unit

3

Electrochemistry

- Electrochemistry is a branch of science which deals with interactions of electrical energy with chemical processes.
- If chemical changes occur by the use of electrical energy then the phenomenon is known as electrolysis.
- When chemical changes cause production of electrical energy, the phenomenon is used in electrochemical cells.

ELECTROLYSIS

- When electric current is passed through an electrolytic solution, chemical reaction *i.e.* oxidation and reduction occur at electrodes, the phenomenon is known as electrolysis.
- Due to the redox reactions, different ions are produced and due to the movement of these ions, electricity flows.

FARADAY'S LAW OF ELECTROLYSIS

- Quantitative aspects of electrolysis were originally developed by Michael Faraday in 1834.

Faraday's First Law

- According to Faraday's first law of electrolysis. "weight of ions deposited on an electrode of an electrolytic cell is directly proportional to the quantity of electricity passed." *i.e.*

  $$w \propto Q \text{ or } w = ZQ = Zit$$

  where Q = quantity of electricity (in Coulombs)
  i = current (in Amperes), t = time (in second)
  Z = electrochemical equivalent of material deposited on the electrode. When 1 ampere current flows through conductor for 1 second the quantity of electricity will be 1 coulomb, *i.e.* $w = Z$.
  - The quantity of electricity required to liberate one gram equivalent of a substance is 96500 coulomb. This quantity of electricity is known as Faraday and is denoted by symbol F.
  - The quantity of electricity required to deposit 1 mole of the substance is given as $Q = n \times F$
    Where n = valency of ion.

Faraday's Second Law

- According to Faraday's second law of electrolysis, "when same quantity of electricity is passed through different electrolytes, the amount of different substances deposited at the electrodes is directly proportional to their equivalent weights." *i.e.*

  $$\frac{w_1}{w_2} = \frac{E_1}{E_2}$$

  $$\text{or } \frac{Z_1 it}{Z_2 it} = \frac{E_1}{E_2} \text{ or } \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

  Thus the electrochemical equivalent (Z) of an element is directly proportional to its equivalent weight.
  i.e. $E \propto Z$ or $E = FZ$
  or $E = 96500 \times Z$

Illustration 1

Three electrolytic cells A, B and C, containing electrolytes zinc sulphate, silver nitrate and copper sulphate respectively, were connected in series. A steady current of 1.5 amperes was passed through them, until 1.45 g of silver were deposited at the cathode of cell B.

(a) How long did the current flow?
(b) What weights of copper and zinc were deposited?

Soln.:

(a) 1 mol of silver (108 g) would be deposited at cathode when one mol of electrons are taken by silver ions.

$$\begin{array}{cccc} Ag^+ & + \; e^- & \longrightarrow & Ag \\ 1\text{ mol} & 1\text{ Faraday} & & 1\text{ mol (108 g)} \end{array}$$

108 g of silver requires = 1 Faraday or 96500 coulombs

$$1 \text{ g of silver requires} = \frac{96500}{108} \text{ C}$$

$$1.45 \text{ g of silver required} = \frac{96500 \times 1.45}{108} = 1295.6 \text{ C}$$

We know that $Q = i \times t$, where Q = charge passed (coulomb), i = current (amperes), t = time (s)

$$\text{or} \quad t = \frac{Q}{i} = \frac{1295.6}{1.5} = 863.7 \text{ s}$$

(b) All the cells are connected in series, therefore, 1295.6 coulomb charge is passed through each cell.

Hence, in the cell of $CuSO_4$ the reaction will be

$$\begin{array}{ccc} Cu^{2+} + \; 2e^- & \rightarrow & Cu_{(s)} \\ 2\text{ mol} & & 1\text{ mol} \end{array}$$

or, 2 Faraday for 63.5 g or, 2 × 96500 coulomb

$\because$ 2 × 96500 C will deposit the copper = 63.5 g

$$\therefore \quad 1 \text{ C will deposit the copper} = \frac{63.5}{2 \times 96500} \text{ g}$$

$$\therefore \quad 1295.6 \text{ C will deposit the copper} = \frac{63.5 \times 1295.6}{2 \times 96500} = 0.426 \text{ g}$$

In the cell of $ZnSO_4$ the reaction will be

$$\begin{array}{lccc} & Zn^{2+} + 2e^- & \rightarrow & Zn_{(s)} \\ & 2\text{ mol} & & 1\text{ mol} \\ \text{or} & 2 \times 96500\text{ C} & & 65.4\text{ g} \end{array}$$

$\because$ 2 × 96500 C are reqired to deposit = 65.4 g Zn

$\therefore$ 1 C is required to deposit $= \dfrac{65.4}{2 \times 96500}$ g Zn

$\therefore$ 1295.6 C is required to deposit $= \dfrac{65.4 \times 1295.6}{2 \times 96500}$

$= 0.439$ g Zn

Electrolytic Conductance

- The property of facilitating the flow of electricity through it, is known as the conductance of the conductor. Mathematically;

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

$$\boxed{C = \frac{1}{R}\ \text{ohm}^{-1}}$$

Specific Conductance

- The resistance of any conductor
  is $R \propto l$ l = length

$$R \propto \frac{1}{a} \quad a = \text{cross-sectional area}$$

$$R = \rho \frac{l}{a}$$

ρ = specific resistance.

The reciprocal of specific resistance is known as specific conductance or conductivity.

$$\text{Specific conductance} = \frac{1}{\text{Specific resistance}}$$

$$\kappa = \frac{1}{\rho} = \frac{l}{R \cdot a} = \frac{l}{a} \times C\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

$$\frac{l}{a} = \text{cell constant}$$

Specific conductance = cell constant × conductance

$l = 1$ cm and $a = 1\ \text{cm}^2$

$\kappa = C$

Thus specific conductance is the conductance of 1 cm^3 cell.

Equivalent and Molal Conductance

- It is defined as the conducting power of all the ions produced by one gram equivalent of an electrolyte in the solution.

$$\Lambda_{eq} = \kappa \times V_{eq} = \kappa \frac{1000}{C_{eq}} = \kappa \times \frac{1000}{\text{Normality}}$$

where V_{eq} = Volume of solution containing 1 g equivalent of electrolyte.

If 1 cm^3 solution contains 1 g equivalent weight of electrolyte then conductance of the solution

= specific conductance = equivalent conductance

The unit of equivalent conductivity is $\text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$ or $\text{S cm}^2\ \text{eq}^{-1}$.

Molar Conductance

- "Molar conductance" (Λ_m) or molar conductivity is defined as the conducting power of all the ions produced by one mole of the electrolyte in solution.

$\therefore \Lambda_m = \kappa \times V_m$ where V_m = volume of solution containing 1 mole of electrolyte.

If C_m is concentration in moles litre^{-1} then,

$$\Lambda_m = \kappa \times \frac{1000}{C_m}; \ C_m = \text{molarity}$$

Unit of Λ_m is $\text{ohm}^{-1}\ \text{cm}^{-2}\ \text{mol}^{-1}$, in SI system it is $\text{ohm}^{-1}\ \text{m}^2\ \text{mol}^{-1}$ or $\text{S m}^2\ \text{mol}^{-1}$.

If Z is total positive or negative charge per formula unit of electrolyte then,

$$\Lambda_m = Z \times \Lambda_{eq}$$

Illustration 2

The conductivity of a 0.12 N solution of an electrolyte of the type A^+B^- is 0.024 S cm^{-1}. Calculate its (i) equivalent (ii) molar conductivities.

Soln.: Normality of a solution is given by the number of equivalent per dm^3 (or per litre) of the solution. Therefore,

Concentration of the given solution = 0.12 equiv/dm^3

Conductivity of the solution, (κ) = 0.024 S cm^{-1}

Then,

(i) The equivalent conductivity is given by,

$$\Lambda_{eq} = \frac{1000\kappa}{C_{eq}} = \frac{1000 \times 0.024}{0.12} \text{S cm}^2\ \text{equiv}^{-1}$$

$$= 200\ \text{S cm}^2\ \text{equiv}^{-1}$$

(ii) The given electrolyte is of the type A^+B^-. This means that each cation (or anion) carries a charge equivalent to the charge carried by one electron. So, $Z = 1$.

Then, $\Lambda_m = 1 \times \Lambda_{eq} = 1 \times 200\ \text{S cm}^2\ \text{mol}^{-1}$

$= 200\ \text{S cm}^2\ \text{mol}^{-1}$

Effect of Dilution on Conductance

- Since conductivity of a solution is due to the presence of ions in the solution, greater the number of ions in a solution greater will be its conductivity. The equivalent and molar conductivities of a solution increase with dilution while the specific conductivity of a solution decreases with dilution. The specific conductance of a solution falls with dilution because the number of current-carrying particles, *i.e.* ions present per centimeter cube of the solution becomes less and less on dilution.Thus although the total number of ions increases with dilution, the number of ions per unit volume of the solution goes on decreasing with increase of dilution because increase in the number of ions on dilution is much less than increase in the volume of the solution.

  The equivalent (and similarly molar) conductivity increases with dilution and acquires a maximum (constant) value at infinite dilution because at this dilution the electrolyte dissociates completely (*i.e.* 100%). The maximum (limiting) value of equivalent and molar conductivities at infinite dilution (or zero concentration) is represented by λ_∞ (or λ_0) and μ_∞ (or μ_0) respectively.