

# ELECTROCHEMISTRY

## ELECTRODE POTENTIAL

For any electrode  $\rightarrow$  oxidation potential = - Reduction potential

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

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

$E_{\text{cell}}$  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 :

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

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

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

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

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

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

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



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

At chemical equilibrium

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

$$\log K_{\text{eq}} = \frac{nE^{\circ}_{\text{cell}}}{0.0591}$$

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

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

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

### CONCENTRATION CELL :

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

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

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

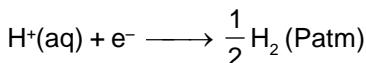
$$E = \frac{0.0591}{2} \log \left( \frac{P_1}{P_2} \right)$$

### 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



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

3. Oxidation-reduction Electrode Pt / Fe<sup>2+</sup>, Fe<sup>3+</sup>  
as a reduction electrode  $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$

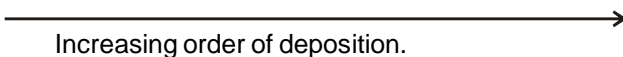
$$E = E^\circ - 0.0591 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

4. Metal-Metal insoluble salt Electrode eg. Ag/AgCl, Cl<sup>-</sup>  
as a reduction electrode  $\text{AgCl}(\text{s}) + \text{e}^- \longrightarrow \text{Ag}(\text{s}) + \text{Cl}^-$

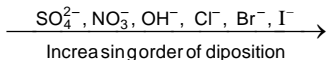
$$E_{\text{Cl}^- / \text{AgCl} / \text{Ag}} = E_{\text{Cl}^- / \text{AgCl} / \text{Ag}}^0 - 0.0591 \log [\text{Cl}^-].$$

### ELECTROLYSIS:

- (a) K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup>, H<sup>+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Au<sup>3+</sup>.



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



### **FARADAY'S LAW OF ELECTROLYSIS:**

#### **First Law:**

$$w \propto zq$$

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

#### **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:**

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



☞ **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  $\lambda_{eq}$  /  $\lambda_M$  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  $\lambda$  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  $\lambda_M^0$  of weak electrolytes :**

$$\lambda_{M(\text{CH}_3\text{COOH})}^0 = \lambda_{M(\text{CH}_3\text{COONa})}^0 + \lambda_{M(\text{HCl})}^0 - \lambda_{M(\text{NaCl})}^0$$

2. To calculate degree of dissociation of a weak 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 :**

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

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