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**B.TECH. FIRST YEAR**

## **Handouts**

**ENGINEERING CHEMISTRY**

**(BAS102 / BAS202)**

**Unit - 3**

*(Electrochemistry and Corrosion,  
Chemistry of Engineering Materials)*

**ABES  
ENGINEERING COLLEGE**

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## Unit - 3

### Electrochemistry and Batteries, Corrosion, Chemistry of Engineering Materials

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## Summary

### Electrochemistry and Batteries

• Electrochemistry - It is a branch of physical chemistry which deals with the relationship between electrical and chemical energy.

Electrochemistry is the study of process of transformation of electrical energy into chemical energy and vice-versa.

Standard Hydrogen Electrode (SHE) - It consist of platinum wire coated with platinum black dipped in 1M solution of  $H^+$  ions. Hydrogen gas at 1 atmosphere pressure is continuously passed through it at 298K

Standard Reduction Potential ( $E^\circ$ ) - It is the reduction potential of an electrode with respect to standard hydrogen electrode

Electrochemical Cell - A device for conversion of chemical energy to electrical energy

Electrolytic Cell - A device for conversion of electrical energy to chemical energy.

Galvanic cell - It is a device in which chemical energy from a spontaneous redox reaction is changed into electrical energy.

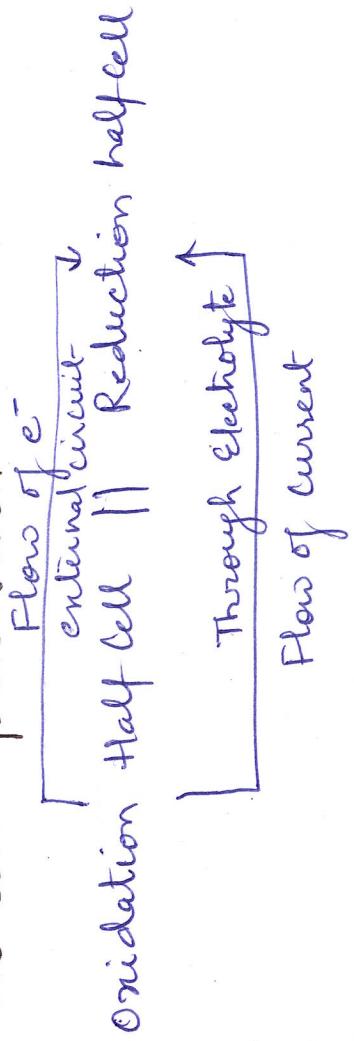
EMF of electrochemical cell - It is the maximum potential difference between two electrodes of a cell

EMF of cell = (Reduction Potential of cathode - Reduction potential of anode)

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

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

Electrochemical cell Representation -



Nernst Equation for the electrode - It gives the effect of electrolyte concentration on electrode potential.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 \frac{RT}{nF} \log \frac{[\text{ap}]}{[\text{ar}]}}{}$$

Electrochemical Series - It is a series in which electrodes are arranged in the increasing order of their reduction electrode potential.

Battery - It is a device, which transforms chemical energy into electrical energy. It is usually group of two or more electric cells connected in series.

Primary Batteries - They are constructed to obtain one continuous discharge.

Secondary Batteries - They are constructed so that they can be recharged after partial or complete discharge

# Chemistry of Engineering Materials

## Cement

Cement - It is a material possessing adhesive and cohesive property and helps in binding materials like brick, sand etc.

Portland Cement - It is also known as "magic powder". It consists of compounds of lime, silica, alumina and iron as primary constituents.

Gypsum - The presence of gypsum in cement retards the speed of initial set, due to the formation of calcium sulphoaluminate by reaction between  $C_3A$  and gypsum.

Fineness - The surface area of fine-ground cement is greater than coarse-ground cement which affects the hydration of cement. The hydration process is more rapid in fine-ground cement.

Soundness - It is the ability of the cement to maintain a stable volume of cement after setting. A sound cement resist cracking and eventually disintegration of cement mass.

Decay of Cement - The cement constituents are susceptible to attack by salt water and acidic solution and undergo deterioration under direct contact and long exposure.

Plaster of Paris - It is hemihydrate of calcium sulphate ( $2CaSO_4 \cdot H_2O$ ).

# UNIT - 3

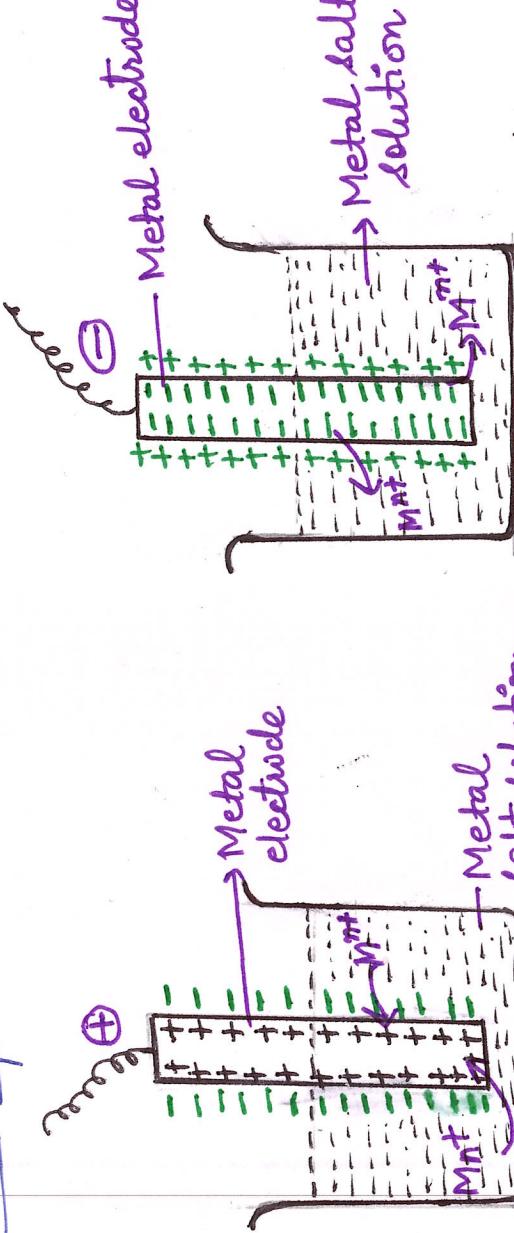
## Electrochemistry and Corrosion

1. Electrochemistry is the branch of chemistry which deals with the interaction between electrical energy and chemical energy.

### Electrode Potential

When a metal is in contact with a 1M solution of its own ions at 25°C, it may either undergo oxidation reaction ( $M \rightarrow M^{n+} + ne^-$ ) or reduction reaction ( $M^{n+} + ne^- \rightarrow M$ ). Due to this, negative or positive charge is developed on the metal, which attracts oppositely charged free ions in the solution.

This leads to the formation of a layer of negative ions or positive ions around the metal electrode. This layer is known as Helmholtz electrical double layer. Due to this, potential difference is set up between the electrode and solution and known as electrode potential.



M<sup>n+</sup> ions from solution enter in the metal leaving behind counter ion in the solution (1)

M<sup>n+</sup> ions moving from electrode to solution leaving free ions on metal electrode

## Measurement of Electrode Potential

### 2. Standard Hydrogen Electrode (SHE)

Electrode Potential is measured with reference to reference electrode, SHE (Standard Hydrogen Electrode). It is done by using Potentiometer which measures the difference between two electrodes.

SHE consists of platinum foil or wire coated with platinum black dipped in 1M solution of  $H^+$  ions.  $H_2$  gas at 1 atmosphere pressure is constantly bubbled through 1 M  $H^+$  ions solution at 298 K. The standard electrode potential of SHE is arbitrarily fixed at zero. SHE serves as reversible electrode.

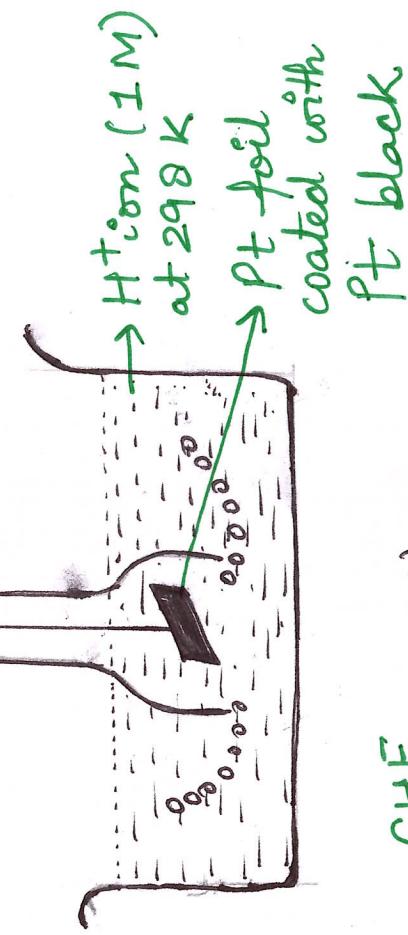
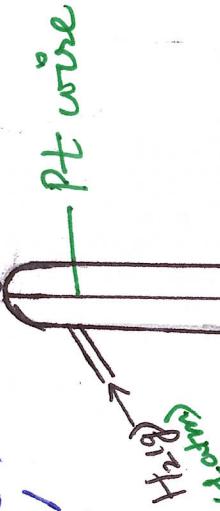
SHE serves as anode as well as cathode depending upon the nature of the another electrode to which it is connected.



Representation of SHE       $\text{Pt}, H_2(g) (1 \text{ atm}) / H^+(\text{aq.}) (1 \text{ M})$

Standard Electrode ( $E^\circ$ )

Potential of SHE = 0 V

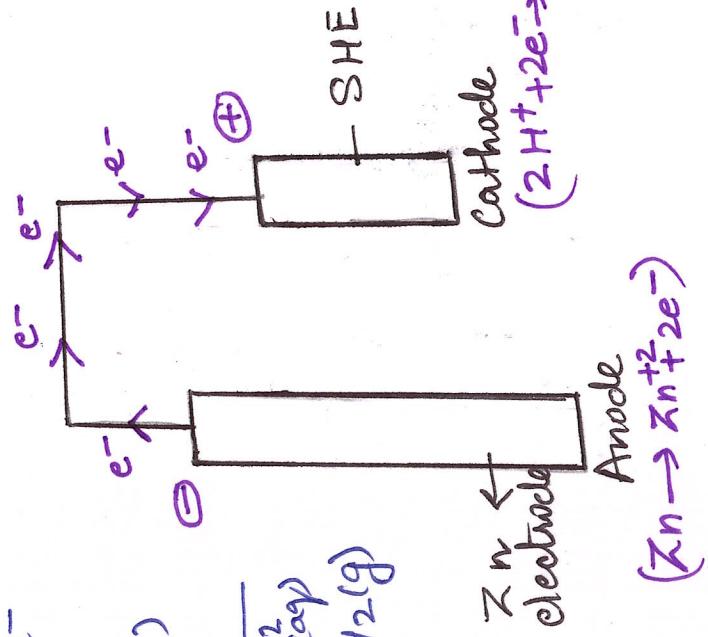


## SHE as Cathode

Anode:  $Zn(s) \rightarrow Zn^{+2}(aq) + 2e^-$   
(oxidation)

Cathode:  $2H^+(aq) + 2e^- \rightarrow H_2(g)$   
(reduction)

Net reaction:  $Zn(s) + 2H^+(aq) \rightarrow Zn^{+2}(aq) + H_2(g)$

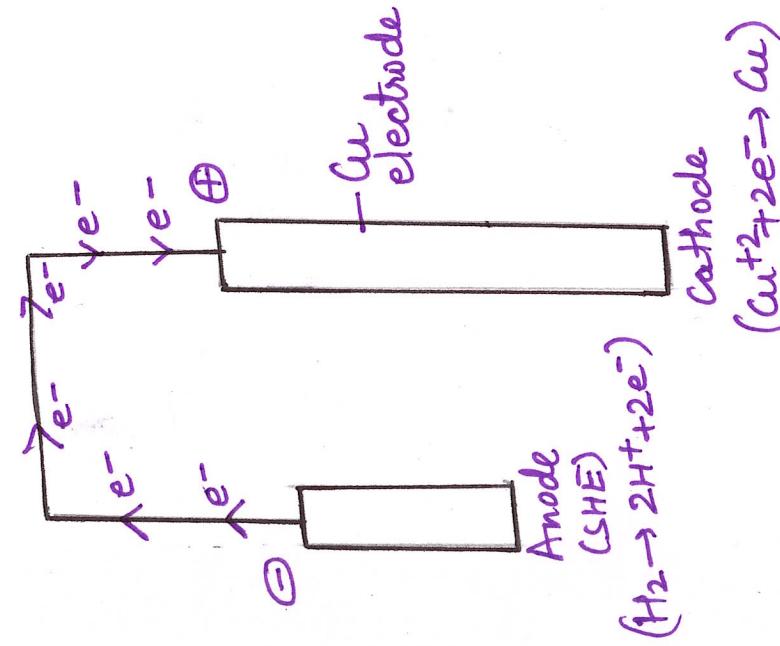


## SHE as Cathode

Anode:  $H_2(g) \rightarrow 2H^+(aq) + 2e^-$   
(oxidation)

Cathode:  $Cu^{+2}(aq) + 2e^- \rightarrow Cu(s)$   
(reduction)

Net Reaction:  $H_2(g) + Cu^{+2}(aq) \rightarrow 2H^+(aq) + Cu(s)$



(3)

### 3. Electrochemical Series

Electrochemical series is the arrangement of electrodes in the increasing order of their standard reduction potential in volts. It is also called as activity series.

Electrode (25 °C)	Standard Reduction Potential of Electrode (V)
$\text{Li}^{\circ} + \text{e}^{-} \rightarrow \text{Li}$	+ 3.05 Volts
$\text{K}^{\circ} + \text{e}^{-} \rightarrow \text{K}$	- 2.93
$\text{Ca}^{+2} + 2\text{e}^{-} \rightarrow \text{Ca}$	- 2.90
$\text{Na}^{\circ} + \text{e}^{-} \rightarrow \text{Na}$	- 2.71
$\text{Mg}^{+2} + 2\text{e}^{-} \rightarrow \text{Mg}$	- 2.37
$\text{Al}^{+3} + 3\text{e}^{-} \rightarrow \text{Al}$	- 1.66
$\text{Zn}^{+2} + 2\text{e}^{-} \rightarrow \text{Zn}$	- 0.76
$\text{Cr}^{+3} + 3\text{e}^{-} \rightarrow \text{Cr}$	- 0.74
$\text{Fe}^{+2} + 2\text{e}^{-} \rightarrow \text{Fe}$	- 0.44
$\text{Ni}^{\circ} + 2\text{e}^{-} \rightarrow \text{Ni}^{\circ}$	- 0.23
$\text{Sn}^{+2} + 2\text{e}^{-} \rightarrow \text{Sn}$	- 0.14
$\text{Pb}^{+2} + 2\text{e}^{-} \rightarrow \text{Pb}$	- 0.13
$2\text{H}^{\circ} + 2\text{e}^{-} \rightarrow \text{H}_2$	0.00
$\text{Cu}^{+2} + 2\text{e}^{-} \rightarrow \text{Cu}$	+ 0.34
$\text{Ag}^{\circ} + \text{e}^{-} \rightarrow \text{Ag}$	+ 0.80
$\text{Pt}^{+4} + 4\text{e}^{-} \rightarrow \text{Pt}$	+ 0.86
$\text{Au}^{\circ} + \text{e}^{-} \rightarrow \text{Au}$	+ 1.69
$\frac{1}{2}\text{F}_2 + \text{e}^{-} \rightarrow \text{F}^{-}$	+ 2.07

(4)

4. Cell is a device used for conversion of electrical energy into chemical energy, or conversion of chemical energy into electrical energy.



Difference between Electrochemical cell and Electrolytic cell

Electrochemical cell

1. It converts chemical energy into electrical energy.

2. The electrodes are made up of different metals.

3. At both electrodes, spontaneous redox reaction takes place.

4. Each electrode is dipped in its electrolytic solution of own ions.

5. Salt bridge is used.

6. Anode is +ve and cathode is -ve.

Electrolytic cell

1. It converts electrical energy into chemical energy.

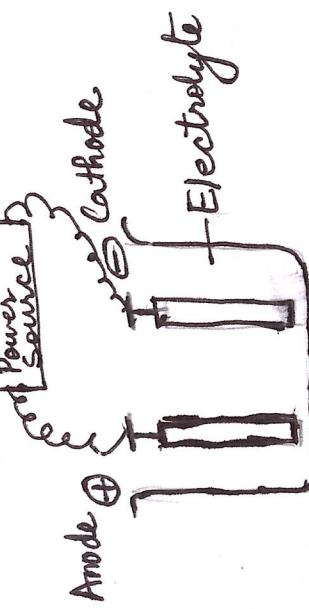
2. The electrodes may be of different metals.

3. At both electrodes, reaction occurs when electrical energy is supplied.

4. Both the electrodes are dipped in same electrolytic solution.

5. Salt bridge is not used.

6. Anode is +ve and cathode is -ve.



(5)

## 4.2 ELECTROCHEMICAL CELL

Electrochemical cell converts the chemical energy into electrical energy. e.g. Galvanic cell

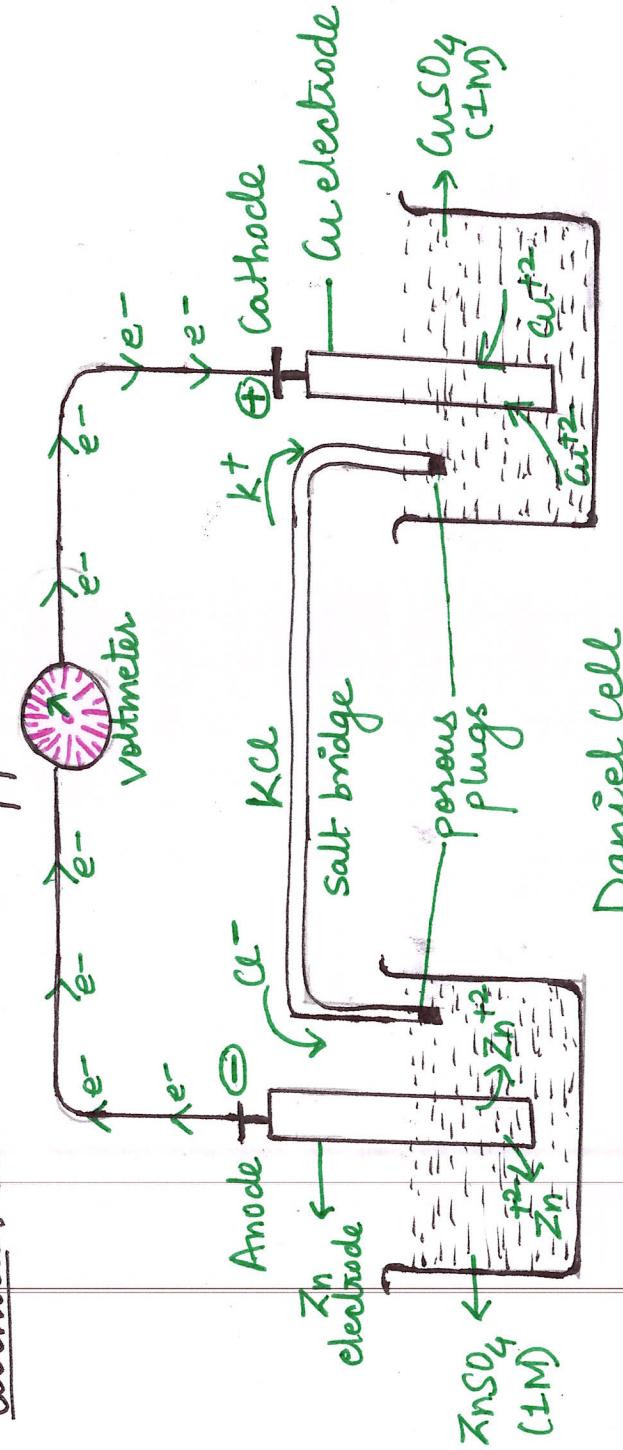
### 4.2.1 Galvanic cell

It is a device in which chemical energy from a spontaneous reaction (redox) is converted into electrical energy that can be used to perform work. Practical example of galvanic cell is Daniel cell.

### Daniel cell

Anode: Zn electrode dipped in 1M  $\text{ZnSO}_4$  solution

Cathode: Cu electrode dipped in 1M  $\text{CuSO}_4$  solution



### Reactions

Anode: (Oxidation)



Cathode: (Reduction)



Net Reaction:  $\text{Zn}(s) + \text{Cu}^{+2}(aq) \longrightarrow \text{Zn}^{+2}(aq) + \text{Cu}(s)$

Representation:  $\text{Zn}(s)/\text{ZnSO}_4(aq)(1M) \parallel \text{CuSO}_4(aq)(1M)/\text{Cu}(s)$

(6)

#### 4.2.2 Function of salt bridge

1. It maintains the electrical neutrality of the two solutions in the half cells.
2. It allows the flow of current by completing the circuit.
3. It prevents the intermixing of solutions of both halves.

(v)

## 5. Nernst Equation

Nernst equation tells us effect of concentration on electrode potential.



$$\Delta G = \Delta G^\circ + RT \ln \left[ \frac{\alpha_{\text{product}}}{\alpha_{\text{reactant}}} \right]$$

$$\Delta G = -nFE \quad \text{and} \quad \Delta G^\circ = -nFE^\circ$$

$$\text{Hence } E = E^\circ - \frac{2.303RT}{nF} \log \left[ \frac{\alpha_{\text{product}}}{\alpha_{\text{reactant}}} \right]$$

$E$  = Electrode potential

$E^\circ$  = Standard electrode potential

$F$  = Faraday constant (96500 C)

$T$  = Temperature (298 K)

$R$  = Gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>)

$\alpha$  = activity of reactants / products

$$E = E^\circ - \frac{0.0591}{n} \log \left[ \frac{\alpha_{\text{product}}}{\alpha_{\text{reactant}}} \right]$$

In dilute solutions, activity may be replaced by molar concentration

For pure solid  $[M(s)] = 1$

$$E = E^\circ - \frac{0.0591}{n} \log \left[ \frac{[M(s)]}{[M^{n+}(aq)]} \right] \quad (8)$$

For a given cell Nernst equation can be written as



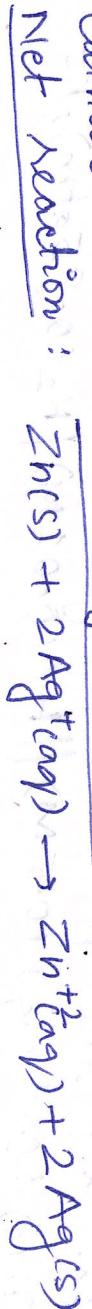
$$E = E^\circ - \frac{2.303RT}{nF} \log \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right) \quad (T=298K)$$

$$\boxed{E = E^\circ - \frac{0.0591}{n} \log \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)}$$

### 5.) Questions on Nernst Equation

- Q. A cell uses Zn and Ag electrodes. Write the cell representation, half cell reactions and net cell reaction. Calculate the EMF of the cell. Given:  $E^\circ_{(Zn^{+2}/Zn)} = -0.76V$  and  $E^\circ_{(Ag^+/Ag)} = 0.80V$ .

Ans Half cell reactions:



Cell representation:  $Zn^{(s)} | Zn^{+2}_{(aq)} || Ag^+_{(aq)} | Ag^{(s)}$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$
$$= 0.8 - (-0.76) = 1.56V$$

(9)

Q2 Calculate the emf of the given cell



$$E^\circ_{\text{cell}} = 1.54\text{V}$$

Answer Cell Reaction:  $\text{Zn(s)} + 2\text{Ag}^{+}(\text{aq}) \rightarrow \text{Zn}^{+2}(\text{aq}) + 2\text{Ag(s)}$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{+2}]}{[\text{Ag}^+]^2}$$

$$E_{\text{cell}} = 1.54 - \frac{0.0591}{2} \log \frac{[0.2]}{[0.002]^2} = 1.401\text{V}$$

Q3 A Zinc rod is placed in 0.1 M solution of  $\text{ZnSO}_4$  at  $25^\circ\text{C}$ . Calculate the potential of electrode at this temp. assuming 96% dissociation of  $\text{ZnSO}_4$ .  $E^\circ(\text{Zn}^{+2}/\text{Zn}) = -0.76\text{V}$ .

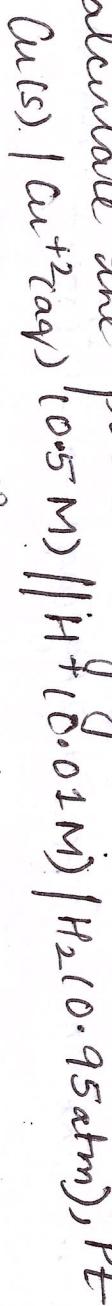
Answer  $\text{Zn}^{+2} + 2e^- \rightarrow \text{Zn(s)}$

$$[\text{Zn}^{+2}] = \frac{96}{100} \times 0.1 = 96 \times 10^{-3}\text{M}$$

$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn}^{+2}]}{[\text{Zn}^{+2}]^2} = -0.76 - \frac{0.0591}{2} \log \frac{1}{[96 \times 10^{-3}]}$$

$$E = -0.79\text{V}$$

Q4 calculate the potential of given cell at  $25^\circ\text{C}$ .



$$E^\circ_{\text{Anode}} = 0.34\text{V}$$

$$E^\circ_{\text{cathode}} = 0\text{V}$$

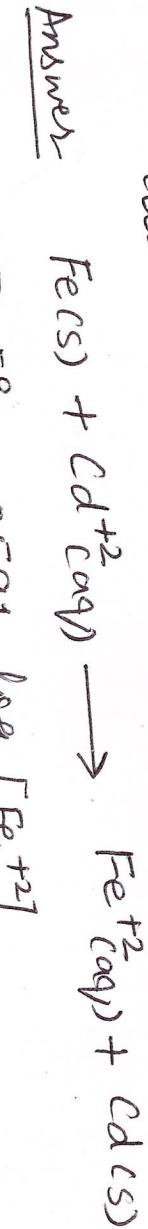
Answer  $\text{Cu(s)} + 2\text{H}^{+}(\text{aq}) \rightarrow \text{Cu}^{+2}(\text{aq}) + \text{H}_2(\text{g})$

$$E = E^\circ - \frac{0.0591}{2} \log \frac{[(\text{Cu}^{+2}) \cdot \text{H}_2]}{[H^+]^2} = (0 - 0.34) - \frac{0.0591}{2} \log \frac{[(0.5)(0.95)]}{[(0.01)]^2}$$

$$E_{\text{cell}} = -0.449\text{V}$$

(10)

B5: Determine the concentration of  $\text{Cd}^{+2}$  ions in the given cell:  $\text{Fe}, \text{Fe}^{+2}(0.1\text{M})/\text{Cd}^{+2}(x\text{M}), \text{Cd}$  at  $25^\circ\text{C}$ .  
 $E_{\text{cell}} = -0.02\text{V}$        $E^{\circ}_{\text{cell}} = 0.04\text{V}$



$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{+2}]}{[\text{Cd}^{+2}]}$$

$$-0.02 = 0.04 - \frac{0.0591}{2} \log \frac{(0.1)}{x}$$

$$x = 0.00093 \text{ or } x = 0.001\text{M}$$

## 5.2 Applications of Nernst Equation

1. Nernst Equation is used to determine the potential of electrodes.
2. Used to determine the potential of cell.
3. Used to determine the ionic concentrations.
4. Used to determine the pH of solutions.
5. Used to determine the solubility of sparingly soluble salts.
6. Used to determine the feasibility of cell reaction.
7. Used to determine the valency of an ion involved in cell reaction.

## BATTERY

Battery is a device which converts chemical energy into electrical energy. The term battery is applied to two or more combination of cells connected in series. The battery act as portable source of energy.

Batteries consist of two types of cells

- 1) Primary cell
- 2) Secondary cell

### 6.1 Primary cell

In primary cell, there is fixed amount of chemical energy is stored and once it is discharged, cannot be charged again. Eg: Dry cell (Leclanche cell) and Mercury cell.

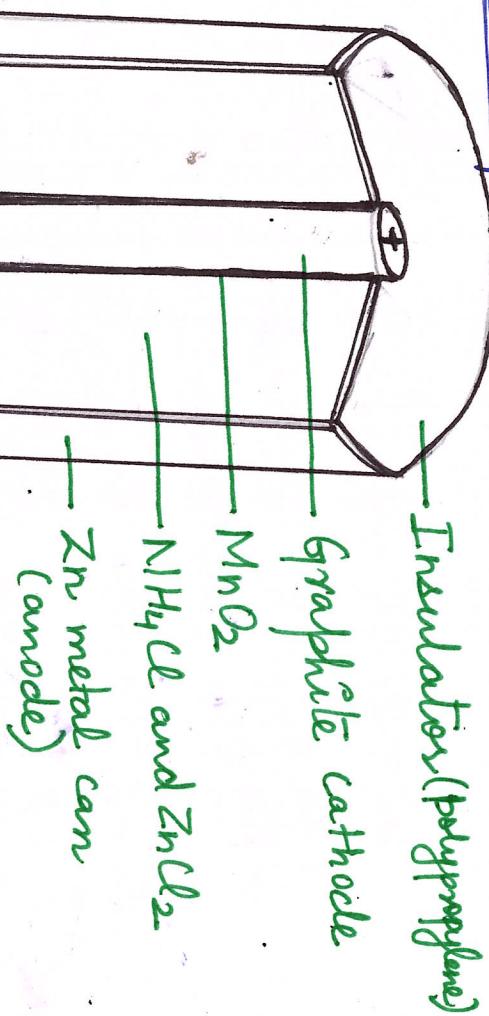
### Dry cell or Leclanche cell

Anode: Zn anode in the form of container

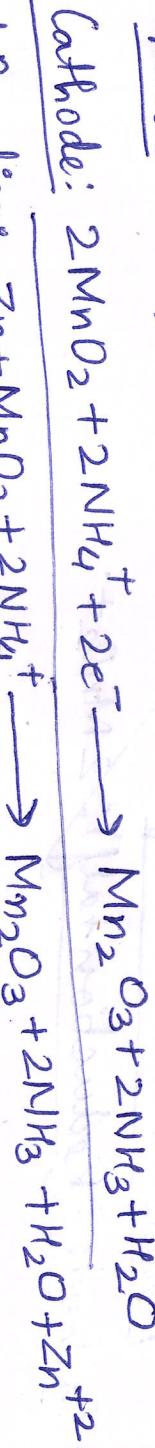
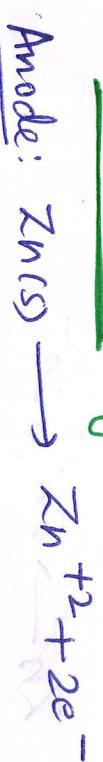
Cathode: Graphite rod surrounded by  $MnO_2$

Electrolyte: moist paste of  $NH_4Cl$  and  $ZnCl_2$

Voltage: Dry cell couple produce about 1.5 Volts

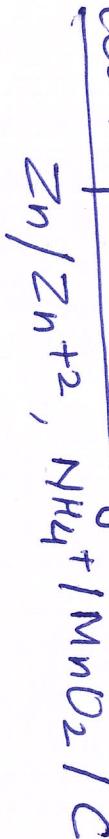


## Reactions of Leclanche cell



The  $NH_3$  which is liberated reacts with  $Zn^{+2}$  from  $ZnCl_2$  to form the complex  $[Zn(NH_3)_2]Cl_2(s)$ .

### Cell Representation of Leclanche cell



## b2 Secondary Cell or Secondary Battery

Secondary battery is the one which can be

recharged again. It has longer life.

Example Lead Acid storage battery

## Lead-Acid Storage Battery

It works both as electrochemical cell and electrolytic cell. When it works as voltaic cell it converts electrical energy into chemical energy. This is charging process of battery. It works as electrochemical

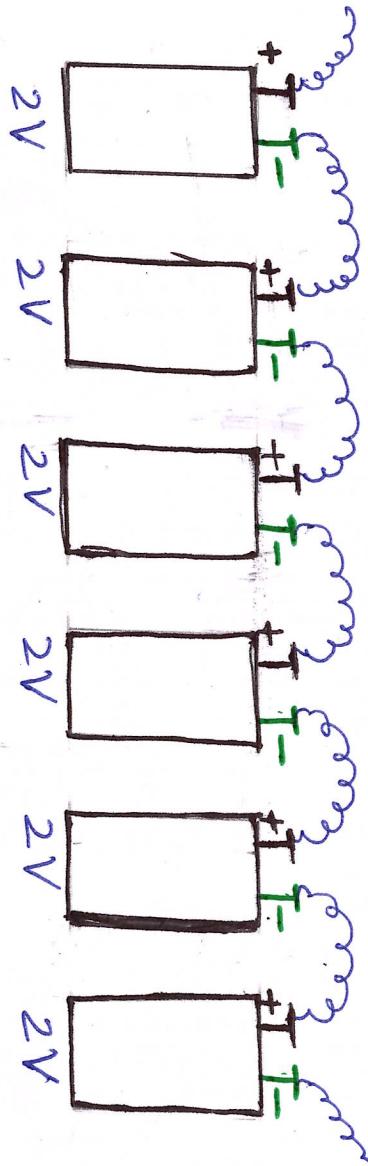
During discharging it works as electrochemical cell and converts chemical energy into electrical energy.

Anode: Spongy lead

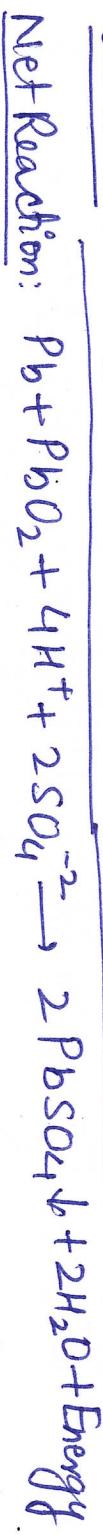
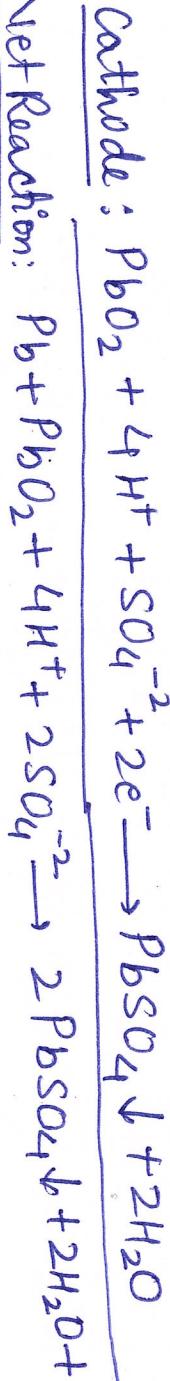
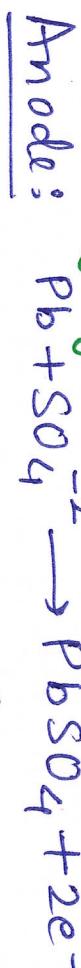
Cathode: Lead-antimony alloy coated with  $PbO_2$

Electrolyte: 21.4% solution of  $H_2SO_4$ .  
(specific gravity 1.15 at  $25^\circ C$ )

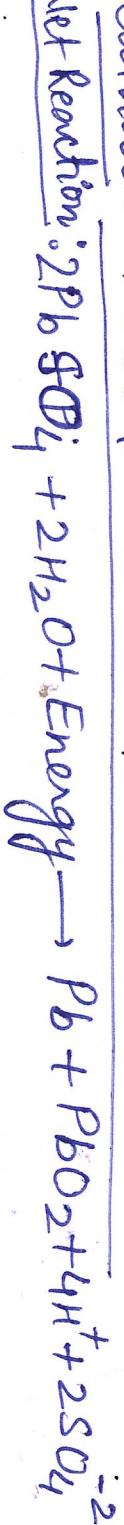
Voltage of battery : 6 cells of 2 V each connected in series  
Total voltage = 12 V



### Discharging Reactions



### Charging Reactions



## 7. Thermodynamic function of cell

Gibb's Free Energy change  $\Delta G = -nFE$

Enthalpy change of reaction  $\Delta H = \Delta G + T\Delta S$

Entropy change of reaction  $\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$

- Q1 For a Weston cell, emf is 1.018 V at 293 K. Temperature coefficient per cell is  $-4 \times 10^{-5} \text{ V K}^{-1}$ . Calculate  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  for the cell reaction. ( $n=2$ )

$$\text{Ans: } \Delta G = -nFE = -2 \times 96500 \times 1.018 = -1.964 \times 10^5 \text{ J}$$

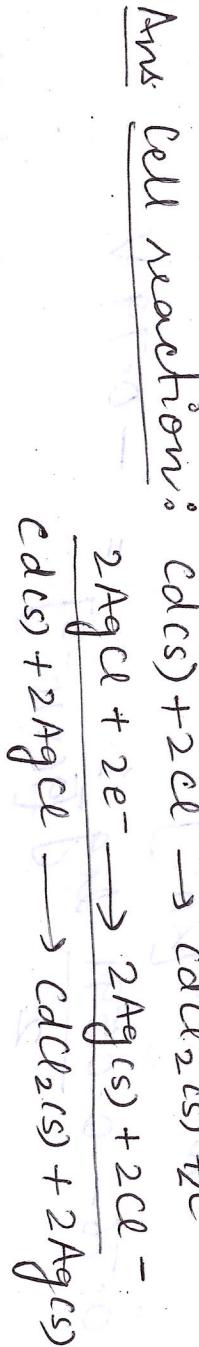
$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P = 2 \times 96500 \times (-4 \times 10^{-5}) = -7.72 \text{ JK}^{-1}$$

$$\Delta H = -nFE + TnF\left(\frac{\partial E}{\partial T}\right)_P$$

$$= -2 \times 96500 \times 1.018 + 293 \times 2 \times 96500 \times -4 \times 10^{-5}$$

$$= -1.99 \times 10^5 \text{ J}$$

- Q2 For a cell:  $\text{Cd}/\text{CdCl}_2 \cdot 2\text{H}_2\text{O}/\text{AgCl(s)}/\text{Ag}$ . Emf at 15°C is 0.67531 V. Temperature coefficient is  $0.00065 \text{ V deg}^{-1}$ . Calculate  $\Delta G$ ,  $\Delta S$ ,  $\Delta H$  if the process is carried out reversibly.



$$\Delta G = -nFE = -2 \times 96500 \times 0.67531 = -130.335 \text{ kJ}$$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P = 2 \times 96500 \times 0.00065 = 125.45 \text{ JK}^{-1}$$

$$\Delta H = \Delta G + T\Delta S = -130.335 \text{ kJ} + 280 \times 125.45 \text{ JK}^{-1}$$

$$= -166.465 \text{ kJ} \quad (15)$$

Q2 Calculate the emf of cell  $Zn(s) \mid Zn^{+2}(0.2\text{M}) \parallel Ag^+(0.002\text{M}) \mid Ag(s)$ . Write the cell reaction.  $E_{cell}^\circ = 1.54\text{V}$

Ans: Net cell reaction:  $Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{+2}(aq) + 2Ag(s)$

(i) Reaction:

$$(ii) E = E_{cell}^\circ - \frac{0.0591}{n} \log \frac{[Zn^{+2}]^{2+}}{[Ag^{+}]^2}$$

$$= 1.54 - \frac{0.0591}{2} \log \frac{[0.2]}{[0.002]^2} = 1.401\text{V}$$

Q3 A zinc rod is placed in 0.1M solution of  $ZnSO_4$  at  $25^\circ\text{C}$ . Calculate the potential of electrode at this temperature, assuming 96% dissociation of  $ZnSO_4$  and  $E_{(Zn^{+2}/Zn)}^\circ = -0.76\text{V}$ .

Ans: Concentration of  $Zn^{+2}$  ions =  $\frac{96}{100} \times 0.1 = 96 \times 10^{-3}\text{M}$



$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[Zn^{+2}]}$$

$$E = -0.76 - \frac{0.0591}{2} \log \frac{1}{[96 \times 10^{-3}]} = -0.79\text{V}$$

Q4 Predict the spontaneity of cell reaction with the help of standard potential values.

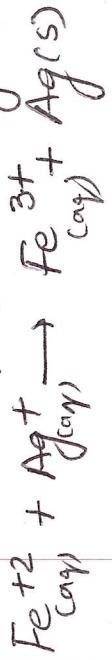
a)  $Fe + 2H^+ \rightarrow Fe^{+2} + H_2$   $E_{(Fe^{+2}/Fe)}^\circ = -0.44\text{V}$

$$E_{cell} = E_{cathode}^\circ - E_{anode}^\circ$$

$$= 0 - (-0.44) = 0.44\text{V}$$

Cell potential is positive, hence reaction is spontaneous.

Q3 Calculate  $\Delta G^\circ$  for the given cell reaction



$$E^\circ_{Fe^{+3}/Fe^{+2}} = 0.77V$$

$$E^\circ_{Ag^+/Ag} = 0.80V$$

Ans.  $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$$E^\circ_{cell} = E^\circ_{(Ag^+/Ag)} - E^\circ_{(Fe^{+3}/Fe^{+2})}$$

$$E^\circ_{cell} = 0.80 - 0.77 = 0.03V$$

$$\Delta G^\circ = -nFE^\circ = -1 \times 96500 \times 0.03$$

$$\boxed{\Delta G^\circ = -2895J}$$

Q4. Calculate  $\Delta G$ ,  $\Delta S$  and  $\Delta H$  for the given cell at 25°C.  
Temperature coefficient is  $1.74 \times 10^{-4} \text{ J K}^{-1}$ . Voltage  
of cell 0.9647 V.



Ans. Cell reaction:  $Pb(s) + Hg_2SO_4 \rightarrow PbSO_4(s) + 2Hg(l)$ .

$$\Delta G_{cell} = -nFE^\circ = -2 \times 96500 \times 0.9647 = \frac{-1.86 \times 10^5}{186 \text{ K}}$$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P = \frac{2 \times 96500 \times 1.74 \times 10^{-4}}{335820 \times 10^{-5} \text{ J/K}} = \frac{= 33582 \text{ J/K}}{3.3582 \text{ J/K}}$$

$$\Delta H = \Delta G + T\Delta S = -186 \text{ KJ} + 298 \times \frac{3.3582}{3.3582} \text{ KJ} = -176 \text{ KJ}$$

(17)

## CORROSION

8. The word corrosion is derived from a latin word 'corrodere'. It is defined as : "

"The destruction or deterioration and consequent loss of metals or alloys through unwanted chemical or electrochemical attack by the surrounding environment."

The primary factors that initiate corrosion on metals are :-

(a) Atmospheric air (b) Water and (c) conducting surface of the metal.

Examples - (1) Rusting of iron (Hydrated Ferric Oxide  $Fe_2O_3 \cdot nH_2O$ ,  
(Reddish-brown scales)

(2) Corrosion of Copper (Basic cupric carbonate)  
 $CuCO_3 + Cu(OH)_2$   
Green-Scales

(3) Fogging of Nickel

- Father of modern Science of Corrosion -

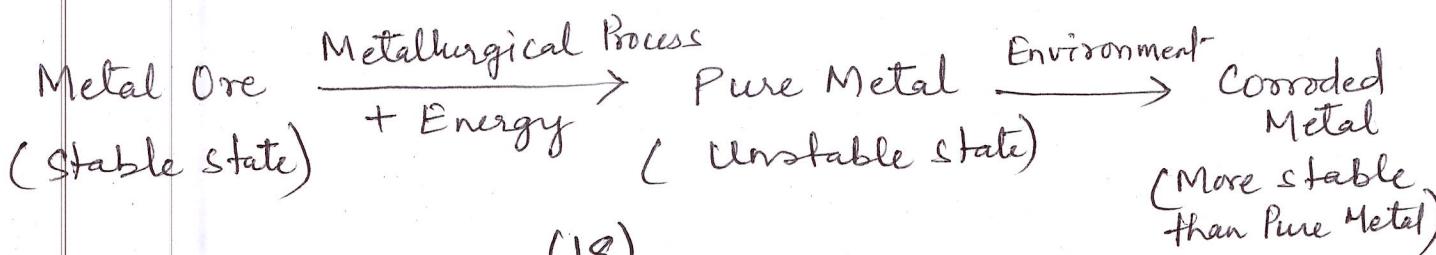
'Wick Richardson Evans'

9. Cause of Corrosion -

Metal exist in nature as carbonates, sulphates & sulphides (Ore) which is thermodynamically stable.

Though during extraction of pure metal from ore through metallurgical process huge amount of energy is required.

This makes the pure metal thermodynamically unstable and thus metal starts interacting with environment to attain stable state.



(18)

## 10. Units of Corrosion

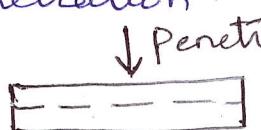
Corrosion rate is expressed in :

- a) Mile per year (mpy) - It is defined as miles of metal corroded by environment in one year.

$$1 \text{ mil} = \frac{1}{1000} \text{ inch}$$

It gives corrosion rate in terms of penetration.

$$\boxed{\text{mpy} = \frac{534 W}{D A T}}$$



Here,  $W$  = weight loss in milligram

$D$  = Density of metal / alloy in  $\text{gm/cm}^3$

$A$  = Area in square inch

$T$  = Time in hour

- b) Milligram per decimeter square per day (mgdd) -

It is defined as milligrams of metal lost from a sample of one decimeter square area per day. ( $\text{mg/dm}^2/\text{day}$ )

## 11. Types of Corrosion

Corrosion of metal occurs by attack of corrosive environment on metal either by :

- (1) Chemical attack or Dry Corrosion
- (2) Electrochemical attack or Wet Corrosion.

### 11.1(1) Chemical or Dry Corrosion

It occurs when the metal surface is in direct chemical interaction with the atmospheric gases or anhydrous liquid in absence of moisture or electrolyte and at elevated temperature.

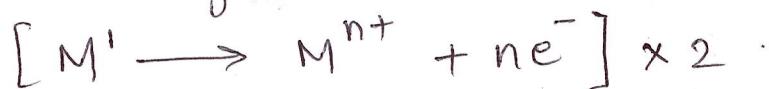
Dry corrosion can be of following types :-

- (a) Corrosion by  $O_2$  or Oxidation corrosion
- (b) Corrosion by other gases ( $H_2S$ ,  $N_2$ ,  $SO_2$ , Halogen etc)

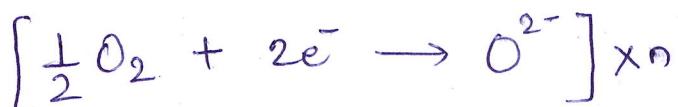
#### (a) Mechanism of Oxidation Corrosion

According to Wagner's theory Oxidation corrosion may be summarized as ;

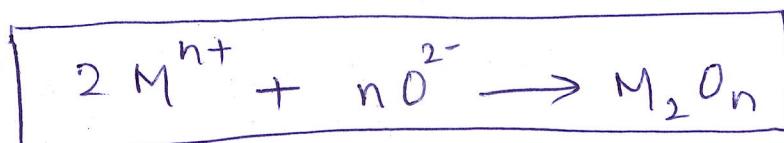
Anode - Oxidation of metal takes place



Cathode - Electrons from anode is transported to cathode and combined with the oxidant



Net Reaction - Formation of metal oxide by direct chemical interaction



## 11.(2) Electrochemical or Wet corrosion

It occurs when the transfer of electron from the anodic part of metal towards the cathodic part takes place through the conductive medium.

Wet corrosion involves electrochemical attack on metals in aqueous environment.

Mechanism of Electrochemical Corrosion : It involves

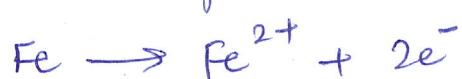
- Formation of different anodic and cathodic parts, between which current flows through conducting medium.
- Oxidation occurs at anodic area, which generates metallic ions ( $M^{n+}$ ) at anode
- Electrons released at anode are absorbed at cathode, which generates non-metallic ions ( $OH^-$  or  $O^{2-}$ ) at cathodic area
- Diffusion of metallic and nonmetallic ions towards each other through conducting medium results in formation of corrosion product somewhere between anodic and cathodic area.

The electrons released at the anode area are conducted to the cathode and shows following reactions:

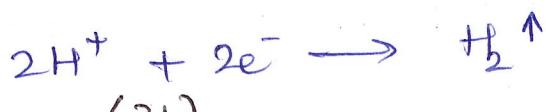
- Evolution of hydrogen
  - Absorption of Oxygen
- (ii) Evolution of Hydrogen - (In absence of Oxygen)

Let's consider the metal Iron (Fe)

Anode - Oxidation of Metal takes place



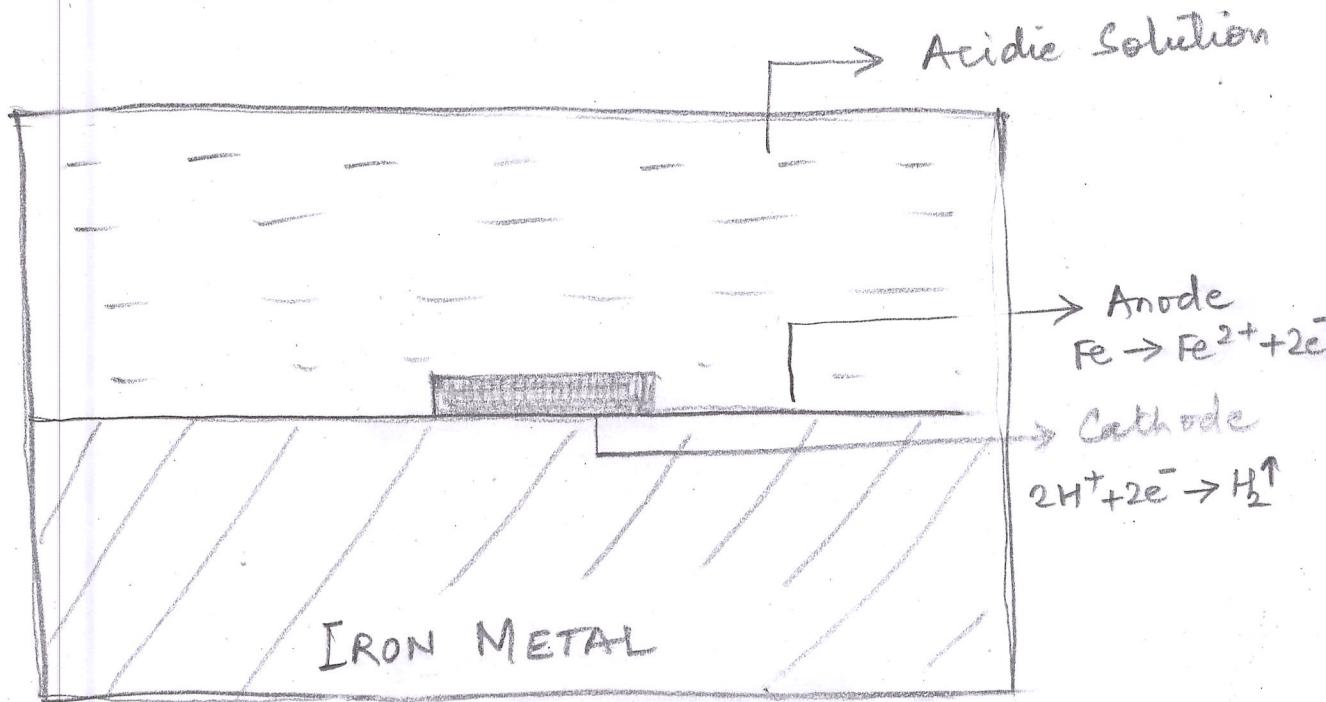
Cathode - (a) in acidic medium (Anode Area)  $\rightarrow$  (Cathode Area)



(b) In neutral or alkaline medium



Net Overall Reaction in acidic Medium



(ii) Absorption of Oxygen - (In presence of dissolved Oxygen)

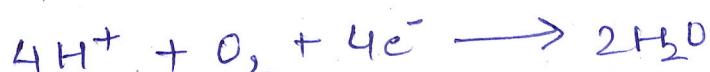
Usually metal surface is covered with thin oxide layer and when this oxide layer is broken, the bare surface of metal gets in contact with environment and acts as anode while remaining area acts as cathode.

Let's consider a metal Iron (Fe)

Anode - Oxidation of metal takes place



Cathode - (a) In acidic medium

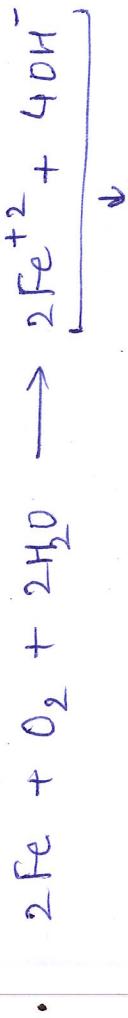


(b) In neutral or alkaline medium:



(Anode Area  
Cathode Area)

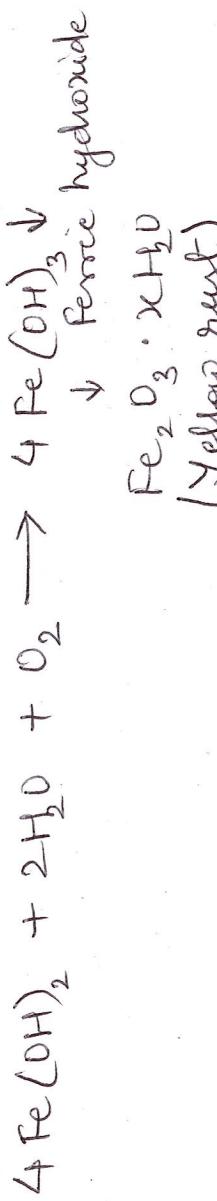
Net Overall Reaction in alkaline medium



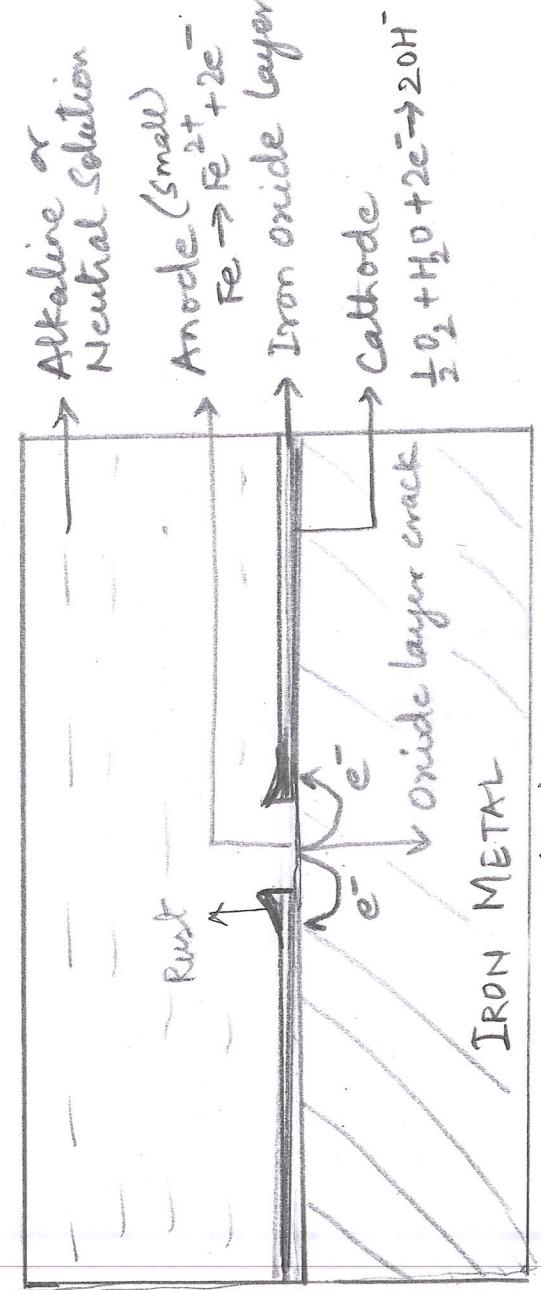
Ferrous hydroxide is deposited near to cathode because  $\text{Fe}^{2+}$  (smaller in size) diffuse faster than  $\text{OH}^-$  (larger in size)

→ Depending on the availability of Oxygen Two types of corrosion products are formed -

(i) In excess supply of Oxygen  $\text{Fe}^{2+}$  Ferrous hydroxide is easily oxidised into Ferric hydroxide.



(ii) In Limited supply of Oxygen :- Black magnetite ( $\text{Fe}_3\text{O}_4$ ) or Ferro ferric oxide is formed



## 12. Numerical on Rusting of Iron -

Numerical 1 - How much rust ( $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) will be formed, when 50 kg of iron have completely rusted away?

Solution 1 - We know, atomic weights of:

$$\text{Fe} = 56, \text{ O} = 16 \text{ and H} = 1$$

So, the molecular weight of rust

$$\begin{aligned}\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} &= (2 \times 56) + (3 \times 16) + 3(2 \times 1 + 16) \\ &= 102 + 48 + 3(2 + 16) \\ &= 102 + 48 + 54 \\ &= 214 \text{ gm/mole}\end{aligned}$$

Each  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  has 2 Fe atoms or 112 g iron.

Since 214 gm of rust contains = 112 g iron  
 $\therefore$  112 gm of iron produces = 214 gm rust

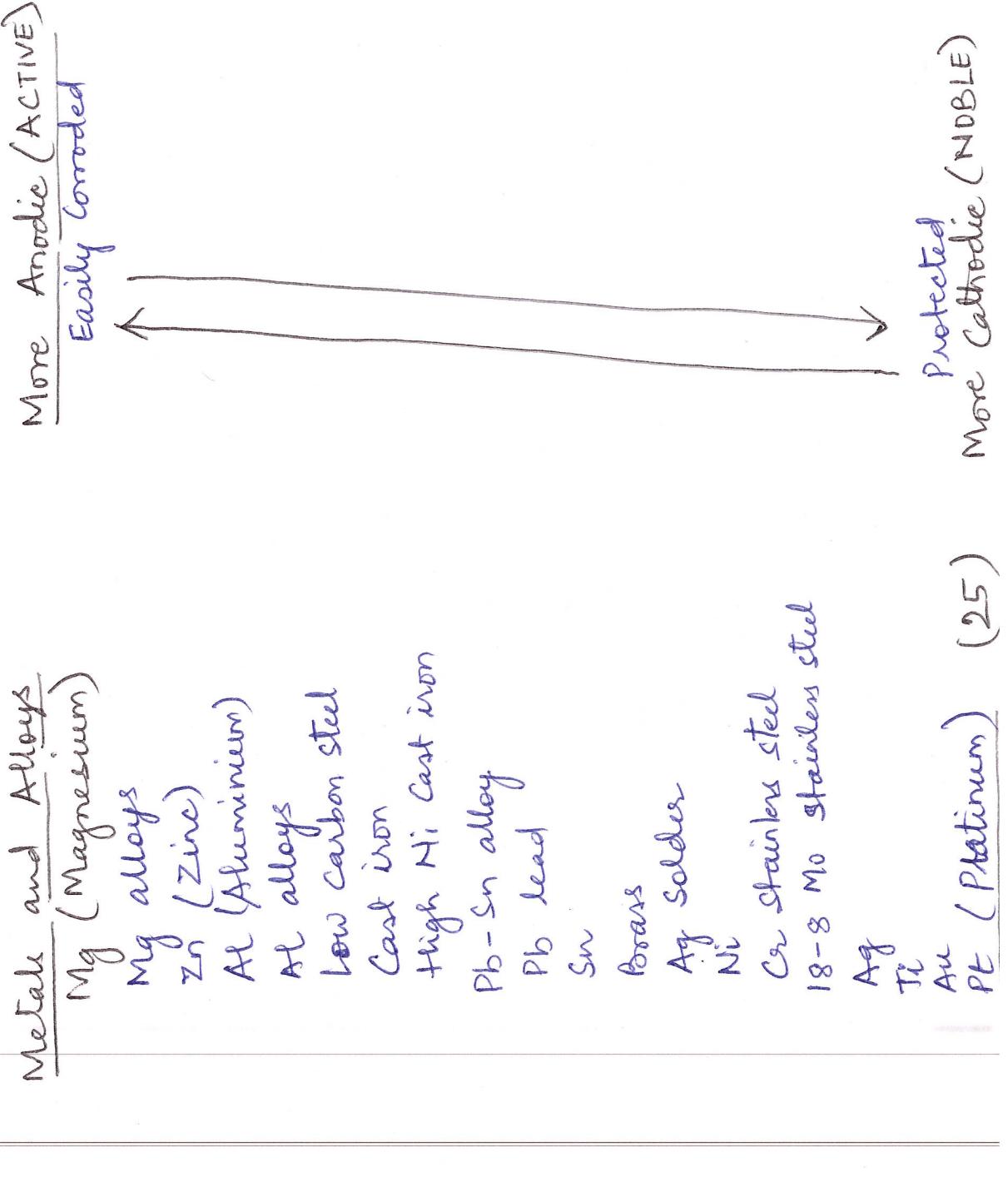
$$\begin{aligned}\text{or } 50 \text{ kg of iron produces} &= \frac{214 \times 50}{112} \\ &= \frac{10,700}{112} \\ &= 95.53 \text{ kg rust}\end{aligned}$$

(24)

### Galvanic Series -

Galvanic series gives real and useful information regarding the corrosion behaviour of metals and alloys in a given environment.

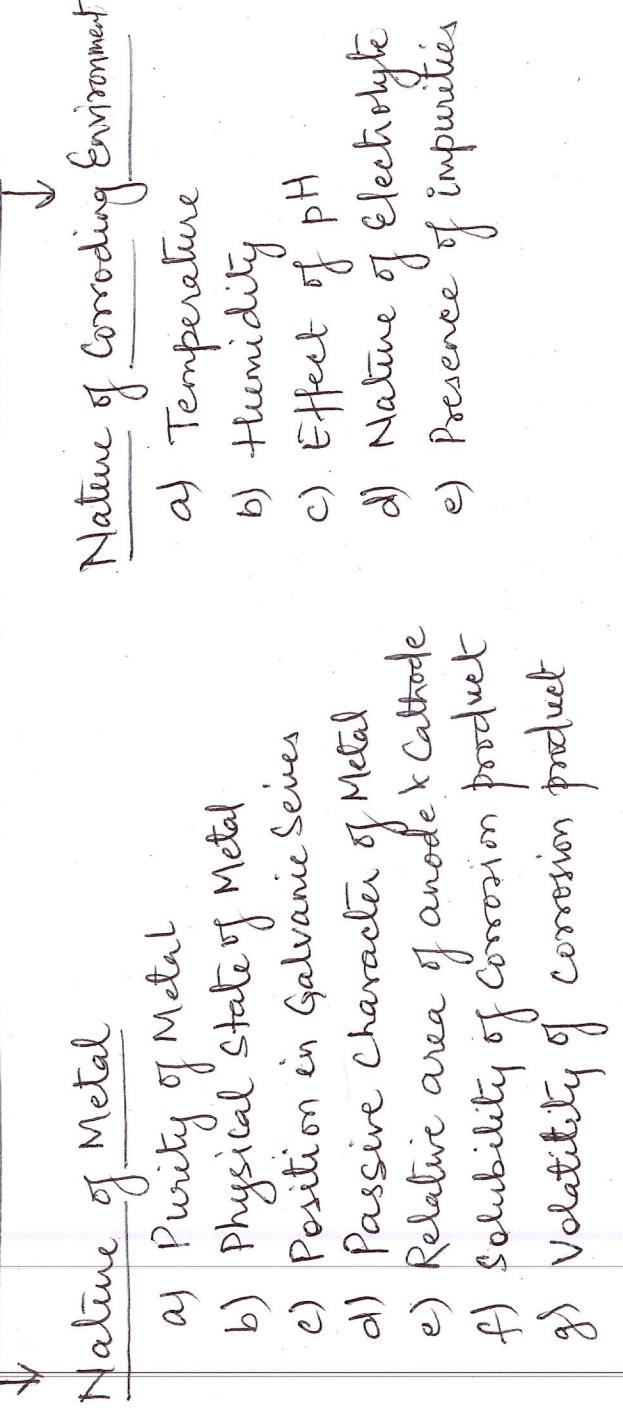
1. Galvanic series is the relative hierarchy of metals arranged in order from Magnesium (least anodic) at the anodic corroded end to Platinum (most noble) at the cathodic, protected end.
2. Greater the difference between two metals or alloys, greater the corrosion will occur.



#### 14. Factors Affecting Corrosion

The rate and extent of corrosion is influenced by the following factors:

Factors influencing corrosion



#### 14(a) Nature of Metal

(a) Purity of metal - Impure metal corrodes faster than a pure metal. Impurity causes 'heterogeneity' and forms tiny electrochemical cells and the anodic part gets corroded.

Example - Rate of corrosion of Al in HCl increases as given for 99.99% purity of Al - relative rate of corrosion is 1  
99.97% purity of Al - relative rate of corrosion is 1000  
99.90% purity of Al - relative rate of corrosion is 30000

(b) Physical State of Metal - It means orientation of crystal, grain size, stress etc.

- The larger the grain size lower is its solubility and lesser will be the corrosion
- Areas under stress (bends, joints, rivets in boilers) act as anode and gets corroded.
- Metals with unevenly distributed stress are also corroded easily.

(26)

### (c) Position in Galvanic Series -

- When two metals are in direct contact, the metal higher up in the galvanic series becomes anode and gets corroded.
- Greater is the potential difference between the two metals coupled, greater is the rate of corrosion.  
Example - As Ag and Cu are below Fe in galvanic series, so, they do not undergo much corrosion.

### (d) Passive character of Metal -

Some metals form thin adherent and self-healing protective film on their surface which acts as barrier between metal and environment thus, resist the corrosion.

Eg:- Metals like Al, Cr, Ti, Co etc are passive and resistant to corrosion.

### (e) Relative area of Anode and Cathode -

When two dissimilar metals are in contact, the corrosion of anodic part is proportional to the ratio of area of cathode to area of anode i.e.

$$\text{Rate of corrosion of anode} \propto \frac{\text{Cathode Area}}{\text{Anode Area}}$$

Rate of corrosion is less if cathode area is small as demand of  $e^-$  is less

Eg:- Steel pipe fitted in large Cu tank undergoes, localised rapid corrosion.

### (f) Solubility of Corrosion Product -

Insoluble corrosion product forms a physical barrier between metal and environment, thus prevents the corrosion. But, if corrosion product is soluble in corroding medium, corrosion becomes faster.

Example - Pb in  $\text{H}_2\text{SO}_4$  forms  $\text{PbSO}_4$  (insoluble in  $\text{H}_2\text{SO}_4$  medium)  
(27)  
Hence, rate of corrosion is less.

## (g) Volatility of Corrosion Product -

Volatile corrosion products leaves the underlying metal surface in direct contact with corroding medium. Thus rate of corrosion becomes faster.

Example - The oxidation product of Molybdenum (Mo) is  $\text{MoO}_3$  (Molybdenum oxide) which is volatile in nature and thus increase the corrosion rate.

## 14.3 Nature of Environment

### (a) Temperature -

The rise in temperature increases the rate of diffusion of ions thus, increasing the rate of corrosion.

### (b) Humidity -

The greater humidity acts as a solvent for gases like  $\text{O}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , also for salts, and furnishes electrolyte essential for setting up a corrosion cell. This increases the rate and extent of corrosion.

Example - Rusting of iron increases when moisture content increases from 60% to 80%.

### (c) Effect of pH -

Rate of corrosion is maximum when the corrosive medium is acidic and can be reduced by increasing the pH of the environment.

Example - Corrosion of  $\text{Zn}$  can be minimised by increasing the pH to 11.

### (d) Nature of Electrolyte -

If the conductance of electrolyte is high then corrosion current is easily conducted and hence rate of corrosion is increased  
Anions - silicate ions in electrolyte form insoluble silicates and prevent further corrosion (28)

- Chloride ions in electrolytes destroy the protective film and the surface undergoes corrosion. Eg - Al corrodes in sea water
- Cations -  $\text{NH}_4^+$  ions in corroding medium increases the corrosion of metals.

conductance of clayey and mineralized soil is more than that of dry sandy soil.

(e) Presence of Impurities

- Corrosive gases (like  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{CO}_2$ ) and fumes of  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  near industries result in increased conductivity of liquid layer on metal surface thus increase corrosion rate.
- Sodium chloride salt near sea also increase the ~~conductivity~~ of liquid layer on metal surface thus increasing corrosion.

## 15. Types of Wet or Electrochemical Corrosion

### 15(1) Galvanic Corrosion (or Bi-metallic corrosion)

This type of corrosion occurs when two dissimilar metals are in contact with each other in a corrosive conducting medium. A potential difference is set up resulting in a galvanic current.

Example :- Iron and Copper couple  $\rightarrow$  Corrosive Environment

#### Mechanism -

- Iron has lower electrode potential acts as anode.

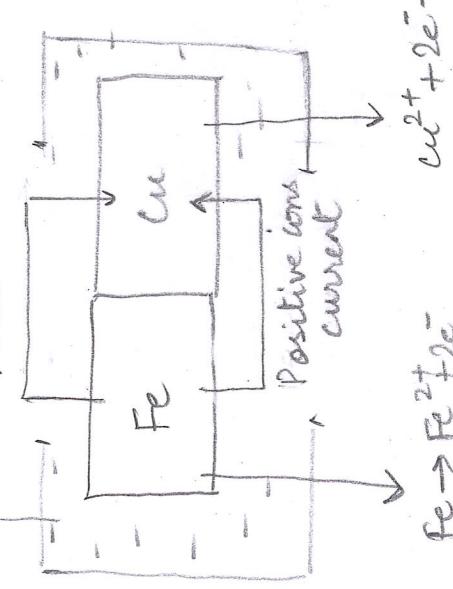


- Copper having higher electrode potential acts as cathode.



Thus, Cu remains unaffected

#### Mechanism -



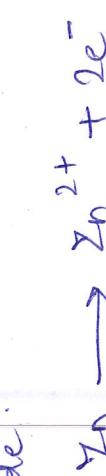
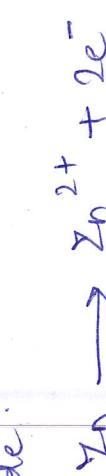
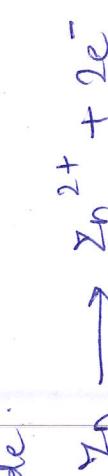
### 15(2) Concentration Cell (or Differential Aeration) Corrosion

This type of corrosion occurs when metal surface is exposed to differential aeration concentration; which develops galvanic cell and initiates corrosion.

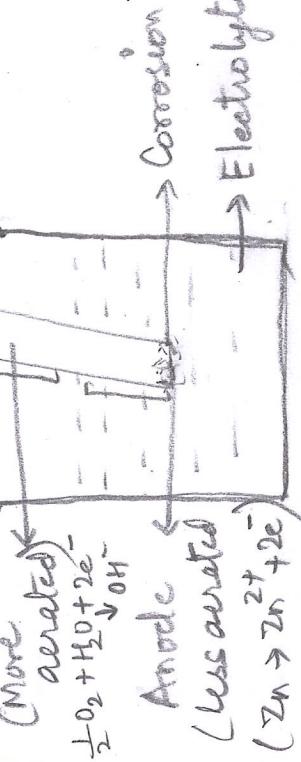
Example - Zinc rod partially immersed in an electrolyte and partially exposed to air.

#### Mechanism -

Anode - Part of zinc rod dipped (More aerated) in electrolyte is less oxygenated and acts as anode.



#### Lithode



(30)

Concentration cell corrosion

Cathode - Part of zinc rod exposed to air acts is more oxygenated and acts as cathode



Net Reaction -  $Zn^{2+}$  and  $OH^-$  interacts to give  $Zn(OH)_2$  and corrosion occurs at anode.

Thus, Pure Zinc rod half immersed in  $H_2O$  starts corroding at bottom.

→ Examples of differential aeration corrosion

- (i) Part of nail inside the wall (less aerated) undergoes corrosion.
- (ii) Window rods inside the frame (less aerated) undergoes corrosion.
- (iii) Paper pins inside the paper (less aerated) gets corroded.

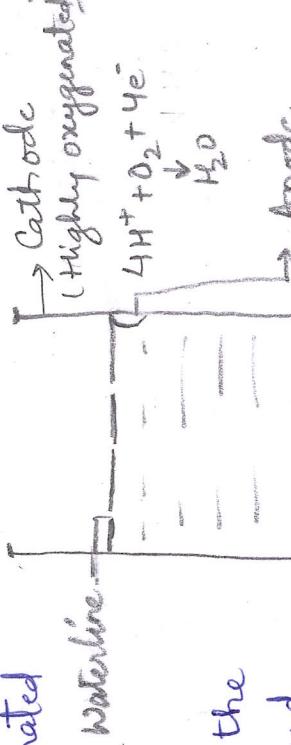
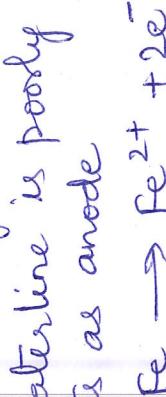
### 15.3) Water line Corrosion

This type of corrosion is one of the case of differential aeration corrosion. and is observed in steel water tanks, ocean going ships etc. in which a portion of metal is always under water.

Example - Water stored in a steel tank

Mechanism -

Anode - Part of tank just beneath the waterline is poorly oxygenated and acts as anode



cathode - Part of tank just above the waterline is more oxygenated and acts as cathode



Waterline Corrosion

(31)

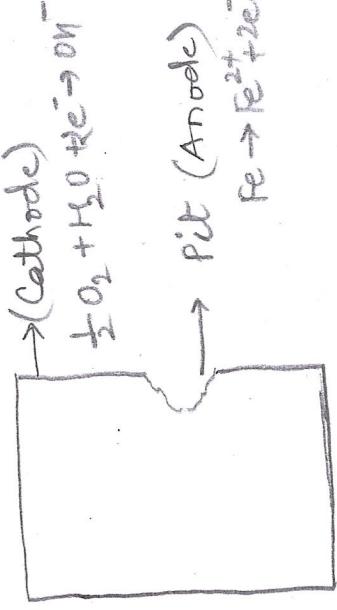
#### 15(4) Pitting Corrosion

This type of corrosion occurs when there is breakage in protective layer or deposition of extraneous matter (eg sand, water droplet, dust etc) on metal surface.

Pitting corrosion is non uniform corrosion and results from a localized accelerated attack resulting in the formation of pits. Pitting corrosion is autocatalytic, self stimulating and takes place exclusively in chloride containing environment.

##### Mechanism -

Anode - Breakage in protective film results in formation of small anodic area which shows dissolution of metal and creates pit.



Cathode - The coated area acts as cathode

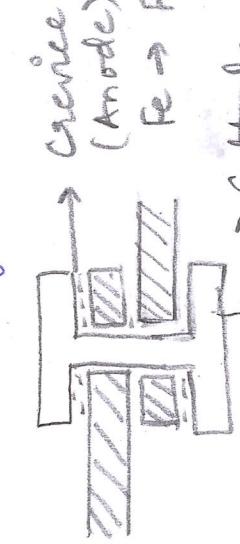


#### 15(5) Crevice Corrosion

This type of corrosion is the accelerated attack at the junction of two metals exposed to corrosive environment. It is a localized corrosion of metal or alloy surface

##### Mechanism -

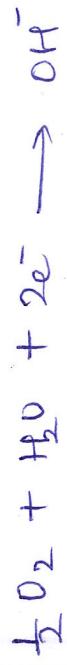
Anode - Joining surface has low oxygen and acts as Anode



(32)

Crevice Corrosion

Cathode - The exposed area acts as cathode



Net Reaction -



Example - bolts, nuts, screws in contact with liquid.

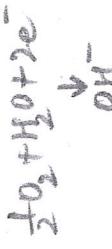
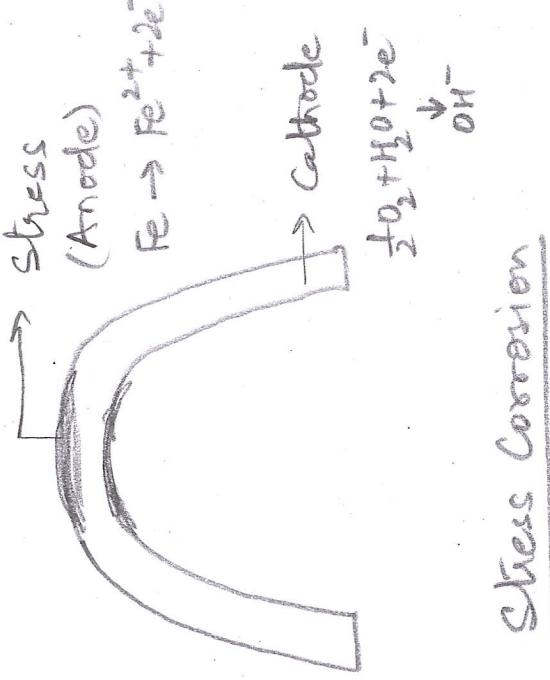
### Stress Corrosion

This type of corrosion occurs due to combined effect of static tensile stress and specific corrosive environment. Mechanical process such as pressing, hammering, bending etc cause stress, which produces strain and results in localized zone of high energy.

Mechanism

Anode - Area under stress has high energy and acts as anode

Cathode - Stress-free part acts as cathode



Stress Corrosion

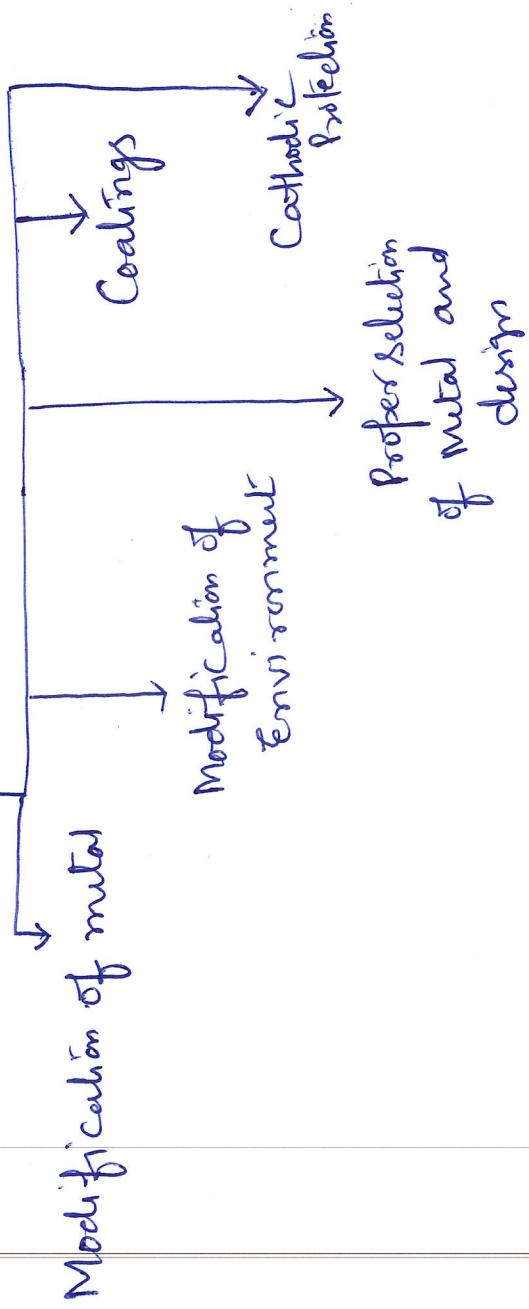
Example - (i) Season cracking of brass in ammonia and ammonia containing environment  
(ii) Caustic Embrittlement of mild steel boiler in alkaline solution at high temperature & stress.

(33)

## 16: Prevention of Corrosion :-

### Corrosion :-

#### Prevention



(34)

## 16.1 Modification of the properties of the metal :-

The properties of the metal can be modified to decrease the effect of corrosion.

Alloying :- Al is used to improve the corrosion resistance of the metal Al, Be, Mg etc. are added to Cu to improve its oxidation resistance.

b) Cu is added to stainless steel as it Cr is added to stainless steel as it improves the corrosion resistance by forming a layer of  $\text{Cr}_2\text{O}_3$ .

Refining of metal :- It is done to remove the impurities (Decrease the concentration of sulphur and phosphorus due to which corrosion rate is minimized).

Annealing :- It is a heat treatment given to metals to remove the residual stress and strain from it.

Passivation :- It is the phenomenon in which metal develops a protective layer on its surface (thickness about 0.0004 mm) called film. This film being protective does not cause corrosion.

Examples Ni-Cr, Ti-Mo (35)

## 16.2 Modification Environment: Metals are protected

from corrosion either by removal of corrosive substances or by the use of Inhibitors.

- >To control the corrosion by moisture can be removed by dehumidification.
- To prevent the corrosion by salts, they are removed by using Ion - exchange resins.
- To prevent the corrosion by acids, they are neutralized with lime.
- To control the corrosion by oxygen present in water deoxygenation agents like  $\text{N}_2\text{H}_4$  and  $\text{NaNO}_2$  are used.

## 16.3 Proper selection of metal and Design

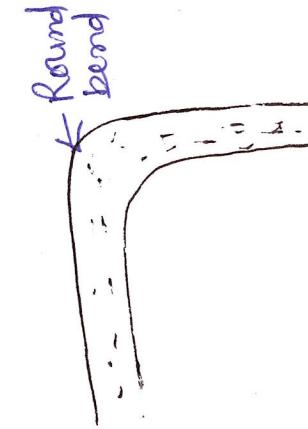
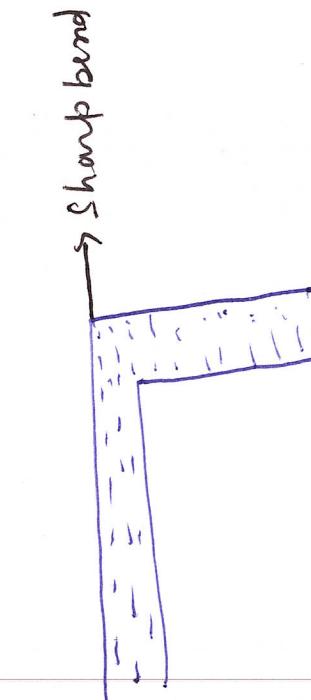
1. Avoid galvanic coupling :- Two metals selected to build a structure should be taken in such a way that there should be insulator between them.



- (II) Two materials selected should have minimum gap in the galvanic series i.e. They have minimum potential difference.

### Proper Designing :-

1. Avoid sharp bend and sharp corners:-

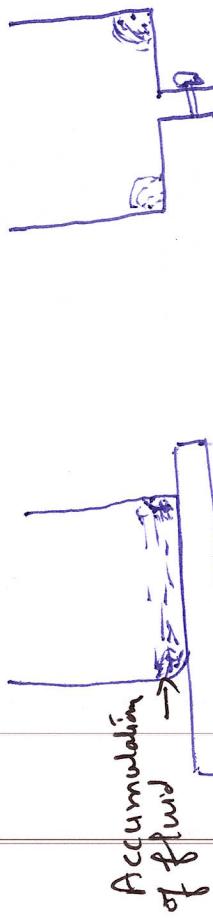


Faulty design

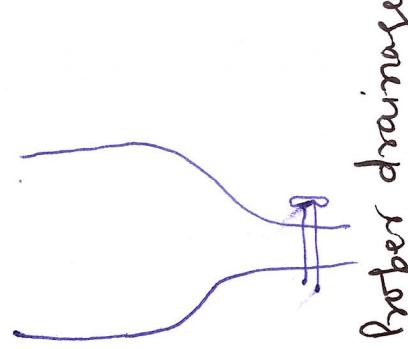
Proper design

(37)

Proper drainage :- Imposter drainage leads to stagnation condition leading to the intense localized corrosion.



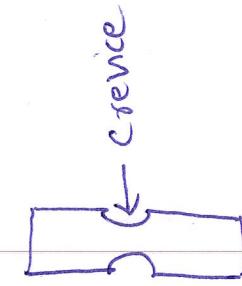
Faulty  
design



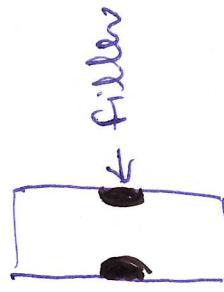
Proper drainage

No accumulation of fluid

Good design



Avoid crevices:



Poor design

Good design

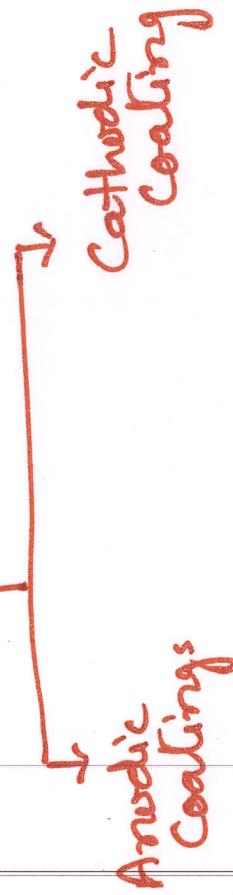
(38)

## Organic Coatings

16.4

### Coatings :-

- a. organic coatings
- b. metallic coatings



a) Organic coatings :- To prevent

the corrosion organic

coating like paints, varnishes, enamels  
lacquers. These coatings not only  
prevent corrosion but also provide aesthetic  
look to the metal.

(39)

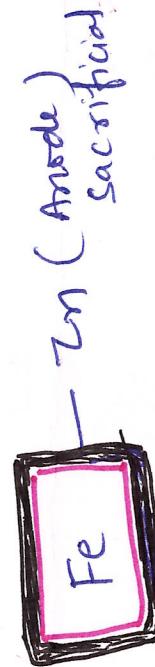
## Metallic Coatings :

### a) Sacrificial anodic Coating :-

In this process the metal structure which is to be protected from corrosion is coated with more active metal which become anode and protects the base metal from corrosion sacrificially.

#### Example

Galvanisation of Fe  
(Coating of Zn on Fe)



b) Cathodic Coating :- In this process the metal structure which is to be protected from corrosion is coated with corrosion resistant metal (cathode) which has no tendency or less tendency to oxidise.

Example :- Tinning of Iron  
(Coating of Tin on Iron)  
Sn Fe

(40)

## Corrosion Inhibitors :-

Corrosion inhibitors are organic and inorganic substances which are added to the corrosion scale to control the rate of corrosion.

### Types of corrosion inhibitors:

- a) Anodic Inhibitors
- b) Cathodic Inhibitors
- c) Vapour phase Inhibitors

Anodic Inhibitors :- Anodic inhibitors like alkalis, molybdates, phosphates, chromates.

They react with the cations of the anode and produce insoluble precipitate and precipitate deposit on the metal surface forming a protective layer thereby reducing the corrosion rate



Cathodic Inhibitors: Cathodic reaction in acidic medium



For this purpose Compounds like amines, urea thiourea, mercaptans are added to the reaction mixture which diffuse the  $\text{H}^+$  ions present in the medium.

Vapour phase / volatile inhibitors: These are organic compounds which readily sublime and form a protective layer on surface of metal.

Example

DCHAN  
(diethyl benzyl ammonium nitrate)

DCHAN are added to corrosion sites in the form of tablets. These materials sublime and form a protective layer on the metallic parts which are to be protected. They are used in sophisticated marine parts like cockpits, tanks, army vehicles, condensers, turbines, compressors etc.

(42)

## 16<sup>o</sup> Cathodic Protection :-

It is the method of preventing the metal from corrosion by forcefully making the metal Cathode.

If there is no anodic area on metal then corrosion would not occur.

### Types of Cathodic Protection :-

1. Sacrificial anodic protection
2. Impressed Current Cathodic Protection

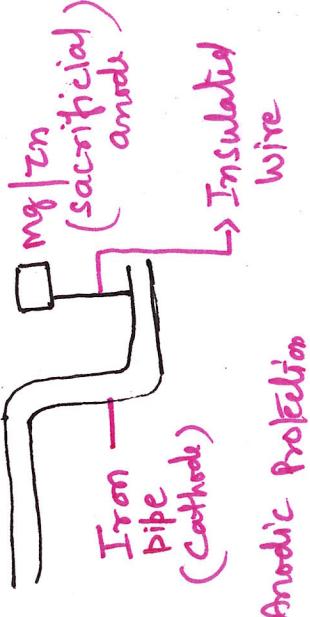
### Sacrificial anodic Protection :-

(Galvanic Protection)

The metal structure which have to protect from corrosion is connected with wire to a more active metal (more anodic) so that the corrosion occurs at more active metal and another metal structure will get protected.

More active metals commonly used for Sacrificial anodic Protection are Mg, Zn, Al and their alloys.

Earth Surface



Sacrificial Anodic Protection  
(43)

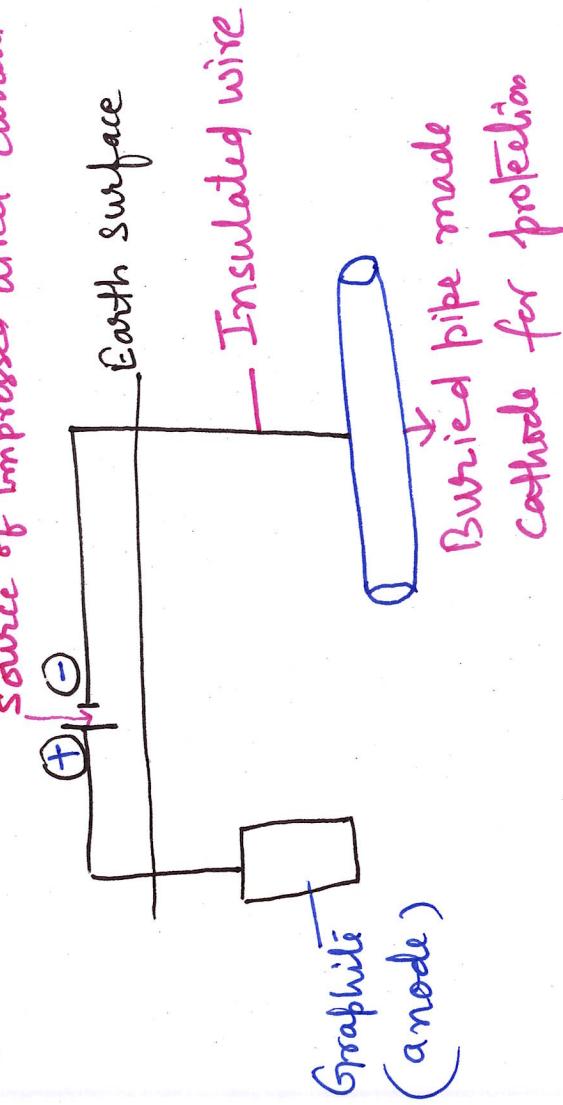
Applications:- This process is used for the

protection of buried / underground pipelines  
transmission lines (phone, gas), Railway  
bridges, flyovers, railway tracks  
marine structures etc.

## Impressed Current cathodic Protection:

### Impressed Current cathodic Protection:

In this process, the object (metal structure) to be protected is made cathode and it is connected to the negative terminal of a DC (direct current) source. The positive terminal of the source is connected to the other electrode made of graphite or platinum. Current from external source is applied to nullify the corrosion current. This is done to make the corroding metal cathode instead of anode. On becoming cathode the metal gets protected from corrosion.



Applications : This method is used for the protection of underground pipelines, transmission cables, storage tanks, towers, pillars of bridges & flyovers.

## CHEMISTRY OF ENGINEERING MATERIALS

### 17. CEMENT:-

It is a material which possesses the adhesive and cohesive properties and it is capable of binding the materials like bricks, stones and building blocks etc.

#### 17.1 PORLAND CEMENT:-

Portland cement is also known as Magic Powder. It has given the name because it resembles the stone like material on Isle of Portland, England.

→ It consists mainly of silica ( $\text{SiO}_2$ ), lime ( $\text{CaO}$ ), alumina ( $\text{Al}_2\text{O}_3$ ) and iron.

→ It is made by calcining this mixture at about  $1500^{\circ}\text{C}$  in definite proportion.

→ William Aspidius is recognised as Father of Modern Portland Cement Industry.

→ All portland cements are hydraulic cement because they set and harden when water is added to them.

#### 18. COMPOSITION OF PORTLAND CEMENT:-

##### Name of constituent

1.  $\text{CaO}$  (lime)

2.  $\text{SiO}_2$  (silica)

3.  $\text{Al}_2\text{O}_3$  (alumina)

##### Percentage

60 - 69%

17 - 25%

3 - 8%

##### function / application

Provides strength to the cement.

Provides strength to the cement.

• Prolong the setting time of cement.

• Provides strength to the cement.

• Reduces the setting time.

(47)

4.  $\text{Fe}_2\text{O}_3$  (iron oxide) 2-4%

- Provides the characteristic grey colour to the cement.
- Provides hardness to the cement.

5.  $\text{MgO}$  (magnesium oxide) 1-5%

- Provides soundness to the cement.

6.  $\text{SO}_3$  (sulphur tri oxide)

1-3%

- Provides smoothness & strength to the cement.

7.  $\text{Na}_2\text{O}$  &  $\text{K}_2\text{O}$  (alkali oxides) 0.3-1.5%

- Provides smoothness & soundness to the cement.
- If it is present in excess, it makes the cement efflorescent.

## MANUFACTURING OF PORTLAND CEMENT:-

### 1. Raw Materials:-

- (i) Lime component ( $\text{CaO}$ ) :- It consists of calcareous materials such as shale, calcite, limestone, marl (these are calcium ore).
- (ii) Silica component ( $\text{SiO}_2$ ) :- It consists of silicious material such as clay, shale, marl & sand.
- (iii) Alumina component ( $\text{Al}_2\text{O}_3$ ) :- It consists of argillaceous material (containing Al) such as aluminum ore, clay, flyash and shale.
- (iv) Iron component ( $\text{Fe}_2\text{O}_3$ ) :- It consists of ferriferous materials (containing Fe) such as clay, iron ore, mill scale etc.

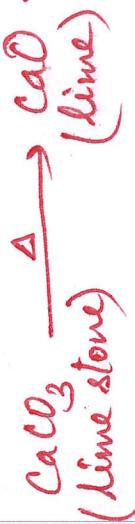
## 2. Manufacturing processes :-

- (i) crushing :- It is done in primary crusher which reduces the size of raw material upto 5-inch and then in secondary crusher which reduces the size upto 0.75 inch.
- (ii) Mixing :- In this process, raw materials are mixed in definite proportions either by dry or wet processes.  
In dry process, fine powder is stored in bin (container) and in wet process slurry is formed which is pumped into storage bins.
- (iii) Burning :- After the mixing process, the material is fed into rotary kiln (furnace) where burning process takes place.

Rotary kiln is a long steel cylinder with length 30 - 160 meter and diameter 2 - 4 meter. It is slightly inclined towards the exit end and mounted on rollers to move it at desired speed. As the material passes through the rotary kiln, temperature is raised where actual reactions takes place.

### Reactions in different zones of Rotary kiln :-

- a - Drying Zone :- In this zone, temperature is around 100 - 500 °C and it is about  $\frac{1}{4}$  th portion of the kiln. Here, moisture is given out and raw material is completely dry.
- b - Calcination Zone :- Temperature of this part around 1000 °C. It is the middle portion of the kiln.  $\text{CO}_2$  is removed from lime stone in this portion.



(49)

c- Burning zone:- Temperature is about  $1400$ - $1500^{\circ}\text{C}$  in this zone. It is the bottom portion of the kiln. In this zone, mixture melts down and form a round party masses of pear size, called as clinkers. The clinkers produced are greenish, bluish or greenish-black in colour.

Clinkers  $\rightarrow$  small round masses present in cement.



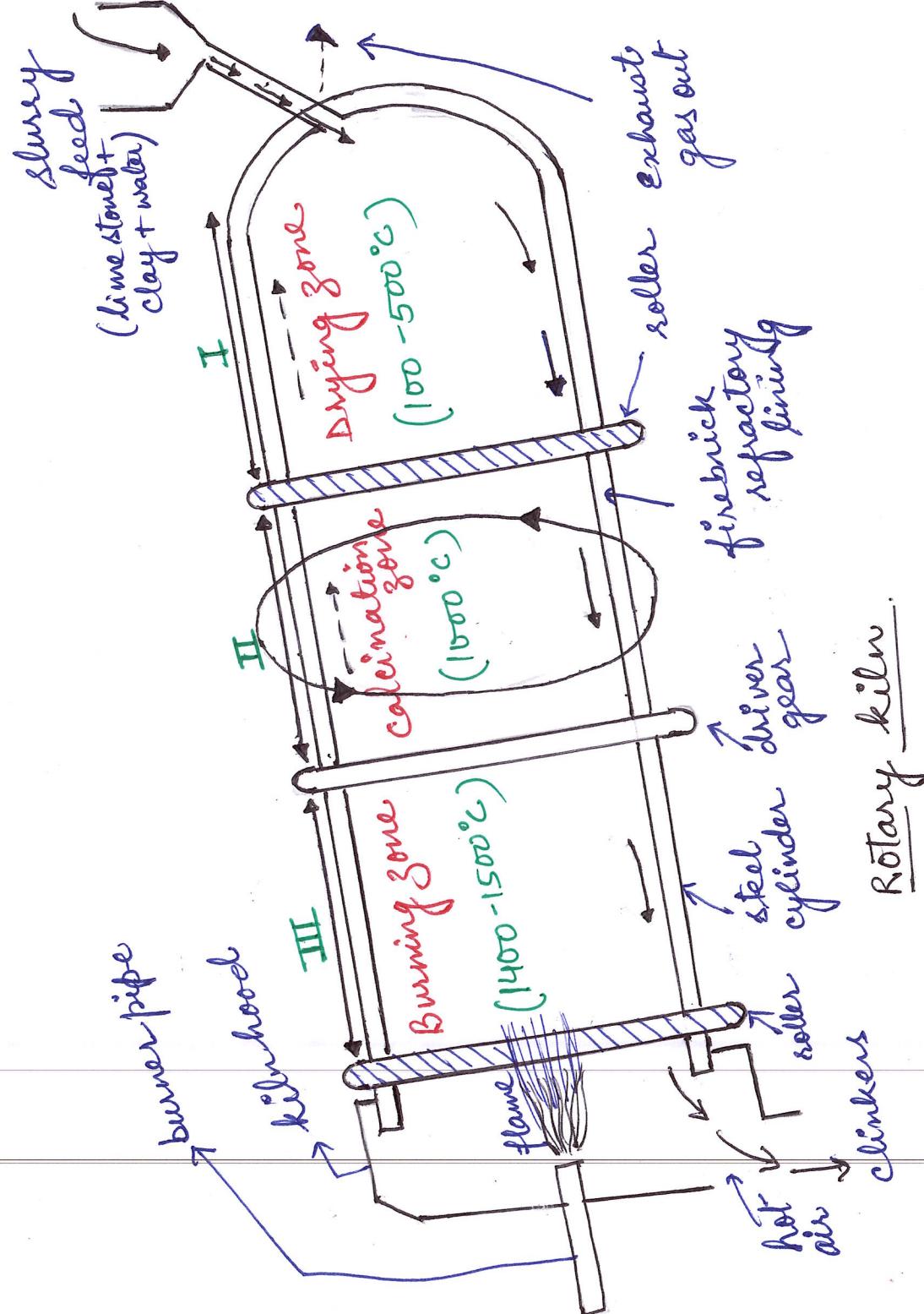
(iv) Grinding:- Clinkers formed are stored in storage bins and transported for fine grinding. Finely ground material sets very fast. Hence, to control the setting time of Portland cement, 2-3% gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is added.

Role of Gypsum in Cement:- Gypsum is added to the cement to slow down the setting time of cement. This happens due to the formation of calcium sulpho-aluminate:



$$x=3.2$$

(50)



**Clinkers :**  
mixture of silicates  
and abundances  
of calcium

Burnt in  
rotary kiln

slurry of  
lime stone +  
clay + water

mixed with  
gypsum

**PORTLAND CEMENT**

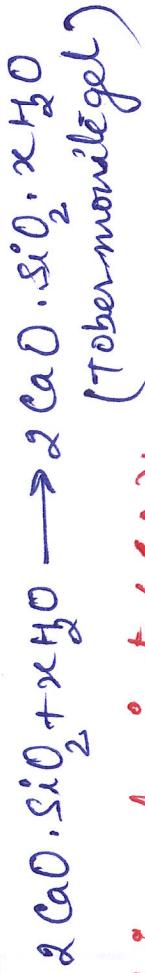
(51)

## 20. REACTIONS OF SETTING AND HARDENING OF CEMENT!:-

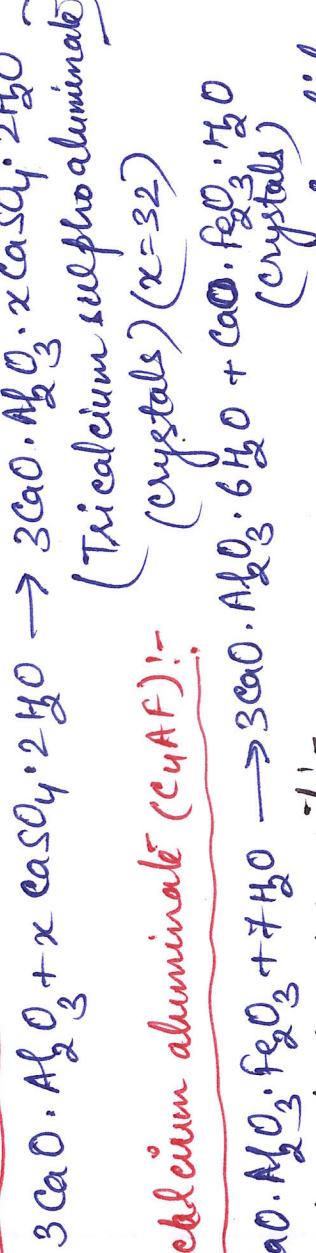
### (i) Tricalcium silicate ( $\text{C}_3\text{S}$ ):-



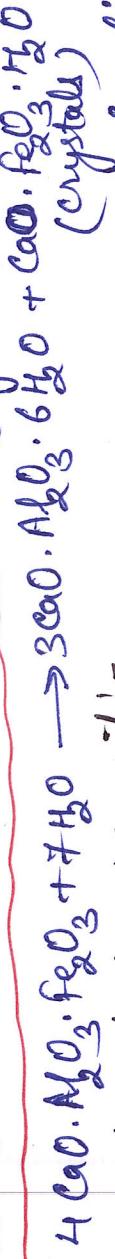
### (ii) Dicalcium silicate ( $\text{C}_2\text{S}$ ):-



### (iii) Tricalcium aluminate ( $\text{C}_3\text{A}$ ):-

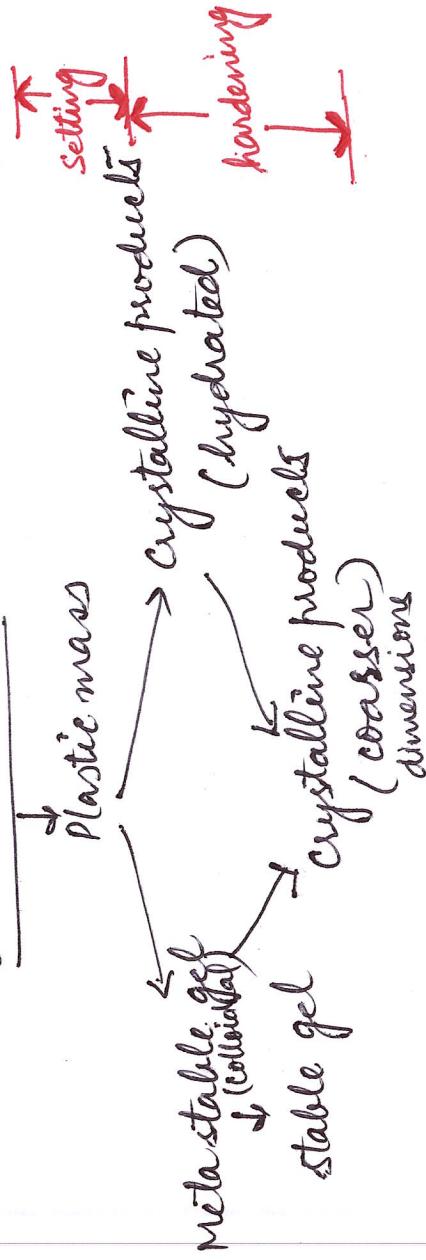


### (iv) Tetra calcium aluminate ( $\text{C}_4\text{AF}$ ):-



Setting and hardening of cement: When water is added to the cement, hydration of cement takes place. This mixture then paste, hydration of cement becomes hard and stiff; this process is known as setting of cement. After hydration, anhydrated compounds become hydrated and sand and other materials bind with it firmly / strongly.

Cement + water



Schematic diagram for setting Rotatory kiln

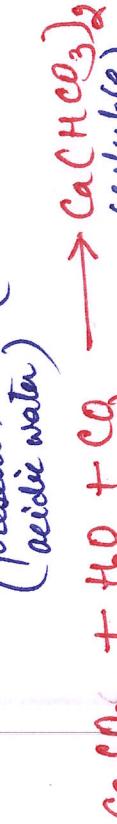
## 21 PHYSICAL PROPERTIES OF CEMENT:

(i) fineness:- This property affects the hydration of cement. The hydration of finely ground cement is more rapid due to the larger surface area which raises the heat of hydration, resulting in the accelerated strength gain.

(ii) Soundness!:- It is the ability to maintain the stable volume after the setting. Portland cement has good soundness property.

## DECAY OF CEMENT!:-

(i) Cement is decayed due to the leaching out of free lime from it. Till the consumption of all  $\text{CO}_2$ , the cycle of reactions continues as:-



(ii) Cement is decayed due to the hydrolysis of silicates and aluminates which will also be dissolved out.

## PREVENTION!:-

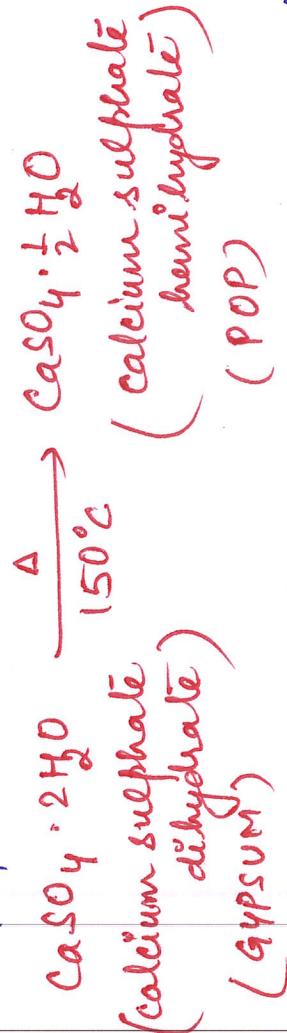
Decay of cement can be minimized by coating the surface by paints or drying oils.

## 22. PLASTER OF PARIS (POP)



Preparation of POP :-

It is prepared by gypsum on heating.



During the preparation of POP from gypsum, following operations take place :-

- (i) crushing and grinding of gypsum;
- (ii) calcination of ground gypsum in kiln by heating it at  $150^\circ\text{C}$ ;

- (iii) Pulverising the calcined product.

### Setting & Hardening of POP :-

→ POP forms a plastic mass when it is mixed with water. This plastic mass sets or hardens very quickly. During this process, it slightly expands and regain the closely packed crystalline structure of gypsum.  
→ Alum or alkali sulphates like  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  are also added to initiate the crystallization process. Hence, they are used to accelerate the setting of POP.

### Applications of POP:-

- It is used for making moulds as it expands slightly on setting.
- It is used for making surgical bandages (plaster), structural tiles and castings.
- It is used for making plaster boards which are made up of alternate layers of gypsum and fibrous material such as felt or paper.