Electrochemistry

Electrochemical Cells

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).

An electrode and its electrolyte comprise an **Electrode Compartment.**

Electrochemical cells can be classified as:

(i) Electrolytic Cells in which a non-spontaneous reaction is driven by an external source of current.

(ii) Galvanic Cells which produce electricity as a result of a spontaneous cell reaction.

Electrolysis

The decomposition of electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis.

Electrolytic Cell

This cell converts electrical energy into chemical energy.

The entire assembly except that of the external battery is known as the electrolytic cell.

Electrodes

The metal strip at which positive current enters is called anode; which is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called cathode. Cathodes are negatively charged.

Faraday's Laws of Electrolysis

(i) **First law of electrolysis:** $w \propto Q$

w = weight liberated

Q = charge in coluomb

$$w = ZQ = ZCt = \frac{A}{nF} Ct$$

(ii) **Second law of electrolysis:** $w_1/w_2 = E_1/E_2$ (Q = Constant)

Conductance

Introduction: i.e. $V = IR$

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho \frac{l}{A} \qquad (\rho = \text{Specific resistance})$$

$$\frac{1}{R} = \frac{A}{\rho l} \quad \text{or} \quad G = \kappa \frac{A}{l}$$

where G = conductance ohm^{-1};

κ = specific conductance ohm^{-1} cm^{-1}.

Mho and siemens are other units of conductance

$$\kappa = \frac{l}{A} G$$

Specific conductance = Cell constant × Conductance $\left(G \times \frac{l}{A} \right)$

Specific conductance is conductance of 1 cm^3 of an electrolyte solution.

1. **Equivalent Conductance:**

    $\Lambda = \kappa \times V$

    $(\Lambda = \text{ohm}^{-1} \text{ cm}^{-1} \times \text{cm}^3 = \text{ohm}^{-1} \text{ cm}^2)$

    Thus, $V = \dfrac{1000}{N}$

    Thus, $\Lambda_{eq} = \kappa \times \dfrac{1000}{N}$

2. **Molar Conductance:**

    $\Lambda_m = \kappa V$

    Thus, $V = \dfrac{1000}{M}$

    Hence, $\Lambda_m = \kappa \times \dfrac{1000}{M}$

Application of Kohlrausch's Law

(A) **Determination of Λ_m^0 of a weak electrolyte:**

In order to calculate Λ_m^0 of a weak electrolyte say CH_3COOH, we determine experimentally Λ_m^0 values of strong electrolytes:

(B) **Determination of degree of dissociation (α):**

$$\alpha = \frac{\text{Number of molecules ionised}}{\text{Total number of molecules dissovled}} = \frac{\Lambda_m}{\Lambda_m^0} = \frac{\Lambda_{eq}}{\Lambda_{eq}^0}$$

(C) **Determination of solubility of sparingly soluble salt:**

$$\Lambda_m^0 = \frac{1000\kappa}{C}$$

where C is the molarity of solution and hence the solubility.

Relationship Between ΔG and Electrode Potential

Work done = Charge × Potential = nFE

$\therefore \Delta G = -nFE$

Under standard state

$\Delta G^0 = -nFE^0$

Concept of Electromotive Force (emf) of a Cell

E_{cell} = Reduction potential of cathode

$\qquad\qquad\qquad$ – Reduction potential of anode

Similarly, standard e.m.f. of the cell (E°) may be calculated as

$E°_{cell}$ = Standard reduction potential of cathode – Standard Reduction potential of anode

$E°_{cell} = E°_{Red}(R) = E°_{Red}(L)$

Nernst Equation

$\Delta G = \Delta G° + RT \ln Q$ $\qquad\qquad\qquad$ ...(i)

$\therefore -\Delta G = nFE \qquad$ and $\qquad -\Delta G° = nFE°$

Thus from Eq. (i), we get $-nFE = -nFE° + RT \ln Q$

(i) Determination of equilibrium constant:

$$K_{eq} = \text{antilog}\left[\frac{nE^0}{0.0591}\right]$$

(ii) Heat of Reaction inside the cell:

$$\therefore \Delta H = -nFE + nFT\left[\frac{\partial E}{\partial T}\right]_P$$

(iii) Entropy change inside the cell:

$$\text{or } \Delta S = nF\left[\frac{\partial E}{\partial T}\right]_P$$

(iv) $E = E°_{cell} - \dfrac{0.059}{n}\log\dfrac{[\text{Product}]}{[\text{Reactant}]}$

$E°_{cell} = E°_{Red}(R) = E°_{Red}(L)$

Concentration Cell

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell.

(i) Electrode Gas concentration cell:

$$E = \frac{0.059}{2F}\log\left[\frac{p_1}{p_2}\right]$$

For spontanity of such cell reaction, $p_1 > p_2$

(ii) Electrolyte concentration cells:

$$\text{or} \quad E = \frac{2.303RT}{2F}\log\left[\frac{C_2}{C_1}\right]$$

For spontaneity of such cell reaction, $C_2 > C_1$