

ELECTROCHEMISTRY

ELECTRODE POTENTIAL

For any electrode \rightarrow oxidation potential = – Reduction potential

$$E_{\text{cell}} = \text{R.P of cathode} - \text{R.P of anode}$$

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

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

$$E^{\circ}_{\text{Cell}} = \text{SRP of cathode} - \text{SRP of anode.}$$

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

GIBBS FREE ENERGY CHANGE :

$$\Delta G = -nFE_{\text{cell}}$$
$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

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

$$\Rightarrow \Delta G = \Delta G^\circ + RT \ln Q \quad (\text{where } Q \text{ is reaction quotient})$$

$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log Q$$

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

At chemical equilibrium

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

$$\bigcirc \quad \log K_{\text{eq}} = \frac{nE_{\text{cell}}^\circ}{0.0591}.$$

$$E_{\text{cell}}^\circ = \frac{0.0591}{n} \log K_{\text{eq}}$$

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

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

CONCENTRATION CELL : A cell in which both the electrodes are made up of same material.

For all concentration cell $E_{\text{cell}}^\circ = 0$.

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

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

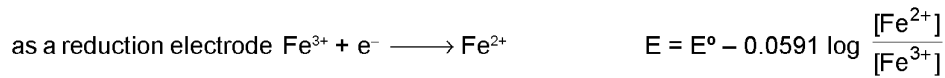
DIFFERENT TYPES OF ELECTRODES :

1. Metal-Metal ion Electrode $M(s)/M^{n+}$. $M^{n+} + ne^- \longrightarrow M(s)$ $E = E^\circ + \frac{0.0591}{n} \log [M^{n+}]$

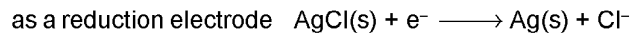
2. Gas-ion Electrode $Pt/H_2(P_{\text{atm}})/H^+(XM)$

as a reduction electrode $H^+(aq) + e^- \longrightarrow \frac{1}{2} H_2(P_{\text{atm}})$ $E = E^\circ - 0.0591 \log \frac{P_{H_2}^{\frac{1}{2}}}{[H^+]}$

3. Oxidation-reduction Electrode Pt / Fe²⁺, Fe³⁺



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



○ $E_{\text{Cl}^- / \text{AgCl} / \text{Ag}} = E_{\text{Cl}^- / \text{AgCl} / \text{Ag}}^\circ - 0.0591 \log [\text{Cl}^-].$

CALCULATION OF DIFFERENT THERMODYNAMICS FUNCTION OF CELL REACTION

○ $\Delta G = -n F E_{\text{cell}}$

○ $S = - \left[\frac{dG}{dT} \right]_p$ (At constant pressure).

○ $\Delta S = - \left[\frac{d(\Delta G)}{dT} \right]_p = nF \left(\frac{d}{dt} (E_{\text{cell}}) \right)_p$

○ $\left[\frac{\partial E}{\partial T} \right]_p$ = Temperature coefficient of e.m.f of the cell.

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

○ $\Delta H = nF \left[T \left(\frac{\partial E}{\partial T} \right)_p - E \right]$

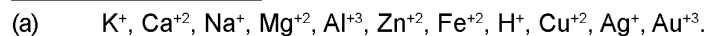
○ **ΔC_p of cell reaction**

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

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

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

○ **ELECTROLYSIS :**



$\xrightarrow{\hspace{10em}}$
 Increasing order of deposition.

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

$\text{SO}_4^{2-}, \text{NO}_3^-, \text{OH}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$
 $\xrightarrow{\hspace{10em}}$
 Increasing order of deposition

FARADAY'S LAW OF ELECTROLYSIS :

First Law :

$$w = zq \quad w = Z it \quad Z = \text{Electrochemical equivalent of substance}$$

Second Law :

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

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

$$\text{CURRENT EFFICIENCY} = \frac{\text{actual mass deposited/produced}}{\text{Theoretical mass deposited/produced}} \times 100$$

○ CONDITION FOR SIMULTANEOUS DEPOSITION OF Cu & Fe AT CATHODE

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

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 :

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

☞ Molar conductance :

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

$$\text{specific conductance} = \text{conductance} \times \frac{\ell}{a}$$

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_M^0 of weak electrolytes :**

$$\lambda_{M(CH_3COOH)}^0 = \lambda_{M(CH_3COONa)}^0 + \lambda_{M(HCl)}^0 - \lambda_{M(NaCl)}^0$$

2. To calculate degree of dissociation of a weak electrolyte

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

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

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

$$K_{sp} = S^2.$$

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

Absolute ionic mobility :

$$\lambda_c^0 \propto \mu_c ; \quad \lambda_a^0 \propto \mu_a$$
$$\lambda_c^0 = F \mu_c^0 ; \quad \lambda_a^0 = F \times \mu_a^0.$$

$$\text{Ionic Mobility } \mu = \frac{v}{(V/\ell)} \begin{matrix} \longrightarrow \text{speed} \\ \longrightarrow \text{potential gradient} \end{matrix}$$

Transport Number :

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

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