# 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 -

# $\Delta_r G^{\Theta} = -RT \ln K$

The standard potential of a cell is given by

$$\Delta_r G^{\Theta} = -nFE_{cell}^{\odot}$$

The potential of an individual half cell cannot be measured.

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

$$\Delta_r G^{\Theta} = -nFE^{\odot}_{cell}$$

Relation between standard Gibbs energy and the equilibrium constant:

 $\Delta_r G^{\Theta} = -RT \ln K$ 

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

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$$\mathbf{E}_{cell} = \mathbf{E}_{cell}^{\odot} - \frac{\mathbf{R}T}{nF} \ln \frac{\left[\mathbf{C}\right]^{c} \left[\mathbf{D}\right]^{d}}{\left[\mathbf{A}\right]^{a} \left[\mathbf{B}\right]^{b}}$$

• For a general electrochemical reaction of the type

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

Nernst equation is given by  $E_{cell} = E_{cell}^{\odot} - \frac{RT}{nF} \ln \frac{[C]^{c} [D]^{d}}{[A]^{a} [B]^{b}}$ 

# **Conductance of electrolytic solutions:**

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

Where,

 $l \rightarrow \text{Length}$ 

 $A \rightarrow Area of cross-section$ 

 $P \rightarrow Resistivity$  or specific resistance

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

Where, K Conductivity or specific conductance

The SI unit of conductance is  $\Omega^{-1}$  (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

### $1F = 96487 \text{ C mol}^{-1}$

- **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