Unit-3

Assignment

Ques-1 Derive Nernst Equation. give its significance. Consider a cell redction. Zn / Zn^{2+} [0.1 M] // Cu^{2+} [0.2 M] / Cu. standard reduction potential of Zn^{2+} and Cu^{2+} are -0.76 V and 0.34 V respectively. write half cells reactions, complete cell reaction and calculate EMF of the cell

Ans- **Derivation of Nernst Eqn :-**

WKt,

$$\Delta G = -nF E_{cell}$$

under standard conditions,

$$\Delta G^\circ = nF E^\circ_{cell}$$

where n = no of electrons transfer

Also, $\Delta G = \Delta G^\circ + 2.303 RT \log Q$

R = universal gas constant (8.314 $JK^{-1} mol^{-1}$)

F = Faraday constant (96500 C mol^{-1})

So, $-nF E_{cell} = -nF E^\circ_{cell} + 2.303 RT \log Q$

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log_{10} \frac{[Product]}{[Reactant]}$$

Significance -

It helps in the determination of cell potential under non-standard conditions.

It relates the measured cell potential to the quotient of the reaction and allows the exact determination of constants of equilibrium.

$$Zn / Zn^{2+}[0.1M] // Cu^{2+}[0.2M.] / Cu$$

At Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

At Cathode: $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

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

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= 0.34 - (-0.76)$$
$$= 1.1 \text{ volts}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log_{10} \frac{[Product]}{[Reactant]}$$

$$= 1.1 - \frac{0.059}{2} \log_{10} \frac{[0.1]}{[0.2]}$$

$$= 1.1 + 0.0088$$
$$= 1.1088\,V$$

Ques-2 The voltage of the cell Pb/PbSO$_4$ $Na_2SO_4 \cdot 10H_2O$ / Hg_2SO_4 / Hg is 0.9647 V at 25°C. The temperature coefficient is $1.74 \times 10^{-4}\ VK^{-1}$. Calculate the values of ΔG, ΔS and ΔH.

Ans. $$\Delta S = nF\left(\frac{dE}{dT}\right)_P$$

$n = 2$, $F = 96500\,C/mol$

$$\left(\frac{dE}{dT}\right)_P = 1.74 \times 10^{-4}$$

$$\Delta S = 96500 \times 2 \times 1.74 \times 10^{-4}$$
$$= 33.58\ JK^{-1}$$

$$\Delta H = nF\left[T\left(\frac{dE}{dT}\right)_P - E\right]$$

$$= 96500 \times 2\left[298 \times 1.74 \times 10^{-4} - 0.964\right]$$

$$= -1.76\,KJ$$

$\Delta G = \Delta H - T\Delta S$

$= -176 - 298 \times 33.58$

$= -176 - 10$

$= -186\ KJ\ mol^{-1}$.

Ques-3 Explain why :-

(a) sheets of zinc metal are hung around the ship hull of ocean-going ships.

Ans- The hull of a ship is the water-tight body that is exposed to water. To protect the hulls, the ship builders put pieces of zinc on these hulls. The zinc components used on ships are called 'sacrificial anodes". sacrificial anodes are linked electrically to the ship's hull.

(b) A block of magnesium attached through an insulated metallic wire to an underground iron pipeline

Ans It is done to protect iron by cathodic protection because the reduction potential of Mg is less

than iron, so when it is connected to iron through an insulated metallic wire, it start acting as anode and starts corroding. Iron acts as cathode and is saved from corrosion.

Ques-5 Give the reactions of lead acid storage battery during discharging and recharging.

Ans- **During discharging :-**

Works as voltaic cell when the battery supplies current i.e when chemical energy is converted to electrical energy.

Anode- $Pb \longrightarrow Pb^{2+} + 2e^-$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

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

Cathode- $PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4$

Determination

Net reaction during discharging :-

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

H_2SO_4 is used up during discharging so, the level of acid falls when the density falls below 1.20 g/cm³ the battery needs recharging.

During Recharging -

It acts as electrolytic cell.

Anode :

$$Pb^{2+} + 2H_2O \longrightarrow PbO_2 + 4H^+ + 2e^-$$

$$PbSO_4 \longrightarrow Pb^{2+} + SO_4^{2-}$$

$$PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$$

Cathode :

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

$$PbSO_4 \longrightarrow Pb^{2+} + SO_4^{2-}$$

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

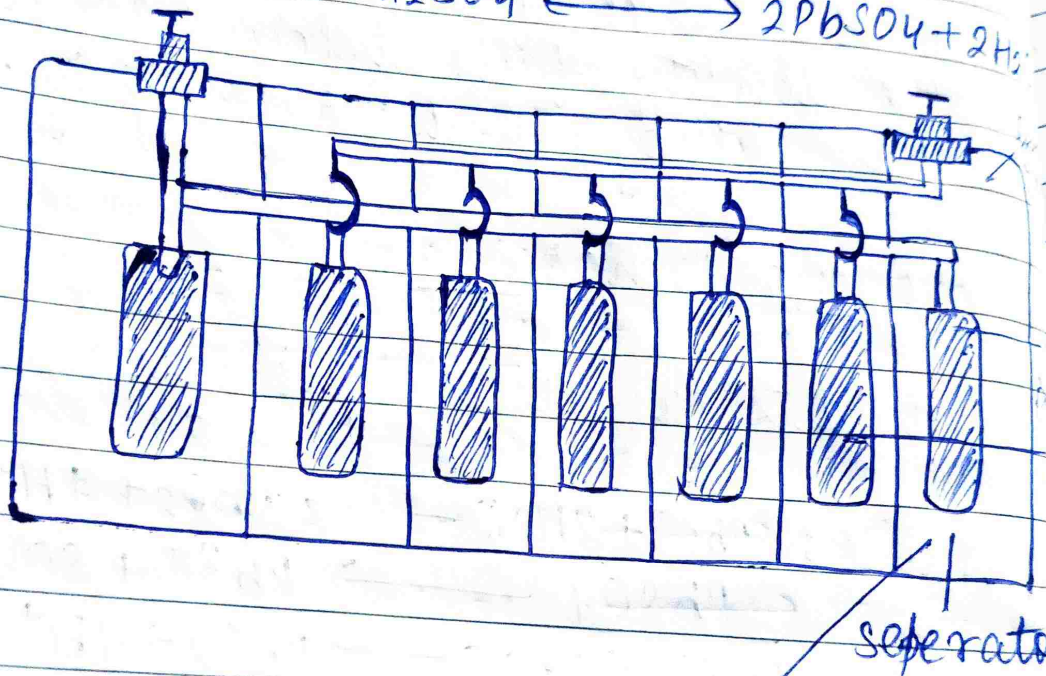
Net reaction during Recharging -

$$2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$$

Recharging is done by passing an external emf greater than ... Ans.

- The net reaction during charg... & recharging process for a rech...

$Pb + PbO_2 + 2H_2SO_4 \longleftrightarrow 2PbSO_4 + 2H_2$



(lead acid storage battery)

Ques-6 Discuss the electrochemical theory of corrosion along with equations. How much rust ($Fe_2O_3 \cdot 6H_2O$) can be produced by 3gm of iron?

Ans. Electrochemical corrosion envolves the formation of large no of galvanic cells on the surface of material.
The reactions takes place in presence of electrolyte and there occurs flow of electrons from anode to cathode. Corrosion products are formed towards cathode.
Eg- Rusting of Iron

Electrochemical corrosion or wet corrosion can be explained by two mechanisms-

- Oxygen absorption mechanism (in alkaline/neutral medium)
- Hydrogen evolution mechanism (in acidic medium)

Mechanism-

- Oxygen absorption mechanism (in basic or neutral medium)-

Anode:- $Fe \longrightarrow Fe^{2+} + 2e^-$

Cathode- $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

$Fe + 1/2\,O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^-$

If enough O_2 is present - $Fe(OH)_2$ is oxidised to rust.

$Fe_2O_3 \cdot xH_2O$ (yellow rust)

In limited supply of O_2 Black magnetite is formed -

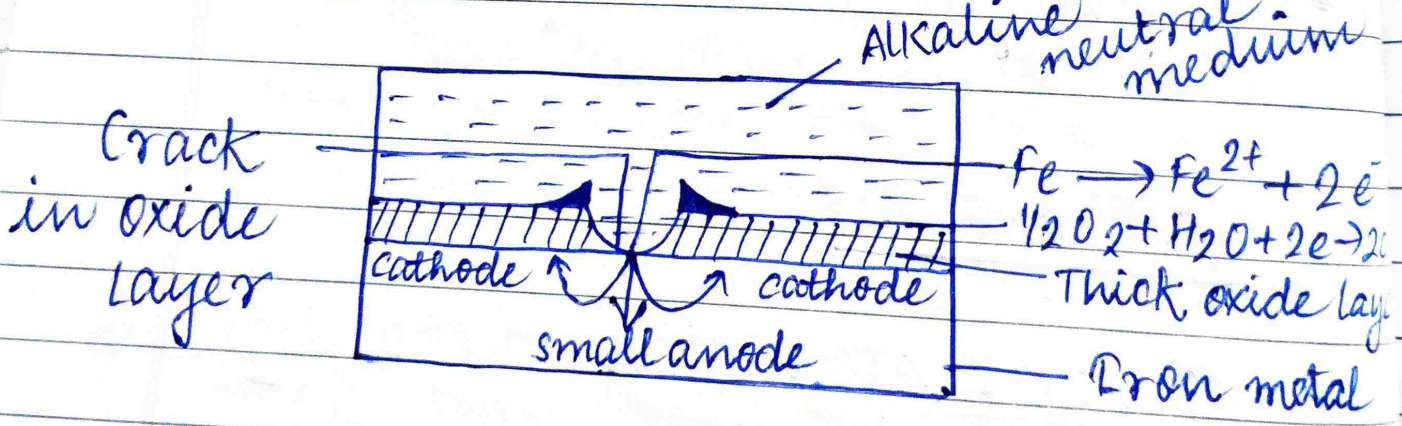
$Fe_2O_3 \cdot FeO \cdot 6H_2O$ (Black magnetite)

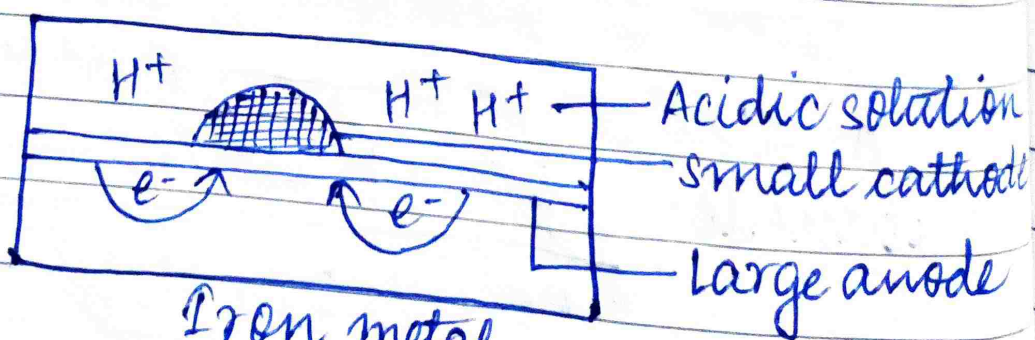
- **Hydrogen evolution mechanism (in acidic medium) -**

Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2\uparrow$

$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2\uparrow$





Ques-7 Define corrosion. How corrosion can be minimised by -

(a) Proper designing
(b) Cathodic protection or sacrificial anodic protection and impressed cathodic protection.

Ans - Corrosion - It is defined as a process of gradual destruction or deterioration of materials by chemical or electrochemical attack of environment.
Eg - Rusting of Iron

Corrosion can be minimised by -

(a) Proper designing - It plays an important role in the control of corrosion of metallic equipments and structures. General guidelines for the design of material and components to control corrosion are -

1) Always use simple design and structures. Avoid sharp bends and corners.

2) Avoid contact of dissimilar metals in presence of electrolyte.

3) When two dissimilar metals are to be used together insulating should be used between them.

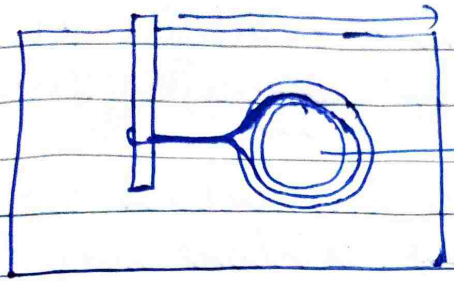
4) Bolts and rivets should be replaced by proper welding.

5) Metal washers should be replaced by rubber or plastic washers as they do not absorb water. They also act as insulations.

(6) Sacrificial Anodic Protection -

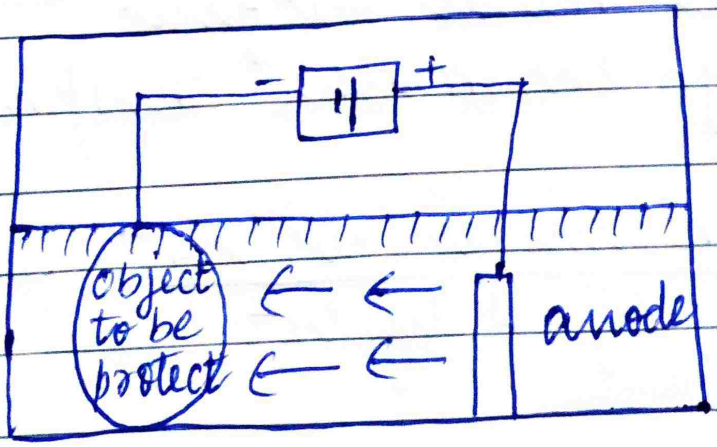
In this method, the metallic structure to be protected is made cathode by connecting it with more reactive metal which acts as anode. Hence, corrosion will occur only on the active metal. The main structure is thus protected. The more active metal used is called sacrificial anode.

The corroded sacrificial anode block is replaced by a fresh one



(ii) Impressed current cathode Protection-

In this method an impressed current is used in opposite direction to reverse the corrosion current and convert the corroding metal from anode to cathode. The impressed current is slightly higher the corrosion current and is derived from an direct current sources.



Ques-8 what are corrosion inhibitors? Explain with examples how anodic and cathodic inhibitor against corrosion.. Explain corrosion issue in different industries.

Ans- Corrosion inhibitors are the substances which are added from outside the inhibit or to decrease the rate of corrosion. Usually they are added in small amount to the corrosive medium.

(a) Anodic inhibitors - They retard the corrosion of metals by reacting with the metallic ions of anode and forming insoluble precipitate which is adsorbed on metal surface. Anodic inhibitors are used to repair crack of the oxide film over the metal surface
Eg- Chromate, Phosphate etc.

(b) Cathodic inhibitors - These are of 2 types-

(i) In acidic solution - Main cathodic reaction is the liberation of H_2 gas, the corrosion reaction is the liberation of H_2 diffusion of H^+ ions.

Eg - Amines, Mercaptans

$$2H^+ + 2e^- \longrightarrow H_2 \uparrow$$

(ii) In Neutral/Alkaline - The cathodic reaction that occurs during corrosion is -

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

Eg - N_2H_4, salts of Mg, Zn or Ni.

- Corrosion issues in different industries -

① Sweet Corrosion (CO_2 corrosion) -

- CO_2 is one of the main corroding agents in the oil and