ELECTROCHEMISTRY

ELECTRODE POTENTIAL

For any electrode $\rightarrow$ oxidiation potential = – Reduction potential

E_{cell} = R.P of cathode – R.P of anode

E_{cell} = R.P. of cathode + O.P of anode

E_{cell} is always a +ve quantity & Anode will be electrode of low R.P

E^o_{Cell} = SRP of cathode – SRP of anode.

- **Greater the SRP value greater will be oxidising power.**

GIBBS FREE ENERGY CHANGE :

$\Delta G = -nFE_{cell}$

$\Delta G^o = -nFE^o_{cell}$

NERNST EQUATION : (Effect of concentration and temp on emf of cell)

$\Delta G = \Delta G^o + RT\ \ell nQ$ (where Q is raection quotient)

$\Delta G^o = -RT\ \ell n\ K_{eq}$

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ \ell n\ Q$$

$$E_{cell} = E^o_{cell} - \frac{2.303\,RT}{nF}\log Q$$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log Q \qquad [\text{At } 298 \text{ K}]$$

At chemical equilibrium

$\Delta G = 0$; $E_{cell} = 0$.

- $$\log K_{eq} = \frac{nE^o_{cell}}{0.0591}.$$

$$E^o_{cell} = \frac{0.0591}{n} \log K_{eq}$$

For an electrode $M(s)/M^{n+}$.

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}.$$

CONCENTRATION CELL :

A cell in which both the electrods are made up of same material.

For all concentration cell $E^o_{cell} = 0$.

(a) Electrolyte Concentration Cell :

eg. $Zn(s) / Zn^{2+} (c_1) || Zn^{2+}(c_2) / Zn(s)$

$$E = \frac{0.0591}{2} \log \frac{C_2}{C_1}$$

(b) Electrode Concentration Cell :

eg. Pt, $H_2(P_1 \text{ atm}) / H^+ (1M)$ / $H_2 (P_2 \text{ atm})$ / Pt

$$E = \frac{0.0591}{2} \log \left(\frac{P_1}{P_2}\right)$$

DIFFERENT TYPES OF ELECTRODES :

1. Metal-Metal ion Electrode $M(s)/M^{n+}$. $M^{n+} + ne^- \longrightarrow M(s)$

$$E = E^o + \frac{0.0591}{n} \log[M^{n+}]$$

2. Gas-ion Electrode Pt /H_2(Patm) /H^+ (XM)

as a reduction electrode

$$H^+(aq) + e^- \longrightarrow \frac{1}{2} H_2 \text{ (Patm)}$$

$$E = E^o - 0.0591 \log \frac{P_{H_2}^{\frac{1}{2}}}{[H^+]}$$

3. Oxidation-reduction Electrode   Pt / Fe^{2+}, Fe^{3+}

as a reduction electrode $Fe^{3+} + e^- \longrightarrow Fe^{2+}$

$$E = E^o - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

4. Metal-Metal insoluble salt Electrode   eg. Ag/AgCl, Cl^-

as a reduction electrode $AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$

$$E_{Cl^-/AgCl/Ag} = E^0_{Cl^-/AgCl/Ag} \mathbf{- 0.0591 \log [Cl^-].}$$

<u>ELECTROLYSIS :</u>

(a) K^+, Ca^{+2}, Na^+, Mg^{+2}, Al^{+3}, Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}.

$\longrightarrow$

Increasing order of deposition.

(b) Similarly the anion which is strogner reducing agent(low value of SRP) is liberated first at the anode.

$$\xrightarrow[\text{Increasing order of diposition}]{SO_4^{2-},\ NO_3^-,\ OH^-,\ Cl^-,\ Br^-,\ I^-}$$

FARADAY'S LAW OF ELECTROLYSIS :

First Law :

w = zq   w = Z it   Z = Electrochemical equivalent of substance

Second Law :

$W \propto E$ $\frac{W}{E}$ = constant $\frac{W_1}{E_1} = \frac{W_2}{E_2} = \dots\dots\dots\dots$

$$\frac{W}{E} = \frac{i \times t \times \text{current efficiency factor}}{96500}.$$

Current efficiency = $\frac{\text{actual mass deposited/produced}}{\text{Theoritical mass deposited/produced}} \times 100$

CONDITION FOR SIMULTANEOUS DEPOSITION OF Cu & Fe AT CATHODE

$$E^o_{Cu^{2+}/Cu} - \frac{0.0591}{2} \log \frac{1}{Cu^{2+}} = E^o_{Fe^{2+}/Fe} - \frac{0.0591}{2} \log \frac{1}{Fe^{2+}}$$

Condition for the simultaneous deposition of Cu & Fe on cathode.

CONDUCTANCE :

☞ Conductance = $\frac{1}{\text{Resistance}}$

☞ **Specific conductance or conductivity :**

(Reciprocal of specific resistance) $K = \frac{1}{\rho}$

K = specific conductance

☞ **Equivalent conductance :**

$$\lambda_E = \frac{K \times 1000}{\text{Normality}}$$ unit : -$ohm^{-1}\ cm^2\ eq^{-1}$

☞ **Molar conductance :**

$$\lambda_m = \frac{K \times 1000}{\text{Molarity}}$$ unit : -$ohm^{-1}\ cm^2\ mole^{-1}$

specific conductance = conductance × $\frac{\ell}{a}$

KOHLRAUSCH'S LAW :

Variation of λ_{eq} / λ_M of a solution with concentration :

(i) Strong electrolyte

$$\lambda_M^c = \lambda_M^\infty - b\sqrt{c}$$

(ii) Weak electrolytes : $\lambda_\infty = n_+ \lambda^\infty_+ + n_- \lambda^\infty_-$

where λ is the molar conductivity

n_+ = No of cations obtained after dissociation per formula unit

n_- = No of anions obtained after dissociation per formula unit

APPLICATION OF KOHLRAUSCH LAW :

1. Calculation of λ^0_M of weak electrolytes :

$$\lambda^0_{M\,(CH3COOHl)} = \lambda^0_{M(CH3COONa)} + \lambda^0_{M(HCl)} - \lambda^0_{M(NaCl)}$$

2. To calculate degree of diossociation of a week electrolyte

$$\alpha = \frac{\lambda_m^c}{\lambda_m^0} \quad ; \quad K_{eq} = \frac{c\alpha^2}{(1-\alpha)}$$

3. Solubility (S) of sparingly soluble salt & their K_{sp}

$$\lambda_M^c = \lambda_M^\infty = \kappa \times \frac{1000}{\text{solubility}}$$

$K_{sp} = S^2$.

Transport Number :

$$t_c = \left[\frac{\mu_c}{\mu_c + \mu_a}\right], \qquad t_a = \left[\frac{\mu_a}{\mu_a + \mu_c}\right].$$

Where t_c = Transport Number of cation & t_a = Transport Number of anion