ELECTROCHEMISTRY

Get well-prepared for exams with quick revision of important concepts of physical chemistry.

CONCEPT MAP

CLASS XII

Basic Terms

- **Conductance :**
  $C = \frac{1}{R}$; Unit : Ω^{-1} or S
- **Specific resistance or resistivity :**
  $R = \rho\frac{l}{a} \Rightarrow \rho = R\frac{a}{l}$; Unit : Ω cm or Ω m
  ($1\ \Omega\ m = 100\ \Omega\ cm$ or $1\ \Omega\ cm = 0.01\ \Omega\ m$)
- **Specific conductance or conductivity :**
  $\kappa = C \times \frac{l}{a}$; Unit : $\Omega^{-1}\ cm^{-1}$ or S cm^{-1}
- **Equivalent conductivity**
  $\Lambda_{eq} = \frac{\kappa \times 1000}{\text{Normality}}$; Unit : S $cm^2\ eq^{-1}$
- **Molar conductivity**
  $\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$; Unit : S $cm^2\ mol^{-1}$

Kohlrausch's law

For a strong electrolyte A_xB_y,

$\Lambda_m^\circ = x\lambda_+^\circ + y\lambda_-^\circ$

where, Λ_m° = Limiting molar conductivity

Nernst Equation

- $E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$ (at 298 K)
  $E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[\text{Oxidised}]}{[\text{Reduced}]}$ (at 298 K)
- **For concentration cell :**
  $E_{cell} = \frac{0.0591}{n}\log\frac{C_2}{C_1}$; E_{cell} = +ve if $C_2 > C_1$
- **For a reaction in equilibrium :**
  $E^\circ_{cell} = \frac{0.0591}{n}\log K$ at 298 K
  $\Delta_rG^\circ = -nFE^\circ_{cell}$
  $\Delta_rG^\circ = -RT\ln K$

- $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$ (when different number of electrons are involved)
  $-n_3FE_3^\circ = -n_1FE_1^\circ - n_2FE_2^\circ$
  $E_{H^+/H_2} = -0.0591$ pH
- **Relation between free energy and cell potential :**

Type of reaction	ΔG	E	Type of cell
Spontaneous	–ve	+ve	Galvanic
Non-spontaneous	+ve	–ve	Electrolytic
Equilibrium	0	0	Dead battery

Types of Cell

Electrolytic Cell

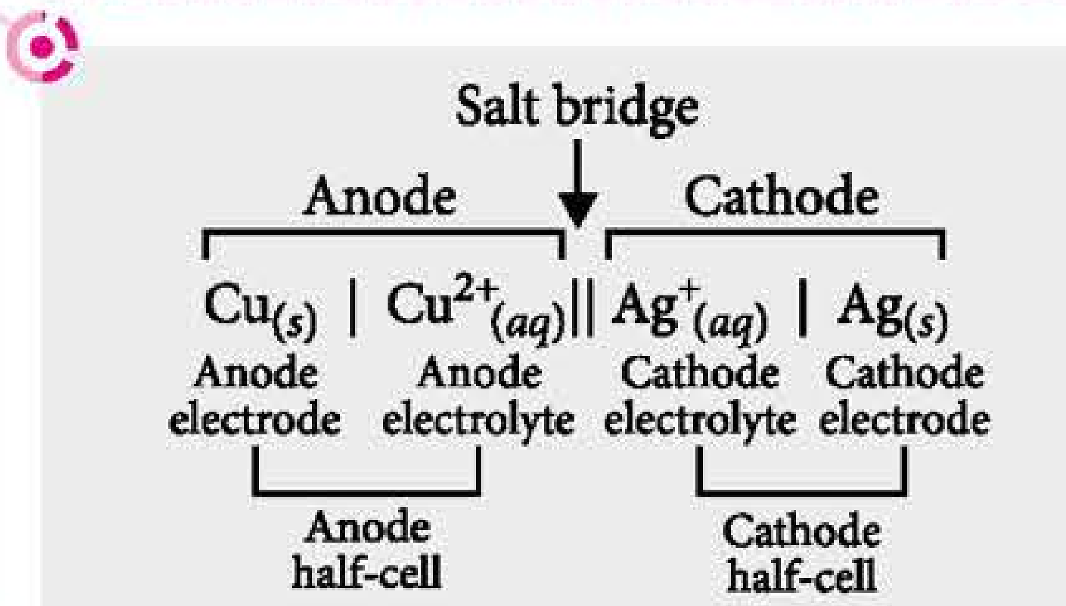
A device which uses electrical energy to carry out some non-spontaneous chemical reactions.

Faraday's first law
$W = Zit$

Faraday's second law
$\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2}$

Electrochemical Cell

A device which converts chemical energy into electrical energy.



$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

or, $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$

Fuel Cells

- **H_2-O_2 Fuel Cell**
  Anode : $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$
  Cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$
  Net reaction : $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$
  Uses : In automobiles on experimental basis, for producing electricity in Apollo Space program, etc.
- **Thermodynamic efficiency** (η) of a fuel cell $= \frac{\Delta G}{\Delta H} = -\frac{nFE}{\Delta H}$

Corossion

- **Rusting of iron** : Formation of brown complex of $Fe_2O_3 \cdot xH_2O$ in presence of O_2 and H_2O.
- **Tarnishing of metals :** Formation of thin layer of corrosion over metals such as copper, silver, aluminium, etc.

Some Commercial Cells

Primary Cells

- **Dry cell**
  Anode : Zinc container
  Cathode : Carbon (graphite)
  Electrolyte : Moist paste of $NH_4Cl + ZnCl_2$
  Net reaction : $Zn_{(s)} + 2NH^+_{4(aq)} + 2MnO_{2(s)} \rightarrow Zn^{2+}_{(aq)} + 2MnO(OH)_{(s)} + 2NH_{3(g)}$
  Uses : In transistors and clocks, etc.
- **Mercury cell**
  Anode : Zn-Hg amalgam
  Cathode : Mercury (II) oxide
  Electrolyte : Paste of KOH + ZnO
  Net reaction : $Zn(Hg)_{(s)} + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$
  Uses : In watches, hearing aids, etc.

Secondary Cells

- **Lead storage cell**
  Anode : Pb; **Cathode :** PbO_2
  Electrolyte : 35-38% H_2SO_4 solution
  Net reaction : $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$
  The reverse reaction takes place during recharging :
  $2PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)}$
  Uses : In automobiles and inverters.
- **Nickel-cadmium cell**
  Anode : Cadmium
  Cathode : Nickel (IV) oxide
  Electrolyte : KOH solution
  Net reaction : $Cd_{(s)} + 2Ni(OH)_{3(s)} \rightarrow CdO_{(s)} + 2Ni(OH)_{2(s)} + H_2O_{(l)}$
  The reverse reaction takes place during recharging :
  $CdO_{(s)} + 2Ni(OH)_{2(s)} + H_2O_{(l)} \rightarrow Cd_{(s)} + 2Ni(OH)_{3(s)}$
  Uses : In portable electronic devices, emergency lighting, photography equipments, etc.