. The sol-gel coating process usually consists of 4 steps:
(1) The desired colloidal particles once dispersed in a liquid to form a sol.
(2) The deposition of sol solution produces the coatings on the substrates by spraying, dipping or
spinning.
(3) The particles in sol are polymerized through the removal of the stabilizing components and produce a
gel in a state of a continuous network.
(4) The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating. There are two distinct reactions in the sol-gel process: hydrolysis of the alcohol groups and condensation of the resulting hydroxyl groups. In the case of isomorphous γ-AlOOH precursor, it exists as the un-hydrolyzed species $[Al(OH_2)_6]^{3+}$below pH 3, and can be hydrolyzed extensively with increasing pH:

$$[Al(OH_2)_6]^{3+} + kH_2O \rightarrow [Al(OH)_k(OH_2)_{6-k}]^{(3-k)+} + kH_3O^+ \quad (1)$$

$$hH_3O^+ + kOH^- \rightarrow 2kH_2O \quad (2)$$

where *h* is defined as the molar ratio of hydrolysis. People generally agree that the preferred condensation sites are those that maximize the interactions between lone pair electrons on a bound hydroxide ligand on one aluminium species with a proton on a water-molecule bound to another aluminium species.

[1] For example, two singly-hydrolyzed monomers (*h*=1) condense to a dimmer via an olation reaction:

$$2[Al(H_2O)_6^{3+} - H^+ \rightarrow Al(H_2O)_5OH^{2+}] - 2H_2O \rightarrow Al_2(OH)_2(H_2O)_8^{4+} \quad (3)$$

However, the condensation mechanism of aluminium isopropoxide is more complex than the above description. People do not have very well understanding of the hydrolysis of the aluminium alkoxides.

## Advantages of Sol-Gel Technique

* Can produce thin bond-coating to provide excellent adhesion between the metallic substrate and the top Introduction to Sol-Gel coat.
* Can produce thick coating to provide corrosion protection performance.
* Can easily shape materials into complex geometries in a gel state.
* Can produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel, the composition can be highly controllable.
* Can have low temperature sintering capability, usually 200-600°C.
* Can provide a simple, economic and effective method to produce high quality coatings.

**CVD methods:-**

Chemical vapor deposition (CVD) is a widely used materials-processing technology.The majority of its applications involve applyingsolid thin-film coatings to surfaces, but it is alsoused to produce high-purity bulk materials andpowders, as well as fabricating compositematerials via infiltration techniques. It has beenused to deposit a very wide range of materials. The majority of the elements in the periodic tablehave been deposited by CVD techniques, somein the form of the pure element, but more oftencombined to form compounds.

In its simplest incarnation, CVD involvesflowing a precursor gas or gases into a chambercontaining one or more heated objects to becoated. Chemical reactions occur on and nearthe hot surfaces, resulting in the deposition of athin film on the surface. This is accompanied bythe production of chemical by-products that areexhausted out of the chamber along withunreacted precursor gases. As would be expectedwith the large variety of materials deposited andthe wide range of applications, there are manyvariants of CVD. It is done in hot-wall reactorsand cold-wall reactors, at sub-torr total pressuresto above-atmospheric pressures, with andwithout carrier gases, and at temperaturestypically ranging from 200-1600°C. There arealso a variety of enhanced CVD processes,which involve the use of plasmas, ions, photons,lasers, hot filaments, or combustion reactions toincrease deposition rates and/or lower depositiontemperatures. There are also many derivativesof the CVD terminology, such as metal-organicchemical vapor deposition (MOCVD) or, lesscommonly and organo-metallic chemical vapordeposition (OMCVD).

CVD has a number of advantages as amethod for depositing thin films. One of theprimary advantages is that CVD films aregenerally quite conformal, i.e., that the filmthickness on the sidewalls of features iscomparable to the thickness on the top. Anotheradvantage of CVD is that, in addition to the widevariety of materials that can be deposited, theycan be deposited with very high purity. Thisresults from the relative ease with whichimpurities are removed from gaseous precursorsusing distillation techniques. Other advantagesinclude relatively high deposition rates, and thefact that CVD often doesn’t require as high avacuum as PVD processes.

## Carbon Nanotubes:-

Carbon nanotubes (CNTs) are an allotrope of carbon.They take the form of cylindrical carbon molecules and have novel properties that make them potentially useful in a wide variety of applications in nanotechnology, electronics, optics and other fields of materials science.They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat.Inorganic nanotubes have also been synthesized.Nanotubes are members of the fullerene structural family, which also includes buckyballs.Whereas buckyballs are spherical in shape, a nanotube is cylindrical, with at least one end typically capped with a hemisphere of the buckyball structure.Their name is derived from their size, since the diameter of a nanotube is on the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair), while they can be up to several millimeters in length.There are two main types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

SWNTs are an important variety of carbon nanotube because most of their properties change significantly with the $(n,m)$ values, and this dependence is non-monotonic. In particular, their band gap can vary from zero to about 2 eV and their electrical conductivity can show metallic or semiconducting behavior. Single-walled nanotubes are likely candidates for miniaturizing electronics. The most basic building block of these systems is the electric wire, and SWNTs with diameters of an order of a nanometer can be excellent conductors. One useful application of SWNTs is in the development of the first intermolecular field-effect transistors (FET). SWNT that acts as a NOT logic gate with both p and n-type FETs within the same molecule.

Double-walled carbon nanotubes (DWNT) form a special class of nanotubes because their morphology and properties are similar to those of SWNT but their resistance to chemicals is significantly improved. This is especially important when functionalization is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT. In the case of SWNT, covalent functionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotube and, thus, modifying both its mechanical and electrical properties. In the case of DWNT, only the outer wall is modified.

## Fullerenes:-

A **fullerene** is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, tube, and many other shapes. Spherical fullerenes are also called **buckyballs**, and they resemble the balls used in football (soccer). Cylindrical ones are called carbon nanotubes or buckytubes. Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings; but they may also contain pentagonal (or sometimes heptagonal) rings.

The first fullerene molecule to be discovered, and the family's namesake, buckminsterfullerene ($C_{60}$), was prepared in 1985 by Richard Smalley. The name was a homage to Buckminster Fuller, whose geodesic domes it resembles. The structure was also identified from an electron microscope image, where it formed the core of a "bucky onion." Fullerenes have since been found to occur in nature. The discovery of fullerenes greatly expanded the number of known carbon allotropes, which until recently were limited to graphite, diamond, and amorphouscarbon such as soot and charcoal. Buckyballs and buckytubes have been the subject of intense research, both for their unique chemistry and for their technological applications, especially in materials science, electronics, and nanotechnology.

**Semiconductors Sensors:-**

The development of gas sensor devices with optimized selectivity and sensitivity has been gaining prominence in recent years. Fundamental materials and processing issues, which are critical for a high-performance gas sensor, need to be addressed. Among the new technologies, a nanocrystalline material offers immense promise for improved sensitivity. This article provides a rationale for using nanocrystalline materials in gas sensors, and outlines the challenges facing commercialization of this new class of material.

In recent years, interest has grown in the development of an electronic "nose," capable of detecting mixed gases and even odors. Instead of analyzing all of the gas constituents by a technique such as gas chromatography, an electronic nose looks for specific patterns or fingerprints of the gas mixture. Such a device generally consists of 4-22 chemical sensors, each one sensitive to a specific gas and a pattern recognition system. Various prototypes, based on organic as well as inorganic sensing materials, have appeared in the market.

Sensitivity is generally enhanced either by doping, which modifies the carrier concentration and mobility, or by microstructural changes such as reduction of the oxide particle size to the nanometer scale. In recent years, the sensitivity of semiconductor oxide materials has been improved by reducing the particle size, with greatly improved properties reported for sizes in the 5-50 nanometer range. The effect of particle size on the sensitivity of a $SnO_2$ sensor for $H_2$ . where an order of magnitude increase in sensitivity occurs when the particle size decreases to below 10 nm. The critical particle size where substantial improvement is observed depends on oxide material, dopant, and processing method. For instance, another study showed that sensitivity for $H_2$ can be increased tenfold by reducing the average particle size to 22 nm. For $In_2O_3$ a particle size effect starts to occur below 50 nm with an order of magnitude increase in sensitivity for particles in the 20 nm to 30 nm range. This particle size effect is due, in part, to an increase in the surface area since, in this size range, a large fraction of the atoms (up to 50%) are present at the surface or the interface region with structure and properties that are different from that of the bulk.

**Nanocomposites:-**

A **nanocomposite** is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material. In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Size limits for these effects have been proposed, <5 nm for catalytic activity, <20 nm for making a hard magnetic material soft, <50 nm for refractive index changes, and <100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocationmovement.Nanocomposites are found in nature, for example in the structure of the abalone shell and bone. The use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials.

In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally highaspect ratio. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibres (e.g. carbon nanotubes or electrospun fibres). The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement note that with polymer nanocomposites, properties related to local chemistry, degree of thermoset cure, polymer chain mobility, polymer chain conformation, degree of polymer chain ordering or crystallinity can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix.

**Nanowires:-**

A **nanowire** is a nanostructure, with the diameter of the order of a nanometer ($10^{-9}$ meters). It can also be defined as the ratio of the length to width being greater than 20. Alternatively, nanowires can be defined as structures that have a thickness or diameter constrained to tens of nanometers or less and an unconstrained length. At these scales, quantum mechanical effects are important — which coined the term "quantum wires". Many different types of nanowires exist, including metallic (e.g., Ni, Pt, Au), semiconducting (e.g., Si, InP, GaN, etc.), and insulating (e.g., $SiO_2$, $TiO_2$). Molecular nanowires are composed of repeating molecular units either organic (e.g. DNA) or inorganic (e.g. $Mo_6S_{9-x}I_x$). The nanowires could be used, in the near future, to link tiny components into extremely small circuits. Using nanotechnology, such components could be created out of chemical compounds.

A suspended nanowire is held up by the ends in an evacuated chamber, and then is chemically etched or bombarded with high-speed atom s or molecule s to reduce its diameter. Another method involves indenting the surface of a wire in the center of a suspended span, raising the temperature, and then stretching the wire while it is near its melting point. A deposited nanowire is fabricated on a surface consisting of some non-conducting substance such as plastic or glass. The process is similar to that by which semiconductor chips are grown, except that the result is a linear (one-dimensional) structure rather than a flat (two-dimensional) or solid (three-dimensional) structure. Fields expected to benefit from nanotechnology include water purification, sanitation, agriculture, alternative energy (particularly photovoltaics), home and business construction, computer manufacturing, communications, and medicine.

## Nanorods:-

**nanorods** are one morphology of nanoscale objects. Each of their dimensions range from 1–100 nm. They may be synthesized from metals or semiconducting materials. Standard aspect ratios (length divided by width) are 3-5. Nanorods are produced by direct chemical synthesis. A combination of ligands act as shape control agents and bond to different facets of the nanorod with different strengths. This allows different faces of the nanorod to grow at different rates, producing an elongated object.One potential application of nanorods is in display technologies, because the reflectivity of the rods can be changed by changing their orientation with an applied electric field. Another application is for microelectromechanical systems (MEMS). Nanorods, along with other noble metal nanoparticles, also function as theragnostic agents. Nanorods absorb in the near IR, and generate heat when excited with IR light. This property has led to the use of nanorods as cancer therapeutics. Nanorods can be conjugated with tumor targeting motifs and ingested. When a patient is exposed to IR light (which passes through body tissue), nanorods selectively taken-up by tumor cells are locally heated, destroying only the cancerous tissue while leaving healthy cells intact.

## Nano Sheets:-

A **nanosheet** is a two-dimensional nanostructure with thickness in a scale ranging from 1 to 100 nm. A typical example of nanosheet is graphene, the thinnest two-dimensional material (0.34 nm) in the world. It only consists of single layer of carbon atoms with hexagonal lattices.Currently, the most commonly used synthesis methods for nanosheet are based on bottom-up approach, e.g., solution phase synthesis andchemical vapor deposition (CVD). For example, CdTe nanosheets could be synthesized by precipitating and aging CdTe nanoparticles in deionized water. The formation of free-floating CdTe nanosheets were due to directional hydrophobic attraction and anisotropic electrostatic interactions causing by dipole moment and small positive charges. Molecular simulations through a coarse-grained model with parameters from semi-empirical quantum mechanics calculations can be used to prove the experimental process. Under high temperature conditions, nanosheets can also be prepared at room temperature. For instance, hexagonal PbO nanosheets were synthesized using gold nanoparticles (Au NPs) as seeds under room temperature. The size of the PbO nanosheet can be tuned by Au NPs and $Pb^{2+}$ concentration in the growth solution. No organic surfactants were employed in the synthesis process. Oriented attachment, in which the sheets form by aggregation of small nanoparticle that each has a net dipole moment, and ostwald ripening are the two main reasons for the formation of the PbO nanosheets.

# unit V

## ENGINEERING MATERIALS - I

Lubricants and their functions – Mechanisms of lubrication – classification of lubricants with example – lubricating oils – properties of lubricating oils (viscosity index, flash and fire points, cloud and pour points, oiliness, carbon residue and aniline point) – Solid lubricants – Greases – emulsion lubricants.

### Lubricants

### 33. 1. INTRODUCTION

In all types of machines, the surfaces of moving or sliding or rolling parts rubs against each other. Due to this a resistance is developed and is known as friction.

Any substance introduced between two moving or sliding surfaces with a view to reduce the frictional resistance between them is known as lubricant. The process of reducing frictional resistance between two moving or sliding surfaces by the introduction of lubricants is known as lubrication.

## 34. 2. FUNCTIONS OF A LUBRICANT

**THE FOLLOWING ARE THE MAIN FUNCTIONS OF A LUBRICANT.**

**i.** It prevents direct contact between the surfaces and reduces wear and tear.

**ii.** It reduces wastage of energy. iii. It reduces expansion of metal by frictional heat. iv. It saves maintenance and running cost of machine.

v. It provides smooth, uniform motion. vi. It avoids seizure of moving surfaces vii. It acts as a seal in preventing the deposition of dust in machine parts or holes.

## 35. 3. CLASSIFICATION

On the basis of physical state of the lubricants the classification is as follows:

Lubricants

| Solid | Semi solid<br>(greases) | Liquid<br>(lubricating oils) |
|---|---|---|
| 1. graphite, | 1. Calcium – based | 1. Animal and Vegetable |
| 2. $MoS_2$ | 2. Soda – based | 2. Mineral or Petroleum |
| 3. Lithium – based | | |

## 36. 4. REQUIREMENTS OF A SOLID LUBRICANT

The solid lubricants should be,

**i.** Very strong adhesion power to the applied surfaces.

**ii.** Chemically inert iii. Good thermal conductivity iv. Good stability at operating temperature

v. Low shear strength vi. High boiling point and low vapour

pressure vii. High fire and flash point and low cloud and pour

point.

## 37. 5. SOLID LUBRICANTS

Solid lubricants are used, where

i. Operating conditions are such that a lubricating film cannot be obtained by the use of

lubricating oils or greases ii. Operating temperature or the load is too high iii.

Combustible lubricants are not suitable.

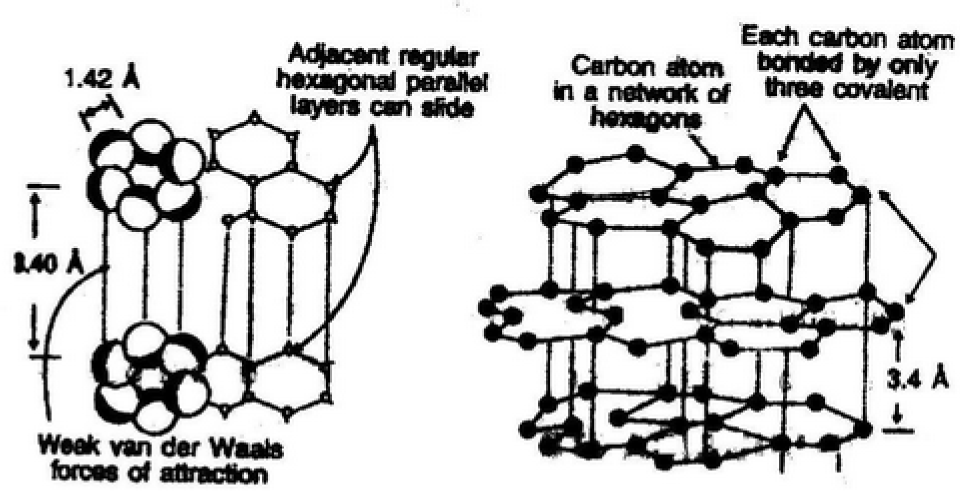
The two common solid lubricants used are graphite and molybdenum disulphide.

### 5.1. Graphite

Graphite is the most widely used of all solid lubricants. In graphite, each carbon atom is attached to three other carbon atoms by strong covalent bonds to form hexagonal rings. Graphite contains layers of these hexagonal rings. The bonding between atoms within a layer is strong. The bonding between adjacent layers is by weak van der Waals force of attraction.

Graphite is soapy in touch, non inflammable and is not condensed in air below 375qC. In the absence of air, it can be used even at a high temperatures. Graphite is used either in powdered form or as suspension of graphite in oil or in water.

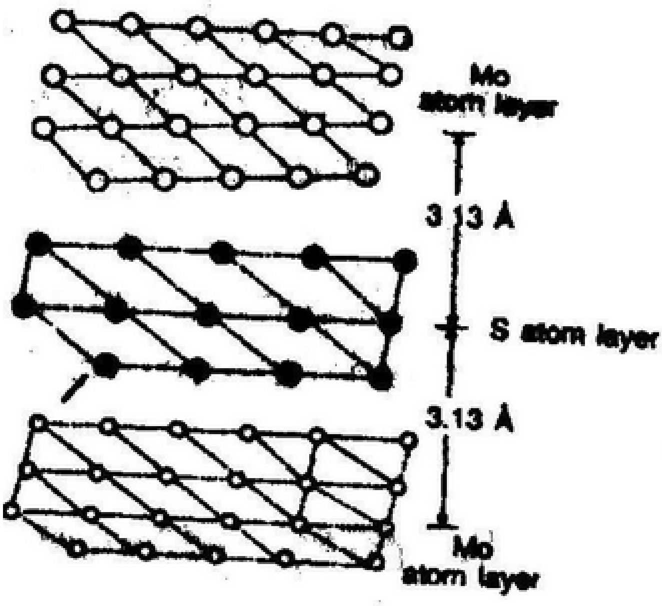
Suspension of graphite in oil (oildag) or in water (aquadag) is brought about with the help of an emulsifying agent like tannin. Oildag is used in internal combustion engines and aquadag is used in food industry where as lubricant free from oil is needed
(Fig. 1).



**38. Fig. 1. Layered structures of graphite**

### *5.2. Molybdenum disulphide ($MoS_2$)*

Molybdenum disulphide possesses similar properties as that of graphite. It has a sandwich like structure in which Mo atom of one layer lies between sulphur atoms of two adjacent layers. The atoms in the layer are held by strong covalent bonds and the adjacent layers are held by weak van der Waals force of attraction. It posses very low coefficient of friction and is stable in air upto 400qC. Its fine powder may be sprinkled on surfaces sliding at high velocities. It can be used along with solvents and greases (Fig.
2).



## 39. Fig. 2. Sandwitch structure of $MoS_2$ 6. LIQUID LUBRICANTS (OR) LUBRICANTING OIL (OR) LUBE OIL

Liquid lubricants are used to a greater extent than solid and semi solid lubricants. Lubricating oils reduce friction and wear between the sliding or moving metallic surfaces by providing a continuous fluid film in between them. They also act as 1) cooling medium, 2) sealing agent, 3) corrosion preventer, 4) continuous and uniform film.

A good lubricating oil must have

i. Low vapour pressure or high boiling point ii.

Adequate viscosity iii. Low freezing point iv.

High oxidation resistance v. Thermal stability vi.

Non-corrosive properties vii. Low pour point

Lubricating oils are further classified as,

### 6.1. Animal oils and vegetable oils

They have good oiliness but they are costly 1) Undergo oxidation easily and get thickened on coming in contact with air. 2) Have some tendency to hydrolyse when allowed to remain in contact with aqueous medium or moist air, (so at present they are used as blending agent, with other oils to produce desired effect). The important vegetable oils are olive oil, palm oil, castor oil, linseed oil etc. The important animal oil are whale oil, lard oil, tallow oil etc.

### *6.2. Petroleum oil (or) mineral oil*

They are obtained by the distillation of crude petroleum. They are used widely because they are a) cheap, b) available in abundance, c) high thermal stability. But they posses poor oiliness as compared to that of animal and vegetable oils. To improve the oiliness small quantities of vegetable or animal oils are added.

## 40. 7. BLENDED (OR) COMPOUNDED OILS (OR) ADDITIVES TO LUBRICANTS

Certain substances called additivites are added to the lubricating oils in order to further improve the properties of the refined lubricating oils. They are added in amounts upto 10%. The oils thus prepared are known as blended oils or compounded oils.

**i) Oiliness carriers:**

Additives are added to increase the oiliness.

Example : vegetable oil, fatty acid, animal oil etc. **ii)**

**Extreme pressure additives :**

Added to make lubricating oil to bear extreme pressure. Example : organic phosphorus, sulphur and chlorocompounds. **iii) Pour point depression additives :**

This helps to reduce the flow rate. Example : alkylnaphthalene, phenol etc. **iv) Viscosity index**

**improvers**

Prevents thinning of oil at high temperature. Example : polyisobutylene **v)**

**Thickness**

Give the lubricating oil a higher viscosity. Example : polystyrene, polyesters

**vi) Anti Oxidants**

It prevents oxidation, Example : aromatic phenols and amines

**vii) Corrosion inhibitors**

Helps to prevent corrosion, Example : phosphorus or antimony **viii)**

**Abrasion inhibitors**

Resists abrasion, Example : Tricresyl phosphate **ix)**

**Antifoaming agent**

It minimizes the foam formation, Example : glycols and glycerol

**41. x) Deposit inhibitors**

It prevents the deposit of dull and foreign substances. Example : Salts of phenol and carboxylic acid.

## 42. 8. SYNTHETIC LUBRICANTS

It can be used in special circumstances like below -26qC and above 121qC. Example : polyglycol, ethers, silicon, fat fluids etc., possesses improved properties like non inflammable, high flashpoint, high viscosity index, good thermal stability, etc.

Drawbacks : costly, some are toxic and corrosive.

## 43. 9. SEMI SOLID LUBRICANTS (OR) GREASES

Grease is a semi solid lubricant obtained by mixing liquid lubricating oil (petroleum oil) with soap at elevated temperatures with constant stirring.

Greases have higher frictional resistance than oils and therefore can support much heavier loads at lower speeds. Greases are used under the following condition.

**i.** In situation where oil does not remain in place due to high load, low speed intermittent operations, sudden jerks etc. Example : rail axle boxes.

**ii.** In bearing and gears that work at high temperature. iii.In situation where bearing needs to be sealed against entry of dust, dirl or moistures.

iv.In situation where spurting or dripping of oil is undesirable.

Example : in machines, preparing paper, textiles, etc.

**Preparation:**

Greases are prepared by the saponification of fat with alkali NaOH, $Ca(OH)_2$ etc., followed by adding hot lubricating oil while under agitation. The main functions of soap are

i. it act as a gelling agent ii. as a thickening agent (so that grease sticks firmly to the

metal surfaces).

The nature of the soap decides

i. the temperature upto which the grease can be used ii.

the consistency iii. resistance to water iv. resistance to

oxidation.

## 9.1 Classification

### 9.1.1. Calcium based greases

They are formed from calcium soap and petroleum oil. First, calcium soap is prepared by adding required amount of $Ca(OH)_2$ to hot tallow oil. Then hot petroleum oil is added and mixed. The calcium base greases are the cheapest and most commonly used grease. They are known as cup grease. Calcium soap grease are water resistant.

They are good for use at low temperature because above 80qC oil and soap begins to separate out.

### 9.1.2. Soda based greases

They are prepared by thickening petroleum oil with sodium soap. They are not water resistant because sodium soap is soluble in water. They can be used upto 175qC.

### 9.1.3. Lithium based greases

They are petroleum oils thickened by lithium soap. They are water resistant and are suitable for use at low temperature only (150qC).

### 9.1.4. Axle greases

They are prepared by adding lime to resin and fatty oils. The mixture is mixed thoroughly and allowed to stand when grease floats on the top.

They are very cheap and water resistant and suitable for less delicate equipments working under high load at low speeds. Besides this, there are greases prepared by mixing graphite, soap stone etc, in mineral oil. They are used in rail axle boxes, tractor rollers, wire ropes etc.

## 44. 10. PROPERTIES OF LUBRICANTS

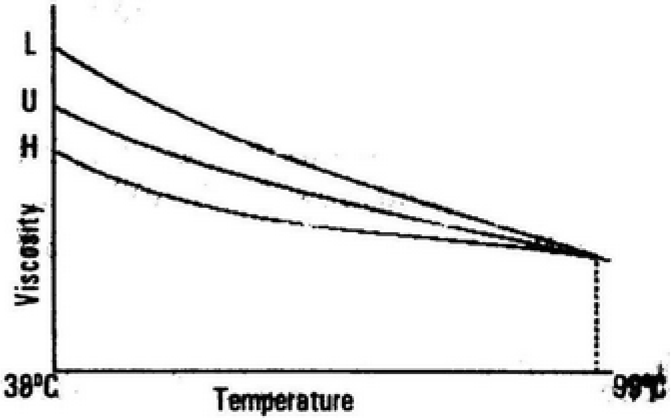
### 10.1. Viscosity and viscosity index

Viscosity of an oil is the internal resistance of a fluid during flow. The unit of viscosity is poise or Newton/sec/$m_2$. Viscosity is the important property of lubricating oil because it determines the operating characteristics of lubricant.

Viscosity of liquids decreases with increases of temperature. This makes the lubricating oil thinner and is unsuitable. Hence a good lubricant should have minimum change in viscosity with rise of temperature.

The rate at which the viscosity of an oil changes with temperature is measured by viscosity index scale. The variation of viscosity with temperature (38 to 99qC) is indicated by viscosity temperature curves (Fig. 3). The viscosity index (V.I) of the lubricating oil is given by the formula.

$$V.I = \frac{L - U}{L - H} u100$$



**45. Fig. 3. Viscosity index**

Where L is the viscosity of low viscosity index oil as 38qC. H is the viscosity of the high viscosity index oil at 38qC and U is the viscosity of the test oil at 38q.

Naphthenic base Gulf oil, the viscosity index is assigned as zero and for paraffinic base Pennsylvanian oils, the viscosity index is 100.

The viscosity of an oil can be measured using Rewood or Saybolt viscometer.

### 10.2. Flash and fire points

Flash point is the lowest temperature at which the lubricating oil gives off enough varpours that ignite for a moment when a small flame is brought near it.

Fire point is the lowest temperature at which the vapours of the oil burn continuously for atleast 5 seconds when a small flame is brought near it.

A good lubricating oil should have flash and fire points well above the operating temperature. Generally the fire point is 5 to 40qC higher than the flash point.

Flash and fire points can be determined by Pensky Martens apparatus.

### 10.3. Cloud and pour point

Could point is the temperature at which a slowly cooled lubricating oil becomes cloudy or hazy in appearance.

The temperature at which a slowly cooled lubricating oil ceases to flow or pour is called pour point.

Normally the pour point is lower than the cloud point. Lubricants used in machine working at low temperature should possess low pour point, otherwise solidification of lubricant will cause jamming of the machine.

### 10.4. Aniline point

Aniline point of an oil is the temperature at which equal volumes of oil and aniline are just miscible.

Aniline point gives an indication of the possible deterioration of an oil in contact with rubber bearings, packing, etc.

A higher aniline point means lower percentage of aromatic hydrocarbons and less solvent effect on rubber sealings, packings, etc., A good lubricating oil posses higher aniline point.

### 10.5. Oiliness

Oiliness is the capacity of a lubricant to stick either physically or chemically or both onto the surface of the machines under conditions of heavy pressure or load.

A good lubricant should have high oiliness. Mineral oils have poor oiliness. Vegetable and animal oils have high oiliness. So small amount of vegetable or animal oils are added to increase the oiliness of mineral oils.

### 10.6. Precipitation number

It is the percentage of asphalt present in the oil. A known weight of lubricant is dissolved in petroleum ether, asphalt gets precipitated. It is filtered, washed, dried and weighed. It is then expressed as percentage of weight of oil taken.

Precipitation number is used for classifying the lubricants.

### 10.7. Neutralisation number

This is a measure of acidic or basic constituent of oil. It is defined as the number of milligrams of alkali required to neutralize the free acid in 1 gm of an oil.

### 10.8. Saponification number

This test is used to ascertain whether the oil under test is animal oil, vegetable oil or mineral oil or compounded oil.

It is the number of milligrams of KOH or NaOH required to saponify one gram of oil.

## 46. 11. SELECTION OF LUBRICANTS

Different types of lubricants are selected for different jobs. The property of a selected lubricant should not change under service conditions. So the selection of lubricant is essential. Some example of lubricant selections for typical jobs are illustrated as follows.

### 11.1. Lubricant for cutting tools

The main function of the cutting fluid is

i. to cool the tool, so as to reduce wear and prevent metal losses. ii. to

cool the metal work piece, so as to prevent the deformation iii. to reduce

power consumption. iv. to improve surface finish.

For heavy cutting mineral oil with high fatty acids are used.

For light cutting oil emulsion is the good lubricant. It is an effective media.

## 11.2. Lubricants for internal combustion engine

In the internal combustion engine the lubricant is exposed to high temperature. So it posses high viscosity index and high thermal stability *i.e.,* it should neither evaporate or decompose at high temperature. The suitable lubricant for this purposes is mineral oil with hexonal and other suitable additives.

## 11.3. Lubricants for gears

For this purposes, the lubricant should

i. possess good oiliness ii. possess

high oxidation resistant iii. possess

high load changing capacity

Example: mineral oil with extreme pressure additive like organic chloride, phosphate or sulphate are employed.

## 11.4. Lubricants for delicate instruments

Delicate instruments like watches, clocks, scientific equipments, sewing machines etc. are lubricated by the vegetable and animal oil.

## 11.5. Lubricants for high pressure and low speed machines

The high pressure and low speed machine, like tractor, rollers, concrete mixtures, lathes, railway track etc, are lubricated by solid lubricant.

## 11.6. Lubricants for transformers

The function of the transformer oil is to insulate the windings and to carry away the heat generated, when the transformer is on load. So the oil used in transformer should posses, high insulating quality, optimum oxidation resistance and chemical stability.

## 11.7. Lubricants for refrigeration system

Oils with low cloud and pour point, low viscosity are employed in refrigeration systems. Eg. Naphthalene based mineral oils are used.

Richard Feynman in 1959, remarked. ‘The Principles of physics as far as I can see do not speak against the possibility of maneuvering things atom by atom’.

In 1990, Drexler in his famous book ‘Engines of creation, the coming age of nanotechnology’ noted that nano science and nanotechnology would enable the mankind to build molecular systems with atom by atom precision yielding a variety of nano machines.

**Unit V** **ENGINEERING MATERIALS II**

Refractories – classification (acidic, basic and neutral refractories) – properties (refractoriness, refractoriness under load, dimentional stability, porosity, thermal spalling) – fire clay bricks, alumina bricks and zirconia bricks.

---

## REFRACTORIES

## 1. INTRODUCTION

Refractories are material that can withstand high temperatures without softening or deformation in shape. Refractories are mainly used for construction of lining in furnaces converters, kilns, crucibles etc. and employed in metallurgical and industrial purposes. The refractories main function is to withstand and maintain high temperatures and to resist the abrasive and corrosive action of molten metals, slags, gases etc.

## 2. CLASSIFICATION

Refractories are mainly classified into three kinds on the basis of their chemical properties.

i. Acid refractories are refractories made of acidic materials like alumina ($Al_2O_3$) silica ($SiO_2$) etc. They are not attacked by acidic materials but can be easily affected by basic materials.

ii. Basic refractories are refractories made of basic materials like lime (CaO), magnesia (MgO) etc. They are not attacked by basic materials but can be easily affected by acidic materials.

iii. Neural refractories are refractories of neutral materials like carbon, chromite (FeO. $CrO_2$), ziconia (ZrO) etc.

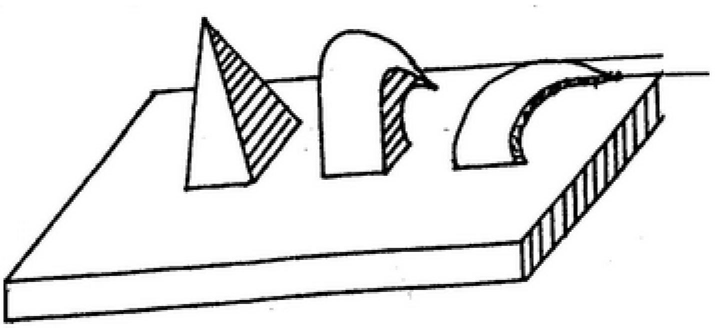
## 3. PROPERTIES OF REFRACTORIES

The important properties of refractories are given below.

### a. Refractoriness

Refractoriness is the ability of the refractory to withstand high temperatures without appreciable deformation or softening under particular service conditions. Refractoriness is generally measured by the softening temperature of the refractories material. The softening temperatures are measured by using pyrometric cones of refractory materials.

**Measurement of refractoriness :**The refractoriness of refractories are measured in terms of pyrometric cone equivalents (PCE). Pyrometric cones of same dimension (38 mm hight and 19 mm sides) which are made of different mixtures of refractory materials that can soften at different temperatures are placed along the sample cone. The standard cones have particular number with



softened and deformedapex just touching thebase known softening point.

**Fig. 3.1. Pyrometric cone test**

Sample cone along with standard cones are heated under standard conditions of 10°C per minute. The pyrometric cone equivalent (PCE) value of the sample cone or test cone is taken as the number of the standard cone which softens along with the sample cone whose softening point is known. If the sample cones soften earlier than one standard cone but later than the next one, then the PCE value of the sample cone is taken as the average softening point values of the two standard cones. A good refractory should have high refractoriness.

### b. Refractoriness under load

Refractoriness used in metallurgical operations and industries have to withstand varying loads. Hence refractories should have high mechanical strength under operating temperatures. The load bearing capacity of a refractory can be measured by means of R.U.L test.

In R.U.L (Refactoriness under Load) test a constant load (1.75 kg/cm$^2$ or 3.5 kg/cm$^2$) is applied to the sample refractory specimen of rectangular shape (base 5 cm$^2$ and height 75 cm) and heated at standard rate (approx 10°C/minute) in a furnace. The temperature at which atleast 10% of the specimen started get destroyed or deformed is taken as the R.U.L value. A good refractory should have high R.U.L. value

### c. Thermal conductivity

Most of the furnaces are lined inside with refractory materials of low thermal conductivity in order to reduce heat loses to the outside by radiation. Some furnaces like muffle furnace, coke oven batteries etc. require a good conductivity of heat. Hence such furnaces should be lined inside with refractories of good heat conductivity. The least porous refractories will have high thermal conductivity due to the absence of air-voids.

### d. Thermal expansion

The construction of the furnace should be designed in such a manner that allowance has to be made for thermal expansion. A good refractory will generally have less thermal expansion. Repeated expansion and contraction of refractory materials will lead to the breakdown of refractory materials.

### e. Chemical inertness

Refractories should be chemically inert and especially they should not react with the slags, furnace gases etc. It is always advisable to use acid refractory linings for acid materials or products formed inside the furnaces. Similarly basic refractory linings are used for furnaces using basic raw materials or products formed.

### f. Dimensional stability

The dimensional stability of a good refractory should be high. Dimensional stability may be defined as the volume change of the refractory when subjected to high temperature. The shrinkage of a refractory can also be due to the transformation from one form to another form. Magnesite (MgO) brick with specific gravity 3.05 is gradually converted to a mere dense form a Periclase with specific gravity 3.54. Due to the increase in density of the material there will be shrinkage of the material.

### g. Porosity

Porosity is the ratio of its porous volume to the bulk volume. Porosity of a refractory has many bad effects along with few advantages also. Due to porosity slags, gases etc. are likely to enter more easily to greater depth and also react with the refractory. Hence porosity reduces the strength, resistance to abrasion, resistance to corrosion etc. But lower porosity increases thermal conductivity owing to the absence of air voids and increases resistance to thermal spalling.

### h. Thermal spalling

It is the property of breaking, cracking or peeling off of a refractory material. So a good refractory should be resistant to thermal spalling. Thermal spalling can be reduced by the following factors (i) low porosity and low co-efficient of expansion (ii) avoiding sudden changes in temperatures (iii) during the construction and finishing of internal lining of refractories, over firing should be avoided.

## 4. COMMON REFRACTORY BRICKS

### 1. Fire clay bricks

These bricks are prepared from finely ground fire clay ($Al_2O_3$ $2SiO_2$ $2H_2O$) with powdered calcined fireclay. The composition of these fire clay bricks are as follows:

$SiO_2$ = 55% $Al_2O_3$ = 35% the remaining composition are $K_2O$, FeO, CaO, MgO etc.

These bricks are slightly acidic in nature. The extend of acidity depends upon the $SiO_2$ content. The bricks are fired at about 1300°C under a load of 2 $kg/cm^2$. The bricks are yellow to reddish brown in colour. They have better resistance to spalling and hence suitable for checker works of regenerative furnaces. The fire clay bricks are cheaper than silica bricks.

The fire clay bricks are largely used as refractory bricks. They are used in blast furnaces, open hearth furnaces, ovens, kilns, generators, charging doors etc.

### 2. Silica bricks

Silica bricks are made of the basic material quartz, quartzite, ganister, sand, sand stone etc., which are present in crushed silicious rock. The powdered silicious rock is mixed with 2% lime and water and made into paste which are converted into bricks. The bricks are dried and gradually heated upto 1500°C nearly for 12 hours in kilns. During the process quartzite is converted into another form known as cristobalite. After burning in the kilns the bricks are taken out of the kiln and gradually cooled for 10 to 14 days time. On cooling cristabalite gradually changes to tridymite and the mixture of the two contribute to the final brick.

Silica bricks are acidic in nature and contains about 25% pores. The bricks can expand upto 15% on heating and cooling contract to its original size. This is due to the following reversible allotropic transformations.

$$\textbf{Quartzite} \xrightleftharpoons{\mathbf{90^{o}C}} \textbf{Tridymite} \xrightleftharpoons{\mathbf{120^{o}C}} \textbf{Cristobalite}$$

The bricks can withstand a load of about 3.5 kg/cm$^{-2}$ at 1500°C-1600°C. Silica bricks possess high mechanical strength.

The silica bricks are used in lining open hearth furnaces, coke oven walls, lining of acid converters, by product coke-ovens, electric furnaces etc.

### 3. High Alumina Refractories

Alumina refractory which consists of aluminum oxide and traces of other materials is the most mature of the engineering ceramics. Alumina is one of the most chemically stable oxides known, which offers excellent hardness, strength and spalling resistance. It is insoluble in water and super heated steam, and in most inorganic acids and alkalis. Alumina refractories carry the all purpose characteristics of fire-clay brick into higher temperature ranges that makes it suitable for lining furnace operating up to 3350°F. It has a high resistance in oxidizing and reducing atmosphere and is extensively used in heat processing industries.

The refractoriness of high alumina refractories increases with increase of alumina percentage. The 50%, 60%, 70% and 80% alumina classes contain their respective alumina contents with an allowable range of plus or minus 2.5%. High-alumina brick are classified by their alumina content according to the following ASTM convention. These are:

a) ***Mullite refractory***: Mullite brick is about 72% alumina with 28% silica. These have excellent volume stability and strength at high temperatures. They are highly suitable for electric furnace roofs, blast furnaces and blast furnaces stoves, and the superstructure of glass tank furnaces.

b) ***Corundum refractories-*** The 99% alumina class of refractories is called corundum. These refractories comprise single phase, polycrystalline, and alpha-alumina.

High alumina bricks are most commonly used in cement, lime and ceramic kilns, glass tanks, crucibles for melting a wide range of metals, hearth & shaft of blast furnaces and in lead drossing furnaces. Studies indicate that these are very economical for the lower sections of soaking pits in the steel industry, primarily because of their resistance to iron oxide slags.

Manufacturing cost and, therefore, price of these brick increase more rapidly with % alumina content, so it is essential to determine experimentally or by test installations the most economical alumina content for each service.

## 4. Zirconia Refractories

Zirconium dioxide ($ZrO_2$) is a polymorphic material. There are certain difficulties in its usage and fabrication as a refractory material. It is essential to stabilize it before application as a refractory. This is achieved by incorporating small quantities of calcium, magnesium and cerium oxide, etc. Its properties depend mainly on degree of stabilization and quantity of stabilizer as well as the quality of original raw material. Zirconia refractories have a very high strength at room temperature which is maintained up to temperatures as high as 2700°F. They are, therefore, useful as high temperature construction materials for furnaces and kilns. The thermal conductivity of zirconium dioxide is found to be much lower than that of most other refractories and the material is therefore used as a high temperature insulating refractory. Since Zirconia exhibits very low thermal losses and does not react readily with liquid metals, it is particularly useful for making refractory crucibles and other vessels for metallurgical purposes. Zirconia is useful refractory material for glass furnaces primarily since it is not easily wetted by molten glass and because of its low reaction with them.