MODULE 1

ELECTROCHEMISTRY

CLASS 1

Electrochemistry is the branch of physical chemistry which deals with the interdependence of chemical change and electrical energy.

➤ Electrode potential

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of unit molar concentration at 25^0c.

➤ Oxidation potential

- The tendency of an electrode to lose electron is a direct measure of its tendency to get oxidized and this tendency is called oxidation potential.

➤ Reduction Potential

The tendency of an electrode to gain electron is a direct measure of its tendency to get reduced and is called reduction potential.

➤ Standard electrode potential

➤ Electrode potential measured under standard conditions i.e. , at 298K ,one atmospheric pressure and unit molar concentration of electrolyte (1M) relative to Standard Hydrogen Electrode (SHE) is called standard electrode potential.

➤ Electrochemical Cell

It is a device which converts chemical energy into electrical energy.
It consists of two electrodes in contact with an electrolyte. These two electrodes may share the same compartment if the electrolyte is same.

If the electrolytes are different, the two compartments are joined by a salt bridge.

Eg: Daniel Cell

Here anode is Zn in $ZnSO_4$

Cathode is Cu in $CuSO_4$

Oxidation reaction takes place in Zn electrode ie, Zn is oxidized to Zn^{2+} ions. The released electrons are passed through the external wire and Zn^{2+} ions are released into the solution. Zn electrode will be dissolved with time.

Reduction occurs at Cu electrode. Here the electrons coming from the external circuit are taken by Cu^{2+} ions in solution and are reduced to Cu metal. Thus mass of Cu electrode will be increased with time.
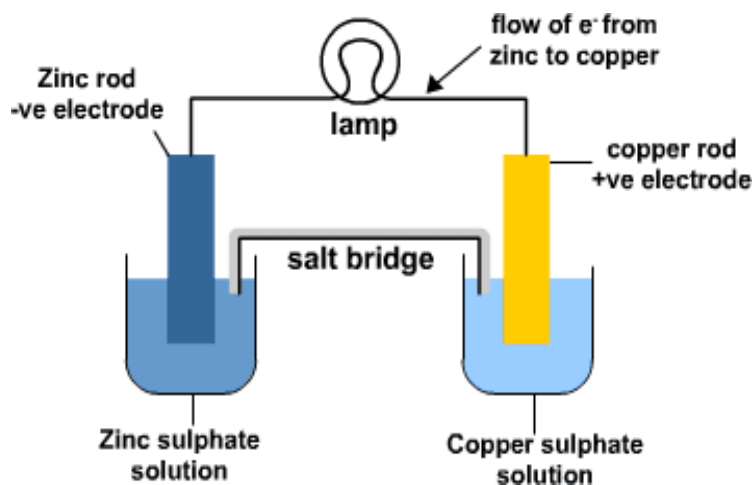
Representation: $Zn / Zn^{2+} // Cu^{2+} /Cu$

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

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

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

Difference between Electrolytic cell and Electrochemical cell

ELECTROCHEMICAL CELL	ELECTROLYTIC CELL
Electrical energy is produced .	Electrical energy is consumed
Reaction taking place is spontaneous	Reaction taking place is non-spontaneous
The half cells are set up in different containers and are connected through salt bridge	Both the electrodes are placed in the solution or molten electrolyte in the same container
Anode is negative and cathode is positive	Anode is positive and cathode is negative
Electrons move from anode to cathode in external circuit	Electrons are supplied by the external source .They enter through cathode and comes out through anode.
The amount of electricity passed is measured by Coulometer.	EMF of the cell is measured by a potentiometer.

NERNST EQUATION FOR SINGLE ELECTRODE POTENTIAL

Consider a general electrode reaction,

$$M^{n+} + n\bar{e} \rightleftharpoons M$$
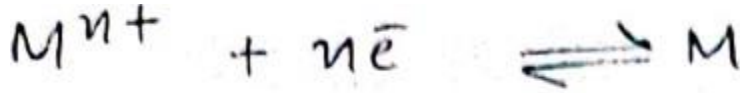
In the case of a reversible reaction , the free energy change ΔG and its equilibrium constant K are inter related as,

ΔG = ΔG⁰ +RT ln K   →1 (Vant Hoff's reaction isotherm)

ΔG^{0-} Standard free energy change

R – Universal Gas Constant

$$K = \frac{[M]}{[M^{n+}]}$$

ΔG related with electrode potential by the equation ,

ΔG =-nFE or ΔG⁰ =-nFE⁰ →2

F- Faraday constant(96500C)

Substitute equation 2 in 1 , we get,

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

$$-nFE = -nFE^0 + RT \ln \frac{1}{[M^{n+}]}$$

$$-nFE = -nFE^0 - RT \ln [M^{n+}]$$

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

OR
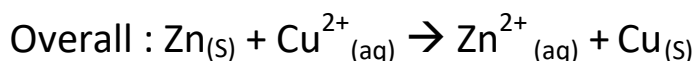
$$\boxed{E = E^0 + \frac{2.303\ RT}{nF} \log [M^{n+}]}$$
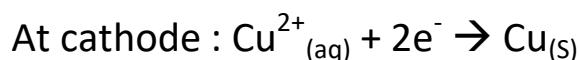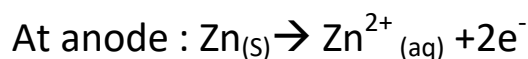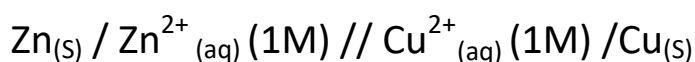
This is Nernst equation for electrode potential.

Substituting the values of R (8.314 $JK^{-1}mol^{-1}$) , T(298K) and F(96500 C), Nernst equation becomes,

$$E = E^0 + \frac{0.0592}{n}\log [M^{n+}]$$

NERNST EQUATION FOR CELL REACTION

EMF of a cell depends on the concentration of electrolyte used in both electrodes. Consider Daniel cell,

$$Zn_{(S)} / Zn^{2+}_{(aq)} (1M) // Cu^{2+}_{(aq)} (1M) /Cu_{(S)}$$

$$\text{At anode : } Zn_{(S)} \rightarrow Zn^{2+}_{(aq)} +2e^-$$

$$\text{At cathode : } Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(S)}$$

$$\text{Overall : } Zn_{(S)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(S)}$$

Nernst equation for Anode:

$$E_{Zn2+ / Zn} = E^0_{Zn2+ / Zn} + \frac{2.303\ RT}{nF}\log [Zn^{2+}]$$

Nernst equation for Cathode:

$$E_{Cu2+ / Cu} = E^0_{Cu2+ / Cu} + \frac{2.303\ RT}{nF}\log [Cu^{2+}]$$

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

$$= (E^0_{Cu2+ / Cu} + \frac{2.303\ RT}{nF}\log [Cu^{2+}]) - (E^0_{Zn2+ / Zn} + \frac{2.303\ RT}{nF}\log [Zn^{2+}])$$

$$= (E^0_{Cu2+ / Cu} - E^0_{Zn2+ / Zn} + \frac{2.303\ RT}{nF} \log \frac{[Cu2+]}{[Zn2+]}$$

$$\boxed{E_{cell} = E^0_{cell} + \frac{2.303\ RT}{nF} \log \frac{[Cu2+]}{[Zn2+]}}$$

In general for aA + Bb → Cc + Dd

$$E_{cell} = E^0_{cell} + \frac{2.303\ RT}{nF} \log \frac{[A]^a\ [B]^b}{[C]^c\ [D]^d}$$

In terms of equilibrium constant, K_C or $K_{eq} = \frac{[C]^c[D]^d}{[A]\ [B]^b}$

$$E_{cell} = E^0_{cell} - \frac{2.303\ RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a\ [B]^b}$$

At equilibrium $E_{cell} = 0$

$$0 = E^0_{cell} - \frac{2.303\ RT}{nF} \log \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

$$\boxed{E^0_{cell} = \frac{2.303\ RT}{nF} \log K_C \qquad \textbf{at 298K}}$$

CLASS 3

Applications:

- Used to study the effect of electrolyte concentration on electrode

  Potential.
- Used for the calculation of potential of a cell under non – standard conditions.
- Determination of unknown concentration of one of the ionic species in a cell provided E^0_{cell} and concentration of other ionic species is known.
- Determination of P^H of a solution:
  The solution whose P^H is to be determined is taken in a vessel and a platinum electrode is half dipped in it. A slow current of hydrogen gas at 1 atm is bubbled through the solution.

$$H^+_{(aq)} + e^- \rightarrow \tfrac{1}{2} H_{2\,(g)}$$
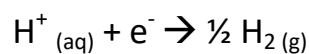
$$E = E^0 - \frac{.303\,RT}{nF} \log \frac{[H_2]^{1/2}}{[H^+]}$$

$$= 0 - \frac{0.0592}{1} \log \frac{1}{[H^+]}$$

$$= -\frac{0.0592}{1} \log \frac{1}{H^+}$$

$$= 0.0592 \log [H+]$$
$$= -0.0592\ pH$$

The above cell is connected with SHE. The two solutions are separated by salt bridge. EMF of the reference electrode is zero. The cell can be represented as,

$$Pt, H_2(1\ atm), H^+(c=?) // H^+(1M), H_2(1\ atm), Pt$$

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

$$E_{cell} = E_{SHE} - (-0.0592\ P^H)$$

$$E_{cell} = 0.0592\ P^H$$

$$P^H = \frac{cell}{0.0592}$$

- Used for finding the valency of an ion or the number of electrons involved in the electrode reaction.
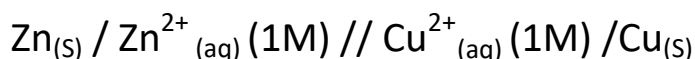
$$Oxidised\ state + ne^- \rightarrow Reduced\ state$$

According to Nernst equation,

$$E_{cell} = E^0_{cell} + \frac{2.303\ RT}{nF} \log \frac{[Oxidised\ state]}{[Reduced\ state]}$$
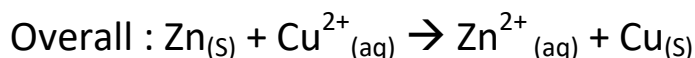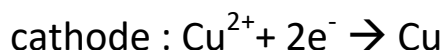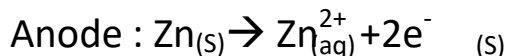
VARIATION OF EMF WITH TEMPERATURE

Nernst equation for a general redox reaction,

$$A_{(s)} + B^{n+}_{(aq)} \rightarrow A^{n+}_{(aq)} + B_{(s)}$$

$$E_{cell} = E^0_{cell} + \frac{2.303\ RT}{nF} \log \frac{[Bn+]}{[An+]}$$

$$Zn_{(S)} / Zn^{2+}_{(aq)} (1M) // Cu^{2+}_{(aq)} (1M) / Cu_{(S)}$$

Eg: Daniel Cell

$$Anode : Zn_{(S)} \rightarrow Zn^{2+}_{(aq)} + 2e^-_{(S)}$$

$$cathode : Cu^{2+} + 2e^- \rightarrow Cu$$

$$Overall : Zn_{(S)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(S)}$$

For Daniel Cell:

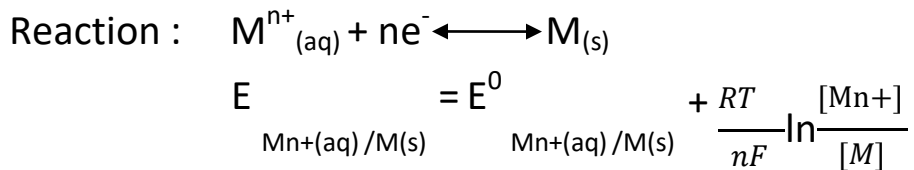$$E_{cell} = E^0_{cell} + \frac{2.303\ RT}{nF} \log \frac{[Cu2+]}{[Zn2+]}$$

➤ When $[Cu^{2+}] = [Zn^{2+}]$, then $E_{cell} = E^0_{cell.}$ ie, EMF is independent on temperature.
➤ When $[Cu^{2+}] > [Zn^{2+}]$, then logarithmic term becomes more postive ie, $E_{cell} > E^0_{cell}$ and EMF increases with rise of temperature.
➤ When $[Cu^{2+}] < [Zn^{2+}]$, then logarithmic term becomes negative ie,te

cell

Types of Electrodes

1. Metal -metal Ion electrode

It consists of a pure metal (M) in contact with the solution of its on cation (M^{n+}).
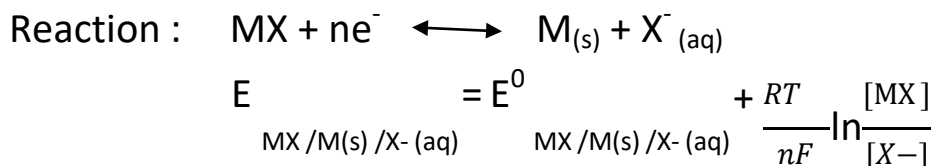
Representation : $M^{n+}_{(aq)} / M_{(s)}$

Reaction : $M^{n+}_{(aq)} + ne^- \longleftrightarrow M_{(s)}$

$$E_{Mn+(aq)/M(s)} = E^0_{Mn+(aq)/M(s)} + \frac{RT}{nF} \ln \frac{[Mn+]}{[M]}$$

2. Metal- metal in soluble salt electrode

It consists of a metal (M) coated by a layer of its sparingly soluble salt (MX) and immersed in a solution containing a common anion (X^-)

Representation: $MX / M_{(s)} / X^-_{(aq)}$

Reaction : $MX + ne^- \longleftrightarrow M_{(s)} + X^-_{(aq)}$

$$E_{MX/M(s)/X-(aq)} = E^0_{MX/M(s)/X-(aq)} + \frac{RT}{nF} \ln \frac{[MX]}{[X-]}$$
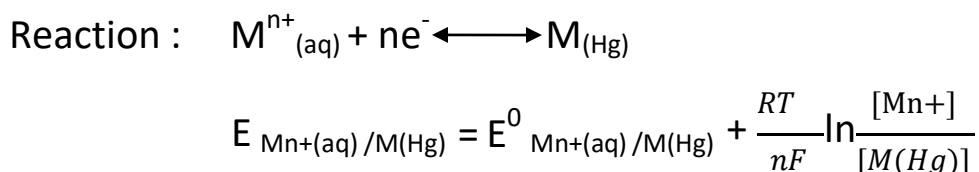
E.g.: Calomel Electrode

3. Metal amalgam electrode

It consists of a metal amalgam remaining in contact with the solution of metal ions.

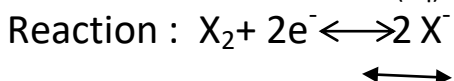Representation : $M^{n+}_{(aq)} / M_{(Hg)}$

Reaction : $M^{n+}_{(aq)} + ne^- \longleftrightarrow M_{(Hg)}$

$$E_{Mn+(aq)/M(Hg)} = E^0_{Mn+(aq)/M(Hg)} + \frac{RT}{nF} \ln \frac{[Mn+]}{[M(Hg)]}$$

4.Gas electrode

It contains an inert metal like Platinum dipped in a solution containing ions to which the gas is reversible. The gas is bubbled continuously through the solution.
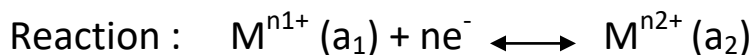
Representation: $X_2 / X^-_{(aq)} / Pt$
Reaction : $X_2 + 2e^- \longleftrightarrow 2 X^-$

$$E_{X2 / X^- (aq) / Pt} = E^0_{X2 / X^- (aq) / Pt} + \frac{RT}{nF} \ln \frac{[P(X2)]}{[X-]2}$$

Eg: Hydrogen electrode

5.Redox electrode

It contains an inert electrode like Platinum dipped in a solution containing ions of the same substance in two oxidation states.

Representation: $Pt / M^{n1+} (a_1) / M^{n2+} (a_2)$

Reaction : $M^{n1+} (a_1) + ne^- \longleftrightarrow M^{n2+} (a_2)$

$$E_{Pt / Mn1+ (a1) / Mn2+ (a2)} = E^0_{Pt / Mn1+ (a1) / Mn2+ (a2)} + \frac{RT}{nF} \ln \frac{a1}{a2}$$

CLASS 4

Reference electrodes

The electrode of standard potential with which we can compare the potentials of another electrode is called a reference electrode.

Standard hydrogen electrode (SHE)

It is a primary reference electrode and its EMF is arbitrarily fixed at zero. It consists of a small Platinum foil which is sealed through the end of a glass tube. This tube is surrounded by another tube which is sealed to the inner glass tube at the top. The outer glass tube is provided with side arm for passing hydrogen gas into the in between space. The bottom of the outer tube is shaped into a bell and its opening allows the escape of hydrogen gas.

Platinum foil is coated with a layer of finely divided platinum black which absorbs hydrogen gas and speeds up the equilibrium between hydrogen gas and hydrogen ions.
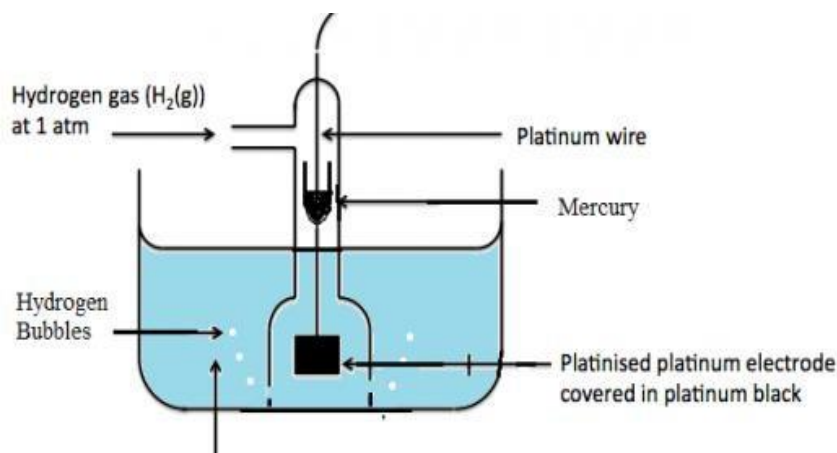
This electrode when dipped in 1 M HCl and when hydrogen at one atmosphere is passed through, it as the standard or normal hydrogen electrode (SHE/ NHE). It can act both as anode and cathode.

Representation(Anode) : Pt , ½ H_2(1 atm) /H^+(1M)

Cell reaction: $H_2(g) \longrightarrow 2H^+ + 2e^-$

Representation (Cathode): H^+(1M) / ½ H_2(1 atm) , Pt

Cell reaction: $2H^+ + 2e^- \longrightarrow H_2(g)$

Limitations

1. SHE is affected by Mercury, arsenic etc. So this electrode cannot be used.

2. SHE cannot be used in the presence of ions of many metals.

3. SHE cannot be used in solutions with redox system.

Calomel electrode (secondary reference electrode)

It consists of a glass tube - bottom of which is a layer of Mercury over which paste of Mercury and Hg_2Cl_2. The remaining portion is filled with a solution of normal or decinormal or saturated potassium chloride(KCl). A Platinum wire is dipped into the Mercury layer for making electrical contact. Side tube is for making electrical contact with Salt Bridge.

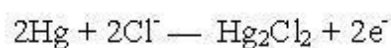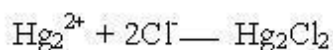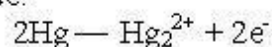Representation- cathode : KCl, Hg_2Cl_2 ,Hg

Representation – anode : Hg , Hg_2Cl_2(s) ,KCl(saturated)
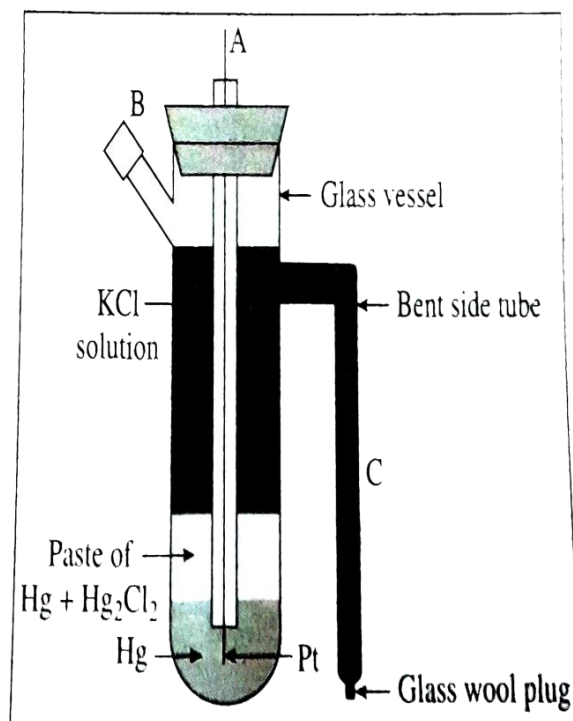
Calomel electrode

The electrode reactions are represented as follows.

As anode:

$$2Hg — Hg_2^{2+} + 2e^-$$

$$Hg_2^{2+} + 2Cl^- — Hg_2Cl_2$$

$$2Hg + 2Cl^- — Hg_2Cl_2 + 2e^-$$

As cathode:

$$Hg_2Cl_2 — Hg_2^{2+} + 2Cl^-$$

$$Hg_2^{2+} + 2e^- — 2Hg$$

$$Hg_2Cl_2 + 2e^- — 2Hg + 2Cl^-$$
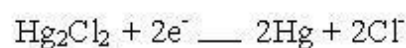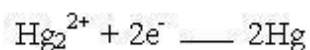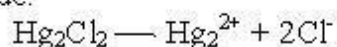
Calomel electrode is reversible with respect to chloride ions (Cl^-).

The reduction potential of this electrode at 25^0c for different concentration of KClsolution is given below.

KCl(concentration)	0.1N(Decinormal)	1N(Normal)	Saturated
Electrode potential(volts)	0.3335	0.2810	0.2422

Determination of electrode potential of Zn electrode using Calomel electrode

 In order to measure the electrode potential of any electrode (example Zn in Zinc sulphate) it is coupled with saturated calomel electrode through a salt bridge. Voltmeter directly gives the cell EMF.

 Electrode having higher production potential undergoes reduction (cathode) and the other undergoes oxidation (anode). E_{SCE} = 0.2422 is higher than $E_{Zn2+ /Zn}$ = -0.76V.Therefore SCE undergoes reduction reaction.

$$Zn /Zn^{2+} //Cl^- /Hg_2Cl_2 /Hg$$

Cathode : $Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$

Anode : $Zn \longrightarrow Zn^{2+} + 2e^-$
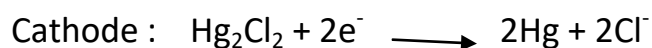
$$E_{cell} = E_{cathode} - E_{anode}$$

$$E_{cell} = 0.2422 - E_{Zn/Zn}^{2+}$$

$$E_{Zn/Zn}^{2+} = 0.2422 - E_{cell}$$

From the E_{cell} value, zinc electrode potential can be calculated.
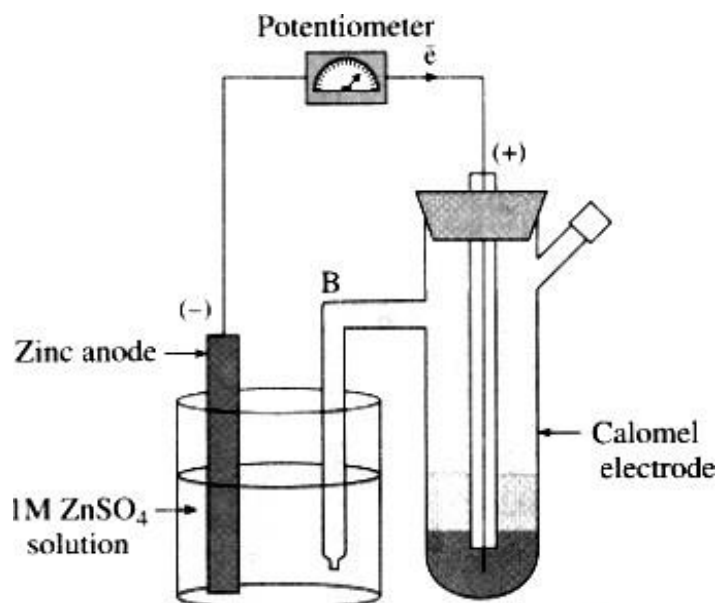
Determination of electrode potential of Cu electrode using Calomel electrode

In order to measure the electrode potential of any electrode (example Cu in Copper sulphate) it is coupled with saturated calomel electrode through a salt bridge. Voltmeter directly gives the cell EMF.

Electrode having higher production potential undergoes reduction (cathode) and the other undergoes oxidation (anode). E_{SCE} = 0.2422 is higher than $E_{Cu^{2+}/Cu}$ = 0.34V.Therefore SCE undergoes reduction reaction.

Hg   / Hg_2Cl_2/ Cl^- // Cu^{2+} /Cu

Cathode : $2Hg + 2Cl^- \longrightarrow Hg_2Cl_2 + 2e^-$

Anode : $Cu^{2+} + 2e^- \longrightarrow Cu$
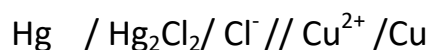
$$E_{cell} = E_{cathode} - E_{anode}$$

$$E_{cell} = E_{Cu2+/Cu} - 0.2422$$

$$E_{Cu2+/Cu} = E_{cell} + 0.2422$$

From the E_{cell} value, Copper electrode potential can be calculated.

GLASS ELECTRODE

When two solutions of different pH values are separated by a thin glass membrane there develops a difference of potential between the two surfaces of the membrane. The potential difference is proportional to the difference in pH value.

For a glass electrode potential difference varies with H $^+$ ion concentration and is given by,

$$E_G = E^0_G + 0.0592 \, P^H \text{ at } 25^0 c$$

A glass electrode consists of thin walled glass bulb containing AgCl coated Ag electrode or simply a platinum electrode in 0.1M HCl.

AgCl /Ag(s) ,HCl(0.1M) / Glass

Pt, HCl (0.1M) / Glass
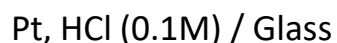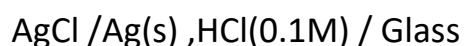
HCL in the bulb furnishes a constant H$^+$ ion concentration. It is silver -silver chloride electrode reversible with respect to chloride ions (Cl$^-$).

Wires to pH meter
Filling hole
AgCl covered silver wire
Ag/AgCl reference electrode
Reference electrode internal solution
Permeable porous junction
Glass electrode internal solution
Glass membrane
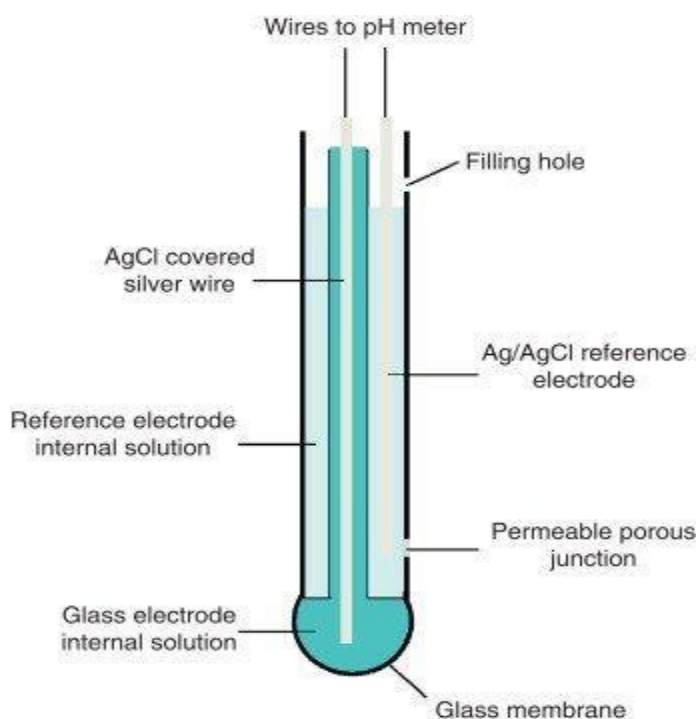
<u>Advantages</u>

1. It is simple and can be easily used.

2. Used to find pH of both oxidizing and reducing solution and coloured solutions.

3. Results are accurate

4. It is not easily poisoned.

<u>Limitations</u>

1. Cannot be used for solution with P^H about 12.

2. Class membrane is having high resistance and thus potential can be measured only by special electronic Potentiometer.

<u>Determination of pH using glass electrode</u>

In order to determine the pH of a solution the glass electrode is placed in the solution under test and this half-cell is coupled with saturated calomel electrode.

$$Ag(s) /AgCl(s) /HCl(0.1M) /Glass /H^+(c=?) // KCl(saturated) /Hg_2Cl_2 /Hg$$
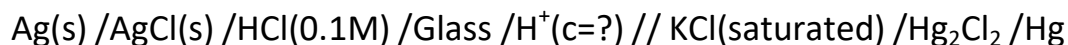
These two electrodes form two half cells.

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

$$E_{cell} = E_{calomel} - E_G$$

$$\text{But, } E_G = E^0_G + 0.0592 \ P^H$$

$$E_{cell} = 0.2422 - [E^0_G + 0.0592 \ P^H]$$

$$P^H = (0.2422 \text{-} E \ cell \text{-} E^0_G) \ / \ 0.0592$$

E^0G value of a glass electrode is first measured by dipping the electrode in buffer solution of known PH.

Vacuum tube

Platinum wire

Glass electrode

KCl satd. solution

Solution of unknown pH

Hg

0·1 M HCl

Hg + Hg_2Cl_2

Calomel electrode
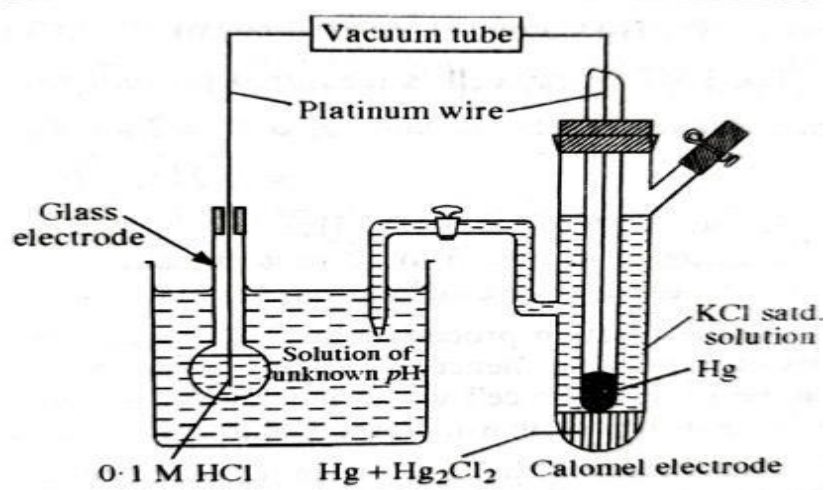
ELECTROCHEMICAL SERIES

The arrangement of various elements in the increasing order of their standard reduction potential is called electrochemical series or activity series.

Some typical elements are given below.

$$Li^+ + \bar{e} \rightarrow Li \qquad -3.05 V \quad Anodic$$

$$K^+ + \bar{e} \rightarrow K \qquad -2.93$$

$$Ca^{2+} + 2\bar{e} \rightarrow Ca \qquad -2.90$$

$$Al^{3+} + 3\bar{e} \rightarrow Al \qquad -1.66$$

$$Zn^{2+} + 2\bar{e} \rightarrow Zn \qquad -0.76$$

$$Fe^{2+} + 2\bar{e} \rightarrow Fe \qquad -0.44$$

$$Pb^{2+} + 2\bar{e} \rightarrow Pb \qquad -0.13$$

$$Fe^{3+} + 3\bar{e} \rightarrow Fe \qquad -0.04$$

$$H^+ + \bar{e} \rightarrow H \qquad 0 \quad Reference$$

$$Cu^{2+} + 2\bar{e} \rightarrow Cu \qquad 0.34$$

$$Ag^+ + \bar{e} \rightarrow Ag \qquad 0.80$$

$$F_2 + 2\bar{e} \rightarrow 2F^- \qquad 2.87 \quad Cathodic$$

Applications

1. Relative ease oxidation or reduction.

A system with the high reduction potential has a great tendency to undergo reduction.

Eg: F_2 / F^-

2. To predict which metal will react with acid to give hydrogen gas.

Metal above hydrogen in the electrochemical series have great tendency for oxidation so they displace hydrogen from acids.

3. Replacing tendency

Higher value of reduction potential shows a great tendency to assume the reduced form.

Eg: $E^0_{Cu2+/Cu}$ =0.34 V   and $E^0_{Zn2+/Zn}$ =-0.76 V

Cu^{2+} has a greater tendency to acquire Cu form than Zn^{2+} has for acquiring Zn. That is Zn will displace copper from its solution. ie, Metals above hydrogen will displace metals below hydrogen.

4. Predicting spontaneity of redox reaction

Positive value of E_{cell} indicates that reaction is spontaneous. If E is negative then the reaction is not feasible. In general and element having lower reduction potential can displace another metal having higher reduction potential from its salt solution.

$$\Delta G = -nFE$$

5. Calculation of equilibrium constant

$$E = E^0 + \frac{RT}{nF} \ln \frac{[Reactan\ ]}{[Products\ ]}$$

Or

$$\mathbf{E = E^0} - \frac{RT}{nF} \ln \frac{[Produc\ ]}{[Reactants\ ]}$$

$$E = E^0 - \frac{RT}{nF} \ln K_{eq}$$

$$0 = E^0 - \frac{RT}{nF} \ln K_{eq} \qquad \text{(At equilibrium } E_{cell} = 0)$$

$$\boxed{\ln K_{eq} = \frac{nFE^0}{RT}}$$

OR

$$\boxed{\log K_{eq} = \frac{nFE^0}{2.303 \ RT}}$$

CLASS 6

CONDUCTIVITY

The substance which allows the passage of electric current through them is called conductors and this phenomenon is called conductivity.

Electrical resistance (R)

It measures the obstruction to the flow of current. Resistance proportional to length and inversely proportional to area of cross section of the conductor.

$$R \propto \frac{l}{a}$$

$$R = \rho \frac{l}{a}$$

ρ is Specific resistance or resistivity

When l= 1 cm and a= 1 cm^3, then R = **ρ**

Ie, Specific resistance is the resistance of a conductor of unit length and unit area of cross section.

Unit-ohm cm

Electrical conductance(C)

It measures the ease with which the current flows through a conductor. Reciprocal of resistance.

Unit – Ohm^{-1} or mho or Siemen(S)

$$C = 1/R$$

Specific conductance (conductivity -K)

Reciprocal of specific resistance (ρ)

$$K = (1/R) (l/a)$$

It is defined as the conductance of 1 cm^3 of a conductor held between two electrodes of area 1 cm^2.

Cell constant

Ratio of distance between two electrodes and area of electrodes.

$$K = l /a$$

Unit – cm^{-1}

Measurement of conductivity

Kohlrauch's conductance ridge is widely used for measuring conductance.

Conductivity cell is connected to the resistance box R on one side and to a long thin wire AB is stretched along a scale on the other side.

An alternating current is passed and a point X at which the sound in the headphone P is minimum is located by moving the sliding contact along the wire AB. At every point other than X current will flow through the headphone and buzzing noise would be heard in the headphone. At point X, when no sound heard ,no current flows through the head phone.

At this point

$$\frac{Resistance\ of\ the\ solution}{Resistance\ R} = \frac{Length\ AX}{Length\ XB}$$

$$Resistance\ of\ the\ solution = \frac{Length\ AX}{Length\ XB}\ X\ R$$

$$\textbf{Conductance} = \frac{1}{R}\frac{XB}{AX}$$

∴ Conductance $= \frac{1}{R} \cdot \frac{XB}{AX}$
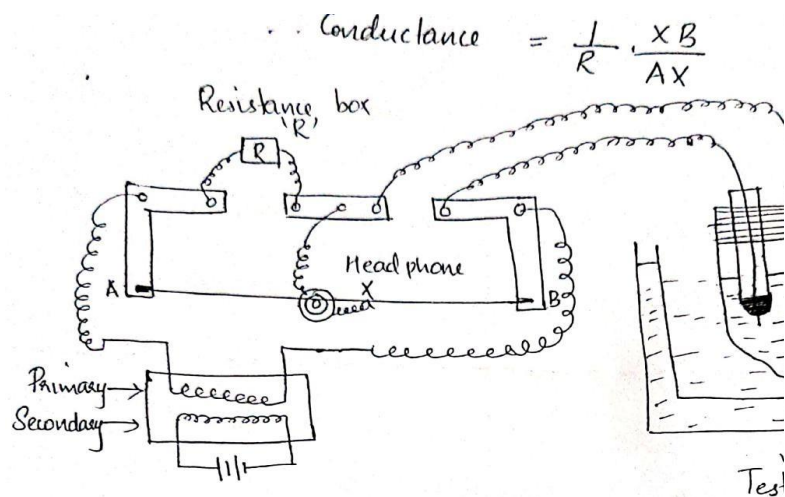
BATTERIES

Battery is an electrochemical cell or several electrochemical cells connected in series, that can e used as a source of direct electric current at a constant voltage. Batteries are of two types:

a). Primary battery

    Primary battery is in which the cell reaction is not reversible.

Eg. Dry cell and mercury cell.

b). Secondary battery

    Secondary battery is in which the cell reactions can be reversed by passing direct electric current in opposite directions.

Eg. Lead-storage battery, Nickel- cadmium battery and Lithium ion battery

LITHIUM ION BATTERY

It is a rechargeable battery in which lithium ion moves between anode and cathodeduring charging and discharging.

Positive electrode is made by using a crystalline mixed oxide, $LiCoO_2$ or $LiOCo_2O_3$. This crystal contains both Li^+ ion and Co^{3+} ion occupying the voids of the oxide array.Negative terminal is graphite. Electrolyte is a solution of lithium salt in an organic solvent such as ether or a solid phase polymer electrolyte which can transport Li^+ ions.

Charging

Anode - $LiCoO_2$

Cathode - Graphite

During charging the cell act as an electrolytic cell that is electrical energy is converted into chemical energy.

At anode - Some Li^+ ions get removed from the crystal lattice and in the respective lattice sites Co^{3+} ions get oxidized to Co^{4+}.

$$LiCoO_2 \rightarrow Li_{1-x}CoO_2 + x\ Li^+ + xe^-$$

At Cathode - Li^+ ion produced at the anode get migrated through the electrolyte and get reduced to Lithium atom at the graphite electrode.

$$C_{(G)} + x \ Li^+ + xe^- \rightarrow Li_xC_G$$
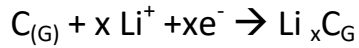
Lithium atoms are inserted between the layers of carbon atoms. This is called lithiated graphite

Fig.2.10: Lithium ion battery- Charging process

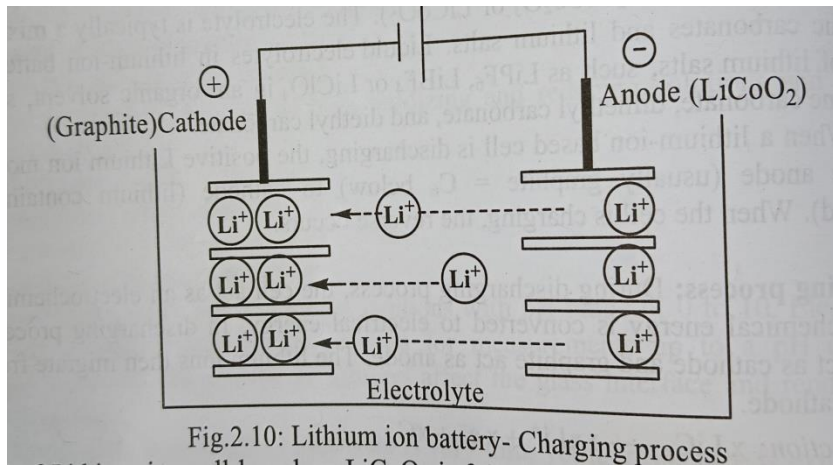## Discharging

During discharging the cell act as an electrochemical cell that is chemical energy is converted to electrical energy. During the discharging LiCoO2 act as cathode and graphiteacts as anode.

$$\text{At cathode}: \ Li_{1-x}CoO_2 + x \ Li^+ + xe^- \rightarrow LiCoO_2$$

$$\text{At anode}: Li_xC_G \rightarrow C_{(G)} + x \ Li^+ + xe^-$$
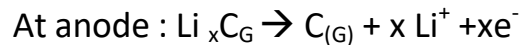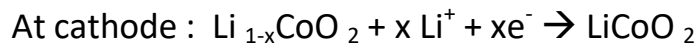
Lithium ion cell based on $LiCoO_2$ has an EMF of 3.7 V. Lithium ion cell with $LiFePO_4$ has an EMF of 3.3 V. The cell is suitable for cell phones, laptop, computers, digital cameras etc.

Fig.2.10: Lithium ion battery- Discharging process
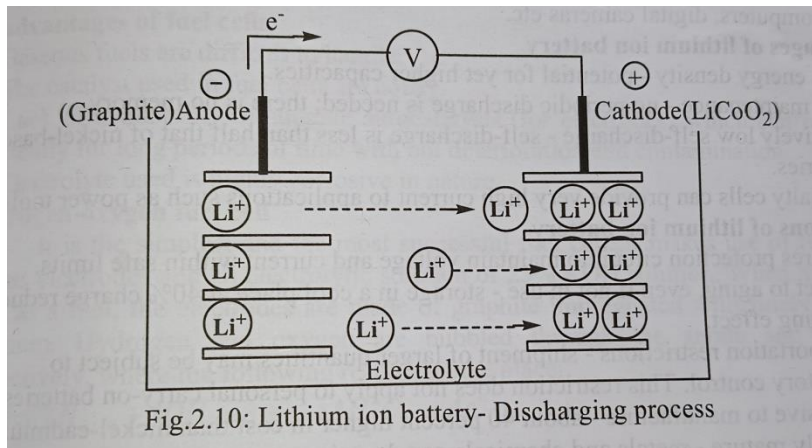
Advantages

- ➢ High energy density
- ➢ No maintenance (no period discharge is needed)
- ➢ Relatively low self discharge
- ➢ These can provide very high current application

Limitations

- ➢ Requires protection circuit to maintain voltage and current within safe limit
- ➢ Subject to ageing even if not in use
- ➢ Transportation restrictions
- ➢ Expensive to manufacture

CLASS 7

FUEL CELLS

When a fuel cell is burned, the electron exchange takes place only when the atoms of the oxidizing agent (oxygen or air) come in direct contact with the atoms of the substance being oxidized. In a fuel cell, electric energy is obtained without combustion from oxygen and a gas that can be oxidized. Hence, a fuel cell converts the chemical energy of the fuels directly to electricity. The essential process in a fuel cell is:

$$\text{Fuel + Oxygen} \longrightarrow \text{Oxidation product + Electrical Energy}$$

Fuel cells do not store chemical energy. In a fuel cell, the reactants are fed continuously and the products are removed continuously. A fuel cell remains in operation as long as the supply of the reactants is continued. The most common fuel cell is the hydrogen-oxygen fuel cell.

Advantages of fuel cells

(a) Fuel cells are more efficient. Efficiency of fuel cell is about 75%.

(b) Fuel cells can supply energy continuously without any drop in voltage/ current with time as seen in conventional cells or batteries.

(c) The concentration of the electrolyte remains unchanged.

(d) Fuel cells do not cause any pollution and they are free of noise, vibration, heat transfer etc. For example, in a hydrogen-oxygen fuel cell, the only product formed is water.

(e) It is compact, simple and easy to operate.

Disadvantages of fuel cells

(a) Gaseous fuels are difficult to handle.

(b) The catalyst used in fuel cells are costly.

(c) Lack of availability of suitable autocatalysts (for electrodes) which can function efficiently for long periods of time without deterioration and contamination.

(d) Electrolyte used is highly corrosive in nature.

Hydrogen-oxygen fuel cell

It is the simplest and the most successful fuel cell. It makes use of two inert porous electrodes and an electrolytic solution of 25% KOH solution. When hydrogen used as a fuel, the electrodes are made of graphite impregnated with finely divided platinum. Hydrogen and oxygen are bubbled through the anode and cathode respectively, where the following reactions take place:

Anode: $2H_{2(g)} + 4OH_{(aq)} \longrightarrow 4H_2O + 4e^-$

Cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH_{(aq)}$

Net reaction: $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$
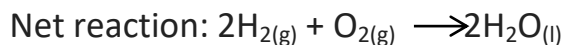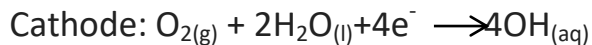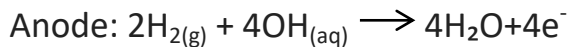
Standard emf of the cell, $E^\circ_{Cell} = E^\circ_{ox} + E^\circ_{red} = 0.83V + 0.40V = 1.23V$

In actual practice, the emf of cell is 0.8 to 1.0V. It may be noted that the only product discharged by the cell is water.

Fig.2.14: Hydrogen-oxygen fuel cell
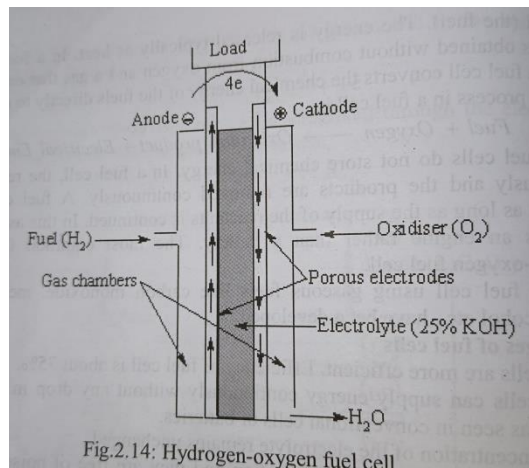
It is also noted that, electrodes must meet stringent requirements. They must:
(a) be good conductors, (b) be good electron sources and (c) not be consumed or deteriorated by the electrolyte heat or electrode reactions. Moreover, they must be excellent catalysts for the reactions that take place on their surfaces. The secret of successful fuel cells probably lies in the development of inexpensive electrodes that are powerful catalysts for the electrode reactions. Electrolyte used for most often are aqueous KOH or H_2SO_4 or ion exchange resin saturated with water. For low temperature operating fuel battery (-54°C to 72°C), potassium thiocyanate dissolved in liquid ammonia is employed.

Applications: Hydrogen -oxygen fuel cells are used as auxiliary energy source in space vehicles (e.g., Appolo spacecraft), submarines or other military vehicles.

CORROSION

Metals exist in nature in Combined forms are their oxides, carbonates, sulphides etc. These are reduced to their metallic states from their ores during their extraction process. When a metal is exposed to environment such as dry gases, moisture etc the exposed metal surface begin to decay.

Metal $\longleftrightarrow$ Metallic product + Energy

Forward reaction – Corrosion (Oxidation)

Backward reaction – Metallurgy(Reduction)

Any process of deterioration or destruction and consequently loss of a metallic material, through an unwanted chemical or electrochemical attack by its environment, starting at its surface is called the corrosion. Does corrosion is a process reverse of extraction of metals.

Eg: Rusting of iron

Fe form oxide Fe_3O_4 when exposed to air

Types of corrosion

- Dry or chemical corrosion

- Wet or electrochemical corrosion

- Galvanic or bimetallic corrosion

- Concentration cell corrosion

- Stress corrosion

- Pitting corrosion

- Waterline corrosion

- Microbiological corrosion

- Crevice corrosion

- Soil corrosion

CLASS 8

ELECTROCHEMICAL OR WET CORROSION

This type of corrosion occurs,

1. When a conducting liquid is in contact with metal.

2. When two dissimilar metals or alloys are dipped partially in a solution.

Electrochemical corrosion involves -

1. Formation of anodic and cathodic areas or parts in contact with each other

Presence of conducting medium

Corrosion of anodic area only

Formation of corrosion product somewhere between anodic and cathodic areas

Corrosion occurs due to the existence of separate anodic and cathodic parts.

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

Anode destroys by oxidation, by dissolution or by formation of compounds. Hence corrosion occurs at anodic area.

$$M^{n+} \text{ --- Dissolve in solution}$$

Form compounds such as oxide

At cathodic area reduction occurs. Cathodic reactions do not affect the cathode since most metals cannot be further reduced. So at cathode dissolved constituents in the conducting medium accepts electrons to form some ions.

The metallic ions (at anode) and non-metallic ions (at cathode) diffuse towards Each other through conducting medium and form a corrosion product somewhere between anode and cathode. The electrons set free at the anode flow through the metal and finally consumed in the cathodic reaction.

Depending upon the nature of corrosive environment cathodic reactions may result in,

**1. Evolution of hydrogen** - **In the absence of Oxygen and in acidic environment** evolution of hydrogen takes place. H^+ ions of acidic solution take up electrons released at anode and are removed as H_2 gas.

$$\text{Acidic medium --------} 2H^+ + 2e^- \rightarrow H_{2(g)} \uparrow$$

In alkaline or neutral solution in the absence of oxygen the reaction will be,

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ (in neutral / alkaline)}$$

Eg: rusting of iron in acidic medium in the absence of oxygen

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (Anode)}$$
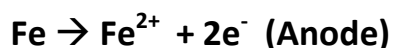
The electrons that are released flow from anode or cathode. The H^+ ions of acidic solution takes up these electrons and eliminated as H_2 gas.

$$2H^+ + 2e^- \rightarrow H_{2(g)} \uparrow \text{ (cathode)}$$

$$\text{Overall : } Fe + 2H^+ \rightarrow Fe^{2+} + H_{2(g)} \uparrow$$
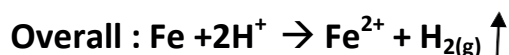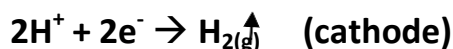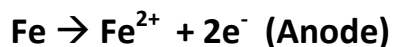
Hence in this corrosion H^+ ions are displaced from the acidic solution by metal ions.

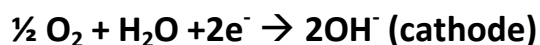**2. Absorption of oxygen** - In the presence of atmospheric oxygen in neutral aqueous solution or weakly alkaline solution oxygen gets reduced as,
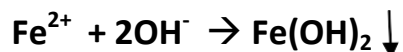
$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$
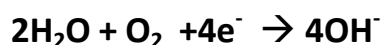
Eg: rusting of iron in neutral aqueous solution in presence of oxygen

$$Fe \rightarrow Fe^{2+} + 2e^{-} \text{ (Anode)}$$

Electrons move from anode to cathode and react with oxygen.

$$½ O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \text{ (cathode)}$$

Fe^{2+} ions produced at anode travel to cathode through the moisture and the react with OH^{-} ions produced at the cathode as follows,

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

The **Fe(OH)₂** produced is oxidized as,

$$Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \quad \text{or} \quad 2Fe_2O_3.3H_2O$$
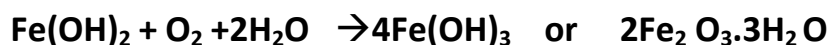
The degree of hydration of the iron (III) oxide affect the colour of the rust which may vary from black (Fe_2O_4) to yellow or reddish Brown ($Fe_2O_3.H_2O$)

It may be noted that all the corrosion occurs at anode , the rust is formed near the cathode. This is because smaller Fe^{2+} ions produced at anode diffuse rapidly towards the cathode as compared to the diffusion of larger OH^{-} ions towards the anode.

Wet corrosion by Hydrogen evolution
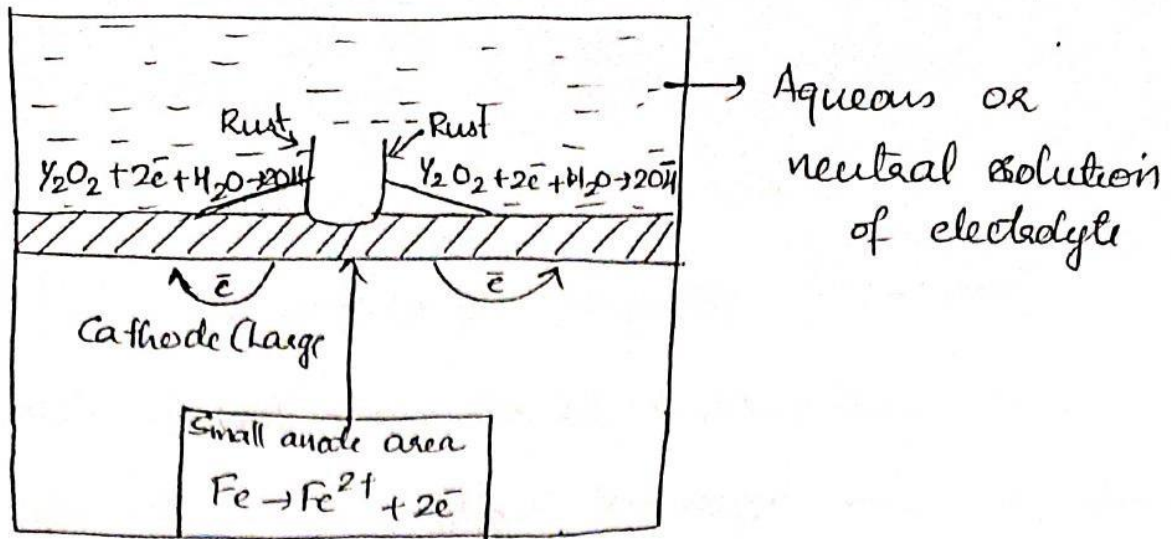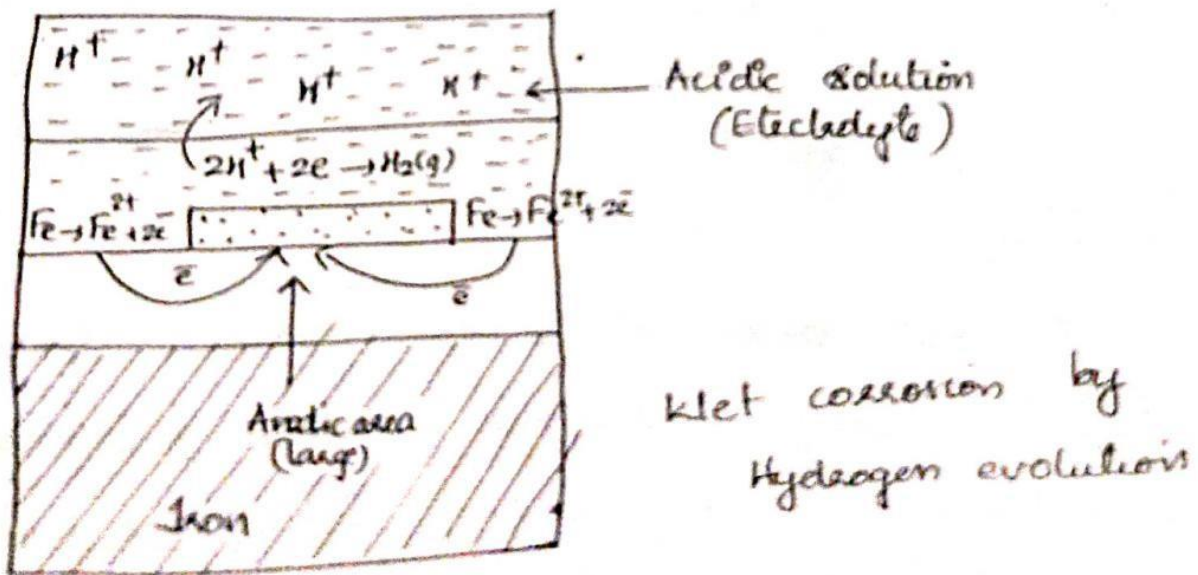
Wet Corrosion by absorption of oxygen.

GALVANIC SERIES

Electrochemical series can provide the basis for predicting the corrosion of the metals. The metals lying at the top of the series is more anodic and undergoes corrosion faster than metals below. However some metals behave exactly opposite to this due to the formation of protective oxide film (Passivity).

Galvanic series is a more reliable series for predicting the corrosion behavior in different environments. This series predicts the corrosion behavior of both metals, non-metals and alloys.

Galvanic series for seawater is given below,

Mg , Mg-alloys , Zn, Al, Cd, Al-alloys, Mild Steel, Cast iron,

_____

Anodic (easily corroded)

High Ni
Cast Iron
Pb-Sn Sold
Pb
Sn
8Ni-Mo-
Fe alloy

← Cathodic (Noble)

Pt, Au, Graphite , Ti, Ag, Cr, Stainless steel , Ni, Cu, Ag solder, Monel, brass
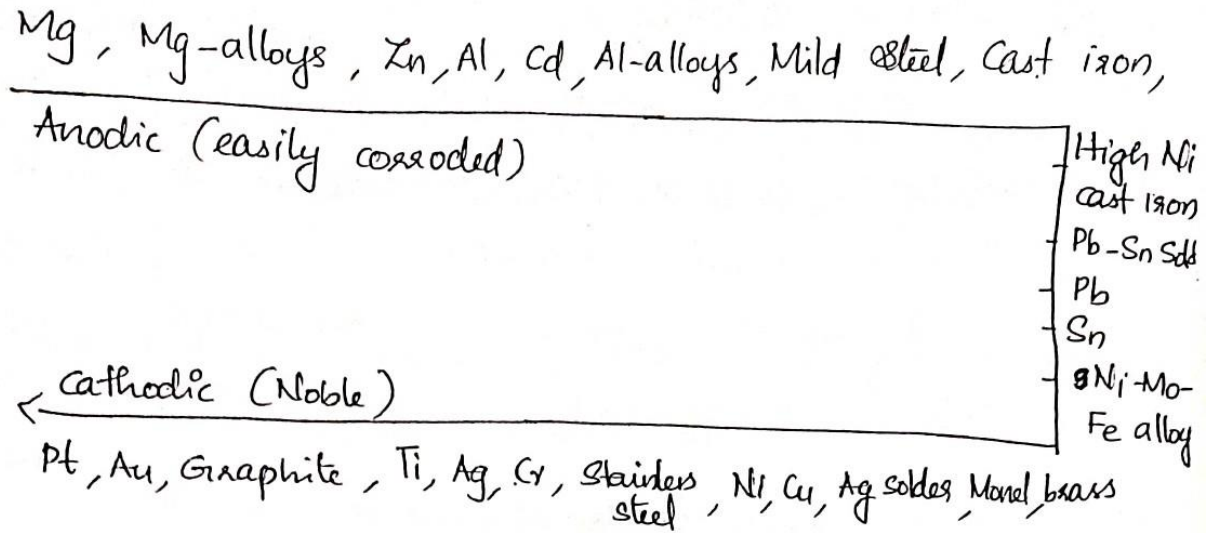
Electrochemical series	Galvanic Series
Electrode potentials are measured by dipping pure metals in their salt solution of C= 1M without any oxide film on them.	This series was developed by studying corrosion of metals and alloys in unpolluted sea water, without their oxide films.
It gives no information regarding position of alloys.	It gives information regarding position of alloys.
The position of a metal in this series is permanently fixed.	The position of a metal, when present in the form of an alloy, is different from that of pure metal.
This series comprises of both metals and non-metals	This series comprises of both metals and alloys.
It predicts the relative displacement tendencies.	It predicts the relative corrosion tendencies.

CATHODIC PROTECTION

Cathodic protection is to force the metal to be protected to behave like a cathode as a result of which it is not corroded.

It can be achieved in two ways,

1. By using Galvanic or sacrificial anode (Galvanic protection)

2. By using impressed current

1. Galvanic protection (sacrificial anodic protection)

In this the metal structure to be protected is made the cathode by connecting it by a wire to a more and anodic material. As a result corrosion takes place at anode and the metal structure is protected from corrosion. The more active (anodic) material used is called sacrificial anode.

Sacrificial anode is replaced by a fresh one when it gets corroded or consumed from time to time. Most commonly used metals are Mg, Al, Zn and their alloys.

At anode : $Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$

At cathode : $O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$
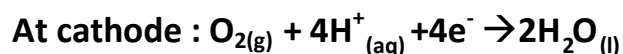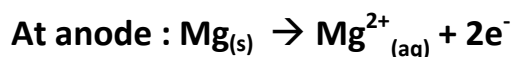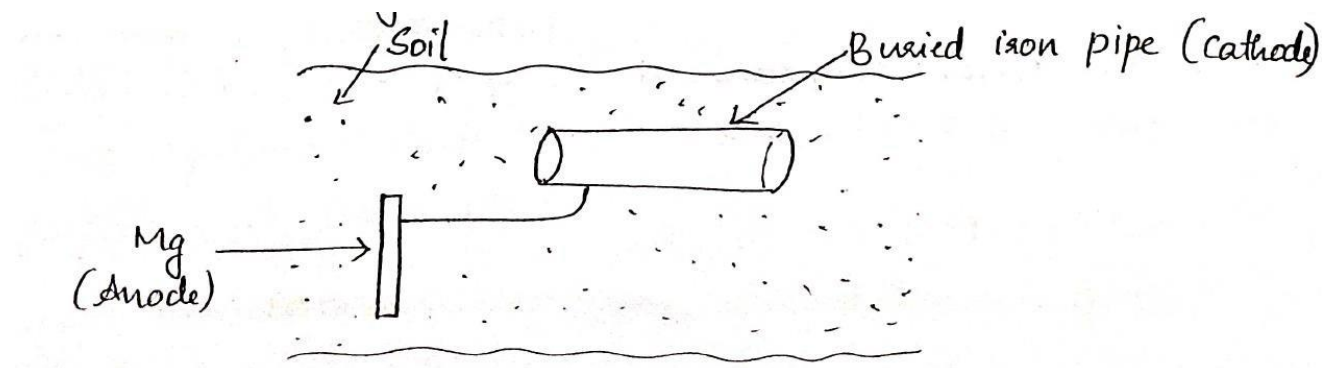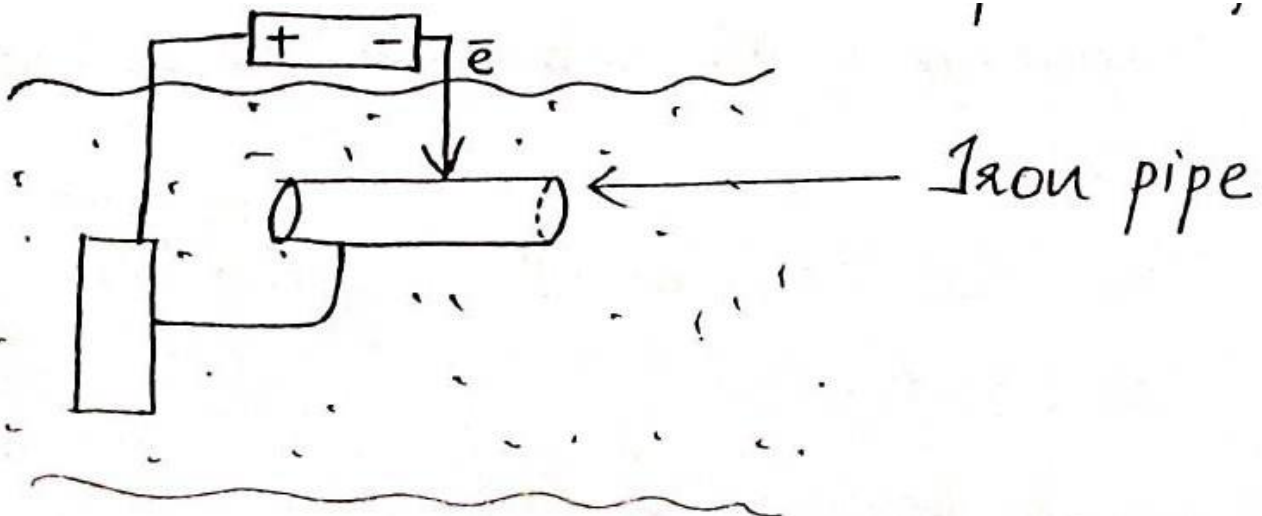
Applications

*   Protection of buried pipelines, underground cables

*   Protection of marine structures

*   Mg rods are inserted into domestic water boilers to prevent the rusting.

2.Impressed current cathodic protection(electrolytic method)

The object to be protected is made cathode by connecting it to negative terminal of DC source. The positive terminal is connected to an insoluble external anode like graphite, Platinum etc. The objective is to apply the current from an external source in the opposite direction of corrosion current. The electrons flow to the metal surface and as a result it act as cathode and is protected. The anode has to be replaced to periodically.

Applications

➢ Buried pipelines, transmission line Towers

➢ Water pipes, water tanks etc

➢ This technique is useful for large structure which requires long-term applications.

ELECTROPLATING

Electroplating is the process of electrolytic deposition of a metal on the surface of substrate; the substrate may be any metal, a polymer, a ceramic or a composite. Coating a layer of metal over the surface of material (metal, alloy, conducting polymer or any other conducting material) by applying an electric current is called as electroplating.

The main components of electroplating process are:

1. **Electroplating bath**: It contains a suitable salt solution of the metal being plated. It also contains other additives.

2. **Anode:** It may be a rod or pellets of the metal being plated. It may be an inert electrode. It should be electrically conducting.

3. **Cathode:** It is the article to be plated. It should have an electrically conducting surface.

4. **Inert vessel:** It may be a vessel made of rubber lined steel, plastic concrete or wood.

5. **DC power supply:** The positive terminal of the power supply is connected to the anode and the negative terminal is connected to the cathode.

CLASS 9

ELECTROPLATING OF COPPER

Electroplating copper is a process that involves depositing a layer of copper onto a surface using an electrical current.

It involves,

1. Preparation of the Surface

   ➢ **Removing Dirt and Oils:** This is typically done using ultrasonic cleaning, degreasing, or acid cleaning.

   ➢ **Etching:** To ensure good adhesion, the surface may be etched or abraded to create a rough texture.

2. Electroplating Solution

   The electroplating process requires a copper plating solution, which is usually an aqueous solution containing:

   - **Copper Sulfate ($CuSO_4$):** This provides the copper ions that will be deposited onto the substrate.
   - **Sulfuric Acid (H_2SO_4):** This helps to maintain the acidity of the solution and ensures good plating quality.
   - **Additives:** Various additives may be used to improve the quality of the plating, such as brighteners, and wetting agents

3. **Electroplating Setup**

The electroplating setup involves:

- **Anode:** The anode is made of copper and will dissolve into the solution, providing copper ions.
- **Cathode:** The cathode is the object to be plated. It is connected to the negative terminal of the power supply.
- **Power Supply:** This provides a direct current (DC) to drive the electroplating process.

4. Electroplating Process

The basic steps in the electroplating process are:

1. **Immersion:** The substrate (cathode) and the copper anode are immersed in the electroplating solution.
2. **Applying Current:** When the electrical current is applied, copper ions from the solution migrate to the cathode (the object to be plated) and are deposited onto its surface.
3. **Monitoring:** The process is monitored to ensure consistent plating thickness and quality. The current, temperature, and pH of the solution are controlled to achieve the desired results.

5. Post-Plating Treatment

After plating, the object typically undergoes:

- **Rinsing:** To remove any residual chemicals from the plating process.
- **Drying:** To prepare the object for use or further processing.
- **Polishing or Finishing:** To enhance the appearance of the plated surface if needed.

Reactions at anode and cathode during electroplating:

At anode oxidation takes place $Cu \longrightarrow Cu^{2+} + 2e^-$

When the anode used is an insoluble (inert) anode, oxygen evolution occurs at the anode: $H_2O \longrightarrow 1/2\ O_2 + 2H^+ + 2e^-$

At cathode, reduction occurs. The metal gets deposited on the cathode surface. For example: $Cu^{2+} + 2e^- \longrightarrow Cu$

<u>**Applications**</u>

Copper electroplating is used in a variety of industries:

➢ **Electronics:** To improve the conductivity of circuit boards.
➢ **Automotive:** For corrosion resistance and aesthetic purposes.
➢ **Jewelry:** For decorative finishes.

ELECTROLESS PLATING

It is the technique of depositing a noble metal from its salt solution on a catalytically active surface of a less noble metal by employing a suitable reducing agent without using electrical energy.

The metal ions undergo reduction to metal in presence of reducing agent and gets plated over the catalytically active surface giving a uniform, thin coating.

Metal + reduing agent →Metal + oxidized products

Various aspects of this are,

1. **Preparation of active surface of the object to be plated**

   ➢ Acid treatment – Etching

   ➢ Electroplating of a thin layer of the metal to be plated followed by heattreatment

   ➢ Treatment of surface with $SnCl_2$ followed by dipping in $PdCl_4$ solution

2. **Composition of the electroless plating bath,**

   • Soluble salt of metal to be plated – Cl^- ,SO_4^{2-}

   • Reducing agent - HCHO

   • Complexing agent - tartrate, citrate

   • Exaltant (enhances plating rate)- Succinate , fluoride

   • Stabilizer (prevent decomposition)- Thiourea

   • Buffer - Sodium acetate

Advantages

- No electrical energy is required

- Better throwing power

- Plating on insulators and semiconductors

- Uniform plating even for irregular shape

- Plated surface possess unique mechanical, chemical property
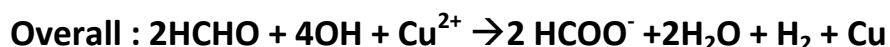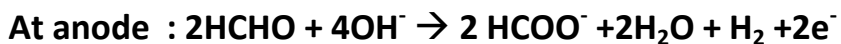
ELECTROLESS COPPER PLATING

It involves,

1. Free treatment and activation of the surface -

➢ Surface to be plated is first degreased followed by acid treatment.

➢ Metals like Fe, Co, Ni etc can be directly copper plated.

➢ Non metallic articles - dipping in $SnCl_2$ solution containing HCl followed by dipping in $PdCl_4$ solution. On drying a thin layer of active Pd is formed.

2. Composition of the bath

➢ Coating solution – $CuSO_4$ (12 g/L)

➢ Reducing agent – HCHO (8 g/L)

➢ Buffer – NaOH and Rochelle salt (14 g/L)

➢ Complexing agent cum exaltant - EDTA (20 g/ L)

➢ Optimum P^H - 11

➢ Optimum temperature – 25 ^{0}c

$$At\ anode : 2HCHO + 4OH^- \rightarrow 2\ HCOO^- + 2H_2O + H_2 + 2e^-$$

$$At\ cathode : Cu^{2+} + 2e^- \rightarrow Cu$$

$$Overall : 2HCHO + 4OH + Cu^{2+} \rightarrow 2\ HCOO^- + 2H_2O + H_2 + Cu$$

Applications

➢ Printed circuit boards(PCB)- double sided and multi-layered boards