4. Electrochemistry

Electrochemical cells:

- Two types – Galvanic cell or voltaic cell, and Electrolytic cell

Galvanic cell:

Converts the chemical energy of a spontaneous redox reaction into electrical energy

Daniell cell -

$$\Delta_r G^\ominus = -RT \ln K$$

The standard potential of a cell is given by

$$\Delta_r G^\ominus = -nFE^\ominus_{cell}$$

The potential of an individual half cell cannot be measured.

Relation between the standard potential of a cell and standard Gibbs energy:

$$\Delta_r G^\ominus = -nFE^\ominus_{cell}$$

Relation between standard Gibbs energy and the equilibrium constant:

$$\Delta_r G^\ominus = -RT \ln K$$

- Nernst equation:
  - Gives the concentration dependence of the potentials of the electrodes and the cells
  - For the electrode reaction

$$aA + bB \xrightarrow{ne^-} cC + dD$$

Nernst equation is given by

$$E_{cell} = E^\ominus_{cell} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- For a general electrochemical reaction of the type

$$aA + bB \xrightarrow{ne^-} cC + dD$$

Nernst equation is given by

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Conductance of electrolytic solutions:

Resistance, R = $\rho \frac{l}{A}$

Where,

$l \rightarrow$ Length

A $\rightarrow$ Area of cross-section

P $\rightarrow$ Resistivity or specific resistance

Conductance, G = $\frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$

Where, κ Conductivity or specific conductance

The SI unit of conductance is Ω^{-1} (siemens or mho).

The conductivity of an electrolyte depends upon

- nature of the solvent
- nature of the electrolyte added
- concentration of the electrolyte
- temperature

Molar conductivity, $\Lambda_m = \frac{\kappa}{C}$

Variation of conductivity

- For both strong and weak electrolytes, conductivity decreases with decrease in concentration.

Variation of molar conductivity

- For both strong and weak electrolytes, molar conductivity increases with decrease in concentration.

Limiting molar conductivity – molar conductivity when concentration approaches zero

- Degree of dissociation, $\alpha = \frac{\Lambda_m}{\Lambda_m^0}$
- **Kohlrausch law of independent migration of ions:**

  According to this law, for an electrolyte, the molar conductivity at infinite dilution is the sum of the contribution of the molar conductivity of the ions in which it dissociates.

Electrolytic cells and electrolysis

1F = 96487 C mol^{-1}

- **Faraday's first law of electrolysis:** The amount of chemical reaction occurring at any electrode during the process of electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.
- **Second law of electrolysis:** The amounts of different substances liberated when same quantity of electricity is passed through the electrolytic solution are proportional to their chemical equivalent weights.

Battery is a galvanic cell in which chemical energy of the redox reaction is converted into electrical energy.

Mainly two types:

Primary batteries
Secondary batteries

- **Primary Batteries**

  In primary batteries, reaction occurs only once.
  After use over a period of time, these become dead and cannot be reused.
  Examples:Dry cell (or Leclanche cell), Mercury cell

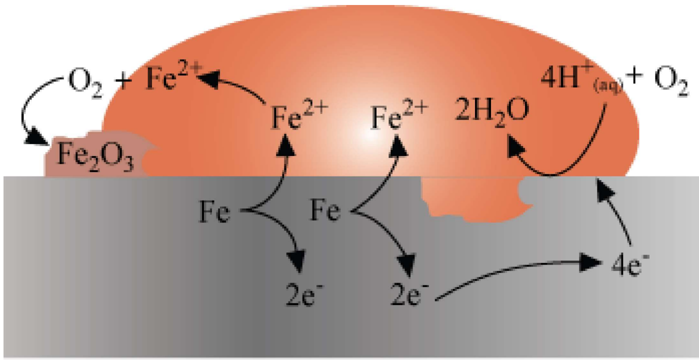
- **Secondary Batteries**

  Secondary batteries can be recharged again by passing current through them in the opposite direction.
  Examples:Lead storage battery, Nickel-cadmium cell

Corrosion: Oxidation of a metal by loss of electrons to oxygen and formation of oxides

Corrosion of Iron

Known as rusting
The spot where oxidation takes place behaves as anode.



Prevention of Corrosion

Preventing the surface of the metal from coming in contact with atmosphere

By covering the surface with paint or chemicals such as bis-phenol

By covering the surface with other metals such as Sn, Zn, Mg.

The Hydrogen Economy: Based on electrochemical principles