

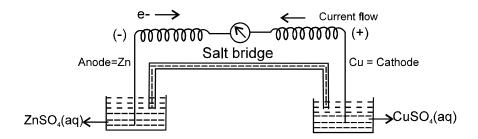
CHAPTER - 02 **ELECTROCHEMISTRY**

Electrochemical cell

It is a device used to convert chemical energy produced in a redox reaction into electrical energy. They are also called galvanic cells or voltaic cells.

Eg : Daniell cell

A zinc rod is placed in $ZnSO_4$ solution in a beaker and a copper rod is placed in $CuSO_4$ solution in another beaker. In each beaker both the reduced and oxidised forms of the same species are present. This is called redox couple. Now the two rods are connected by a wire and the two solution are connected by a salt bridge.



Oxidation occurs at anode (-ve electrode)

Reduction occurs at cathode (+ve electrode)

$$Zn \longrightarrow Zn^{2+} + 2e^{-}$$

$$\underline{Cu^{2+} + 2e^{-} \longrightarrow Cu}$$

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

The cell reactions are redox reactions and exothermic. The e⁻ move from anode to cathode producing current, but conventionally flow of current is represented in the opposite direction. The salt bridge is an inverted glass u-tube containing a saturated solutions of an inert electrolyte, like KCl, KNO $_3$, K $_2$ SO $_4$ or NH $_4$ NO $_3$ in agar-agar and gelatin. These salts are used because their ionic mobilities are equal.

The main functions of salt bridge are:

- 1. To maintain electrical neutrality of both anodic and cathodic compartment
- 2. To obtain continuous current in external circuit
- 3. To prevent the mixing of the two solutions

cell gives an electrical potential equal to 1.1 V (with 1M solutions)

Electrode potential (E)

The potential difference developed between the electrode and the electrolyte is called electrode potential. If the tendency of the electrode is to get oxidised, it is called oxidation potential, and if the tendency of the electrode is to get reduced, it is called reduction potential. At standard conditions (1M, 298K, 1 atm) it is called standard electrode potential (E⁰)

EMF of a cell (Cell potential) (E_{cell})

It is the difference between the reduction potential of cathode and anode. At standard conditions it is called standard EMF and is denoted as $E_{\rm cell}^0$. It can be calculated in 3 ways.

- 1. $E_{cell}^0 = std.R.Pof \ cathode std \ R.P. \ of \ anode = E_C^0 E_A^0 = E_{Right}^0 E_{Left}^0$
- 2. $E_{cell}^0 = std.O.P \text{ of } Anode std O.P. \text{ of } cathode = E_A^0 E_C^0$
- 3. $E_{cell}^0 = std.O.Pof Anode + std R.P. of cathode = E_A^0 + E_C^0$

Conventionally, anode is on the left and cathode is on the right while representing the galvanic cell. Daniell cell is indicated as, $Zn \mid Zn^{2+} \mid Cu^{2+} \mid Cu$

Standard hydrogen electrode (SHE)

It consists of a platinum wire sealed in a glass tube and has a platinum foil attached to it. The foil is coated with finely divided Pt. It is dipped in an acid solution containing 1M H^+ ions. Pure H_2 gas at 1 bar (1 atm) is bubbled into the solution at 298 K.

If SHE acts as anode; $H_2(g) \longrightarrow 2H^+ + 2e^-$

If SHE acts as cathode: $2H^+ + 2e^- \longrightarrow H_2(g)$

The electrode potential of SHE is taken as zero. It is used for calculating the potential of single electrodes. It is also called normal hydrogen electrode (NHE). It is primary standard electrode.

It is represented as : $Pt(s)|H_2(g)|H_{aq}^+$

Some other secondary standard (reference) electrodes are also used.

The most commonly used reference electrode is calomel electrode. Its potential depends on the concentration of KCl solution used:

Electrochemical series

The standard electrode potentials of various electrodes have been measured using SHE. The arrangement of elements in the order of increasing (or decreasing) electrode potential values is called electrochemical series (activity series). The main applications are

- 1. Relative strengths of oxidising and reducing agents. A negative E^0 means that redox couple is a stronger R.A. than H^+/H_2 couple. A positive E^0 value means that the redox couple is a weaker R.A. than H^+/H_2 couple.
- 2. Calculation of EMF of the cell
- 3. Predicting feasibility of a reaction
- 4. To predict whether a metal can liberate H₂ from acid or not.

NERNST EQUATION

The electrode potentials depend on the concentration of the electrolyte solution. Nernst gave a relationship between electrode potentials and the concentration of the electrolyte solution known as

Nernst equation. For a general electrode reaction, $M_{(aq)}^{n^+} + ne^- \longrightarrow M_{(s)}$, the Nernst equation is

$$E_{\left(M^{n^{+}|M}\right)}=E_{\left(M^{n^{+}|M}\right)}^{0}-\frac{RT}{nF}\ell n\frac{\left[M_{(s)}\right]}{\left\lceil M^{n^{+}}\left(aq\right)\right\rceil}.$$

R = gas constant, T = absolute temperature.

n = no.of electrons gained and F = Faraday constant.

$$[M(s)]$$
 = Molar concentration of solid metal = 1

 E^0 = standard reduction potential

$$E_{(M^{n+}|M)} = E_{(M^{n+}|M)} - \frac{2.303RT}{nF} log \frac{[Pr oduct]}{[Re ac tan ts]}$$

ie,
$$E = E^0 + \frac{2.303RT}{nF} log \frac{[Re ac tan ts]}{[Pr oducts]}$$

$$E = E^{0} + \frac{0.059}{n} log \frac{[Re ac tan ts]}{[Pr oducts]}$$
 At 298 K, $\frac{2.303RT}{F} = 0.059$

$$E = E^{0} - \frac{0.059}{n} log \frac{[Pr oducts]}{[Re ac tan ts]}$$

$$[solid] = 1$$

$$[liquid] = 1$$

For gases instead of molar concentration, partial pressure is used.

Equilibrium constant from Nernst equation

Consider the redox reaction,
$$Zn_{(s)} + Cu_{(aq)}^{2+} \longrightarrow Zn_{(aq)}^{2+} + Cu_{(s)}$$

As the reaction proceeds, the conc.of Zn^{2+} increases and its R.P. increases. The concentration of Cu^{2+} decreases and its R.P. decreases with passage of time. Ultimately the R.P. of the two electrodes become equal. Thus the emf of the cell becomes zero and the reaction stops

$$(E_{cell} = R.P.of cathode - R.P.of Anode)$$

Under these conditions, the electrochemical cell is said to have attained equilibrium state, and $E_{cell} = 0$

$$E_{cell} = E_{cell}^{0} - \frac{0.059}{n} log \frac{\left[Zn^{2+}(aq)\right]}{\left[Cu^{2+}(aq)\right]}$$

At equilibrium;
$$0 = E_{\text{cell}}^0 - \frac{0.059}{n} \log K_c$$

or
$$E_{\text{cell}}^0 = \frac{0.059}{n} \log K_c$$

The value of K_c gibes the extent of the cell reaction. If value of K_c is large, reaction proceeds to larger extent.

Electrochemical cell and Gibb's energy of reaction

In the cell the system does work by transferring electrical energy through an electric circuit. Electrical work done in 1 second is equal to the electrical potential multiplied by the total charge passed.

 ΔG of a reaction is a measure of the maximum useful work obtained from a chemical reaction. The work done when amount of charge nF is pushed by the potential of the cell (E_{cell}) is given by nFE_{cell}.

 $W_{max} = nFE_{cell}$. Here work is done by galvanic cell : it is negative.

$$\therefore \Delta G_{\rm r}^0 = -nFE_{\rm cell}^0$$

Also the equilibrium constant can be calculated by the equation:

$$\Delta G_r^0 = -RT \ln K$$

Or,
$$\Delta G_r^0 = -2.303RT \log K$$

1. Concentration cells I Electrolytic concentration cell

It is a cell in which both the electrodes are of the same type but the solutions of the electrolyte have different concentration.

Eg:
$$\operatorname{Cu} | \operatorname{CuSO}_{4(aq)}(\operatorname{C}_1) | | \operatorname{CuSO}_{4(aq)}(\operatorname{C}_2) | \operatorname{Cu}$$

Here the E⁰ terms cancel and the cell potential is given by

$$E_{\text{cell}} = \frac{0.059}{n} \log \frac{C_2}{C_1} \left(C_2 > C_1 \right)$$

II. Electrode concentration cell

Two similar electrodes at different concentrations is immersed in the same solution of the electrolyte. Eg: Two hydrogen electrodes at different gas pressures in the same solution of acid.

$$Pt; H_{2(g)}(P_1) | HCl(1M) | H_{2(g)}(P_2); Pt$$

$$E_{cell} = \frac{0.059}{n} log \frac{P_1}{P_2}$$
 This cell is spontaneous when $P_1 > P_2$

CONDUCTORS

The substances which allow the passage of electric current are called conductors. Conductors are classified into two types.

- **1. Metallic conductors or electronic conductors.** They conduct electricity without undergoing any decomposition. Eg: Metals, graphite etc. The conduction is due to the flow of electrons.
- **2. Electrolytic conductors or electrolytes.** They allow the electricity to pass through them in their molten state of in the form of their aqueous solutions. Eg: Solutions of acids, bases, salts in water. The flow of electricity is due to the movement of ions. Hence are also called ionic conductors.

Electrolytes are classificied into

- **Strong electrolytes**: They are completely dissociated into ions in solution, conduct electricity to large extent. Eg: HCl, HNO₃, H₂SO₄, NaCl, NaOH, NH₄NO₃......
- **Weak electrolytes**: They have low degree of dissociation, hence conduct electricity to a small extent. Eg: CH₃COOH, H₂CO₃, HCN, H₃BO₃, NH₄OH etc.

FACTORS AFFECTING METALLIC CONDUCTANCE

1. Nature and structure (electronic configuration) of the metal

- 2. No.of valence e- per atom
- 3. Metallic conductance decreases with increase of temperature because the positive ions of metal start vibrating and produce hinderance in the flow of electrons.

FACTORS AFFECTING ELECTROLYTIC CONDUCTANCE

- 1. Nature of electrolyte
- 2. The conductance of an electrolyte increases with decrease in concentration or increase in dilution
- 3. Dissociation of an electrolyte increases on increasing the temperature. : conductance increases.
- 4. Electrolytes ionize more in polar solvents. ∴ Greater the polarity of the solvent, greater is the conductance.
- 5. Greater the viscosity of a solvent, lesser is the conductance.

Specific resistance (Resistivity)

 $R \alpha \frac{\ell}{a}$; R - Resistance of conductor; I = length of conductor, a = area of cross section

 $R = \rho \times \frac{\ell}{a} \text{ where } \rho \text{ (rho) is called the specific resistance or resistivity. If } \ell = 1 \text{cm}, \text{ a = 1 cm}^2 \text{ then } R = \rho \text{ ie specific resistance is the resistance of 1 cm}^3 \text{ of the conductor.}$

$$\rho = \frac{Ra}{\ell} = \frac{ohm \times cm^2}{cm} = ohm \ cm \ (unit)$$

Conductance: It is the reciprocal of resistance, denoted by G.

$$\therefore G = \frac{1}{R}; \text{ unit is ohm}^{-1}$$

Conductivity (Specific conductance)

The inverse of resistivity is called conductivity. It is represented by the symbol κ (Kappa). It is the conductance of a solution of 1 cm length and 1 cm² as the area of cross section.

$$\kappa = \frac{1}{\rho}$$
.

It is the conductance of 1cm³ of the conductor. $\kappa = \frac{1}{\rho} = \frac{1}{ohm \ cm} = ohm^{-1} \ cm^{-1} \ (unit \ of \ \kappa) = S \ cm^{-1}$

$\underline{\text{Molar conductivity}}\left(\lambda_{\scriptscriptstyle m}\right)$

It is the total conductance of a solution which contains 1 mole of the substance. λ_m = conductance of 1 cc \times volume of solution in cc. containing 1 mole

$$\boxed{\lambda_{\rm m} = \kappa \times \frac{1000}{M} \ | \ \text{M} = \text{Molarity of solution}}$$

$$\text{Unit of } \lambda_m \text{ is } \lambda_m = \frac{Scm^{-1} \times cm^3L^{-1}}{molL^{-1}} = Scm^2mol^{-1} \text{ = } Sm^2mol^{-1} \text{ (In SI unit)}$$

$$1 \text{ Sm}^2 \text{mol}^{-1} = 1 \text{S} \times (10^2 \text{ cm})^2 \text{ mol}^{-1} = 10^4 \text{S cm}^2 \text{mol}^{-1}$$

$$1 \text{S cm}^2 \text{mol}^{-1} = 1 \text{S} \times (10^{-2} \, \text{m})^2 \, \text{mol}^{-1} = 10^{-4} \, \text{Sm}^2 \, \text{mol}^{-1}$$

Measurement of Resistance/Conductance/Conductivity

Resistance of a metallic conductor can be easily measured by connecting it to a wheatstone bridge. But for measuring the resistance of an electrolytic conductor there are two difficulties. Direct current (DC) cannot be used because it causes electrolysis of the solution. So AC is used. Secondly a solution cannot be connected to wheatstone bridge like a metallic wire. This is solved by using a specially designed vessel called conductivity cell for taking the solution. It is then connected to wheatstone bridge. The conductivity cell contains 2 electrodes separated by a distance *I*, having an area of cross section equal to a.

The resistance is given by: $R=\rho\times\frac{\ell}{a}$

The quantity $\frac{\ell}{a}$ is called cell constant denoted by G^{\times} ; $\therefore G^{\times} = \frac{\ell}{a} = \frac{cm}{cm^2} = cm^{-1}$

$$\therefore R = \frac{1}{\kappa} \times G^{\times} \quad \text{or} \quad \kappa = \frac{1}{R} \times G^{\times} \quad \text{or} \quad \kappa = G \times G^{\times}$$

Thus knowing the value of cell constant and conductance of solution, the conductivity (specific conductance) can be calculated.

Variation of conductivity (specific conductance) with concentration

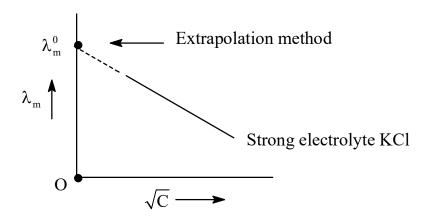
Conductivity is the conductance of 1 cm³ of the solution. Upon diluting the solution, the number of ions per cm³ decreases and therefore the conductivity decreases.

Variation of λ_m (or λ_{eq}) with concentration

1. **Strong electrolytes**. On diluting a strong electrolyte, the interionic attraction decreases ionic mobility increases and the conductance also increases. Finally it reaches maximum value at infinite dilution

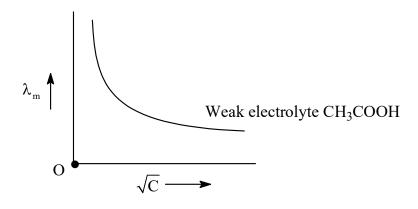
(called molar conductivity at infinite dilution) denoted by λ_m^∞ (or limiting molar conductance). This is also given by Debye-Huckel-Onsager equation.

$$\lambda_{_{m}}=\lambda_{_{m}}^{0}-b\sqrt{C}$$
 (b is a constant and C is the concentration)



 $\lambda_{m}^{\scriptscriptstyle 0}\,$ can be calculated by extrapolating the line to meet the Y-axis

2. Weak electrolytes. On diluting a weak electrolyte, the degree of dissociation increases. The no.of ions increases suddenly and hence the conductance increases, sharply.



 $\lambda_{\rm m}^0$ cannot be determined by the extrapolation method

KOHLRAUSCH'S LAW OF INDEPENDENT MIGRATION OF IONS

The molar conductivity at infinite dilution of an electrolyte is the sum of the molar conductivities at infinite dilution of the cation and anion.

1.
$$\lambda_{m}^{0} (NaC1) = \lambda_{Na^{+}}^{0} + \lambda_{C1^{-}}^{0}$$

$$\lambda_{eq}^{0}\left(NaCl\right) = \lambda_{eq\left(Na^{+}\right)}^{0} + \lambda_{eq\left(Cl^{-}\right)}^{0} = \frac{\lambda_{Na^{+}}^{0}}{1} + \frac{\lambda_{Cl^{-}}^{0}}{1}$$

$$\therefore \lambda_{\rm m}^0 = \lambda_{\rm eq}^0$$

2.
$$\lambda_{m}^{0} (CaCl_{2}) = \lambda_{Ca^{2+}}^{0} + 2\lambda_{Cl^{-}}^{0}$$

$$\lambda_{eq}^{0}\left(CaCl_{2}\right) = \lambda_{eq\left(Ca^{2+}\right)}^{0} + \lambda_{eq\left(Cl^{-}\right)}^{0} = \frac{\lambda_{Ca^{2+}}^{0}}{2} + \frac{\lambda_{Cl^{-}}^{0}}{1}$$

Multiplying by 2;
$$2\lambda_{eq(CaCl_2)}^0=\lambda_{Ca^{2+}}^0+2\lambda_{Cl^-}^0=\lambda_m^0$$

$$\therefore 2\,\lambda_{eq}^0 = \lambda_m^0$$

3.
$$\lambda_{m}^{0} \left[Al_{2} \left(SO_{4} \right)_{3} \right] = 2\lambda_{Al^{3+}}^{0} + 3\lambda_{SO_{4}^{2}}^{0}$$

$$\lambda_{eq}^{0} \left[Al_{2} \left(SO_{4} \right)_{3} \right] = \lambda_{eq(Al^{3+})}^{0} + \lambda_{eq(SO_{4}^{2-})}^{0} = \frac{\lambda_{Al^{3+}}^{0}}{3} + \frac{\lambda_{SO_{4}^{2-}}^{0}}{2}$$

Multiplying by 6;
$$6\lambda_{eq}^0=\lambda_m^0$$

APPLICATION OF KOHLRAUSCH'S LAW

- 1. Calculation of λ_m^0 and λ_{eq}^0 for weak electrolyte
- 2. Calculation of degree of dissociation of weak electrolytes $\alpha = \frac{\lambda_m^c}{\lambda_m^0}$ OR $\alpha = \frac{\lambda_{eq}^c}{\lambda_{eq}^0}$
- 3. Calculation of dissociation constant of weak electrolytes $\text{Ka}\left(\text{CH}_3\text{COOH}\right) = \frac{\text{C}\alpha^2}{1-\alpha}$
- 4. Calculation of solubility of sparingly soluble salt like AgCl, BaSO₄, PbSO₄

For such salts; (1) Molarity (M) = Solubility (S) (2) $\lambda_{\rm m}^0 = \lambda_{\rm m}$

$$\therefore \lambda_{\rm m} = K \times \frac{1000}{M} \, ; \text{ ie } \lambda_{\rm m}^{\rm 0} = K \times \frac{1000}{S} \, \therefore \, \boxed{S = \frac{K \times 1000}{\lambda_{\rm m}^{\rm 0}}}$$

ELECTROLYSIS

Electrolysis is the decomposition of an electrolyte by the passage of electricity through the aqueous solution or the molten state. It is carried out in an electrolytic cell in which anode is the positive electrode where oxidation occurs and cathode is the negative electrode where reduction occurs. It is a non spontaneous process.

1. Electrolysis of molten NaCl using Pt electrodes.

At cathode :
$$Na^+ + 1e^- \longrightarrow Na(s)$$

At anode :
$$Cl^- \longrightarrow \frac{1}{2}Cl_2(g) + 1e^-$$

2. Electrolysis of aqueous NaCl using Pt electrodes. It contains Na⁺, Cl⁻ and H₂O

At cathode : (1)
$$Na_{aq}^+ + 1e^- \longrightarrow Na$$
; $E_{Na^+/Na}^0 = -2.71 \text{ V}$

(2)
$$2H_2O + 2e^- \longrightarrow H_{2(g)} + 2OH_{ag}^-$$
; $E_{H_2O/H_2}^0 = -0.83 \text{ V}$

H₂O has higher reduction potential than Na⁺. ∴ H₂O is reduced into H₂(g)

At anode : (1)
$$Cl^- \longrightarrow \frac{1}{2}Cl_2(g) + le^-$$
; $E_{Cl^-/Cl_2}^0 = -1.36 \text{ V}$

(2)
$$2H_2O \longrightarrow O_{2(g)} + 4H^+ + 4e^-$$
; $E_{H_2O/O_2}^0 = -1.23 \text{ V}$

The oxidation of H_2O into O_2 is a slow process and also over voltage (over potential) is needed. Therefore oxidation of chloride into $Cl_2(g)$ occurs at anode.

After the electrolysis the solution contains Na⁺ and OH[−] ions. (or NaOH). ∴ The solution becomes alkaline and the pH increases.

3. Electrolysis of aqueous CuSO₄ using Pt electrodes.

It contains
$$Cu^{2+}$$
, SO_4^{2-} and H_2O

At cathode : (1)
$$Cu_{aq}^{2+} + 2e^{-} \longrightarrow Cu$$
; $E_{Cu^{2+}/Cu}^{0} = +0.34V$

(2)
$$2H_2O + 2e^- \longrightarrow H_{2(g)} + 2OH_{aq}^-$$
; $E_{H_2O/H_2}^0 = -0.83 \text{ V}$

R.P. of Cu²⁺ is higher. : Cu is deposited.

At anode: (1)
$$2SO_{4(aq)}^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$$
; $E_{SO_8^{2-}/S,O_8^{2-}}^0 = -2 \text{ V}$

(2)
$$2H_2O \longrightarrow O_{2(g)} + 4H^+ + 4e^-$$
; $E_{H_2O/O_2}^0 = -1.23 \text{ V}$

Here no other gas (Only O₂) is formed.

After the electrolysis the solution contains H^+ and SO_4^{2-} (or H_2SO_4) ions. \therefore The solution becomes acidic in nature and pH decreases.

4. Electrolysis of aqueous CuSO₄ using Cu electrodes

It contains Cu²⁺, SO₄²⁻ and H₂O

At cathode: (1) $Cu^{2+} + 2e^{-} \longrightarrow Cu$; $E^{0}_{Cu^{2+}/Cu} = +0.34 \text{ V}$

(2)
$$2H_2O + 2e^- \longrightarrow H_{2(g)} + 2OH^-$$
; $E_{H_2O/H_2}^0 = -0.83 \text{ V}$

At anode : (1) $2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$; $E^0_{SO_4^{2-}/S,O_8^{2-}} = -2~V$

(2)
$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$
; $E_{H,O/O_2}^0 = -1.23 \text{ V}$

(3)
$$Cu \longrightarrow Cu^{2+} + 2e^{-}$$
; $E_{Cu/Cu^{2+}}^{0} = -0.34 \text{ V}$

The net result is that copper is deposited at the cathode from the solution and an equivalent amount of copper from the anode dissolves into solution as Cu²⁺ ions. No acid or base is formed and hence the pH remains the same.

FARADAY'S FIRST LAW OF ELECTROLYSIS

The amount of substance deposited at the electrode is directly proportional to the quantity of electricity passed through the electrolyte.

If w gram substance is deposited by passing Q coulombs of electricity, $w \alpha Q$ or w = ZQ

Where Z = electrochemical equivalent of the substance.

or
$$\boxed{w = ZIt}$$
; I = Current in Amperes; t = time in seconds.

From this the electrochemical equivalent is defined as the mass of substance deposited in gram when 1 ampere current is passed for 1 second. (ie when 1 coulomb is passed). The unit of Z is gram coulomb⁻¹.

Faraday's second law

When the same quantity of electricity is passed through different electrolytes the amount of substances deposited are directly proportional to their respective equivalent weights.

For 2 substances deposited A and B, then $\frac{w_A}{w_B} = \frac{E_A}{E_B}$ w = mass in gram; E = equivalent weight

Faraday (1F = 96500 C)

1F is the quantity of charge on 1 mole of electrons.

OR

1F is the quantity of charge required to deposit 1g equivalent of a substance. 96500 C deposits E gram substance.

$$\therefore$$
 Mass of substance deposited by 1C = $\frac{E}{96500}$ = Z

$$w = ZIt$$

ie
$$w = \frac{EIt}{96500}$$

w = mass deposited in gram, E = equivalent weight, I= current in Ampere, t = time in seconds

Commercial cells (Batteries)

2 types of commercial cells

I. Primary cells

Here the redox reaction occurs only once and they are not chargeable.

Eg: (1) Dry cell (Laclanche cell)

Anode = Zn container

Cathode = Graphite rod

Electrolyte = Paste of NH₄Cl, ZnCl₂, MnO₂ and C powder

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

Cathode : $2NH_4^+ + 2MnO_2 + 2e^- \longrightarrow 2MnO(OH) + 2NH_3$

It gives voltage of 1.2 to 1.5 V

(2) Mercury cell

Anode = Zn amalgam

Cathode = C rod

Electrolyte = HgO + KOH

Anode : $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$

Cathode : $HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^-$

 $Zn + HgO \longrightarrow ZnO + Hg$

It gives a constant voltage of 1.35 V

II. Secondary cells

In this, the reactions can be reversed by an external electric energy source. So they can be recharged and used again.

1. Lead storage battery

Anode = Pb

Cathode = PbO₂

Electrolyte = H₂SO₄

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

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

 $Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$

At battery containing 6 cells gives output of 12 V.

2. Ni-Cd cell

Anode = Cd

Cathode = NiO₂

Electrolyte = KOH

Anode : $Cd + 2OH^{-} \longrightarrow Cd(OH)_{2} + 2e^{-}$

Cathode: $NiO_2 + 2H_2O + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$

 $Cd + NiO_2 + 2H_2O \longrightarrow Cd(OH)_2 + Ni(OH)_2$

It produces a potential of 1.4 V

III. Fuel cells

They are galvanic cells in which the energy of combustion of fuels like H_2 , CH_4 , CH_3OH etc is directly converted into electrical energy.

 $Eg: H_2 - O_2$ fuel cell

 H_2 is used as fuel and O_2 acts as the O.A. The energy of combustion of H_2 is converted into electrical energy.

Electrodes = Porous C rods

Electrolyte = Aqueous NaOH or KOH

Catalysts = Pt, Pd

 $\rm H_2$ and $\rm O_2$ are bubbled into NaOH/KOH solution. $\rm H_2$ at the anode is oxidised. $\rm O_2$ at the cathode is reduced.

Anode :
$$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$$
Cathode : $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^ 2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(\ell)}$

It gives a potential of 0.9 V. They have a high efficiency. It is a pollution free cell.

Efficiency of fuel cell = $\frac{\text{Electrical energy produced}}{\text{Enthalpy change during combustion}}$

ie
$$\eta = \frac{\Delta G}{\Delta H}$$

CORROSION

It is the slow destruction of a metal as a result of its reaction with air or water surrounding it.

Eg: Rusting of iron, tarnishing on silver, formation of a green coating on copper vessels.

Mechanism of rusting of iron

Large number of tiny electrochemical cells are formed on the surface of iron. Anode is pure iron and cathode is the impure surface. Electrolyte is , water vapour on the metal surface which dissolve ${\rm CO_2}$ and ${\rm O_2}$ from air producing carbonic acid.

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

$$H_2CO_3 \longrightarrow 2H^+ + CO_3^{2-}$$

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

Cathode: $2H^{+} + 2e^{-} \longrightarrow 2H$

$$2H + \frac{1}{2}O_{2} \longrightarrow H_{2}O$$

$$2Fe_{(s)} + 4H^{+} + O_{2} \longrightarrow 2Fe_{(aq)}^{2+} + 2H_{2}O$$

Multiply by 2 and add

The ferrous ions formed react with oxygen to form ferric oxide.

$$4Fe_{aq}^{2+} + O_{2(g)} + 4H_2O \longrightarrow 2Fe_2O_3 + 8H_{aq}^+$$

It then undergoes hydration to form rust (hydrated ferric oxide)

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3.xH_2O$$

PREVENTION OF CORROSION

- 1. Barrier protection: Done by
 - (a) painting (b) applying oil/grease (c) electroplating with metals like tin, nickel, zinc, chromium etc.
- 2. Sacrificial protection

Iron is protected from rusting by covering it with a metal which is more active than iron. (Zn, Al etc). Coating with zinc metal is called Galvanization.

3. Electrical protection (Cathodic protection)

Used for protecting iron articles which are in contact with water such as underground water pipes. The article of iron is connected with more active metal like Zn or Mg. The active metal has higher R.P. than iron. Zn or Mg has lower R.P. than iron. \therefore Mg will be oxidised in preference to iron, and iron will be protected from being rusted.

4. Using anti-rust solutions

Solutions of alkaline phosphate or alkaline chromate are used as anti-rust solutions. The alkalinity prevents the availability of H⁺ ions. Also a protective insoluble sticking film of iron phosphate is formed.