CHAPTER ⇒ 3

ELECTROCHEMISTRY

$$\text{Electrical Energy} \underset{\text{Spontaneous}}{\overset{\text{non Spontaneous}}{\rightleftharpoons}} \text{chemical Energy}$$

It is a relationship b/w electrical energy and chemical energy and the interconversion of one form to another form.

Example:- $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

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

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

Conductor

① **Metallic Conductor :-** Cu, fe, Ag, Au, graphite, minerals or ores, etc.

② **Electrolytic conductor :-** Electric current flow by movement of ions.

Ex → Aqueous solution of acids, base or salt etc

③ **Non-conductor :-** plastic, rubber, glass, pure water etc.

⇒ **Electrolytes :-** ~~Aqueous~~ Those substance whose aq. Sol^n conduct electricity

Ex → NaCl (aq)

(a) **Strong electrolytes:** Ex- HCl, NaOH, NaCl, etc.

(b) **weak electrolytes:** Ex- CH_3COOH, H_2CO_3, H_3PO_4, $Al(OH)_3$, NH_4Cl etc.

⇒ **Non-electrolytes:** Ex- Sugar, starch, urea etc.

⇒ Factor affecting of electrolytic conduction-

① **Nature of electrolytes:** Strong electrolytes will increase the conduction of Solution.

② **Solvation of ion:** Increase in the Solvation will decrease the conductivity of electrolytes.

③ **Dilution:** Electrical conductivity increase with increase of dilution.

④ **Nature of Solvent:** polarity of Solvent will increase the electrical conductivity of Solution.

⑤ **Viscosity:** Increase of Viscosity of solution will decrease electrical conductivity.

⑥ **Temperature:** Electrical conductivity increases with increases of Temprature.

⇒ Resistance (R)

$$V \propto I$$

$$V = IR$$

$$\boxed{R = \frac{V}{I}}$$ unit :- Ω

⇒ Conductance (C or G) :- It is the reciprocal of Resistance.

$$\boxed{C = \frac{1}{R}}$$ unit :- Ω^{-1}

⇒ Resistivity (ρ) :- The Resistance provided by one unit volume of medium.

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

unit :- Ω cm

$$R = \frac{\rho l}{A} \Rightarrow \boxed{\rho = \frac{RA}{l}}$$

if $l = 1\,cm$, $A = 1\,cm^2$

$$\Rightarrow \boxed{\rho = R}$$

⇒ Conductivity (κ) :- It is the reverse of Resistivity.

(kappa) ← $\kappa = \frac{1}{\rho}$ or $\rho = \frac{1}{\kappa}$ —— ①

$$R = \frac{1}{C}$$

We know that

$$R = \frac{\rho l}{A} \Rightarrow \frac{1}{C} = \frac{1}{\kappa} \times \frac{l}{A} \Rightarrow \boxed{\kappa = C \times \frac{l}{A}}$$

if, $l = 1\,cm$ & $A = 1\,cm^2$

$$\boxed{\kappa = C}$$ unit :- $\Omega^{-1} cm^{-1}$

⇒ Cell constant :- $\frac{K}{C}$

we know that

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

$\frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$

$K = C \times \frac{l}{A}$

$\text{cell constant} = \frac{K}{C}$

unit :- cm^{-1}

⇒ Molar Conductivity : (Λ_m) :- Conductors provided by one mole of electrolytes present in Solution when distance b/w two electrode is 1 cm apart.

$\Lambda_m = K \times V_m$

$\Lambda_m = \frac{K \times 1000}{M}$

unit : $\Omega^{-1} cm^2 mol^{-1}$

Imp for Boards

Variation of conductance, conductivity & Molar conductivity on dilution

① effect of dilution on conductance → Conductance increase with increase of dilution but it decrease with increase of Concentration.

② Effect of dilution on Conductivity → Conductivity decrease with increase of dilution because no. of ions present per unit Vol. decrease. Conductivity increase with increase of Concentration.

③ Effect of dilution on molar conductivity →

Molar conductivity increase with increase of dilution because total Volume of Solution Containing 1 mole of electrolytes.

ⓐ Variation of Conc. of Strong electrolytes →

Molar conductivity of strong electrolyte very increase with increase of dilution. The relation b/w molar conductivity and Conc. of electrolytes can be described by following relation.

$$\Lambda_m^c = \Lambda_m^\circ - A\sqrt{C}$$

This eq^n is known as Debye - Huckel - Onsager eq^n where

Λ_m^c = ~~limiting~~ molar conductivity at any conc.

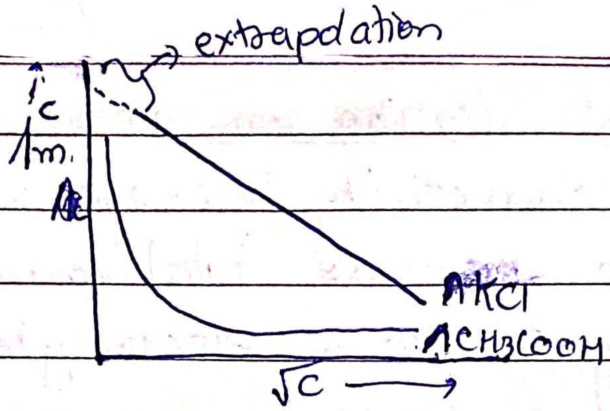
Λ_m° = limiting molar conductivity at Infinite dilution

C = Concentration of electrolytes

A = Constant

ⓑ for weak electrolytes →

The molar conductivity of weak electrolyte steeply increase with the increase of dilution. The limiting molar conductivity for weak electrolyte can not be obtained by Λ_m^c Vs $\sqrt{c}$ graph because it does not obtain straight line



Imp for Boards

⇒ **Kholrausch law:** It state that the limiting molar conductivity of an electrolyte is the Sum of limiting ionic conductivity of Cation as well as Anion

$$\Lambda^{\circ}_m = n^+ \lambda A^+ + n^- \lambda B^-$$

n → Total no of cation & Anion.

λ → limiting M cond of cation & Anion

Application of kholrausch law:

① **Calculation of limiting molar conductivity for weak electrolyte**

Λ°_m of weak electrolyte can be obtain by kholrausch law.

Ex. $\Lambda^{\circ}_{CH_3COOH} = \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{H^+}$ — ①

→ this eqⁿ can be obtained by following ways?

$$\Lambda^{\circ}_{CH_3COONa} = \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{Na^+} \quad —②$$

$$\Lambda^{\circ}_{HCl} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl} \quad —③$$

$$\Lambda^{\circ}_{NaCl} = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Cl} \quad —④$$

add eqⁿ ② & ③ and Substract by eqⁿ ④

$$= (\lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{Na^+}) + (\lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl^-}) - (\lambda^{\circ}_{Na} + \lambda^{\circ}_{Cl})$$

$$\boxed{\Lambda^{\circ}_{CH_3COOH} = \lambda^{\circ}_{CH_3COO^-} + \lambda_{H^+}}$$

② for calculation of degree of dissociation of weak electrolytes

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0}$$

α = dissociation

$\Lambda_m^\infty / \Lambda_m^c$ (limiting molar conductivity):- The Value of molar conductivity when Concentration across to zero is known as limiting molar conductivity.

③ Calculation of dissociation Constant of weak electrolytes:-

$$K_c = \frac{C\alpha^2}{1-\alpha}$$

④ Calculation of Solubility of Sparingly Soluble Salt

$$\Lambda_m^0 = \frac{K \times 1000}{M} = \frac{K \times 1000}{\text{Solubility}}$$

$$\text{Solubility} = \frac{K \times 1000}{\Lambda_m^0}$$

⇒ faraday's law:-

① faraday's first law:- It State that the amount of Substance deposited & liberated at any electrode is directly proportional to quantity of chargepassed through an electrolyte.

$$w \propto Q$$

$$w = Z \times Q \quad \text{—— (1)}$$

or $w = Z \times I \times t$

where Z is electrochemical equivalent

Electrochemical equivalent: It is defined as the Amount of Substance deposited by passing 1A current for 1 Sec through an electrolytes.

1 Mole of e^- = 1F = 96500 C/mol

$$\boxed{Z = \frac{E}{nF}} \quad \text{—— (2)}$$

put the value of eqⁿ (2) in eqⁿ (1)

$$\boxed{w = \frac{EQ}{nF}}$$

⇒ Faraday's Second law :

It state that when Same Amount of electricity pass through an electrolyte, The amount of different Substance deposited at different electrode is directly proportional to equivalent mass of that Substance.

$$\boxed{\frac{W_1}{W_2} = \frac{E_1}{E_2}}$$

Ques- A Solution of $Ni(NO_3)_2$ is electrolysed b/w platinum electrodes using current of 5A for 20 Min. what mass of Nickel is deposited at Cathode?

Solⁿ

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

$I = 5A$

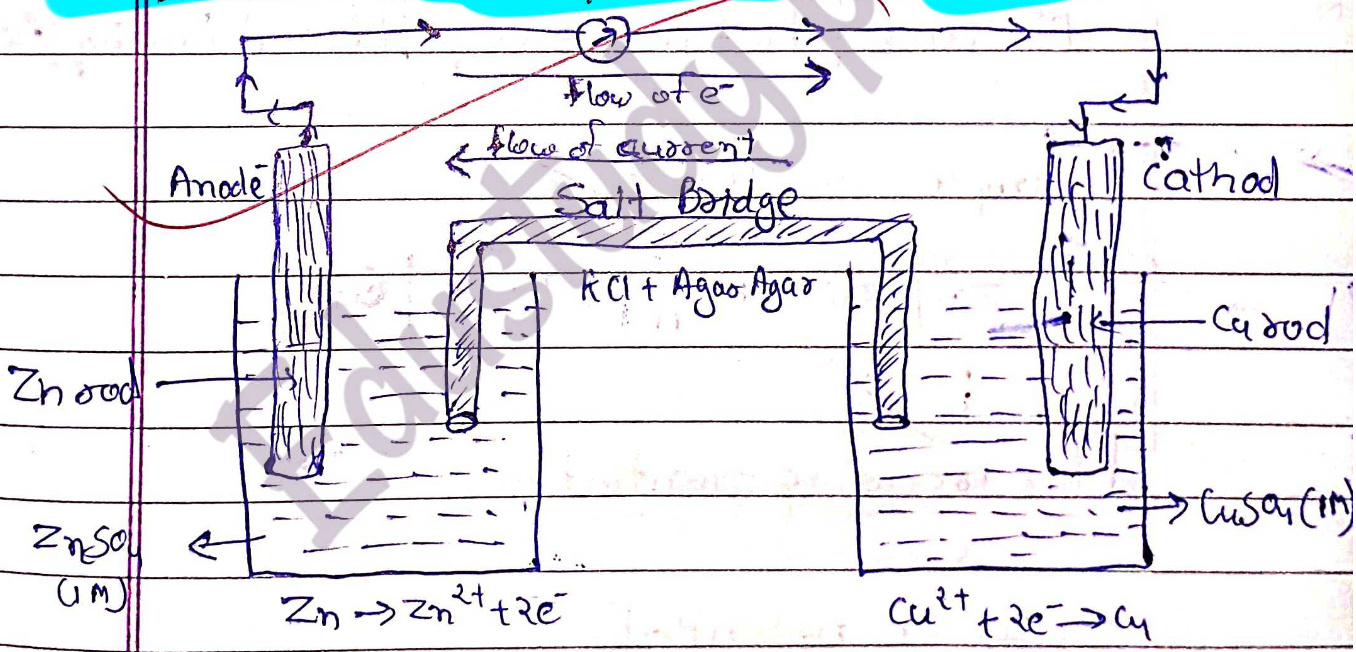
$t = 20min$

$Q = 5 \times 20 \times 60 = 6000\,C$

$$w_n = \frac{E \times Q}{nf} = \frac{58.7 \times 6000}{2 \times 96500}$$

$$w_n = 1.825 \text{ gram.}$$

⇒ Electrochemical / Galvenic / Voltanic Cell :-



At Anode :- $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$; $E_{Zn/Zn^{2+}}$

At Cathode :- $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu(s)$, $E_{Cu^{2+}/Cu}$

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

⟹ Salt Bridge :- It is inverted 'U' Shape tube Containing inert electrolytes like KCl, KNO_3 etc. with Agar-Agar paste

function of salt Bridge

→ Connect oxidation & Reduction half cell

→ It complete the circuit by maintain the flow of ion

→ it maintain electrical neutrility.

→ it prevent junction-junction potential.

Cell Representation :

Metal(s) | Metal ions (aq) || Metal ions (aq) | Metal(s)

Example for Danial cell

$Zn | Zn^{2+} (1M) || Cu^{2+} (1M) | Cu (s)$

⟹ Electrode potential

① oxidation potential

$Zn \longrightarrow Zn^{2+} + 2e^-$, $E_{Zn/Zn^{2+}} = E_{oxidation}$

② Reduction potential

$Cu^{2+} + 2e^- \longrightarrow Cu$, $E_{Reduction} = E_{Cu^{2+}/Cu}$

$$E_{oxd.} = -E_{Red.}$$

⇒ **Standard Reduction potential:** The reduction potential of an electrode when concentration of ions in solution is 1 mole per litre, 1 Mol/e, 1 bar or 1 atm and temperature is 25°C/298 K

⇒ **Standard hydrogen potential:-**

At Anode :- $H_2 \longrightarrow 2H^+ + 2e^-$

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

cell representation:-

$$Pt(s) \mid H_2(aq) \mid H^+(1M) \parallel H^+(1M) \mid H_2(g) \mid Pt(s)$$

$$\boxed{E_{cell} = 0.00 \text{ Volt}}$$

$$Emf = E_{cathode} - E_{Anode}$$

or

$$E^\circ_{cell} = E_{reduction} - E_{oxidation}$$

⇒ **Electrochemical Series :-** The arrangement of different element in order of increasing value of standard Reduction potential.

⇒ **Nernst Equation:** consider a general equation

$$M^{2+}(aq) + ne^- = M(s)$$

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[M]}{[M^{2+}]}}$$

at R = 8.314
T = 298 K
F = 96500

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{1}{[M^{2+}]}}$$

Equilibrium constant from Nernst Equation

Consider cell reaction of Daniel cell

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

$$E_{cell} = 0 = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E^{\circ}_{cell} = \frac{0.0591}{n} \log K_c$$

☆ $$\log K_c = \frac{nE^{\circ}_{cell}}{0.0591}$$

$$K_c = \text{Antilog} \frac{nE^{\circ}_{cell}}{0.0591}$$

Ecell & Gibb's free energy

$$\Delta_r G = -nf E_{cell}$$

$$\Delta_r G^{\circ} = -nf E^{\circ}_{cell} \quad \text{——— (1)}$$

we know that

$$E^{\circ}_{cell} = \frac{2.303\,RT}{nf} \log K_c$$

put the value of E°_{cell} in eq^n (1)

$$\Delta_r G = -nf \cdot \frac{2.303\,RT}{nf} \log K_c$$

$$\Delta_r G = -2.303\,RT \log K_c$$

Battery

① Primary Battery

ⓐ Dry cell / leclanie cell : [Zn – Carbon cell]

→ Non Rechargable

→ cell potential :- 1.25 – 1.50 V

→ Used in Radio, flash light, toys etc.

Anode = Zn

Cathode = $Mg0 + C$

Electrolytes = $NH_4Cl + ZnCl_2$

At Anode:-

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

At Cathode:-

$$MnO_2 + 2NH_4^+ + 2e^- \longrightarrow Mn(OH)_2 + 2NH_3 \uparrow$$

It is not liberate. it React with Zn & form $[Zn(NH_3)_2Cl_2]$

ⓑ Button cell / Mercury cell

[Zn – amalgum cell]

→ Not rechargeable

→ cell potential = 1.35 V

→ used in earphone, wrist watch etc.

Anode = $Zn(Hg)$

cathode = $Hg0 + C$

Electrolytes = $KOH + ZnO$

At Anode:-

$$Zn(Hg) + 2OH^- \longrightarrow ZnO + H_2O$$

At Cathode:-

$$HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$$

$$\boxed{Zn(Hg) + HgO \longrightarrow Hg(l) + ZnO}$$

(2) Secondary Battery

(a) Lead storage battery

→ Rechargeable
→ Cell potential = 12V
→ Used in automobile & inverter

Anode = Pb
Cathode = PbO_2
Electrolytes = H_2SO_4 (38%)

At anode :-

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

At Cathode :-

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

behave as electro chemical cell

$$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O + \text{Electricity}$$

On Recharging

At Anode :-

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

At Cathode :-

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

behave a electrolyte.

$$2PbSO_4 + 2H_2O + \text{Electricity} \longrightarrow Pb + PbO_2 + 2H_2SO_4$$

(b) Nickel - Cadmium battery

→ Rechargable

→ Cell potential = 1.4 V

→ Used in cell phone, electric shaver etc.

Anode = Cd

Cathode = NiO_2

Electrolytes = KOH

At anode:-

$$Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$$

At Cathode:-

$$NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^-$$

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

The cell reaction can be reversed during charging.

⇒ Fuel cell

Anode = H_2

Cathode = O_2

Electrolyte = NaOH

At Anode:-

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

At Cathode:-

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

$$\boxed{2H_2 + O_2 \longrightarrow 2H_2O + E\uparrow}$$

Corrision of Iron

Step 1: $Fe(s) \longrightarrow Fe^{2+} + 2e^-$ —— (1)

Step 2: $H_2O + CO_2 \longrightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$

Step 3: $2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O$ —— (2)

adding eq^n (1) & (2)

$Fe + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{2+} + H_2O$

Step 4: $2Fe + \frac{1}{2}O_2 + H_2O \longrightarrow 2Fe_2O_3 + 4H^+$

Step 5: $Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3 \cdot xH_2O$