ELECTROCHEMISTRY

ELECTRODE POTENTIAL

For any electrode → 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 of an emf of cell)

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

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

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

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

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

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. $Pt, H_2(P_1\ atm) / H^{+}(1M)\ / H_2(P_2\ atm) / Pt$ $$E = \frac{0.0591}{2}\ \log\left(\frac{P_1}{P_2}\right)$$

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 $H^{+}(aq) + e^{-} \longrightarrow \frac{1}{2}H_2\,(Patm)$ $$E = E^{o} - 0.0591\ \log\frac{P_{H_2}^{\frac{1}{2}}}{[H^{+}]}$$

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

as a reduction electrode $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $\qquad$ $E = E^o - 0.0591 \log \dfrac{[Fe^{2+}]}{[Fe^{3+}]}$

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

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

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

CALCULATION OF DIFFERENT THERMODYNAMICS FUNCTION OF CELL REACTION

- $\Delta G = -n\,F\,E_{cell}$
- $S = -\left[\dfrac{dG}{dT}\right]_p$ $\qquad$ (At costant pressure).
- $\Delta S = -\left[\dfrac{d(\Delta G)}{dT}\right]_P = nF\left(\dfrac{d}{dt}(E_{cell})\right)_p$
- $\left[\dfrac{\partial E}{\partial T}\right]_p$ = Temperature cofficient of e.m.f of the cell.

  $E = a + bT + CT^2 + \ldots\ldots\ldots\ldots\ldots$

- $\Delta H = nF\left[T\left(\dfrac{\partial E}{\partial T}\right)_p - E\right]$
- **ΔCp of cell reaction**

  $$Cp = \frac{dH}{dT}$$

  $$\Delta Cp = \frac{d}{dT}(\Delta H)$$

  $$\Delta C_p = n\,F\,T\,\frac{d^2E_{cell}}{dT^2}$$

- **ELECTROLYSIS :**

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

  $\xrightarrow{\hspace{6cm}}$

  Increasing order of deposition.

  (b) Similarly the anion which is stronger 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 :

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

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

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 :**

   $\lambda^0_{M\,(CH_3COOHl)} = \lambda^0_{M(CH_3COONa)} + \lambda^0_{M(HCl)} - \lambda^0_{M(NaCl)}$

2. To calculate degree of diossociation of a week electrolyte

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

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

   $$\lambda_M^{\,c} = \lambda_M^{\,\infty} = \kappa \times \frac{1000}{\text{so lubility}}$$

   $K_{sp} = S^2$.

❍ **IONIC MOBILITY :** It is the distance travelled by the ion per second under the potential gradient of 1 volts per cm. It's unit is $cm^2 s^{-1} v^{-1}$.

Absolute ionic mobility :

$$\lambda^0_c \propto \mu_c \quad ; \quad \lambda_a^{\,0} \propto \mu_a$$

$$\lambda^0_c = F\mu^0_c \quad ; \quad \lambda^0_a = F \times \mu^0_a .$$

Ionic Mobility $\mu = \dfrac{v \longrightarrow \text{speed}}{(V/\ell) \longrightarrow \text{potential gradient}}$

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