BCH101
ENGINEERING CHEMISTRY- I

UNIT – I   WATER TECHNOLOGY

INTRODUCTION

Water is the nature's most wonderful, abundant and useful compound. Of the many essential elements for the existence of human beings, animals and plants, water is rated to be of greatest importance. Without food human being can survive for a number of days, but water is such an essential thing without it one cannot survive. Water is not only essential for the lives of animals and plants but also occupies unique position in industries. Probably its most important use as an engineering material is in the 'steam generation'. Water is also used as a coolant, in power, and chemical plants. In addition to it, water can also be used in the production of steel, rayon, paper, textiles, chemicals, irrigation, drinking fire fighting, etc.

OCCURRENCE:

Water is the only substance that occurs at ordinary temperatures in all three states of matter: Solid, Liquid and Gas. As a so33.3.33lid, ice, it forms glaciers, frozen lakes and rivers, snow, hail and frost. It is liquid as rain and dew, and it covers three- quarters of the earth's surface in swamps, lakes, rivers and oceans. Water also occurs in the soil and beneath the earth's surface asa vast groundwater reservoir. As gas, or water vapour, it occurs as fog, steam and clouds.

WATER PURIFICATION:

Impurities are removed from water by seeming, sedimentation, filtration, chlorination or irradiation. Aeration removes odours and tastes caused by decomposing organic matter, industrial wastes and some gases. Various salts and metals cause hardness in water. Hardness may be removed by boiling, by adding sodium carbonate and lime or by filtering through natural or artificial zeolites. Water is also purified by processes such as desalination, reverse osmosis, electrolysis etc.,

CHARACTERISTICS OF WATER

As per the suggestion given by World Health Organisation (WHO) and by Indian Council of Medical Research (ICMR), the following are the important characteristics of potable water.

1. It should be clear, colourless and odourless.

2. It should be cool and pleasant to taste.

3. It should be free from harmful bacteria and suspended impurities.

4. It should be free from dissolved gases like CO_2, H_2S, NH_3, etc., and poisonous minerals like lead, arsenic, manganese, etc.,

5. Hardness should be less than 500 ppm.

6. Chloride ion content should be less than 250 ppm.

7. Fluoride ion content should be less than 1.5 ppm.

8. Total Dissolved Solids (TDS) content should be less than 500 ppm.

9. pH of the potable water should be 6.5 – 8.5.

Acidic	Neutral	Alkaline
pH=0-7	7	pH=7-14

CHEMICAL CHARACTERISTICS OF WATER

The most important chemical characteristics of water are its acidity, alkalinity, hardness and corrosiveness. Chemical impurities can be either natural, man made (Industrial) or be deployed in raw water sources by enemy forces.

Some chemical impurities cause water to behave as either an acid or a base. Since either condition has an important bearing on the water treatment process, the pH value must be determined. Generally the pH influences the corrosiveness of the water, chemical dosages necessary for proper disinfection and the ability to detect contaminants.
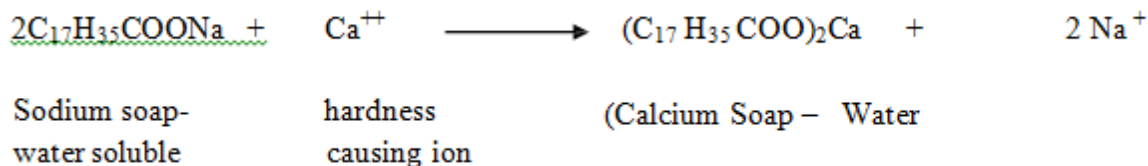
HARDNESS

Hardness is caused by the soluble salts of calcium, magnesium, iron, manganese, sodium, sulphates, chlorides and nitrates. The degree of hardness depends on the type and amount of impurities present in the water. Hardness also depends on the amount of carbon-di-oxide in solution. Carbon-di-oxide influences the solubility of the impurities that cause hardness.

The hardness caused by carbonates and bicarbonates is called carbonate hardness. The hardness caused by all others (chlorides, sulphates, nitrates) is called non-carbonated hardness.

HARD WATER

Water which does not produce lather with soap solution, but produces whiteprecipitate (scum) is called hard water.In other words, water that contains mineral salts (an calcium and magnesium ions)that limit the formation of lather with soap.

This is due to the presence of dissolved Ca and Mg salts.

$$2C_{17}H_{35}COONa \; + \quad Ca^{++} \quad \longrightarrow \quad (C_{17}H_{35}COO)_2Ca \quad + \quad 2\,Na^+$$

Sodium soap-   hardness   (Calcium Soap $-$ Water

water soluble   causing ion

SOFT WATER

Water, which produces lather, readily with soap solution is called soft water. This is due to the absence of Ca and Mg salts.Water that is not hard (ie., does not contain mineral salts that interfere with the formation of lather with soap).

HARDNESS OF WATER

How to detect hardness?

Hardness of water can be detected in two ways.

· When the water is treated with soap solution, if it prevents lathering and forms white scum, the water contains hardness.

· Water containing hardness, gives wine red colour with Eriochrome Black –T indicator.

The total water hardness (including both Ca^{2+} and Mg^{2+} ions) is read as parts per million (ppm) or weight / volume (mg/L) of Calcium Carbonate ($CaCO_3$) in the water. Although water

hardness usually measures only the total concentrations of calcium and magnesium (the two most prevalent, divalent metal ions), iron, aluminum and manganese may also be present at elevated levels in some geographical locations. The predominant source of magnesium is dolomite $(CaMg (CO_3)_2)$.

TYPES OF HARDNESS

Depending upon the types of dissolved salts present in water, hardness of water can be classified into two types:

· Temporary Hardness

· Permanent Hardness

Temporary Hardness (or) Carbonate Hardness (CH) (or) Alkaline Hardness

Temporary hardness is caused by a combination of calcium and magnesium bicarbonate ions in the water. It can be removed by

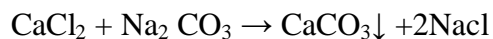· boiling water

· by the addition of lime $(Ca(OH)_2)$

Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon coving.
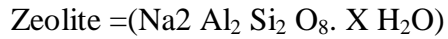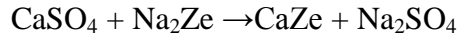
$$Ca (HCO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O + CO_2$$
$$Mg (HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg (OH)_2 \downarrow + 2CaCO_3 \downarrow + 2H_2O$$

Permanent Hardness (or) Non – Carbonate Hardness (NCH) (or) Non – alkaline Hardness

Permanent hardness is hardness (mineral content) that cannot be removed by boiling. It is usually caused by the presence of calcium and magnesium sulphates and /or chlorides which become more soluble as the temperature rises. Despite the name, permanent hardness can be removed using water – softener or ion-exchange column, where the calcium and magnesium ions are exchanged with the sodium ions in the column. It can be removed by

· Lime – Soda process

· Zeolite process

$$CaCl_2 + Na_2 CO_3 \rightarrow CaCO_3 \downarrow + 2Nacl$$

(Soda)

$CaSO_4 + Na_2Ze \rightarrow CaZe + Na_2SO_4$

Zeolite $= (Na_2\ Al_2\ Si_2\ O_8.\ X\ H_2O)$

Hard water causes scaling, which is the left- over mineral deposits that are formed after the hard water had evaporated. This is also known as lime scale.

Total Hardness

The sum of temporary hardness and permanent hardness.

Table 1 :1 Molecular weights of some hardness producing salts.

Hardness producing salt	Molecular weight	Hardness producing salt	Molecular weight
$Ca(HCO_3)_2$	162	$MgSO_4$	120
$Mg(HCO_3)_2$	146	$MgCO_3$	84
$Mg(NO_3)_2$	148	$MgCl_2$	95
$Ca(NO_3)_2$	164	$CaCl_2$	111
$CaCO_3$	100	Ca^{2+}	40
$CaSO_4$	136	Mg^{2+}	24

Expression of hardness in terms of equivalents of CaCO3

The concentration of hardness producing salts are usually expressed in terms of an equivalent amount of $CaCO_3$. $CaCO_3$ is chosen as a standard because,

i) Its molecular weight (100) and equivalent weight (50) is a whole number, so the

Calculations in water analysis can be simplified.

$$\text{Amount equivalent to CaCO}_3 \left\{ \frac{x \times 100}{\text{Molecular weight of hardness producing salt}} \right.$$

ii) It is the most insoluble salt, that can be precipitated in water treatment. If the concentration of hardness producing salt is x mgs/lit. then

$$CaCO_3 = \frac{43 \times 100}{136} \text{ mgs/lit}$$

Example

If the concentration (or) weight of $CaSO_4$ is 43mgs/lit, then weight equivalent to

UNITS OF HARDNESS

1. Parts per million (ppm)

It is defined as the number of parts of $CaCO_3$ equivalent hardness per 106 parts of water.

2. Milligrams per litre (mg/lit)

It is defined as the number of milligrams of $CaCO_3$ equivalent hardness per 1 litre of water.

3. Clarke's degree (oCl)

It is defined as the number of parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

4. French degree (oFr)

It is defined as the number of parts of $CaCO_3$ equivalent hardness per 105 parts of water.

Relationship between various units

1ppm = 1 mg/lit = 0.10 Fr = 0.070 Cl

ESTIMATION OF TOTAL HARDNESS OF WATER BY EDTA METHOD

The hardness of water is estimated by EDTA method using Eriochrome Black –T [EBT].

Principle:

The calcium ion in the water is capable of forming complex with Indicator EBT and also with the EDTA in the pH range 8- 10.To keep the solution at this pH range , a buffer [mixture of ammonium chloride and ammonium hydroxide] is used . The complex between EDTA and indicator is more stable that of between the metal ion and indicator

$$M + In \longrightarrow [M-In] \quad \text{---}(1)$$

$$M + EDTA \longrightarrow [M-EDTA] \text{----}(2)$$
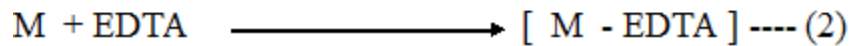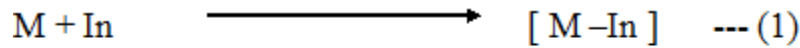
$$(2) \text{ is more stable than } (1)$$

Experiment :

1.Preparation of Standard hard water :

Hard water is prepared in such a way that 100 ml of containing 100 mg of Calcium carbonate;

So , 1 ml of Std. hard water = 1mg

2.Standadisation of EDTA :

EDTA is taken in the burette; 20 ml of Std. hard water is pipette out in beaker; 5ml of buffer solution and 2 a few drops of indicator are added ; now the solution becomes wine –red colour because the colour of the complex between calcium and indicator [M- In] is wine –red. Then it is titrated against EDTA; at the end point the colour changes to Pale blue, which is colour of the free indicator. Since the complex between metal ion -EDTA is more stable that of between the metal ion and indicator , the Metal moves from [M-In] towards EDTA and forms complex with that , which is colourless; now the indicator is freed and the solutions attains steel blue colour , which is the colour of the free indicator. Let the titre value be V_1.

$$1 \text{ml of Std. hard water} = 1\text{mg of CaCO}_3$$
$$20 \text{ ml of Std. hard water} = 20 \text{ mg of CaCO}_3$$
$$V_1 \text{ ml of EDTA} = 20 \text{ of Std. hard water}$$
$$= 20 \text{ mg of CaCO}_3$$
$$1 \text{ ml of EDTA} = 20 / V_1 \text{ X } 20 \text{ mg of CaCO}_3$$
$$= \frac{1}{V_1} \text{ mg of CaCO}_3$$

3. Determination of Total hardness of water :

20 ml of the given sample of water is taken and titration is conducted as before; let the titre value be V_2 ;
$$20\text{ml of Sample of water} = V_2 \text{ ml of EDTA}$$

$$= V_2 \times \frac{1 \text{ mg of CaCO}_3}{V_1}$$

$$= \frac{V_2}{V1} \text{ mg of CaCO}_3$$

1000 ml of sample $= V_2 / V_1 \times 1000$ mg of CaCO3

The weight in milligrams of calcium carbonate in 1000 ml of the sample of water

$= V_2 / V_1 \times 1000$ mg of CaCO3

Total hardness of the given water $= V_2 / V_1 \times 1000$ *ppm*

PREPARATION OF SOLUTIONS;

1. **Standard hard water:** 1 gm of dry CaCO3 is dissolved in minimum quantity of HCl and evaporate the solution to dryness on a water bath, and then diluted to 1 lit with water. Each ml of this solution then contains 1 mg of CaCO3 hardness.

2. **EDTA solution:** 4 gm of EDTA crystals + 0.1 gm MgCl2 in 1lit

3. **Indicator:** 0.5 gm of EBT in100 ml of alcohol.

4. **Buffer solution:** 67.5 gm NH4Cl + 570 ml of Con. Ammonia solution diluted with distilled water to 1 lit.

5. **Titration of permanent hardness of water:** Take 250 ml of the water sample in a large beaker .Boil till the volume is reduced to 50 ml. Filter, wash the precipitate with distilled water collecting filtrate and . Finally make the volume to 250 ml with distilled water. Then titrate 50 ml of the boiled water sample just as in step (5).

Let volume used by V3 ml Calculations: 50 ml of standard hard water = V1 ml of EDTA :.

50 x1 mg of CaCO3 = V1 ml of EDTA :.

1 ml of EDTA = 50/V1 mg of CaCO3 eq.

Now 50 ml. of given hard water = V2 ml EDTA = V2 x 50/V1 mg of CaCO3

eq. :. 1 L (1,000 mL) of given hard water = 1000 V2/V1 mg of CaCO3 eq. :.

Total hardness of water = 1000 V2/V1 mg/L = 1000 V2/V1 ppm Now 50 ml of boiled water = V3 ml of EDTA . . . V3 x 50 /V1 mg of CaCO3 eq

. . . V3 x 50/ V1 mg of CaCO3 eq 1000 ml (= 1 L) of boiled water = 1000 V3 /V1 mg of CaCO3 eq 1000 V3

Permenent hardness = /V1 ppm = . . .

And Temporary hardness = Total hardness – Permanent hardness= ppm =

3.1 Advantages of EDTA method:

This method is definitely preferable to the other methods, because of the

(i) Larger accuracy; (ii) Convenience; (iii) Rapid procedure

ALKALINITY

Alkalinity is classified as

Depending up on the anions that are responsible for the alkalinity of water, there are three types of alkalinity:

1. Hydroxide alkalinity – due to hydroxide ions

2. Carbonate alkalinity - due to carbonate ions

3. Bicarbonate alkalinity - due to bicarbonate ions

The alkalinity due hydroxide and carbonate can be detected by Phenolphthalein indicator and so they are collectively called as Phenolphthalein Alkalinity , represented by P.

The alkalinity due hydroxide, carbonate and bicarbonate can be detected by Methyl orange indicator and so it is called as in Methyl orange Alkalinity, represented by M.

1.Determination of Phenolphthalein Alkalinity ,P :

100 ml of given water sample is taken in the conical flask , a few drops of Phenolphthalein indicated are added and titrated against N/50 H2SO4 ; let the titre value when the solution becomes colourless, be V_1.

2.Determination of Methylorange Alkalinity ,M :

The in the same solution a few drops of Methylorange indicator are added and titrated against the same acid until the colour changes from yellow to red ; let the titre value be X .

So, M = V_1 + X = V_2

(a)Calculation of P:

Volume of the acid $= V_1$ cc

Normality of the acid , $N_1 = 1/50$

Volume of water , V_2 $= 100$ cc

Normality of water N_2 $= V_1 \times 1/50 \times 1/100$

P in terms of $CaCO_3 = N_2$ x equivalent of $CaCO_3 \times 1000$ mg of $CaCO_3$

$= V_1 \times 1/50 \times 1/100 \times 50 \times 1000$ mg of $CaCO_3$

$= 10 V_1$

P = 10 V_1 ppm

(a)Calculation of M:

Volume of the acid $= V_2$ cc

Normality of the acid, $N_2 = 1/50$

Volume of water, V_1 $= 100$ cc

Normality of water N_1 $= V_2 \times 1/50 \times 1/100$

M in terms of $CaCO_3 = N1$ x equivalent of $CaCO_3 \times 1000$ mg of $CaCO_3$

$= V_2 \times 1/50 \times 1/100 \times 50 \times 1000$ mg of $CaCO_3$

$= 10 V_2$

M = 10 V_2 ppm

ALKALINITY	HYDROXIDE	CARBONATE	BICARBONATE
P= 0	0	0	M
P = 1/2 M	0	2P	0
P = M	M or P	0	0
P < 1/2 M	0	2P	M - 2P
P > 1/2 M	2P - M	2(M - P)	0

1. When OH⁻ only present ;   [$HCO_3^- = 0$ & $CO_3^{2-} = 0$]

      P = M

OH	P	M
1/2CO₃		
H CO₃		
H CO₃		

2. when CO_3^{2-} only present ; [$HCO_3^- = 0$ & $OH^- = 0$] ;

      2P = M or   P = M/2

OH		
1/2CO₃	P	
HCO₃⁻	P	M
HCO₃⁻		

3. when HCO_3^- only present [$CO_3^{2-} = 0$ & $OH^- = 0$]

      HCO_3^- =M ;   P = 0

OH	
1/2CO3	
HCO₃⁻	
HCO₃⁻	M

4. When OH & CO_3 are present ; [$HCO_3 = 0$]

	X		
OH	P – (M-P)		
1/2CO3	M - P	P	M
HCO3	M - P		
HCO3			

$X + M – P = P ;\quad X + M = 2P ;$ or $2P > M$; or $P > M/2$

$X = OH = P – (M - P) = (2P – M)$

$CO_3 = (M – P) + (M – P) = (2M – 2P) = \underline{\mathbf{2(M – P)}}$

5. When CO_3 & HCO_3 are present ; [$OH = 0$]

$\qquad CO_3 = 2P ;\quad HCO_3 = (M – 2P)$

OH		
1/2 CO_3	P	
HCO_3	P	M
HCO_3	M - 2P	

SCALE AND SLUDGE FORMATION IN BOILERS

In boilers, water evaporates continuously and the concentration of the dissolved salts increases progressively. When their concentrations reaches saturation point, they are thrown out of water in the form of precipitates which stick to the inner walls of the boiler. If the precipitation takes place in theform of loose or slimy precipitate it is called sludge.

On the other hand, if the precipitated matter forms a hard adhering crust/ coating on the inner walls of the boiler, it is a scale. Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludge can be easily scrapped off with a wire brush. It is formed at comparatively colder portions of the boiler and collects in areas of the system, where the flow rate is slow at bends. Sludges are formed by substances which have greater solubilities in hot water than in cold water. Examples are MgCO3, MgCl2, CaCl2, MgSO4 etc.

Differences between scale and Sludge.

S.No.	Scale	Sludge
1.	Scale is hard and adherent .	Sludge is loose , slimy and non – adherent.
2.	formed by the salts like Calcium bicarbonate , Calcium sulphate , etc.	formed by the salts like magnesium Sulphate , magnesium carbonate , etc,.,
3.	*formation can be prevented by* dissolving scale using dilute acids like HCl , H_2SO_4 .	*formation can be prevented by* i. periodically removing the concentrated water by fresh water ii. taking soft water

4.1 Disadvantages of sludge formation:

1. Sludges are poor conductors of heat, so they tend to waste a portion of heat used.

2. If sludges are formed along with scales, the former get entrapped in the later and both get deposited as scales.

3. Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, gauge glass connection thereby causing even chocking of the pipes.

4.2 Prevention of sludge formation:

1. By using well softened water. 2. By a frequent blow down operation, i.e., drawing off a portion of the concentrated water Scales are hard deposits, which stick very firmly to the inner surface of the boiler. Scales are very difficult to remove even with the help of hammer and chisel. Scales are the main source of boiler troubles. Formation of scales may be due to

1. Decomposition of calcium bicarbonate

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

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

$$CaCO_3 + H_2O \rightarrow Ca(OH)_2 + CO_2$$
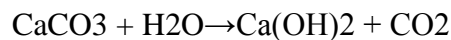
2. Decomposition of calcium sulphate:

The solubility of calcium sulphate in water decreases with increase in temperature. Thus, solubility of calcium sulphate is 3,200 ppm at 15 oC and it reduces to 55 ppm at 230 oC and 27 ppm at 320 oC. In other words, calcium sulphate is soluble in cold water, but almost completely insoluble in superheated water. Consequently calcium sulphate gets precipitated as hard scale on the heated portions of the boiler. This is the main cause in the high pressure boilers.

3. Hydrolysis of magnesium salts:

Dissolved magnesium salts undergo hydrolysis at prevailing high temperatures in the boiler forming magnesium hydroxide precipitate, which forms a soft type of scale.

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$
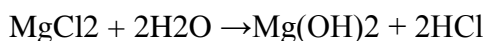
4. Presence of silica: (SiO_2), even if present in small quantities, deposits as calcium silicate ($CaSiO_3$) and/ or magnesium silicate ($MgSiO_3$). These deposits stick very firmly to the inner walls of the boiler surface and are very difficult for removal. One important source of silica in water is the sand filter used.

4.3 Disadvantages of scale formation:

1. Wastage of fuels: Scales have a low thermal conductivity, so the rate of transfer of heat from boiler to inside water is largely decreased. In order to provide a steady supply of heat to

water, excessive or over heating is done which causes unnecessary increase in fuel consumption. Thickness of the scale (mm) 0.325 0.625 1.25 2.5 12 Wastage of fuel 10% 15% 50% 80% 150%

2. Lowering of boiler safety:

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

3. Decrease in efficiency:

Scales may sometimes get deposited in the valves and condensers of the boiler and choke them partially or totally. This results in decrease the efficiency of the boiler.

4. Danger of explosion:

When thick scales crack due to uneven expansion, the water comes in contact with the overheated iron plates. This causes a release of a large amount of steam suddenly, developing a high pressure, which may cause explosion in the boiler.

4.4 Removal of scales:

1. With the help of scraper or piece of wood or wire brush, if they are loosely adhering.

2. By giving thermal shocks like heating the boiler and suddenly cooling it with cold water.

3. Dissolving scales by adding suitable chemicals, if they are adherent and hard. Thus calcium carbonate scales can be dissolved by the addition of 5% HCl. Calcium sulphate scales can be dissolved by the addition of EDTA (ethylene diamine tetra acetic acid), with which they form complexes.

4. By frequent blow down operation, if the scales are loosely adhering.

5. CAUSTIC EMBRITTELMENT

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

$$Na_2CO_3 + H_2O \rightarrow NaOH + CO_2$$
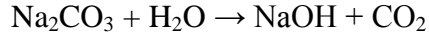
The water containing sodium hydroxide flows into the minute hair cracks always present, by capillary action in to the inner sides of the boiler. Here as water evaporates the dissolved caustic soda concentration increases progressively. This concentrated caustic soda attacks the surrounding area dissolving inner iron side of the boiler by forming sodium ferroate. This causes the embrittlement of the boiler parts, particularly stressed parts such as bends, joints, rivets etc., causing even failure of the boiler operations. Caustic cracking can be explained by the following concentration cell Iron at Bends, rivets and joints

The iron surrounded by the dilute NaOH becomes the cathodic surface and the iron present with the high concentration of NaOH becomes anodic which is consequently dissolved or corroded.

5.1 Caustic embrittlement can be avoided by

1. By using sodium phosphate as a softening agent instead of sodium carbonate.

2. By adding tannin or lignin to the boiler water, since these substances block the hair cracks, thereby preventing the infiltration of the caustic soda solution in to these.

3. By adding sodium sulphate to boiler water: Sodium sulphate blocks the hair cracks preventing the infiltration of caustic soda solution in to these. It has been observed that caustic cracking can be prevented, if sodium sulphate is added to the boiler in the ratio of Na2SO4 : NaOH as 1:1; 2:1; 3:1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

6. BOILER CORROSION

Boiler corrosion is the decay of boiler material (iron) either by chemical or electro chemical attack of its environment. Main reasons for the boiler corrosion are:
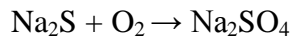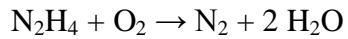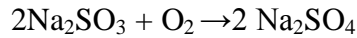
6.1 Dissolved oxygen:

Water usually contains 8 mg of dissolved oxygen per liter at room temperature. Dissolved oxygen in water in the presence of prevailing high temperature of the boiler, attacks the boiler material as

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

$$4 Fe(OH)_2 + O_2 \rightarrow 2 [Fe_2O_3.2 H_2O]$$
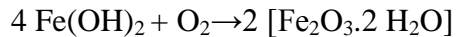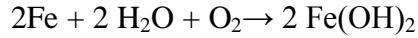
Removal of the dissolved oxygen:

a. By adding calculated amount of sodium sulphite or hydrazine or sodium sulphide.

$$2Na_2SO_3 + O_2 \rightarrow 2 Na_2SO_4$$

$$N_2H_4 + O_2 \rightarrow N_2 + 2 H_2O$$

$$Na_2S + O_2 \rightarrow Na_2SO_4$$

b. Mechanical de-aeration:

In this process water is sprayed in to a tower fitted with perforated plates (Fig), heated from sides and connected to vacuum pump. High temperature, low pressure and large exposed surface area reduce the dissolved oxygen in water.

6.2 Dissolved carbon dioxide:

Carbon dioxide dissolved in water forming carbonic acid, has a slow corrosive effect on the boiler material. Carbon dioxide is also released inside the boiler, if water, containing bicarbonates is used for steam generation
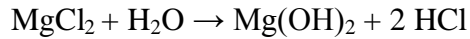
$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$Mg(HCO_3)_2 \rightarrow MgCO_3 + CO_2 + H_2O$$
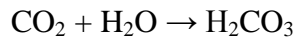
Removal of dissolved carbon dioxide: a. By adding calculated amount of ammonia

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3$$
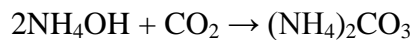
b. By mechanical de-aeration process along with oxygen (described above)

6.3 Acids from dissolved salts:

Water containing dissolved salts of magnesium liberates acids on hydrolysis.

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

The liberated acid reacts with the iron material of the boiler in chain like processes, producing HCl again and again.

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

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2\ HCl$$
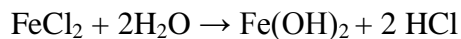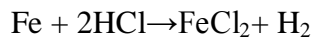
Consequently, presence of even small amount of magnesium chloride will cause corrosion to a large extent and may cause damage to the boiler material. Removal of acids: a) Softening boiler water to remove magnesium chloride, if any. b) By frequent blow down operation of removal of concentrated water with fresh soft water. c) Addition of inhibitors as sodium silicate/sodium phosphate/sodium chromate, which protect the boiler material against acid attack.

7. PRIMING AND FOAMING

When a boiler is producing steam rapidly, some particles of the condensed liquid water are

carried along with the steam. The process of wet steam formation is called priming. Priming is causedby

1. The presence of large amounts of dissolved solids

2. High steam velocities

3. Sudden boiling

4. Improper boiler design

5. Sudden increase in the steam production rate.

Foaming is the production of persistent foam or bubbles in boilers, which do not break easily.

Foaming is due to the presence of substances like oils in water, which reduce the surface tension of water. Priming and foaming usually occur together. They have to be eliminated because

a. Dissolved salts in boiler water are carried by the wet steam to super heater and turbine blade, where they get deposited as water evaporates. This deposit reduces the efficiency of the boiler.

b. Dissolved salts may enter the other parts of the machinery, where steam is being used, thereby decreasing the life of the machinery

c. Actual height of the water column cannot be judged properly making the maintenance of the boiler pressure difficult.

Priming can be avoided by fitting mechanical steam purifiers, avoiding the rapid change in steaming rate, maintaining low water levels in boilers, efficient softening and filtration of the boiler feed water. Foaming can be avoided by adding anti foaming chemicals like castor oil, or removing oil from boiler water by adding compounds like sodium aluminate.

8. SOFTENING METHODS

Water used for industrial purposes (such as for steam generation) should be sufficiently pure. it should, therefore, be freed from hardness- producing salts before it is being put to use. The process of removing hardness-producing salts from water is known as softening of water. In industry three methods are mainly employed for softening of water.

8.1 Lime soda process:

In this method, the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime $[Ca(OH)_2]$ and soda $[Na_2CO_3]$. Calcium carbonate $[CaCO_3]$ and magnesium hydroxide $[Mg(OH)_2]$ are precipitated and removed.

8.2 Ion exchange or de-ionization or de-mineralization process:

Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure, and the "functional groups' attached to the chains are responsible for the ion-

exchanging properties. Resins containing acidic functional groups (-COOH, -SO₃H etc.) are capable of exchanging their H+ ions with other cations, which come into their contact; whereas those containing basic functional groups (-NH₂=NH as hydrochloric acid) are capable of exchanging their anions with other anions, which come into their contact.

The ion-exchange resins may be classified as: (i) Cation exchange resins (RH+) are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation become capable to exchange their hydrogen ions with the cations present in the raw water
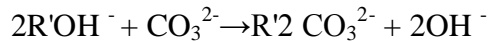
(ii) Anion exchange resins (R1OH-) are styrene-divinyl benzene amineformaldehyde copolymers, which contains amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrixs. These, after treatment with dil. NaOH solution, become capable to exchange their OHanions with anions present in the raw water.
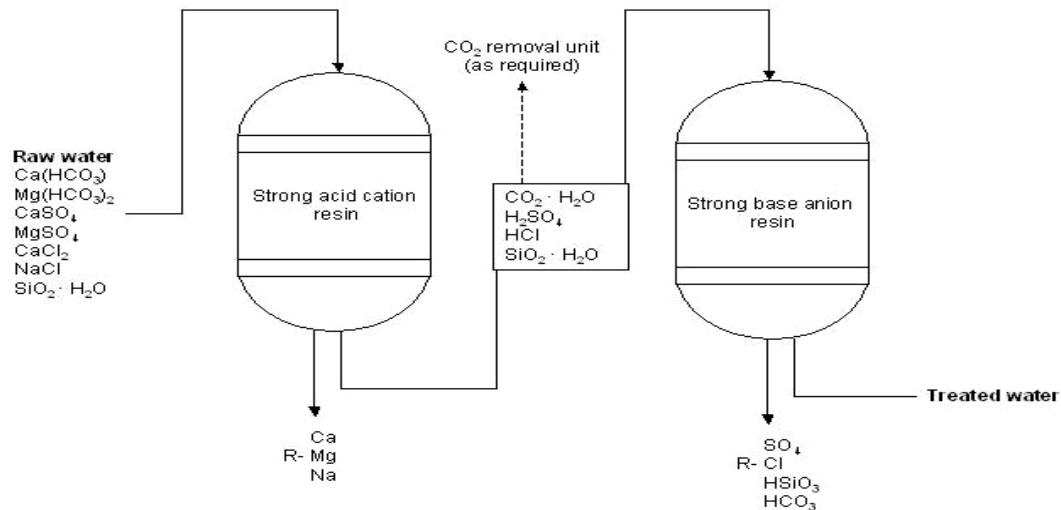
Process: The hard water is passed first through cation exchange column, which removes all the cations like Ca2+.Mg2+, etc., from it and an equivalent amount of H+ ions are released from this column to water. Thus: 2

$$2RH^+ + Ca^{2+} \rightarrow R2Ca^{2+} + 2H^+$$

$$2RH^+ + Mg^{2+} \rightarrow R2Mg^{2+} + 2H$$
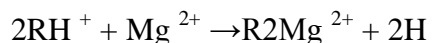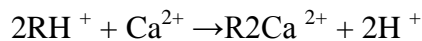
The water which is now free from cations, is passed through anion exchange column, which removes all the anions like SO4 2- , Cletc., present in the water and equivalent amount OHions are released from this column to water. Thus:

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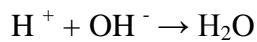
$2R'OH^- + SO_4^{2-} \rightarrow R'2\ SO_4^{2-} + 2OH^-$

$2R'OH^- + CO_3^{2-} \rightarrow R'2\ CO_3^{2-} + 2OH^-$
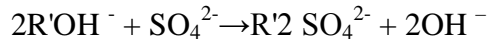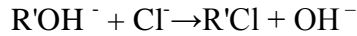
H + and OHions (released from cation exchange and anion exchange columns respectively) combine to produce water.

$H^+ + OH^- \rightarrow H_2O$

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

Regeneration: When capacities of cation and anion exchangers to exchange H+ and OHions respectively are lost, they are then said to be exhausted

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

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

The column is washed with deionized water and such washing (which containing Ca2+, Mg2+, etc. and cation SO_4^{2-}) is passed into sink or drain. The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as:

$R'_2\ SO4^{2-} + 2OH^- \rightarrow 2R'OH^- + SO_4^{2-}$ (Washing)

The column is washed with deionized water and such washing (which contains Na+ and SO_4^{2-} or Clions) is passed into sink or drain.

Advantages

(1) The process can be used to soften highly acidic or alkaline waters. (2) It produces water of very low hardness (2 ppm) .

 Disadvantages

(1) The equipment is costly and expensive chemicals are needed.

 (2) If water contains turbidity, then the output of the process is reduced.

(3) The turbidity must be below 10 ppm. If it is more, it has to be removed first by coagulation followed by filtration.

9. Potable water

 The water which is fit for human consumption is known as potable water

Municipalities have to supply potable water, i.e., water which is safe to human consumption

should satisfy the following essential requirements

1. It should be sparkling clear and odourless.

2. It should be pleasant in taste

3. It should be perfectly cool

4. Its turbidity should not exceed 10 ppm

5. It should be free from objectionable dissolved gases like hydrogen sulphide.

6. It should be free from objectionable minerals such as lead, arsenic, chromium and manganese

salts.

7. Its alkalinity should not be high. Its pH should not be above 8.0

8. It should be reasonably soft

9. Its total dissolved solids should be less than 500 ppm

10. It should be free from disease- producing micro- organisms.

Purification of domestic water for domestic use:

For removing various types of impurities in the natural water from various sources, the following treatment process is employed;

9.1 Removal of suspended impurities :

The treatment water for municipal supply involves the following steps:

1.Screening :

It is a process of removing the floating materials like , leaves , wood pieces ,etc., from water. Here water is passed through a screen having a number of holes .

2.Aeration :

The process of mixing air with water is called aeration; here the gases like CO_2, H_2S and other volatile impurities responsible for the bad taste and odour, are removed; further ferrous and manganeous salts are converted into insoluble ferric and manganic salts .

3.Sedimentation :

In this process suspended impurities are removed by keeping the water undisturbed for 2 – 6 hours in a tank. This removes only 75 % of the suspended *impurities.*

*4.Coagulation :*

In this method by adding coagulants like aluminium sulphate, the colloidal impurities like finely divided clay, silica, etc., are also removed. The aluminium sulphatehydrolysed to give gelatinous precipitate Al(OH)**3** ; The suspended impurities adhere to the precipitate and settle down at the bottom.

$$Al_2(SO_4)_3 + H_2O \longrightarrow Al(OH)_3 + H_2SO_4$$
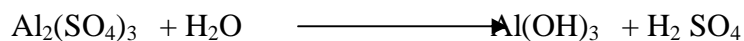
5.Filtration :

The bacterias, colour, taste ,odour and suspended impurities are removed by passing the water through the layers of fine sand , coarse sand and fine gravel and coarse gravel successively placed in a filter tank.


Sand Filter
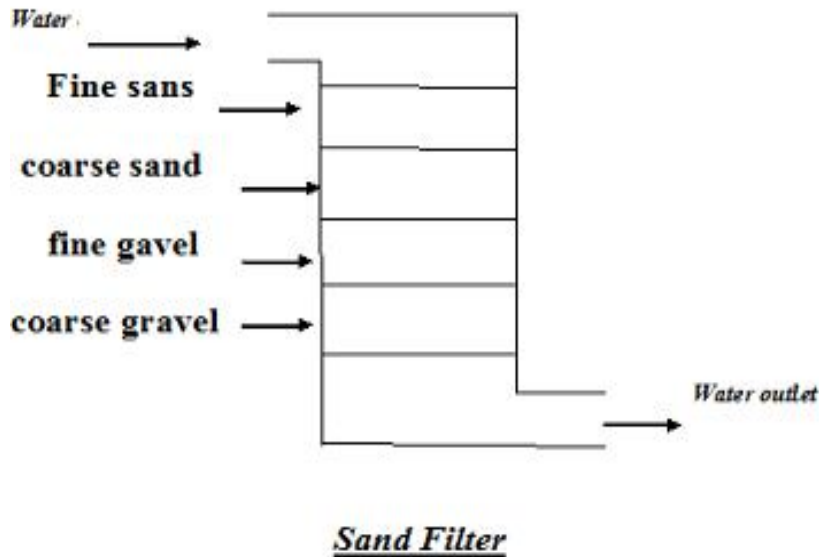
After a long time the rate of filtration is ceased as the holes in the filter are blocked by the impurities; so filtration is stopped and the top concentrated sand layer is scrapped off and replaced by fresh sand .

9.2 Removal of micro-organisms:

The process of destroying /killing the disease producing bacteria, micro-organisms, etc., from the water and making it safe for the use, is called disinfection.

a. Boiling: By boiling water for 10-15 minutes, all the disease producing bacteria is killed and the water becomes safe for use.

b. Adding bleaching powder: In small water works, about 1 kg of bleaching powered per 1000 kiloliter of water is mixed and allowed to standing undisturbed for several hours. The chemical action produces hypochlorous acid (a powerful germicide)

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

Cl2+ H2O → HCl+ HOCl
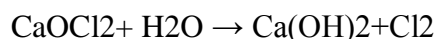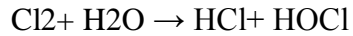
Germs+ HOCl → Germs are killed

c. Chlorination: Chlorination (either gas or in concentrated solution from) produces hypochlorous acid, which is a powerful germicide.

Cl2+ H2O → HCl+ HOCl

Bacteria+ HOCl → Bacteria are destroyed

9.3. Break point chlorination (or) or free residual chlorination :
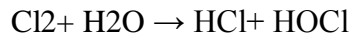
It involves addition of sufficient amount of chlorine to oxidize: (a) organic matter (b)reducing substance and (c) free ammonia in raw water; leaving behind mainly free chlorine, which possesses disinfecting action against disease- producing bacteria The addition of chlorine at the dip or break is called "break point" chlorination. This indicates the point at which free residual chlorine begins to appear..

Advantages:

(1) It oxides completely organic compounds, ammonia and other reducing compounds.

(2) It removes color, odour and taste of water. (3) It removes completely all the disease causing

bacteria/micro-organism (4) It prevents the growth of any weeds in water.

9.4. Using Chloramine ($ClNH_2$):

When chlorine and ammonia are mixed in the ratio of 2:1 by
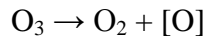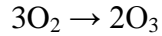
volume, chloramine is formed. $Cl_2+NH_3 \rightarrow ClNH_2+ HCl$

Chloramine is a better bactericidal than chlorine.

9.5. Disinfection by Ozone:

Ozone gas is an excellent disinfectant, which is produced by passing

silent electric discharge through cold and dry oxygen.

$$3O_2 \rightarrow 2O_3$$

$$O_3 \rightarrow O_2 + [O]$$

10. Desalination of brackish water

The process of removing common salt (NaCl) from the water is known as desalination. Water containing high concentration of dissolved salts with a peculiar salty taste is called brackish water. Sea water is an example containing 3.5% of dissolved salts. The common methods for the desalination of brackish water are;

10.1 Eletctrodialysis:

It is a method in which the ions are pulled out of the salt water by passing direct current, using electrodes and thin rigid plastic membrane pair.

An Eletctrodialysis cell consists of a large number of paired sets of rigid plastic membranes. Hard water is passed between the membrane pairs and an electric field is applied perpendicular to the direction of water flow. Positively charged membrane and negatively charged membrane repel positively charged ions and negatively charged ions respectively to pass through. So, in one compartment of the cell, the salt concentration decreases while in the adjacent compartment it increases

Thus, we get alternative stream of pure water and concentrated brine. Advantages: 1. It is most compact unit

10.2 Reverse osmosis:

When two solutions of unequal concentrations are separated by a semi permeable membrane, flow of solvent takes place from dilute to concentrate sides, due to osmosis. If, however a hydrostatic pressure in excess to osmotic pressure is applied on the concentrated side, the solvent flow is reversed, i.e, solvent is forced to move from concentrated side to dilute side across the membrane. This is the principle of reverse osmosis.(RO)

Thus in reverse osmosis method, pure solvent is separated from its contaminants, rather than removing contaminants from the water. The membrane filtration is sometimes also called super-filtration or hyper filtration.

METHOD:

In this process, pressure is applied to the sea water or impure water to force the pure water content of it out the semi-permeable membrane, leaving behind the dissolve solids. The principle of reverse osmosis as applied for treating saline/sea water The membrane consists of very thin film of cellulose acetate, affixed to either side of a perforated tube. However, more recently superior membranes made of polymethacrylate and polyamide polymers have come into use.

ADVANTAGES

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

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

 3. The maintenance cost is almost entirely on the replacement of the semi permeable membrane.
4. The life time of membrane is quite high, about 2 years,

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

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

BCH101
ENGINEERING CHEMISTRY- I

UNIT – II

POLYMERS

A **polymer** (Greek *poly-*, "many" + *-mer*, "parts") is a large molecule, or macromolecule, composed of many repeated subunits. Because of their broad range of properties, both synthetic and natural polymers play an essential and ubiquitous role in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness, viscoelasticity, and a tendency to form glasses and semi crystalline structures rather than crystals.

The term "polymer" derives from the ancient Greek word (*polus*, meaning "many, much") and (*meros*, meaning "parts"), and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. The units composing polymers derive, actually or conceptually, from molecules of low relative molecular mass. The term was coined in 1833 by Jöns Jacob Berzelius, though with a definition distinct from the modern IUPAC definition. The modern concept of polymers as covalently bonded macromolecular structures was proposed in 1920 by Hermann Staudinger, who spent the next decade finding experimental evidence for this hypothesis.

Polymers are of two types:

- **Natural polymeric** materials such as shellac, amber, wool, silk and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper.

- The **list of synthetic polymers** includes synthetic rubber, phenol formaldehyde resin (or Bakelite), neoprene, nylon, polyvinyl chloride (PVC or

vinyl), polystyrene, polyethylene, polypropylene, polyacrylonitrile, PVB, silicone, and many more.

Most commonly, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms. A simple example is polyethylene ('polythene' in British English), whose repeating unit is based on ethylene monomer. However, other structures do exist; for example, elements such as silicon form familiar materials such as silicones, examples being Silly Putty and waterproof plumbing sealant. Oxygen is also commonly present in polymer backbones, such as those of polyethylene glycol, polysaccharides (in glycosidic bonds), and DNA (in phosphodiester bonds).

TYPES OF POLYMERS

1. Oligopolymers   2.Highpolymers

3. Homopolymers   4.Heteropolymers.

MONOMER ARRANGEMENT IN COPOLYMERS

—A—A—A—A—A—A—A—A—A—A—   1

—A—B—A—B—A—B—A—B—A—B—   2

—A—B—B—B—A—B—A—B—A—A—   3

—B—B—B—B—B—A—A—A—A—A—   4

—A—A—A—A—A—A—A—A—A—A—   5
—B—B—B   B—B—B—

Monomers within a copolymer may be organized along the backbone in a variety of ways.

- **Alternating copolymers** possess regularly alternating monomer residues [AB...]$_n$
- **Periodic copolymers** have monomer residue types arranged in a repeating sequence: [A$_n$B$_m$...] m being different from n.

- **Statistical copolymers** have monomer residues arranged according to a known statistical rule. A statistical copolymer in which the probability of finding a particular type of monomer residue at a particular point in the chain is independent of the types of surrounding monomer residue may be referred to as a truly **random copolymer**

- **Block copolymers** have two or more homopolymer subunits linked by covalent bondsPolymers with two or three blocks of two distinct chemical species (e.g., A and B) are called diblock copolymers and triblock copolymers, respectively. Polymers with three blocks, each of a different chemical species (e.g., A, B, and C) are termed triblock terpolymers.

- **Graft or grafted copolymers** contain side chains that have a different composition or configuration than the main chain.

TACTICITY

Tacticity describes the relative stereochemistry of chiral centers in neighboring structural units within a macromolecule. There are three types: isotactic (all substituents on the same side), atactic (random placement of substituents), and syndiotactic (alternating placement of substituents).

POLYMERIZATION.
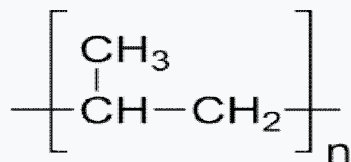
The repeating unit of the polymer polypropylene

Polymerization is the process of combining many small molecules known as monomers into a covalently bonded chain or network. During the polymerization process, some chemical groups may be lost from each monomer. This is the case, for example, in the polymerization of PET polyester. The monomers are terephthalic acid ($HOOC-C_6H_4-COOH$) and ethylene glycol ($HO-CH_2-CH_2-OH$) but the repeating unit is $-OC-C_6H_4-COO-CH_2-CH_2-O-$, which corresponds to the combination of the two monomers with the loss of two water molecules. The distinct piece of each monomer that is incorporated into the polymer is known as a repeat unit or monomer residue.

The process in which a large number of micro molecules, called monomers, are linked to form a giant molecule, called polymer is known as Polymerization.

There are 3 types of Polymerisation:

1. Addition Polymerisation ;
2. Condensation Polymerisation;
3. Co – Polymerisation

1.AdditionPolymerisation :

In this type polymer is produced from the monomers with multiple bonds, without loss of any material; the product polymer is the integral multiple of the monomer. The reaction is conducted by the application of heat, light , pressure or catalyst.

Ex. Formation of Polythene from ethylene

$$n\ CH_2 = CH_2 \xrightarrow{P/T/Cat} (-CH_2 - CH_2-)_n$$

ethylene (monomer) Polyethylene (polymer)
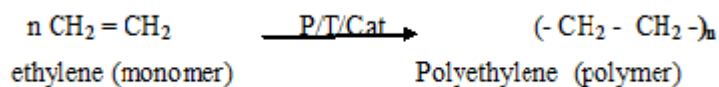
2.CondensationPolymerisation:

In this type , polymer is produced from the monomers with loss of simple molecules such as water, ethanol etc.,

ex. Nylon – 6,6

$$nH2N – (CH2)6 – NH2 + n\ HOOC – (CH2)4 – COOH \longrightarrow$$

hexa methylene diaminesAdipic acid

$$Nylon – 6,6\ + 2nH_2O$$

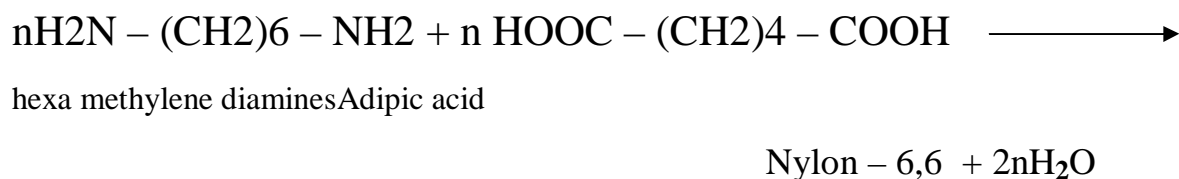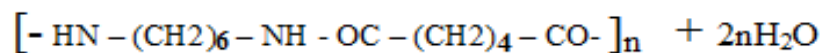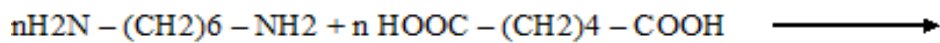$$nH_2N - (CH_2)_6 - NH_2 + n\ HOOC - (CH_2)_4 - COOH \longrightarrow$$

$$[- HN - (CH_2)_6 - NH - OC - (CH_2)_4 - CO-]_n + 2nH_2O$$

Nylon -6,6

3. CopolymerisationPolymerisation:

Here two different type of monomers [one is aliphatic & the other is aromatic] combine to give polymers;

Ex. Butadiene and styrene gives Buna –S – rubber OR

Polybutadiene –co - styrene

$$CH_2 = CH - CH = CH_2 + CH_2 = CH$$
$$|$$
$$C_6H_5$$

$$\xrightarrow{P\ /\ T\ /Cat.}$$

$$- [- CH2 - CH = CH - CH_2 - CH_2 - CH -]_n$$
$$|$$
$$C_6H_5$$
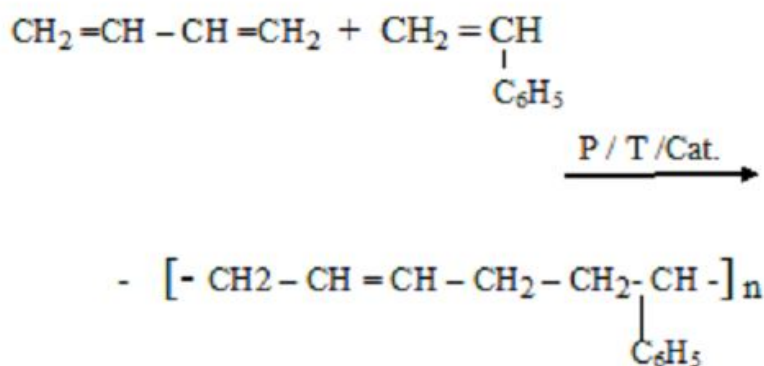
Buna –S – rubber or Polybutadiene –co - styrene

DIFFERENCES BETWEEN ADDITION AND CONDENSATION POLYMERIZATION

S.No	Addition Polymerization.	Condensation Polymerization.
1.	Monomers combine to form polymers without elimination.	Monomers combine to form polymers with elimination.(few exceptions)
2.	Monomers must have at least one multiple bond ; ex. CH2 =CH2	Monomers must have at least two identical or different functional groups; ex. CH2 OH– CH2OH

		H2N(CH2)4-COOH
3.	No other by product is formed.	By product such as H_2S , HCl , etc., are formed.
4.	M.wt. of the polymer is an integral multiple of M.Wt. of the monomer.	M.wt. of the polymer need not be an integral multiple of M.Wt. of the monomer.
5.	High m.wt. polymer is formed at once	M.Wt. of polymer increases steadily.
6.	Longer reaction time give higher yield ; but no effect on M.Wt.	Longer reaction times are essential to get high M.Wt. Polymer.
7.	Homo- chain polymer is obtained.	Hetro - chain polymer is obtained.
8.	Thermo plastics are produced. ex. PVC , polyethylene ,	Thermosetting plastics are produced. Ex. Bakelite , Polyester,

FREE – RADICAL MECHANISM OF POLYMERIZATION.

The free radical mechanism occurs in three major steps:

1.Initiation

2.Propagation

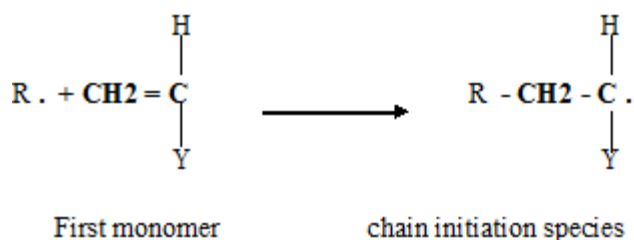3.Termination

I.Initiation :

   This involves two reactions :

 (i)First reaction

involves production of free radical by hemolytic dissociation of an initiator (or

catalyst):

 (ii) Second reaction :

   Addition of the free radical with the first monomer to give chain initiating

species :

R . + CH2 = C(H)(Y) $\longrightarrow$ R - CH2 - C . (H)(Y)

First monomer   chain initiation species

II Propagation :

Here growth of chain initiating species occurs by successive addition of large number of monomers.

R - CH2 - C . (H)(Y) + n CH2 = C (H)(Y) $\longrightarrow$

R - [CH2 = C(H) - CH2]$_n$ CH2 = C . (H)(Y)

C. Growing chain [living polymer]
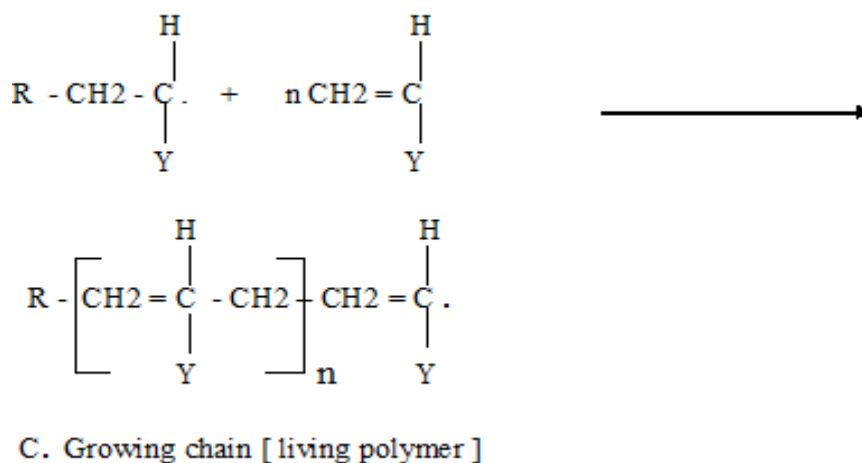
The growing chain of the polymer is known as living polymer.

III Termination :

Termination of a growing chain of polymer may occur by

(i)   Coupling (or) combination

(ii)   Disproportionation

Coupling or combination

Here coupling of free radical of one chain end to another free radical occurs to form a macro molecule.

$$R - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}} \cdot \quad + \quad \cdot \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}} - CH_2 - R \qquad \longrightarrow$$

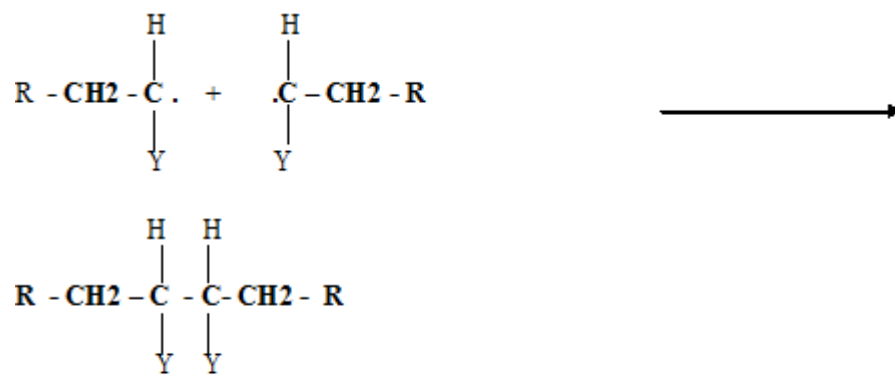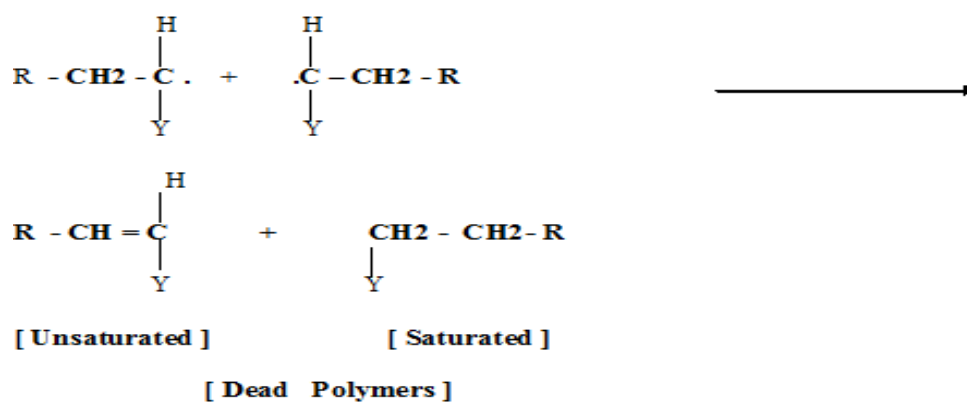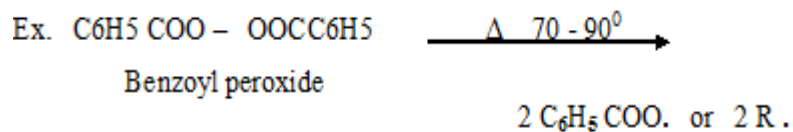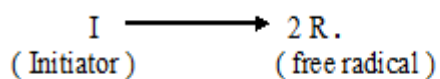$$R - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}} - CH_2 - R$$

Macro molecule [Dead polymer]

Disproportionation :

Here transfer of hydrogen from one radical to another radical occurs to form two macromolecules, one is saturated and the other is unsaturated.

$$R - CH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}} \cdot \quad + \quad \cdot \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}} - CH_2 - R \qquad \longrightarrow$$

$$R - CH = \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}} \quad + \quad \underset{\underset{\displaystyle Y}{|}}{CH_2} - CH_2 - R$$

$$\quad\text{[Unsaturated]} \qquad\qquad \text{[Saturated]}$$

$$\text{[Dead Polymers]}$$

The products of addition polymerisation is known as Dead Polymers.

$$\underset{(\text{Initiator})}{I} \quad \longrightarrow \quad \underset{(\text{free radical})}{2\,R \cdot}$$

Ex. C6H5 COO – OOCC6H5 $\xrightarrow{\quad \Delta \quad 70 - 90^0 \quad}$

      Benzoyl peroxide

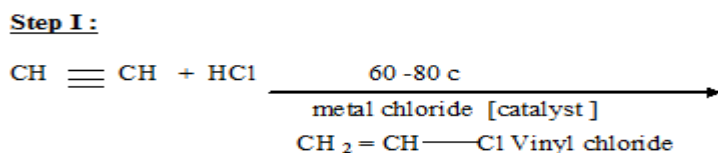$$2\ C_6H_5\,COO \cdot \ \text{ or }\ 2\,R \cdot$$

PREPARATION, PROPERTIES AND USES OF THE POLYMERS

a)   PVC ; b) Teflon ;   c) PET; d) nylon 6-6

a) PVC

Preparation: This involves two steps :

In the Step – I vinyl chloride is formed from acetylene

Step I :

$$CH \equiv CH + HCl \xrightarrow[\text{metal chloride [catalyst]}]{60\text{ -}80\text{ c}}$$
$$CH_2 = CH——Cl \text{ Vinyl chloride}$$

Step II :

 By heating water emulsion of vinyl chloride in the presence of H2O2 or benzoylperoxide under pressure

$$n \ CH_2 = CH — Cl \xrightarrow{\text{H2O2 / Pressure}} [-CH2-CH-]_n$$
Vinyl chloride Cl PVC
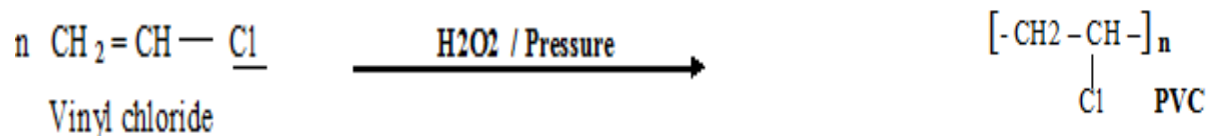
Properties of PVC :
1.colourless , odourless
2.chemically inert powder
      3. insoluble in inorganic & alkalis but soluble in hot chlorinated hydrocarbons like ethyl chloride.
      4. Undergoes degradation in the presence of light or heat.
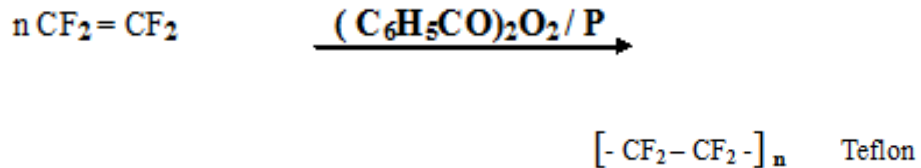*uses :*
      1. production of pipes, cable insulators ,table covers & rain coats
   2. for making sheets which are employed for light fittings ,
   3. Refrigerator   components, etc.,
b)Teflon :

Preparation :

It is nothing but polytetrafluoroethylene (PTFE) which is an Engineering polymer. It is prepared by polymerization of water emulsion of tetrafluoroethylene in the presence of benzoylperoxide under pressure

$$n\,CF_2 = CF_2 \quad \xrightarrow{(C_6H_5CO)_2O_2 / P}$$

$$[-CF_2 - CF_2-]_n \quad \text{Teflon}$$

Properties :

1. Extremely tough & flexible

2. has extremely good electrical & mechanical properties

3. Chemically resistant towards all chemicals (except hot alkali metal & hot

   (Fluorine)

4. excellent thermal stability.

Uses of Teflon ;

1.as a very good electrical insulating material in motors,cables , transformers, electrical fittings

2. For making gaskets, pump parts, tank linings , etc.,

3. For making non-lubricating bearings, chemical pipes, etc.,

4. For making non-sticking stop cocks for burettes.
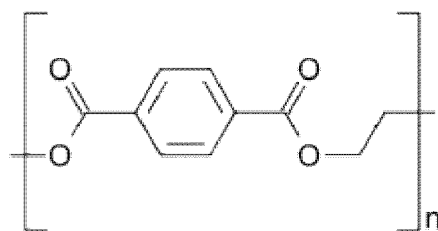
c) PET :

Preparation:

PET is nothing but Polyethyleneteterephthlate; it is prepared by the condensation of ethylene glycol and terephthalic acid(benzene-1,4-dicarboxylic acid).

HOOC—⬡—COOH   HO-CH₂CH₂-OH   ⟶
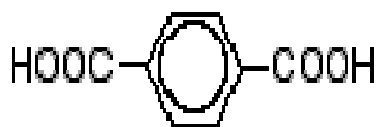
benzene-1,4-dicarboxylic acid   ethane-1,2-diol

PET

Poly (ethyleneterephthalate)

Properties

1.goodfibre – forming material

2.Fibre possess high stretch – resistance & wrinkle – resistance .

3.Highly resistant to mineral & organic acids but less resistant to alkali.
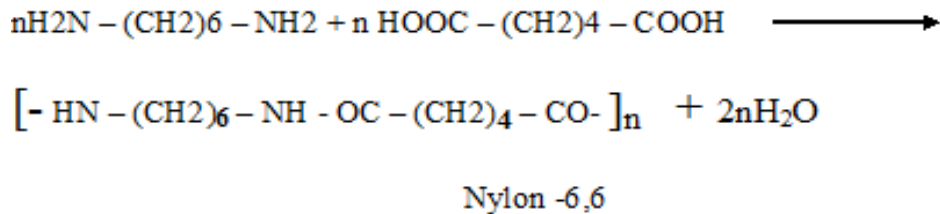
Uses :

1.for making synthetic fibres like terylene , Dacron , etc.,

2.blended with wool to provide better wrinkle – resistance.

3.In safety helmets , aircrafts , battery boxes , etc.,

D) NYLON 6-6

preparation:

it is an engineering plastic obtained by the condensation polymerization of 1 , 6 – hexamethylenediamine with adipic acid . 6,6 indicates the number of carbon atoms in each monomer.

$$nH2N - (CH2)6 - NH2 + n\ HOOC - (CH2)4 - COOH \longrightarrow$$

$$[- HN - (CH2)_6 - NH - OC - (CH2)_4 - CO-]_n + 2nH_2O$$

Nylon -6,6

Properties:

1. Nylons are transparent, whitest and high melting polymers.

2. Possess high temperature stability and good abrasion – resistance.

3. Insoluble in common organic solvents and soluble in phenol and formic acid.

Uses:

1. For making filaments for ropes , bristles for tooth –brushes , etc.,

2. Nylon 6 and nylon 11 are mainly used for moulding purposes for gears , bearings, etc.,

3. Forfibres, which is used in making socks , dresses , carpets, etc.,

PLASTICS

Plastics are high molecular weight organic or inorganic materials, which can be moulded into any stable form when subjected to heat and pressure in the presence of a catalyst. The name plastics or plastic materials in general is given to organic materials of high molecular mass, which can be moulded into any desired form when subjected to heat and pressure in presence of catalysts. Polymer resin is the basic binding material, which forms the major part of a plastic. In recent years plastics have attained greater importance in every walk of life due to their unique properties. Now, plastics substitute all engineering materials like wood, metal, glass etc because of their special advantages over other conventional materials. Plastics are products of polymers

Plastics are classified into two types:

      1. Thermoplastics

They are the resins which soften on heating and set on cooling. Therefore, they can be remoulded any number of times and used. Example: Polythene, PVC, Nylon, etc.

      2. Thermosetting plastics.

They are the resins which set on heating and cannot be resoftened. Hence, their scrap cannot be reused. Examples: Phenol-formaldehyde resin (Bakelite), urea formaldehyde resin, etc. The differences between two types of plastics arise mainly due to the difference in their chemical structure.

Properties of Engineering plastics

They possess

1. High abrasion resistance

2. High load bearing properties

3. Fairly good thermal stability

4. Light weight

5. Readilymoldable into complicated shapes

6. Rigidity

7. Dimensional stability

8. High performance properties which permit them to be used in the same

      manner as metals, alloys and ceramics

DISADVANTAGES OF PLASTICS

1. Softness

2. Embrittlement at low temperature

3. Deformation under load

4. Low heat resistant

5. Combustibility

6. Tend to degrade upon exposure to heat and radiation

7. Non bio – degradable

Differences between Thermo Plastics and Thermosetting Plastics

S.No.	Thermo Plastics	Thermosetting plastics
1	Formed by addition Polymerization	Formed by condensation Polymerization
2.	Consists of linear long chain polymers.	Consists of three dimensional networks.
3.	Polymer chains are held together by weak Vander wall's forces.	Polymer chains are held together by strong covalent forces.
4.	Weak , soft and less brittle	Strong, hard and more brittle.
5.	Soften on heating and harden on cooling.	Harden on heating ;but once hardened they cannot be softened.
6.	Can be remoulded	Cannot be remoulded.
7.	Low M.Wt.	High M.Wt.
8.	Soluble in organic solvents.	Insoluble in organic solvents.

RUBBER

Rubbers are non-crystalline, high polymers (linear polymers) having elastic and other rubber – like properties.Rubber is a natural elastic polymer of isoprene. It is obtained from the milk of rubber called 'Latex'. The structure of natural rubber is as follows.

1. Latex is rubber milk containing about 30 to 45% of rubber.

2. The rubber milk is diluted with water and allowed to stand for sometime.

3. The clear liquid from the top is treated with acetic acid or formic acid to precipitate rubber.

4. The precipitated rubber is collected and passed through rollers to get sheets of rubber.

5. Rubber sheets are finally dried by smoking. This rubber is called 'Smoked rubber'.

6. During the coagulation of rubber milk with acetic or formic acid, retardants like sodium bisulphite (NaHSO) are added to prevent oxidation of rubber. This is called 'Creep rubber'.

The natural rubber obtained from latex cannot be used in industries because it has some defects.

1. It becomes soft and sticky during summer.

2. It became hard and brittle during winter.

3. It swells up in oils.

4. It flows plastically due to prolonged stress.

5. Chemicals easily affect rubber.

NATURAL AND SYNTHETIC RUBBER.

Natural rubber:

Natural rubber is obtained from the tree as a latex , which is a dispersion of Isoprene. During the treatment of latex isoprene molecules undergo polymerization to form long coiled chain of polyisoprene.

$$n \ CH_2 = C - CH = CH_2$$
$$| $$
$$CH_3$$

Isoprene

$$-[CH_2 - C = CH - CH_2]_n-$$
$$|$$
$$CH_3$$
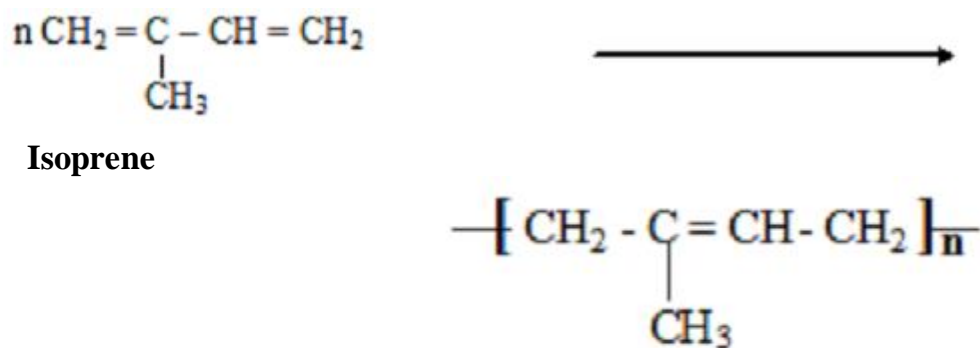
Polyisoprene
Properties :
1. Plastic in nature – soften at high temperature and too brittle at low temperature.

2. Has large absorbing capacity.

3. Tensile strength is very less .

4. non – resistant to non-polar solvents like benzene .

5. attacked by oxidizing agents like nitric acid and con.H_2SO_4

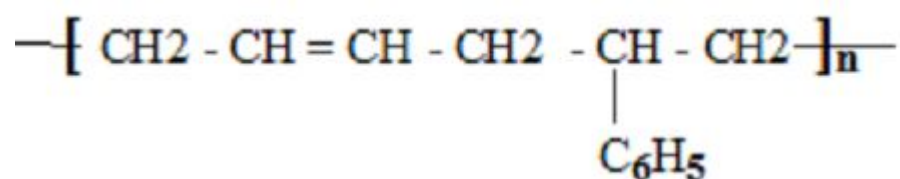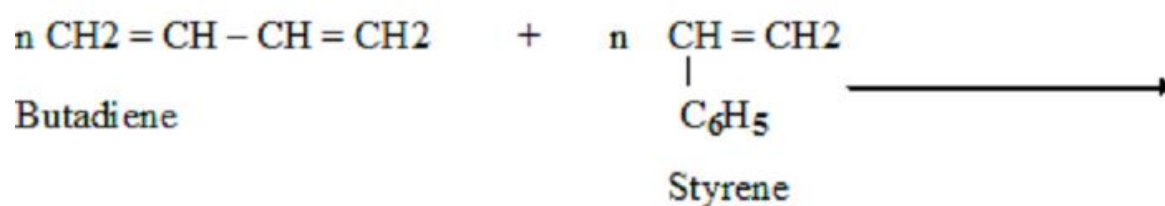6. becomes brittle on long exposure to air.

To improve the properties of rubber, it is mixed with some chemicals like sulphur , hydrogen sulphide etc. the properties of rubber improved using sulphur is called vulcanisation.

SYNTHETIC RUBBER :

Synthetic rubber is nothing but any vulcanisable , manmade rubber like polymer ; it is superior to natural rubber in certain properties.

Ex. Styrene Rubber (Buna – S rubber) or SBR;

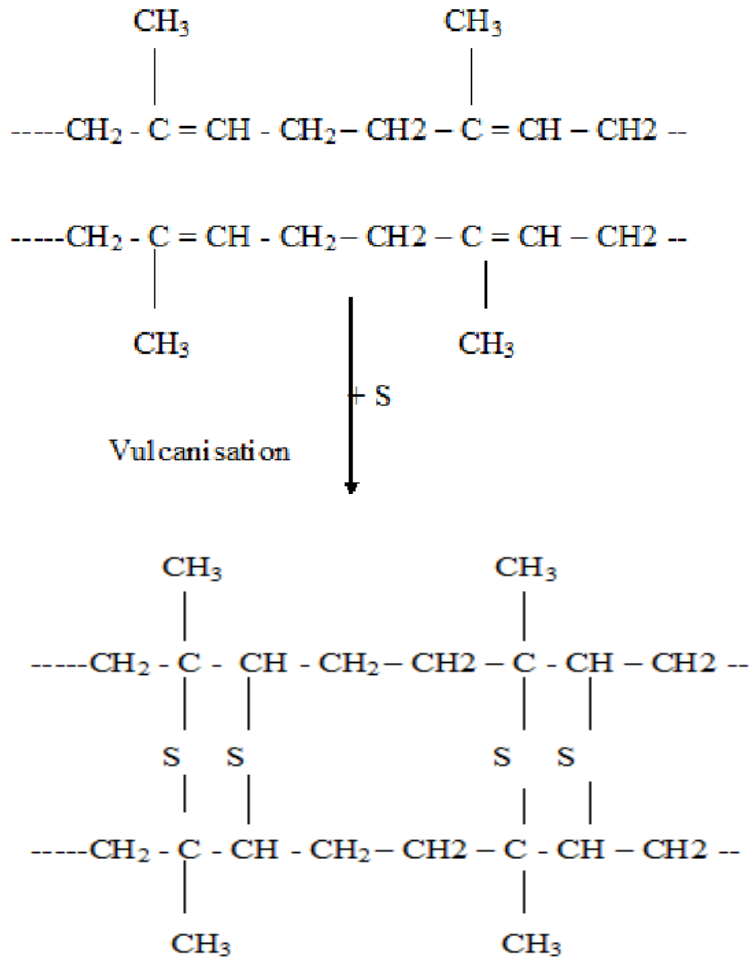It is prepared by copolymerization of Butadiene and Styrene

$$n \; CH_2 = CH - CH = CH_2 \quad + \quad n \quad CH = CH_2$$

Butadiene

C_6H_5

Styrene

$$-[CH_2 - CH = CH - CH_2 - CH - CH_2]_n-$$

C_6H_5

Styrene -butadiene rubber

DRAWBACKS OF NATURAL RUBBER

1.plastic in nature – soften at high temperature and too brittle at low temperature.

2.Has large absorbing capacity.

3.Tensile strength is very less .

4.non – resistant to non-polar solvents like benzene .

5.attacked by oxidizing agents like nitric acid and con. H_2SO_4

VULCANISATION OF RUBBER :

        Vulcanization is a process of heating the raw rubber with Sulphur at about 100 – 140 ^{0}c. to improve its properties. The added Sulphur combines at the double bonds of different long chain rubber springs. Thus vulcanization prevents intermolecular movement of rubber springs. The extent of stiffness of vulcanized rubber depends on the amount of sulphur added.

$$
\begin{array}{ccccccc}
& CH_3 & & & & CH_3 & \\
& | & & & & | & \\
----CH_2 - C & = CH - CH_2 - CH2 - C & = CH - CH2 -- \\
\end{array}
$$

$$
\begin{array}{ccccccc}
----CH_2 - C & = CH - CH_2 - CH2 - C & = CH - CH2 -- \\
& | & & & & | & \\
& CH_3 & & & & CH_3 & \\
\end{array}
$$

+ S

Vulcanisation

$$
\begin{array}{ccccccc}
& CH_3 & & & & CH_3 & \\
& | & & & & | & \\
----CH_2 - C - & CH - CH_2 - CH2 - C - CH - CH2 -- \\
& | \quad | & & & & | \quad | & \\
& S \quad S & & & & S \quad S & \\
& | \quad | & & & & | \quad | & \\
----CH_2 - C - CH - CH_2 - CH2 - C - CH - CH2 -- \\
& | & & & & | & \\
& CH_3 & & & & CH_3 & \\
\end{array}
$$

Ex. 1.Tyre rubber contains 3 – 5 % sulphur
2.Battery case rubber contains 30 % sulphur

***********&&&&&**********

BCH101
ENGINEERING CHEMISTRY- I

UNIT – III
ELECTRO CHEMISTRY

Electrochemistry is the branch of physical chemistry that studies the relationship between electricity, as a measurable and quantitative phenomenon, and identifiable chemical change, with either electricity considered an outcome of a particular chemical change or vice versa. These reactions involve electric charges moving between electrodes and an electrolyte (or ionic species in a solution). Thus electrochemistry deals with the interaction between electrical energy and chemical change.

When a chemical reaction is caused by an externally supplied current, as in electrolysis, or if an electric current is produced by a spontaneous chemical reaction as in a battery, it is called an *electrochemical* reaction. Chemical reactions where electrons are transferred directly between molecules and/or atoms are called oxidation-reduction or (redox) reactions. In general, electrochemistry describes the overall reactions when individual redox reactions are separate but connected by an external electric circuit and an intervening electrolyte.

The term "redox" stands for **reduction-oxidation**. It refers to electrochemical processes involving electron transfer to or from a molecule or ion changing its oxidation state. This reaction can occur through the application of an external voltage or through the release of chemical energy. Oxidation and reduction describe the change of oxidation state that takes place in the atoms, ions or molecules involved in an electrochemical reaction. Formally, oxidation state is the hypothetical charge that an atom would have if all bonds to atoms of different elements were 100% ionic. An atom or ion that gives up

an electron to another atom or ion has its oxidation state increase, and the recipient of the negatively charged electron has its oxidation state decrease.

Electrochemical reactions in water are better understood by balancing redox reactions using the ion-electron method where H^+, OH^- ion, H_2O and electrons (to compensate the oxidation changes) are added to cell's half-reactions for oxidation and reduction.

Acidic medium

In acid medium H^+ ions and water are added to half-reactions to balance the overall reaction. For example, when manganese reacts with sodium bismuthate.

Basic medium

In basic medium OH^- ions and water are added to half reactions to balance the overall reaction. For example, on reaction between potassium permanganate and sodium sulfite

Neutral medium

The same procedure as used on acid medium is applied, for example on balancing using electron ion method to complete combustion of propane

Electrochemical cells

An electrochemical cell is a device that produces an electric current from energy released by a spontaneous redox reaction. This kind of cell includes the Galvanic cell or Voltaic cell, named after Luigi Galvani and Alessandro Volta, both scientists who conducted several experiments on chemical reactions and electric current during the late 18th century.
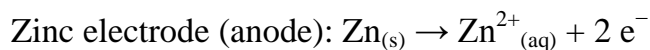
Electrochemical cells have two conductive electrodes (the anode and the cathode). The anode is defined as the electrode where oxidation occurs and the cathode is the electrode where the reduction takes place. Electrodes can be made from any sufficiently

conductive materials, such as metals, semiconductors, graphite, and even conductive polymers. In between these electrodes is the electrolyte, which contains ions that can freely move.

The galvanic cell uses two different metal electrodes, each in an electrolyte where the positively charged ions are the oxidized form of the electrode metal. One electrode will undergo oxidation (the anode) and the other will undergo reduction (the cathode). The metal of the anode will oxidize, going from an oxidation state of 0 (in the solid form) to a positive oxidation state and become an ion. At the cathode, the metal ion in solution will accept one or more electrons from the cathode and the ion's oxidation state is reduced to 0. This forms a solid metal that electrodeposits on the cathode. The two electrodes must be electrically connected to each other, allowing for a flow of electrons that leave the metal of the anode and flow through this connection to the ions at the surface of the cathode. This flow of electrons is an electric current that can be used to do work, such as turn a motor or power a light.

A galvanic cell whose electrodes are zinc and copper submerged in zinc sulfate and copper sulfate, respectively, is known as a Daniell cell.

Half reactions for a Daniell cell are these

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

Copper electrode (cathode): $Cu^{2+}_{(aq)} + 2\ e^- \rightarrow Cu_{(s)}$

In this example, the anode is the zinc metal which is oxidized (loses electrons) to form zinc ions in solution, and copper ions accept electrons from the copper metal electrode and the ions deposit at the copper cathode as an electrodeposit. This cell forms a simple battery as it will spontaneously generate a flow of electric current from the anode to the cathode through the external connection. This reaction can be driven in reverse by applying a voltage, resulting in the deposition of zinc metal at the anode and formation of copper ions at the cathode.

To provide a complete electric circuit, there must also be an ionic conduction path between the anode and cathode electrolytes in addition to the electron conduction path. The simplest ionic conduction path is to provide a liquid junction. To avoid mixing between the two electrolytes, the liquid junction can be provided through a porous plug that allows ion flow while reducing electrolyte mixing. To further minimize mixing of the electrolytes, a salt bridge can be used which consists of an electrolyte saturated gel in an inverted U-tube. As the negatively charged electrons flow in one direction around this circuit, the positively charged metal ions flow in the opposite direction in the electrolyte.

A voltmeter is capable of measuring the change of electrical potential between the anode and the cathode.

Electrochemical cell voltage is also referred to as electromotive force or emf.

A cell diagram can be used to trace the path of the electrons in the electrochemical cell. For example, here is a cell diagram of a Daniell cell:

$$Zn_{(s)} \mid Zn^{2+} (1M) \parallel Cu^{2+} (1M) \mid Cu_{(s)}$$
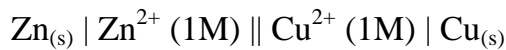
First, the reduced form of the metal to be oxidized at the anode (Zn) is written. This is separated from its oxidized form by a vertical line, which represents the limit between the phases (oxidation changes). The double vertical lines represent the saline bridge on the cell. Finally, the oxidized form of the metal to be reduced at the cathode, is written, separated from its reduced form by the vertical line. The electrolyte concentration is given as it is an important variable in determining the cell potential.

Reversible cell :

Here , the cell reactions will take place in the reverse direction , when the applied voltage is greater than the cell voltage ; The voltage of the **Daniel cell** = 1.1V; Cell reaction ;

$Cu + Zn^{2+}Cu^{2+} + Zn$ $\xrightarrow{\hspace{3cm}}$

when the applied voltage is greater than the cell voltage , the cell reaction is

$Cu^{2+} + Zn$ $\xrightarrow{\hspace{1.5cm} Cu + Zn^{2+} \hspace{0.3cm}}$

Ex. Daniel cell

Irreversible cell :

Here , the cell reactions cannot not be reversed by applying higher voltage greater than the cell voltage.   Ex., Dry cell

Standard electrode potential

To allow prediction of the cell potential, tabulations of standard electrode potential are available. Such tabulations are referenced to the standard hydrogen electrode (SHE). The standard hydrogen electrode undergoes the reaction

$$2 \, H^+_{(aq)} + 2 \, e^- \rightarrow H_2$$
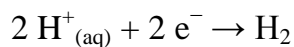
which is shown as reduction but, in fact, the SHE can act as either the anode or the cathode, depending on the relative oxidation/reduction potential of the other electrode/electrolyte combination. The term standard in SHE requires a supply of hydrogen gas bubbled through the electrolyte at a pressure of 1 atm and an acidic electrolyte with H^+ activity equal to 1 (usually assumed to be $[H^+] = 1$ mol/liter).

The SHE electrode can be connected to any other electrode by a salt bridge to form a cell. If the second electrode is also at standard conditions, then the measured cell potential is called the standard electrode potential for the electrode. The standard electrode potential for the SHE is zero, by definition. The polarity of the standard electrode potential provides information about the relative reduction potential of the electrode compared to the SHE. If the electrode has a positive potential with respect to the SHE, then that means it is a strongly reducing electrode which forces the SHE to be the anode (an example is Cu in aqueous $CuSO_4$ with a standard electrode potential of 0.337 V). Conversely, if the measured potential is negative, the electrode is more oxidizing than the SHE (such as Zn in $ZnSO_4$ where the standard electrode potential is −0.76 V).

Standard electrode potentials are usually tabulated as reduction potentials. However, the reactions are reversible and the role of a particular electrode in a cell depends on the

relative oxidation/reduction potential of both electrodes. The oxidation potential for a particular electrode is just the negative of the reduction potential. A standard cell potential can be determined by looking up the standard electrode potentials for both electrodes (sometimes called half cell potentials). The one that is smaller will be the anode and will undergo oxidation. The cell potential is then calculated as the sum of the reduction potential for the cathode and the oxidation potential for the anode.

$$E°_{cell} = E°_{red} \text{ (cathode)} - E°_{red} \text{ (anode)} = E°_{red} \text{ (cathode)} + E°_{oxi} \text{ (anode)}$$

For example, the standard electrode potential for a copper electrode is:

Cell diagram

$$Pt_{(s)} \mid H_2 \text{ (1 atm)} \mid H^+ \text{ (1 M)} \parallel Cu^{2+} \text{ (1 M)} \mid Cu_{(s)}$$
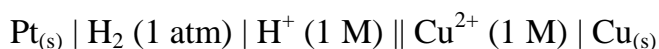
$$E°_{cell} = E°_{red} \text{ (cathode)} - E°_{red} \text{ (anode)}$$

At standard temperature, pressure and concentration conditions, the cell's emf (measured by a multimeter) is 0.34 V. By definition, the electrode potential for the SHE is zero. Thus, the Cu is the cathode and the SHE is the anode giving

$$E_{cell} = E°(Cu^{2+}/Cu) - E°(H^+/H_2)$$

Or,

$$E°(Cu^{2+}/Cu) = 0.34 \text{ V}$$

Changes in the stoichiometric coefficients of a balanced cell equation will not change $E°_{red}$ value because the standard electrode potential is an intensive property

Spontaneity of redox reaction

During operation of electrochemical cells, chemical energy is transformed into electrical energy and is expressed mathematically as the product of the cell's emf and the electric charge transferred through the external circuit.

Electrical energy = $E_{cell}C_{trans}$

where E_{cell} is the cell potential measured in volts (V) and C_{trans} is the cell current integrated over time and measured in coulombs (C); C_{trans} can also be determined by multiplying the total number of electrons transferred (measured in moles) times Faraday's constant (F).

The emf of the cell at zero current is the maximum possible emf. It is used to calculate the maximum possible electrical energy that could be obtained from a chemical reaction. This energy is referred to as electrical work and is expressed by the following equation:

$$\mathbf{W_{max} = W_{electrical} = -nFE_{cell}}$$

where work is defined as positive into the system.

Since the free energy is the maximum amount of work that can be extracted from a system, one can write:[23]

$$\Delta \mathbf{G = -nFE_{cell}}$$

A positive cell potential gives a negative change in Gibbs free energy. This is consistent with the cell production of an electric current from the cathode to the anode through the external circuit. If the current is driven in the opposite direction by imposing an external potential, then work is done on the cell to drive electrolysis.

A spontaneous electrochemical reaction (change in Gibbs free energy less than zero) can be used to generate an electric current in electrochemical cells. This is the basis of all batteries and fuel cells. For example, gaseous oxygen (O_2) and hydrogen (H_2) can be combined in a fuel cell to form water and energy, typically a combination of heat and electrical energy.

Conversely, non-spontaneous electrochemical reactions can be driven forward by the application of a current at sufficient voltage. The electrolysis of water into gaseous oxygen and hydrogen is a typical example.

The relation between the equilibrium constant, *K*, and the Gibbs free energy for an electrochemical cell is expressed as follows:

$$\Delta G^O = -RT \ln K = -nFE^O_{cell}$$

Rearranging to express the relation between standard potential and equilibrium constant yields

$$E^O_{cell} = \frac{RT \ln K}{nF}$$

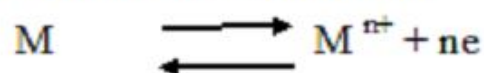The previous equation can use Briggsian logarithm as shown below:

$$E^O_{cell} = \frac{0.0591V \log K}{n}$$

Cell emf dependency on changes in concentration

Nernst's equation

Let us consider the following equilibrium

$$M \rightleftharpoons M^{n+} + ne$$

For this, Equilibrium constant,

$$K_{eq.} = \frac{[M^{n+}]}{[M]} \quad \text{------ [1]}$$

The decrease in the free energy (-ΔG) of a reversible system can be written as

$$-\Delta G = -\Delta G^0 - RT \ln K_{eq.} \quad \text{-------------- [2]}$$

Further , decrease in the free energy (-ΔG)

of a reversible system = Energy produced

$$-\Delta G = n E F; \quad \& \quad -\Delta G^0 == nE^0F$$

Where E = emf of the electrode; F = Faraday [96500 coulombs] ;

n = number of electrons involved in the reaction;

E^0 = Standard emf; nEF = electrical energy produced.

Substituting the values of -ΔG, -ΔG^0 and $K_{eq.}$

in the equation [2] , we get,

$$n EF = nE^0F - RT \ln \frac{[M^{n+}]}{[M]}$$

$$E = \frac{nE^0F}{nF} - \frac{RT}{nF} \ln \frac{[M^{n+}]}{[M]}$$

since the activity of solid metal [M] =1 ,

$$E = E^0 - \frac{RT}{nF} \ln [M^{n+}]$$

$$E = E^0 - \frac{2.303RT}{nF} \log [M^{n+}]$$

where $R = 8.314$ J/K/mole ; $F = 96500$ coulombs ; $T = 298$ K

$$[25^0 C]$$

$$E_{oxi} = E^0_{oxi} - \frac{0.059}{n} \log [M^{n+}] \quad \text{------- [3]}$$

similarly , for reduction process

$$E_{red.} = E^0_{red.} + \frac{0.059}{n} \log [M^{n+}] \quad \text{------ [4]}$$

The above equations 3 & 4 are known as Nernst equation for a single electrode potential, oxidation and reduction reaction respectively.

APPLICATIONS OF NERNST'S EQUATION

The applications of Nernst equation are

1. It can be used to calculate potential of an electrode;

2. Whether a reaction is feasible or not, can be decided;

3. Whether a metal can displace H_2 from the acid solution can be determined ;

4. Equilibrium constant $K_{eq.}$ can be calculated.

GLASS ELECTRODE CONSTRUCTION
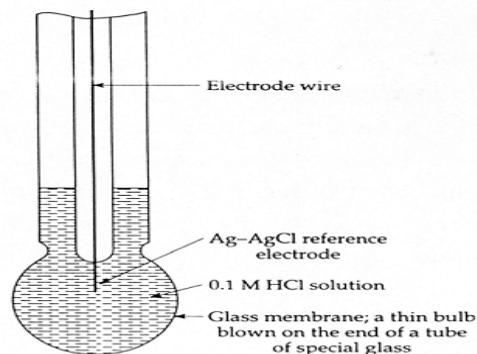
Construction :

A glass electrode consists of thin – walled bulb (the glass is a special type having low melting point and high electrical conductivity) containing a Pt wire in 0.1 M HCl. The glass electrode is represented as

Pt, 0.1 M HCl / glass

The thin walled glass bulb called glass membrane functions as an ion – exchange resin, and equilibrium is established between the Na+ ions of glass and H+ ions in solution and its emf is given by the expression

$E_G = E^0_G - 0.0595 \log [H^+]$

(or)

$E_G = E^0_G + 0.0595\ p[H^+]$

## *ADVANTAGES AND DISADVANTAGES OF GLASS ELECTRODE*

Advantages :

1.It can be easily constructed

2.results are accurate

3.can be used in any solutions.

4.a small solution is sufficient for the determination of Ph.

Disadvantages :

1.it cannot be used in strong alkaline solution as it affects the glass.

2.special electronic potentiometer should be used for measurements.

GLASS ELECTRODE USED TO DETERMINE THE PH OF A SOLUTION

The glass electrode is placed in the solution under test and is coupled with saturated calomel electrode as shown in the fig.
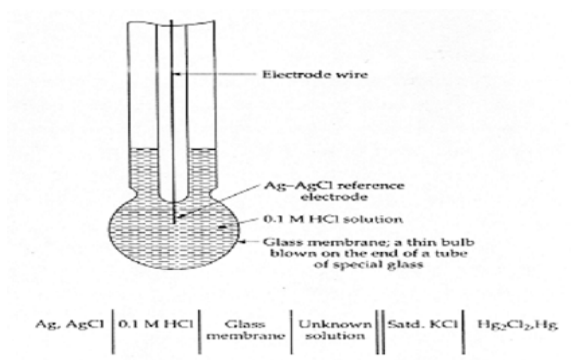
Electrode 1 is glass electrode and electrode 2 is calomel electrode; they are connected through a potentiometer as shown in the diagram.

It is an internal reference electrode. The glass electrode & calomel electrode are in touch with the test solution and connected to a potentiometer; the emf of the cell is determined; then

$$E_{cell} = E_{right} - E_{left} = E_{Cal} - E_{G} \quad \text{------------} \quad [1]$$

E_{Cal} value is taken from tables ; so we can get the value of E_{G} ; and

for oxidn. reaction, $\quad E_{G} = E^{0}_{G} - 0.059 \log[H^{+}]$

$$= E^{0}_{G} + 0.0591 \, pH \quad \text{--------} \quad [2]$$

E^0_G value is taken from the tables ; now ,in the equation [2] ,

E_G and E^0_G are known ; so pH value can be determined.

Thus the pH of a given solution is determined using glass electrode.

STANDARD HYDROGEN ELECTRODE

Construction :

Hydrogen electrode consists of platinum foil connected to Pt wire and sealed in a glass tube. Hydrogen gas is passed through the side arm of the glass tube. The electrode is dipped in a 1N HCl and hydrogen gas at 1 atm. Pressure is passed at a temp. of 25^0c . the electrode potential of SHE is zero at all temp.

It is represented as,

$Pt, H_2 (1atm.) / HCl(1M)$; $E^0 = 0$ V

In a cell , when this acts as anode , electrode reaction can be written as,

H_2 (g) $\longrightarrow$ $2H^+ + 2e$

when this acts as cathode , electrode reaction can be written as,

$2H^+ + 2e$ $\longrightarrow$ H_2 (g)
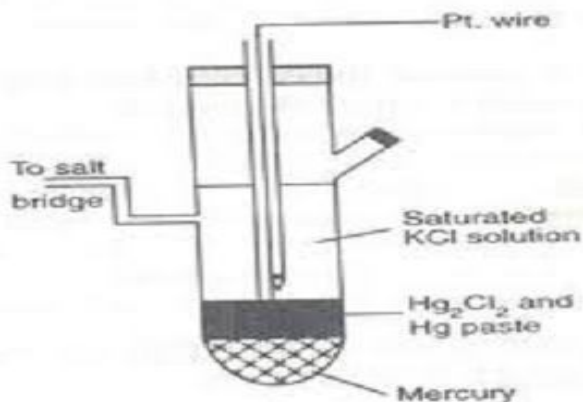
## CALOMEL ELECTRODE WITH A NEAT DIAGRAM.

Fig. 12.15 Calomel electrode

Construction:

It consists of a glass tube containing Hg at the bottom ; above that Hg_2Cl_2 (calomel) paste is placed; above this saturated solution of KCl is taken.

The Pt wire is sealed in a glass tube and its bottom is in contact with Hg as shown in the figure. The side tube is used for making electrical contact as salt bridge. The electrode potential of saturated calomel electrode = 0.2422 V

It is represented as: Pt, Hg, $Hg_2Cl_{2(s)}$/ KCl (saturated)

If this electrode acts as anode, reaction is

$$2Hg_{(l)} \longrightarrow Hg_2{}^{2+} + 2e^-$$
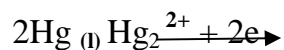
If this electrode acts as cathode , reaction is

$$Hg_2{}^{2+} + 2e^- \longrightarrow 2Hg_{(s)}$$
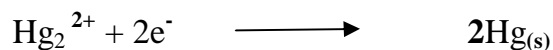
The potential of this electrode depends on the concentration of

Cl^- & it decreases as the concentration of Cl^- increases.

Its reduction potential is given by

$E_{(0.1N.)} = +0.3338$ V ; $\qquad$ $E_{(1N.)} = +0.280$ V ;

$E_{(sat.)} = +0.2422$ V ;

EMF OF A GALVANIC CELL MEASURED BY POGGENDORFF'S COMPENSATIONMETHOD

Principle :

The emf of a cell can is measured on the basis of Poggendorff's compensation method. Here the emf of the test cell is opposed and compensated by an external emf; measurements are are made when there is no flow of current in the circuit ;ie emf of the test cell is balanced (ie., compensated) by the external emf.

Circuit Diagram

$$\frac{\text{emf of } C_2}{\text{emf of } C_1} = \frac{\text{distance } AX_2}{\text{distance } AX_1}.$$
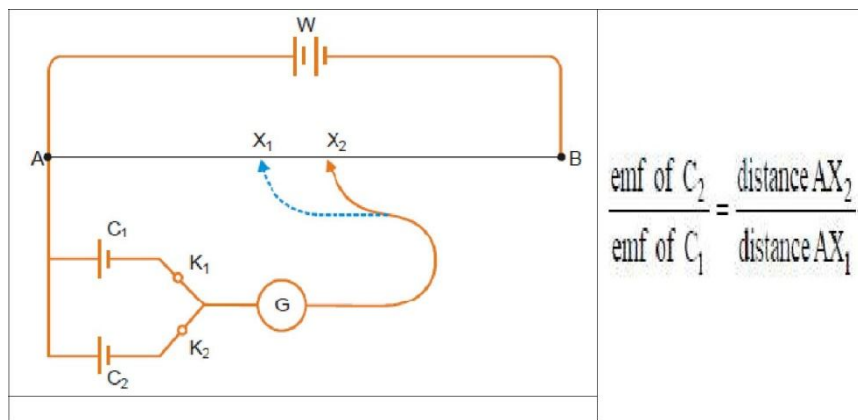
Procedure :

$\qquad$ Standard cell C_1 and the test cell C_2 are connected to a potentiometer through a three way plug and also to a galvanometer G and a sliding contact J as shown the circuit diagram.

$\qquad$ At first the standard cell is connected & J is moved here and there until there is no current flow in G; now the length

$l_1 \alpha \; C_1$

Then test cell is connected & J is moved here and there until there is no current flow in G; now the length

$l_2 \; \alpha \; C_2$

Hence , $\quad C_2 / C_1 \; = \; l_2 / l_1$

$C_2 = l_2 / l_1 \;\; x \; C_1$

Since current C is directly proportional to emf E ,

So , $\qquad E_2 = \; E_1 \; . \; l_2 / l_1$

thus the emf of a cell is determined on the basis of $\qquad\qquad\qquad$ Poggendorff's compensation method.

THE POTENTIOMETRIC TITRATION WITH A SPECIFIC EXAMPLE

$\qquad$ The titration in which the end point is noted by the change in the potential values of the solution .let us consider the titration between ferrous Ammonium Sulphate (FAS) and $K_2Cr_2O_7$.

Principle:

$\qquad$ The *potential* value of a solution depends on its concentration. During titration its concentration changes gradually and so its potential value also changes gradually; at the end point the change will be very sharp; after the end point the change will not be appreciable.

Let us consider the titration of FAS Vs $K_2Cr_2O_7$

$\qquad$ In the titration at the beginning there are only F^{2+} ions and no $Fe^{3}+$ ions; as the dichromate is added , the F^{2+} ions are oxidized in to $Fe^{3}+$; the concentration of to $Fe^{3}+$ ions goes on increases ; so the potential value also goes on increases & at the end

point the emf value will be sharp; further addition will result no appreciable change in emf value.

In the graph plotted drawn between EMF and volume of $K_2Cr_2O_7$, the emf goes on increases gradually as shown ; at the end point all the ions are completely oxidized in to $Fe^{3}+$; so sharp increase results ; further the graph is almost horizontal .

The line which is almost perpendicular, gives the value of dichromate necessary for the end point; from this the strength and hence amount of FAS in the whole of the given solution can be calculated

CONDUCTOMETRIC TITRATION WITH SUITABLE EXAMPLE.
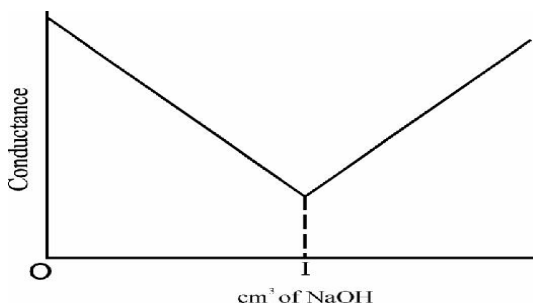
Principle :

A titration, in which concentration changes are followed by the changes in the conductance values, is called Conductometric titration. The basic principle involved in this titration is that for a given electrolyte at a particular temperature, the conductivity value depends on its concentration alone. The variation in conductance of the solution during titration is utilized to locate the end point.

By plotting C values against the volume of titrant, a graph obtained consists of two straight lines; the point of intersection of these two lines gives the end point.

Let us consider the titration of Strong acid (HCl) verses Strong Base (NaOH)

NaOH is taken in the burette and HCl is taken in a beaker; conductivity cell is dipped in it and connected to a Conductometer. Conductance value ,C is noted at the beginning , after each addition(1cc) of NaOH ; C value goes on decreases as the H^+ ions in the HCl is replaced by the bigger Na^+ ions ; when all the H^+ ions are replaced by Na^+ ions , further addition of NaOH increases the value of C as it NaOH is a strong electrolyte.

Then C values are plotted against volume of NaOH added; two straight lines are obtained as shown in the fig. ; the point of intersection gives the end point which give the volume of NaOH required to neutralize the HCl taken in the beaker. From these values , the strength of HCl and the amount of HCl present in the whole volume of the given solution can be calculated.

****

BCH101
ENGINEERING CHEMISTRY- I

UNIT – IV

CORROSION AND CORROSION CONTROL

Corrosion can be defined as the gradual destruction of materials, (usually metals), by the chemical or electrochemical reaction with its environment. **Corrosion** is the breakdown of materials due to reactions. It is usually oxidation with air molecules and often in the presence of water. Corrosion also occurs when an acidic or basic material touches another material. When a material corrodes, it changes and becomes weaker. Materials that corrode include metal, plastic, and wood. Also, corrosion is a form of erosion.

One form of high temperature corrosion can lead to the formation of compacted oxide layer glazes, which under certain circumstances reduces wear.Iron corrosion is called rusting.

Corrosion is a natural process, which converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical and/or electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and stopping corrosion.

In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen or sulfur. Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal, and results in a distinctive orange colouration. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term "degradation" is more common. Corrosion degrades the useful properties of materials and structures including strength, and permeability to liquids and gases.

PILLING –BEDWORTH RULE

According to this rule if the volume of the oxide film formed is at least as large as the volume of the metal consumed , the oxide layer is protective or nonporous ; on the other hand , if the volume of the oxide is less than the volume of the metal consumed , the layer will be porous or non-protective

The **Pilling–Bedworth ratio (P–B ratio)**, in corrosion of metals, is the ratio of the volume of the elementary cell of a metal oxide to the volume of the elementary cell of the corresponding metal (from which the oxide is created).On the basis of the P–B ratio, it can be judged if the metal is likely to passivate in dry air by creation of a protective oxide layer.

MECHANISM OF CORROSION

[1] Chemical Corrosion

Mechanism of chemical or dry Corrosion :
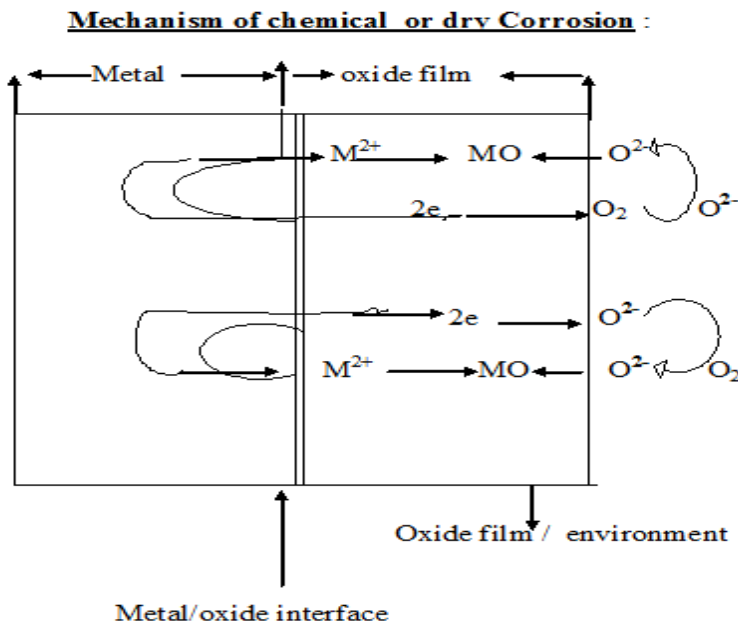
1. Chemical corrosion simply involves reaction between chemicals and materials ; it occurs due to the attack of the metal surfaces by atmospheric gases such as oxygen , nitrogen , hydrogen sulphide ,sulphurdioxide , etc.,
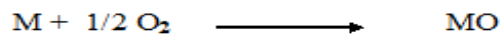
i) At the surface of the metal oxidation occurs resulting formation of M^{2+} ;

$$M \longrightarrow M^{2+}$$

ii) O_2 changes to O^{2-} due to transfer of e s from metal ,
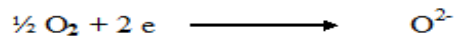
$$\tfrac{1}{2} O_2 + 2 e \longrightarrow O^{2-}$$

iii) M^{2+} **and** O^{2-} react to form metal oxide film on the surface .

$$M + 1/2 O_2 \longrightarrow MO$$

iii) M^{2+} **and** O^{2-} react to form metal oxide film on the surface .

$$M + 1/2 O_2 \quad MO \longrightarrow$$

Once the metal surface is converted to a monolayer of metal oxide , the metal ion diffuses outward through metal oxide film for further corrosion to occur. Thus the growth of oxide film commences perpendicular to the the metal. Surface .

If the oxide layer formed is non-porous &non-volatile ,it stops further O2 attack through diffusion. Such a film behaves as a protective coating; but if it is porous and volatile , further corrosion occurs by diffusion or direct of oxygen in its ionic form with metal ion.
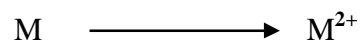
[2] Mechanism of Electro chemical or wet Corrosion:

This type of corrosion occurs under the following conditions :

1. When two dissimilar metals are in contact with each other in the presence of moisture or an aqueous solution.
2. When a metal is exposed to different concentration of O_2 or electrolyte.

Under the above conditions, one part of the metal becomes anode and the another part becomes cathode;
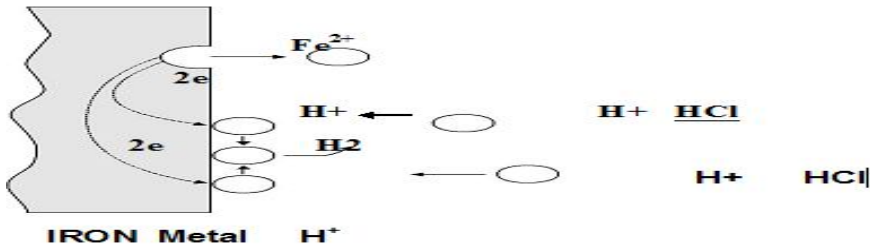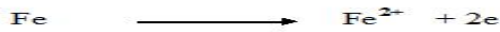
i) **At anode :**

Metal oxidizes to M^{2+}

$$M \longrightarrow M^{2+}$$

ii) **At cathode :**

Here reduction occurs depending on the nature of corrosive environment:

Mechanism :

IRON Metal   H⁺

When Fe metal contacts with acid like HCl , H₂ evolution occurs.

<u>At anode :</u>

$$Fe \longrightarrow Fe^{2+} + 2e$$

<u>At cathode :</u>

The liberated e s flow from anode to cathode where H⁺ ions get reduced;

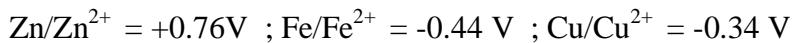$$2H^+ + 2e \longrightarrow H_2$$
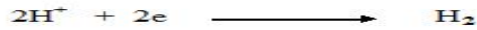
GALVANIC CORROSION.

This is one of the Two types of electrochemical corrosion. This type of corrosion occurs when two different metals are in contact with each other in the presence of an aqueous solution or moisture.

Her , more active metal (with more positive oxidation potential) acts as anode and less active metal (with less positive oxidation potential) acts as cathode.

Zn	Fe

Fe	Cu

We know ,

$Zn/Zn^{2+} = +0.76V$; $Fe/Fe^{2+} = -0.44$ V ; $Cu/Cu^{2+} = -0.34$ V
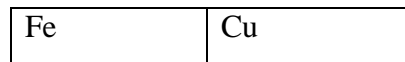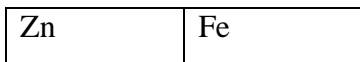
So , in the Zn – Fe couple . since Zn is more active than Fe , Zn acts as anode and undergoes corrosion and Fe acts as cathode;

But in the Fe – Cu couple , since Fe is more active than Cu , Fe acts as anode and undergoes corrosion and Cu acts as cathode.

Ex. Steel screw in a brass material

Here due to galvanic corrosion , iron having more oxidation potential than brass undergoes corrosion ;

Galvanic corrosion can be avoided by having bolt and nut made by the same metal.

Prevention : it can be prevented by providing insulating material between the two metals.

DIFFERENTIAL AERATION CORROSION.

This is one of the Two types of electrochemical corrosion. This type of corrosion occurs when the metal is exposed to varying concentration of oxygen or any electrolyte on the surface of the metal.
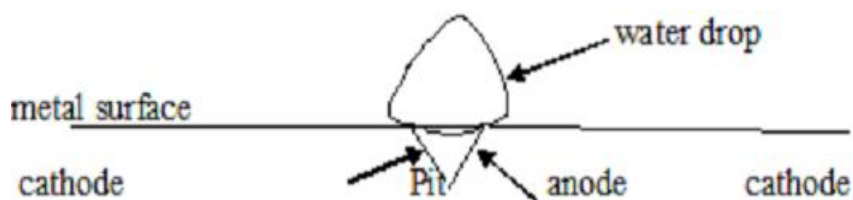
Ex. Metals partially immersed in water

Examples for differential aeration corrosion:

1. Pitting or localized corrosion
2. Crevice corrosion
3. Pipiline corrosion
4. Corrosion on wire fence

Let us discuss one in detail;

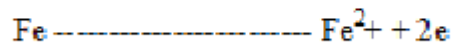**1.Pitting or localized corrosion;**

Pitting is the localized attack , resulting in the formation of a hole around which the metal is relatively unattacked.
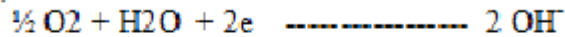
Let us consider a drop of water resting on a metal surface as shown in the fig. the area covered by the drop of water acts as anode due to less oxygen concentration and suffers corrosion. The uncovered area freely exposed to air, acts as cathode due to high oxygen concentration.

Rate of corrosion will be more , when the area of the cathode is larger and the area of anode is smaller. Therefore , more and more material is removed from the same spot. Thus a small hole or pit I formed on the surface of the metal.
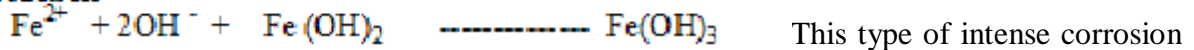
At the anode;

$$Fe \xrightarrow{\hspace{3cm}} Fe^{2+} + 2e$$

At cathode ;

$$\tfrac{1}{2}O_2 + H_2O + 2e \xrightarrow{\hspace{2cm}} 2\ OH^-$$

Net reaction

$$Fe^{2+} + 2OH^- + Fe(OH)_2 \xrightarrow{\hspace{2cm}} Fe(OH)_3$$

This type of intense corrosion is called pitting.

CREVICE CORROSION

Crevice corrosion is a localized form of corrosion occurring in confined spaces (crevices), to which the access of the working fluid from the environment is limited. Formation of a differential aeration cell leads to corrosion inside the crevices. Examples of crevices are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with deposits and under sludge piles.

Crevice corrosion is influenced by the crevice type (metal-metal, metal-nonmetal), crevice geometry (size, surface finish), and metallurgical and environmental factors. The susceptibility to crevice corrosion can be evaluated with ASTM standard procedures. A critical crevice corrosion temperature is commonly used to rank a material's resistance to crevice corrosion.

FACTORS INFLUENCING THE CORROSION.

1.Nature of the metal ;

2.Nature of environment ;

1.Nature of the metal :

a)position in emf series :
when two metals or alloys are in electrical contact , in presence of an electrolyte the more active metal suffers corrosion.

b)relative areas of the anodic and cathodic parts ;
Corrosion is more rapid and severe , if the anodic area is relatively small than the cathodic part.

c) purity of the metal ;
the rate of corrosion increases with increase of the impurities.

d)nature of the corroded products ;
if the corrosion products are porous or volatile , rapid and continuous corrosion takes place.

II. Nature of the environment ;

a) **Temperature:**
The rate of corrosion increases with increase of temperature.

b) **Humidity of air:**
The rate of corrosion increases with increase of humidity.

c) Presence of impurities in atmosphere:
The rate of corrosion increases with increase of impurities , gases likeCO_2,H_2S,SO_2 , and fumes of HCl ,H_2SO_4.

c) **influence of pH :** The rate of corrosion can be reduced by increasing the pH solution.

e) Concentration of O2 ;
when oxygen supply is greater , corrosion rate also increases.

THE ROLE OF THE NATURE OF FILM FORMED ON METAL SURFACE IN THE OXIDATION

Corrosion.
The role of the nature of film formed on metal surface in the oxidation Corrosion can be discussed by "Pilling - Bedworth" rule ;

According to that rule ,

If the volume of the oxide film formed is less than the volume of the metal corroded , the oxide layer is porous and non- protective ;

Ex. The volumes of the oxides of alkali and alkaline earth metals , such as Na , Mg , ca , etc., is less than the volume of the metal consumed. Hence the oxide layer formed is porous and non-protective.

If the volume of the oxide film formed is greater than the volume of the metal corroded , the oxide layer is non-porous and protective ;

Ex. The volumes of the oxides of heavy metals , such as Pb , Sn , etc., is greater than the volume of the metal consumed. Hence the oxide layer formed is non- porous and protective.

CORROSION CONTROL BY
a) Sacrificial anodic protection method
b) Impressed current cathodic protection method

a) Sacrificial anodic protection method

In this method the metal to be protected is connected to more anodic (active) metal by a wire . the more active metal itself gets corroded slowly , while the parent structure is protected. The more active metal used , is called Sacrificial anode. Metals commonly employed as Sacrificial anodes are Mg , Zn , Al ,and their alloys.

Application :

1.ships hull ; 2.marine equipments ; 3. Water tanks

b)Impressed current cathodic protection method.

In this method , an impressed (direct) current is applied in the opposite direction of the corrosion current to nullify it .

In this method , the metal to be protected converted to cathode by connecting to the negative terminal of the battery. The positive terminal of the battery is connected to an inert anode. The inert anodes used for this purpose are graphite ,platinised titanium. The anode is

buried in a "back fill" It is a mixture of gypsum , coke , breeze , sodium sulphate; it provides good electrical contact to anode.

ELECTROPLATING

Electroplating is a process by which the coating metal is deposited on the base metal by passing a direct current through an electrolyte solution containing the soluble salt of the coating metal.

ELECTROLESS PLATING

The surface of the plate is first degreased using organic solvents or alkali followed by acid treatment; then they are dipped in different solutions to activate the surface.

DIFFERENCES BETWEEN ELECTROPLATING AND ELECTROLESS PLATING

S.NO.	ELECTRO PLATING	ELECTROLESS PLATING
1.	It is carried out by passing current	It is carried out By auto catalytic redox reactio
2.	Separate anode is employed	Catalytic surface acts as anode
3.	Anode reaction M --------- $Mn+ + ne$	Anode reaction R --------- $O + ne$
4.	Cathodic reaction $Mn^+ + ne$ ---------- M	Cathodic reaction $Mn^+ + ne$ ---------- M
5.	Not satisfactory for objects with irregular shape.	satisfactory for all objects even with irregular shape.
6.	It is carried out on conducting materials.	It is carried out on conducting , semiconducting (plastics)materials.
7.	Thickness of the plating is $1 – 100\,\mu m$	Thickness of the plating is $1 – 100\,\mu m$

A) ELECTROPLATING OF GOLD OVER COPPER OBJECT

B) ELECTROLESS PLATING OF NICKEL

a) Electroplating of gold over copper object .
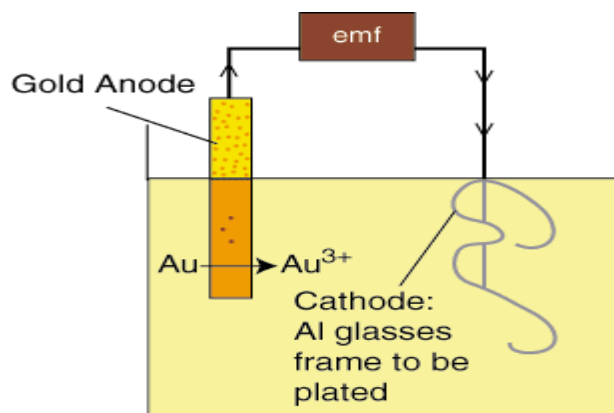
The electroplating is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal.

The base metal to be plated is made cathode of an electrolytic cell and anode is either made of coating metal itself or an inert metal of good electrical conductivity.
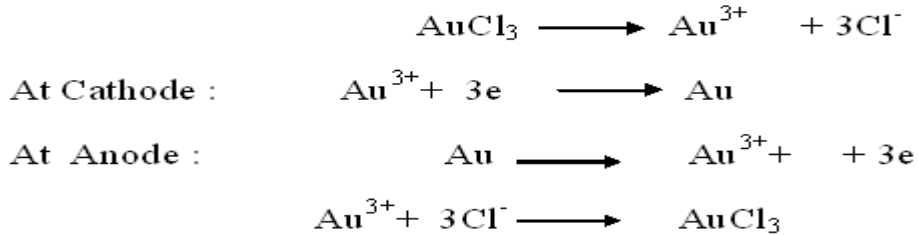
THEORY :

If the anode is made of coating metal itself , the concentration of the electrolyte remains unaffected during electrolysis; since metal ions deposited from solution on cathode , are replaced continuously by the reaction of free negative ions with anode.

PROCESS :

The copper object to be coated is cleaned using dil HCl or H2SO4; then it is made cathode; Au foil is anode ; AuCl3 is the electrolyte; current is passed from battery. Au dissolves in the electrolyte and deposit uniformly on Cu object.

REACTION ;

$$AuCl_3 \longrightarrow Au^{3+} + 3Cl^-$$

At Cathode : $Au^{3+} + 3e \longrightarrow Au$

At Anode : $Au \longrightarrow Au^{3+} + + 3e$

$$Au^{3+} + 3Cl^- \longrightarrow AuCl_3$$

In order to get strong , smooth &adherent deposit , certain additives like gelatin , glue , etc., are added to the bath.

The conditions for a good deposit are :
1. the current density : $1 – 10$ mA / cm^2
2. optimum temperature : 60^0 C
3. low metal ion concentration.

b)   Electroless plating of Nickel

It is the process by the coating metal is deposited on the base metal by passing direct current through an electrolytic solution containing a soluble salt of the coating metal.

It is a technique of depositing a noble metal on an catalytically active surface of the metal to be protected , by using a suitable reducing agent without using electrical energy.

Metal ions + reducing agents ----------- metal + oxidized products.

(deposited)

Step.I ;
Pre treatment and activation of the surface : the surface to be plated is first degreased by using organic solvents or alkali , followed by acid treatment.

Step II ;
Plating bath : this consists of

1. coating solution – $NiCl_2$
2. reducing agent - sodium hypophosphite
3. complexing agent – sodium succinate
4. buffer – sodium acetate
5. optimum ph – 4.5
6. optimum temperature - 93^0C

Step III ;Procedure ;

The pre - treated object is immersed in the plating bath for the required time. During which the following reduction reaction will occur and the Ni gets coated over the object. The reducing agent provides electrons for reduction ,

$$H_2PO_2^- + H2O \longrightarrow H_2PO_3^- + 2H^+ + 2e$$

At cathode : $Ni^{+2} + 2e \longrightarrow Ni$
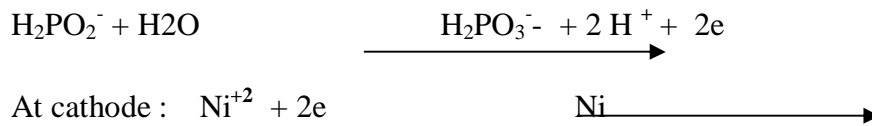
THE CONSTITUENTS OF PAINTS AND THEIRFUNCTIONS.

Paint can be defined as a mixture consisting of a solid pigment or pigments suspended in a medium (mixture of vehicle and thinner) , that when applied to a surface dries to form a hard coating.

THE FUNCTION OF PIGMENT IN A PAINT

Pigments are solid and colour producing substances in the paint. Its functions are

1.it gives colour and opacity to the film

2.also provides strength to the film

3.protects the film by reflecting the destructive UV rays.

THE CONSTITUENTS OF PAINTS AND THEIR FUNCTIONS:

1. **Pigment :**

these are solids and colour producing substances in the paint.

Function :

1. It gives colour and opacity to the film.
2. It also provides the strength to the film.

2.Vehicle or drying oil ;

This is the non- volatile portion of the medium. This is the film forming constituent of the paint.

Function :

1. they form a protective film by the oxidation and polymerization of the oil.
2. They hold the pigment particle together on the metal surface.
3. **Thinner or solvent**

This is a volatile portion of the medium; it easily evaporates after application of a paint.

Function :

1. Reduces the viscosity of the paint
2. Increases the elasticity of the film
3. Increases the penetrating power of the vehicle.
4. **Extender or Filler**

They are white or colourless pigments.

Function :

1. Reduces the cost of the paint.
2. Modifies the shades of the paint
3. Prevents the shrinkage and cracking

5.Driers : They are the substances , used to accelerate the process of drying.

Function ;

1. They act as oxygen – carrier or catalysts
2. Provide oxygen , which is essential for oxidation

6.Plasticisers :

They are chemicals added to the paints to provide elasticity to the film and to prevent the cracking of the film .

7.anti-skinning agents :

These are chemicals added to the paints to prevent gelling and skinning of the paint.

****

BCH101
ENGINEERING CHEMISTRY- I

UNIT – V

NON – CONVENTIONAL ENERGY SOURCES

NUCLEAR FISSION

It can be defined as "the process of splitting of heavier nuclei nucleus into two or more smaller nuclei with simultaneous liberation of large amount of energy." It is always accompanied by two or more neutrons.

NUCLEAR FUSION

It can be defined as "the process of combination of lighter nuclei into heavier nuclei, with simultaneous liberation of large amount of energy. "

ENERGY LOSS IN A NUCLEAR CHAIN REACTION

Some of the neutrons released in the nuclear chain reaction may escape from the surface to the surrounding o may be absorbed by U^{238} present as impurity. This will result in breaking of the chain and the amount of energy released will be less than expected; this less in energy is called Energy loss in a nuclear chain reaction.

(A)NUCLEAR ENERGY CRITICAL MASS .(B) SUPER CRITICAL MASS .

(a)Nuclear Energy Critical mass .

The minimum amount of fissionable material required to continue the nuclear chain reaction is called Critical Mass.

(b) Super Critical mass .

If the amount of fissionable material is more than the Critical Mass , it is called Super Critical mass.

(c) Sub -critical mass:

If the amount of fissionable material is less than the Critical Mass , it is called Sub - Critical mass.

DIFFERENCE BETWEEN NUCLEAR FISSION AND FUSION REACTIONS

S.No.	Nuclear fission	Nuclear fusion
1.	It is a process of breaking a heavier nucleus.	It is a process of combination of lighter nuclei.
2.	Does emits radioactive rays.	Does not emit radioactive rays.
3.	Occurs at ordinary temperature.	Occurs at high temperature; $>10^6$ k
4.	The mass no.& the atomic no. of new elements are lower than that of parent nucleus.	The mass no.& the atomic no. of new elements are lower than that of parent nucleus.
5.	It gives rise to chain reaction.	It doesn't give rise to chain reaction.
6.	Emits neutrons .	Emits positrons .
7.	Can be controlled.	Can't be controlled.

LIGHT WATER NUCLEAR POWER PLANT
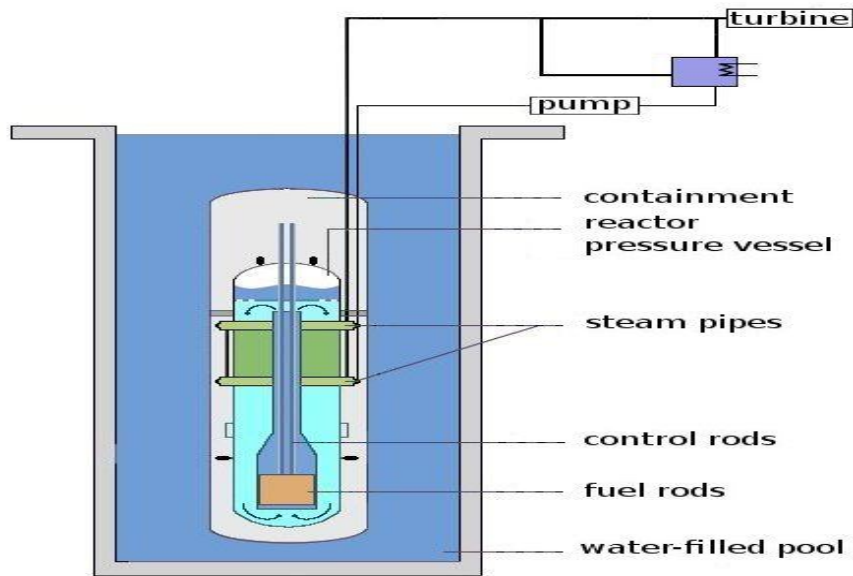
LWNP Plant is the one in which U^{235} fuel rods are submerged in H_2O; here water act as coolant and moderator.

CONTROL ROD

Control rods are usually combined into control rod assemblies — typically 20 rods for a commercial pressurized water reactor assembly — and inserted into guide tubes within a fuel element. A control rod is removed from or inserted into the central core of a nuclear reactor in order to control the number of neutrons which will split further uranium atoms. This in turn affects the thermal power of the reactor, the amount of steam generated, and hence the electricity produced. The control rods are partially removed from the core to allow a chain reaction to occur. The number of control rods inserted and the distance by which they are inserted can be varied to control the reactivity of the reactor.

COOLANT

Nuclear reactor coolant

The light-water reactor also uses ordinary water to keep the reactor cooled. The cooling source, light water, is circulated past the reactor core to absorb the heat that it generates. The heat is carried away from the reactor and is then used to generate steam. Most reactor systems employ a cooling system that is physically separate from the water that will be boiled to produce pressurized steam for the turbines, like the pressurized-water reactor. But in some reactors the water for the steam turbines is boiled directly by the reactor core, for example the boiling-water reactor.

Many other reactors are also light-water cooled, notably the RBMK and some military plutonium-production reactors. These are not regarded as LWRs, as they are moderated by graphite, and as a result their nuclear characteristics are very different. Although the coolant flow rate in commercial PWRs is constant, it is not in nuclear reactors used on U.S. Navyships.

FUEL

Nuclear fuel

The use of ordinary water makes it necessary to do a certain amount of enrichment of the uranium fuel before the necessary criticality of the reactor can be maintained. The light-water reactor uses uranium 235 as a fuel, enriched to approximately 3 percent. Although this is its major fuel, the uranium 238 atoms also contribute to the fission process by converting to plutonium 239; about one-half of which is consumed in the reactor. Light-water reactors are generally refueled every 12 to 18 months, at which time, about 25 percent of the fuel is replaced.

MODERATOR

Neutron moderator

A neutron moderator is a medium which reduces the velocity of fast neutrons, thereby turning them into thermal neutrons capable of sustaining a nuclear chain reaction involving uranium-235. A good neutron moderator is a material full of atoms with light

nuclei which do not easily absorb neutrons. The neutrons strike the nuclei and bounce off. After sufficient impacts, the velocity of the neutron will be comparable to the thermal velocities of the nuclei; this neutron is then called a thermal neutron.

The light-water reactor uses ordinary water, also called light water, as its neutron moderator. The light water absorbs too many neutrons to be used with enriched natural uranium, and therefore uranium enrichment or nuclear reprocessing becomes necessary to operate such reactors, increasing overall costs. This differentiates it from a heavy water reactor, which uses heavy water as a neutron moderator. While ordinary water has some heavy water molecules in it, it is not enough to be important in most applications. In pressurized water reactors the coolant water is used as a moderator by letting the neutrons undergo multiple collisions with light hydrogen atoms in the water, losing speed in the process. This moderating of neutrons will happen more often when the water is denser, because more collisions will occur.

WORKING:-

The fission reaction is controlled by inserting or removing the control rods B^{10} or Cd^{113} from the space between fuel rods.

The heat emitted by fission of U^{235} is absorbed by the coolant; the heated coolant [at 300^0c] then goes to the heat-exchanger containing sea water . The coolant here, transfers heat to sea water, which is converted it into steam; the steam then drives the turbines, generating electricity.

SOLAR ENERGY CONVERSION

Solar energy conversion is the process of conversion of direct sun light into more useful forms. This conversion occurs by two mechanisms:

1. Thermal conversion
2. Photo conversion

1. Thermal conversion:-

It involves absorption of thermal energy in the form of infra-red radiation. Solar energy is an important source for low heat [T< 100 c]which is useful for heating water , building , refrigeration, etc.,

2. Photo – conversion: -

It involves conversion of light energy directly into electrical energy.

Solar cells:-

Photo conversion can be done by Solar cells. Solar cell converts sunlight energy directly into electrical energy; it does not utilize chemical or nuclear reactions to produce electric power.

Principle;-

The basic principle involved in the solar cells is based on the photovoltaic effect. When solar rays fall on a two layer of semi – conductor devices, a potential difference between the two layers is produced. This potential difference causes flow of electrons & produces electricity.

Construction:

Solar cell consists of a p-type semiconductor[such as Si doped with B] & n-type semiconductor [such as Si doped with P].They are in close contact with each other.

Working:-

When solar rays fall on the top layer of p-type semiconductor , the electrons from the valence band get promoted to the conductor band by crossing p-n junction into n-type; thereby potential difference is created between the two layers; this causes flow of electrons
[i.e., an electric current.]

If more solar rays fall on the surface of top layer , the potential difference & hence the current also increases.

Thus when p and n – layers are connectedto an external circuit, electrons flow from n – layer to p-layer, and hence current is generated.

APPLICATIONS OF SOLAR CELLS;

1. for lighting purpose;

2. in boilers to produce hot water;

3. incalculators, electric watches, etc.,

4. Solar energy can be stored in Ni- cd batteries & Pb – acid batteries;

5. To drive vehicles,motors, etc.,

6. used as a source of electricity in space craft& satellites.

7. Solar cells can be used to produce hydrogen by electrolysis of water.

WORKING OF HYDROGEN – OXYGEN FUEL CELL.

Hydrogen – Oxygen fuel cell

It is the simplest and most successful fuel cell. In this , fuel H2 , Oxidizer O2 and the liquid electrolyte are continuously passed through the cell.
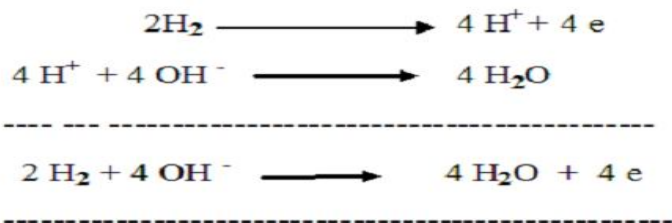
Construction

It consists of two porous carbon electrodes [anode and cathode]. These electrodes are made of compressed carbon containing a small amount of catalyst [Pt, Pd ,Ag]. In between the electrodes , an electrolytic solution , such as 25 % KOH or NaOH is filled. Two electrodes are connected through a voltmeter.

Reactions :

At anode :-

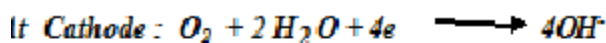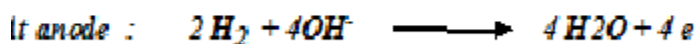H_2 gas , passed through anode , is oxidized to H^+ with liberation of electrons ; these H^+ combine with OH^- to form H_2O .

$$2H_2 \longrightarrow 4H^+ + 4e$$

$$4H^+ + 4OH^- \longrightarrow 4H_2O$$

$$\text{---------------------------------------}$$

$$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e$$

$$\text{---------------------------------------}$$

At cathode :

The electrons produced at anode pass through the external wire to the cathode ; react with O_2 & H_2O to produce OH^-

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

Overall Cell reaction :

It anode : $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e$

It Cathode : $O_2 + 2H_2O + 4e \longrightarrow 4OH^-$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

LEAD – ACID STORAGE BATTERY.

It is a secondary battery which can act as a voltaic cell and as an electrolytic cell. When it acts as a voltaic cell , it supplies electrical energy ; when it is recharged [ie., current is sent in] , the cell operates as an electrolytic cell.

Construction :

It consists of a number of [3 to 6] voltaic cells, connected in series to get 6 to 12 V battery . anode is made of Pb ; cathode is made of PbO2. A number of Pb & PbO2 plates are connected in parallel separately ; the plates are separated from adjacent ones by insulators rubber or glass fibre. The entire set up is immersed in dil. H2SO4 having a density of 1.3 gm/ml. the cell is represented as :

$$Pb / PbSO4 // H2SO4_{(aq.)} / PbO2 / Pb$$
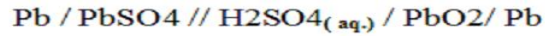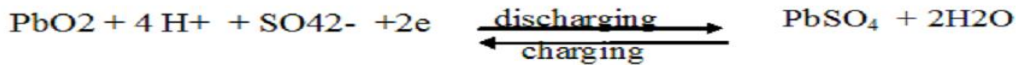
<u>Working (discharging) :</u>

<u>At anode :</u>

Pb is oxidized to Pb2+ which combines with SO_4^{2-} to form insoluble PbSO4

$$Pb + SO_4^{2-}{}_{(aq.)} \xrightleftharpoons[\text{charging}]{\text{discharging}} PbSO4 + 2e$$
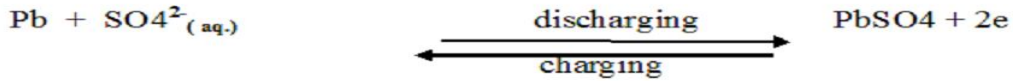
<u>At cathode :</u>

PbO_2 is reduced to Pb^{2+} which combines with SO_4^{2-} to give insoluble $PbSO_4$.

$$PbO2 + 4H+ + SO42- + 2e \xrightleftharpoons[\text{charging}]{\text{discharging}} PbSO_4 + 2H2O$$

Cell reaction during use [discharging]

$$Pb + PbO_2 + 2H2SO_4 \longrightarrow 2PbSO_4 + 2H_2O + energy$$

From these reactions it is clear that $PbSO_4$ is precipitated at both electrodes and H2SO4 is used up. As a result , the concentration of H_2SO_4 decreases & hence the density of H_2SO_4 falls below 1.2 gm/ml; so battery needs recharging.

Recharging:

it is done by sending current in the opposite direction. The electrode reactions get reversed. As a result **Pb** is deposited on anode & PbO_2 on cathode .

NI- CD BATTERY

This is also a rechargeable battery.
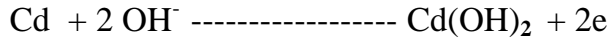
Description :

Nickel – Cadmium cell consists of a Cadmium anode and a metal grid containing a paste of NiO_2 acting as a cathode. The electrolyte is KOH

Cell is represented as : Cd ,$Cd(OH)_2$ // KOH (aq) / NiO_2,Ni

Working :

At anode :

Cadmium is oxidized to Cd^{2+} and further it combines with OH^- to form $Cd(OH)_2$

Cd + 2 OH⁻ ------------------ Cd(OH)$_2$ + 2e

At cathode :

NiO$_2$ + 2 H2O + 2e ------------ Ni(OH)$_2$ + 2 OH⁻

Net cell reaction :

Cd + NiO$_2$ + 2 H2O + 2e ---------- Cd(OH)$_2$ + Ni(OH)$_2$ + energy
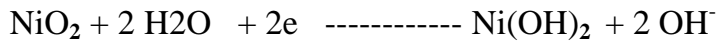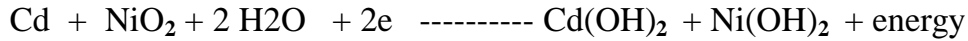
The products Cd(OH)$_2$ and Ni(OH)$_2$ adhere well to the surfaces of the corresponding electrodes.

Recharging:

this is similar to lead storage battery. When the current is passed in the opposite direction, the electrode reaction gets reversed. As a result Cd gets deposited on the anode and NiO$_2$ on the cathode.
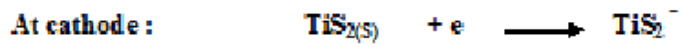
LITHIUM BATTERY

Lithium battery is a solid state battery because instead of liquid or a paste electrolyte , solid electrolyte is used.
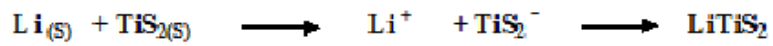
Construction ;

The lithium battery consists of a lithium anode and TiS2 cathode. A solid electrolyte , generally a polymer is packed between the electrolytes. The electrolyte (polymer) permits the passage of ions but not that of electrons

Working (discharging)

When the anode is connected to cathode , lithium ions move from anode to cathode . The anode is elemental lithium, which is the source of the lithium ions and electrons. The cathode is a material capable of receiving the lithium ions and electrons.
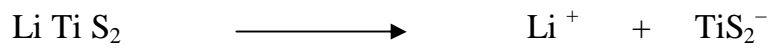
At Anode :

$$Li_{(S)} \longrightarrow Li^+ + e$$

At cathode :

$$TiS_{2(S)} + e \longrightarrow TiS_2^-$$

Overall reaction :

$$Li_{(S)} + TiS_{2(S)} \longrightarrow Li^+ + TiS_2^- \longrightarrow LiTiS_2$$

Recharging the Battery:

The lithium battery can be recharged by supplying an external current , which derives the lithium ions back to the anode . the overall reaction is

$$Li\,Ti\,S_2 \longrightarrow Li^+ + TiS_2^-$$

This cell is rechargeable and produces a cell voltage of 3.0 V

****