MIND MAP

FOR NEET ASPIRANTS

PHYSICAL CHEMISTRY

ELECTROCHEMISTRY

ONE-SHOT

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Topics *to be covered*

1. Electrochemical cell
2. Conductance of electrolytic solution
3. Electrolysis and electrolytic cell
4. Batteries, fuel cell

Electrochemistry

↓

deals with chemical energy and electrical energy and their interconversion.

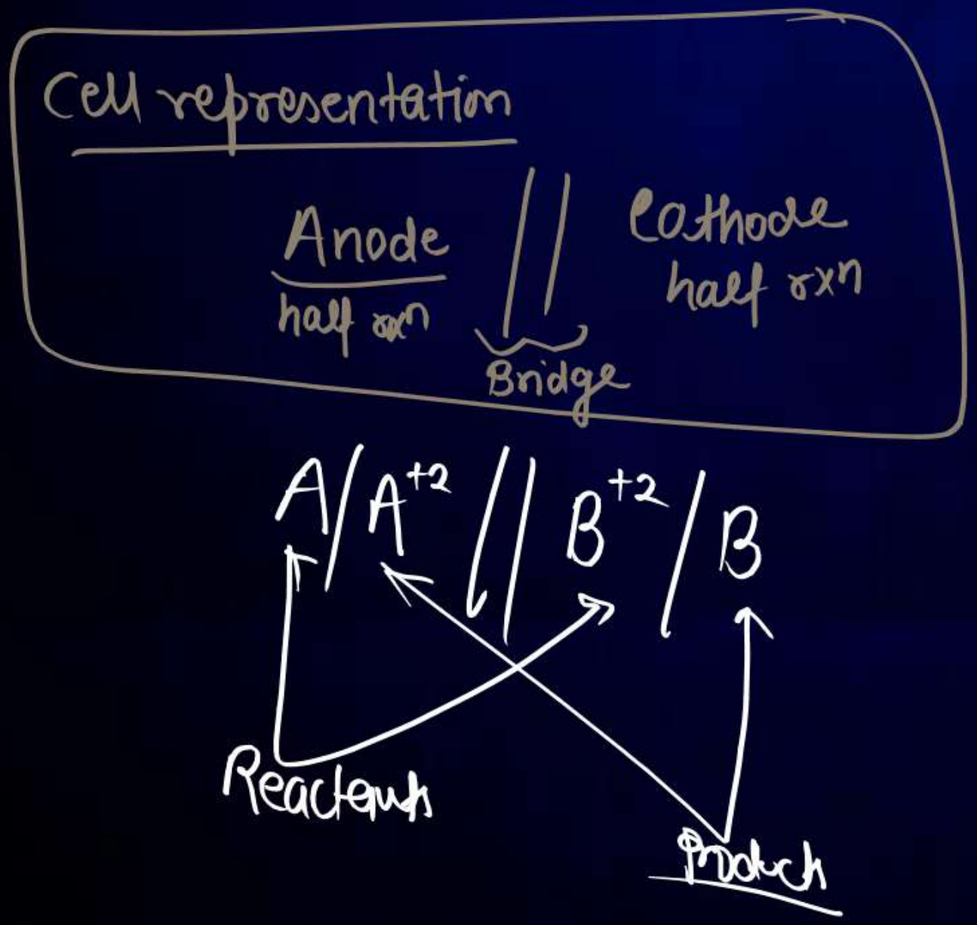
Chemical energy from spontaneous chemical rxn → (electrochemical cell) → electrical energy

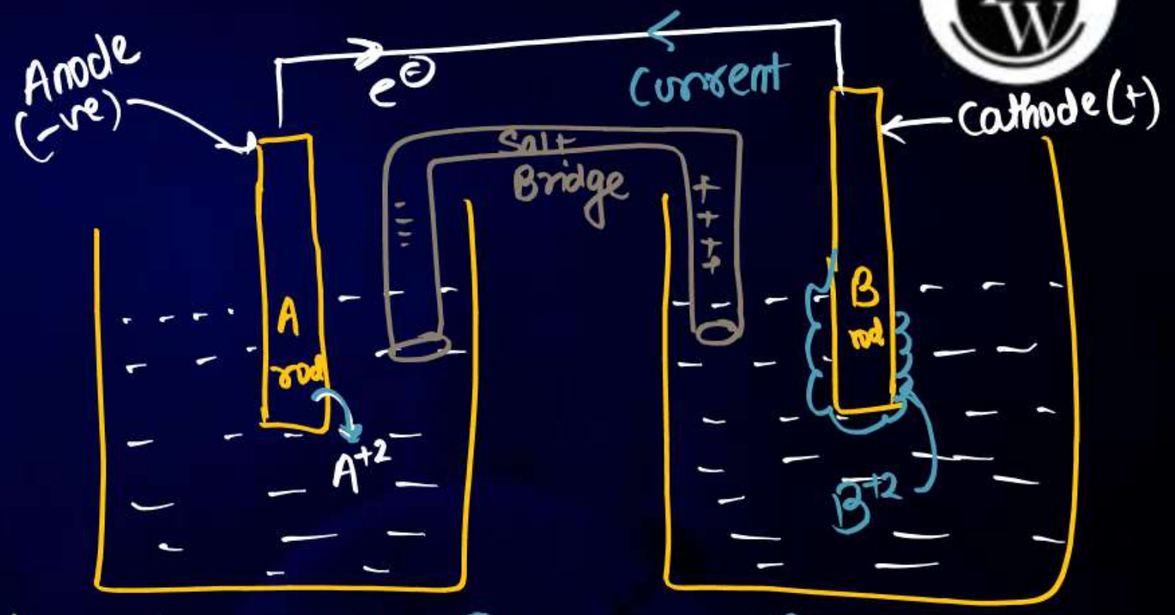
electrical energy → (electrolytic cell) → chemical energy to do non-spontaneous Chemical rxn

	(Oxidation) Anode	(Reduction) Cathode
Electrochemical cell	−	+
Electrolytic Cell	+	−

Electrochemical cell

$$A_{(s)} + B^{+2}_{aq.} \longrightarrow A^{+2}_{aq.} + B_{(s)}$$





Imp. points

⇒ $e^{\ominus}$ flows from anode to cathode.

⇒ Current flows from Cathode to anode.

⇒ Thickness of anode decreases

⇒ Thickness of Cathode increases.

⇒ Solution remains neutral

⇒ $\Delta H = 0$ ⇒

Daniel cell

$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

$Zn/Zn^{+2}//Cu^{+2}/Cu$

$E^\circ_{cell} = 1.1V$

Case-I ⇒ $E_{ext} = 1.1V$ ⇒ no current flows.

Case-II → $E_{ext} < 1.1V$ ⇒ Normal daniel cell
- ↳ $e^\ominus$ flows from Zn to Cu
- ↳ Zn dissolves and Cu deposit.

Case-III → $E_{ext} > 1.1V$ ⇒ Reverse of daniel cell
- ↳ $e^\ominus$ flows from Cu to Zn
- ↳ Zn deposit and Cu dissolve.

⇒ if Conc^n is 1 M
↳ Galvanic cell/Voltaic cell

Salt-bridge

↓ inverted U-shaped to be have electrolyte.

Functions
1. Complete the circuit.
2. maintains neutrality of soln.
3. Liquid-liquid junction potential reduces.

⇒ electrolyte used in Salt bridge must show two conditions
(a) they should be inert
(b) ionic mobility/velocity of cations and anions must be same.

electrode potential ⇒ (E)

→ Oxidation potential ⇒ $E^\circ_{Zn/Zn^{+2}} = 0.76\ V$

→ Reduction potential ⇒ $E^\circ_{Zn^{+2}/Zn} = -0.76\ V$

$$\left|E^\circ_{\text{oxidation potential of A}}\right| = \left|E^\circ_{\text{Reduction potential of A}}\right|$$

$$(\pm)E^\circ_{\text{oxidation potential of A}} = (\mp)E^\circ_{\text{Reduction potential of A}}$$

⇒ Oxidation potential ∝ tendency to get oxidised
∝ Reducing power

⇒ Reduction Potential ∝ tendency to get reduced
∝ Oxidising power

Best choice for anode = Highest O.P
Best choice for Cathode = Highest R.P

⇒ Standard potential = standard reduction Potential E°_{RP} ⇒ on the basis of SRP, we arrange elements known as electrochemical series.

$Li < K < Ba < Sr < Ca < Na < Mg < Al < Mn < H_2O < Zn < Cr < Fe < Cd < Co < Ni < Sn < Pb < (H_2) < Cu <$

$F_2 > Au > Cl_2 > O_2 > Pt > Br_2 > Ag > I_2 > Hg >$

(H_2) ⇒ SRP = 0

Standard emf of cell (E°_{cell}) → when no electric current is withdrawn.

↓ do not depend on stoichiometric coefficient.

→ Conc^n = 1 M and Pressure = 1 bar

$$E^\circ_{cell} = E^\circ_{\text{oxidation potential of anode}} + E^\circ_{\text{Reduction potential of Cathode}}$$

→ In terms of R.P

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

→ In terms of O.P

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

⇒ Feasible cell ⇒ $E^\circ_{cell} > 0$, $\Delta G^\circ < 0$

Non-feasible cell ⇒ $E_{cell} < 0$, $\Delta G^\circ > 0$

Emf of cell (E_{cell}) → $E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q_c$

→ Nernst equation

→ n = no. of e$^\ominus$ lost/gained.

$E^\circ_{cell} > E_{cell}$

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log Q_c$$

For numericals →

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log Q_c$$

at equilibrium

$$\left\{ \begin{matrix} E_{cell} = 0 \\ Q_c = K_c \end{matrix} \right\}$$

$$E^\circ_{cell} = \frac{RT}{nF} \ln K_c$$

$$E^\circ_{cell} = \frac{0.059}{n} \log K_c$$

Gibbs free energy (ΔG)

$\Delta G = -nFE_{cell}$

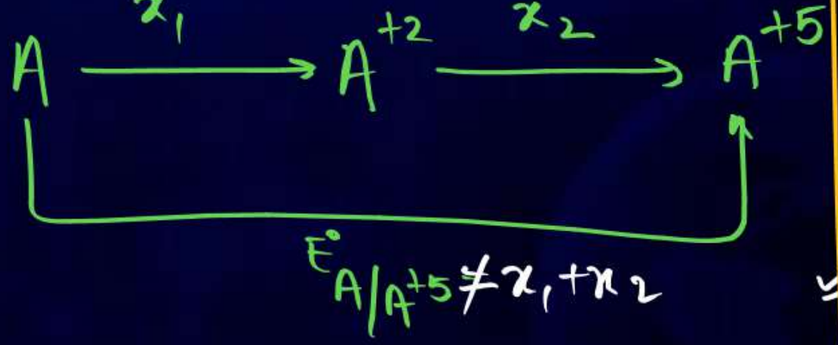
$\Delta G^\circ = -nFE^\circ_{cell}$

Standard gibbs free energy

$\Delta G = \Delta G^\circ + RT \ln Q_C$

Conservation of Gibbs energy

$$(\Delta G^\circ)_{A/A^{+5}} = (\Delta G^\circ)_{A/A^{+2}} + (\Delta G^\circ)_{A^{+2}/A^{+5}}$$



$$2x_1 + 3x_2 = 5E^\circ_{A/A^{+5}}$$

$$E^\circ_{A/A^{+5}} = \frac{2x_1 + 3x_2}{5}$$

Concentration cell $\Rightarrow E^\circ_{cell} = 0$

$M/M^{+n} \,\|\, M^{+n}/M$

Standard Hydrogen electrode

SHE → SRP = 0 = $E^\circ_{H^+/H_2}$

→ SOP = 0 = $E_{H_2/H^\oplus}$

Oxidation potential of H_2 electrode $= 0.059 \times pH$

$E_{H_2/H^\oplus} = 0.059 \times pH$

$E_{H^\oplus/H_2} = -0.059 \times pH$

Conductance of electrolytic solution

metallic conductance

Conductance shown by $e^{\ominus}$

⇒ depends on ① nature of metal
② valence $e^{\ominus}$ of metal
③ Viscosity
④ Temp ↑ Resistance ↑
metallic Conductance ↓

Electrolytic/Ionic conductance

Conductance shown by ions.

depends on ① Nature of electrolyte
② Viscosity and ionic size
③ Temp ↑ dissociation of electrolyte ↑
ionic conductance ↑

$\Rightarrow R = \rho \frac{l}{A}$

R ↓ unit = ohm

ρ ↓ specific or resitivity
resistence
unit = ohm-m or ohm-cm

$\frac{l}{A}$ = cell constant = G^*
unit = m^{-1} or cm^{-1}

$\frac{1}{R}$ = Conductance (G)
Unit = ohm^{-1} or Siemens (S)

$\frac{1}{\rho}$ = specific conductance = K
or
Conductivity
Unit = $S cm^{-1}$ or $S m^{-1}$

$\frac{1}{G} = \frac{1}{k}\frac{l}{A}$

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

$G^* = \frac{l}{A} = R \times \frac{1}{\rho} = R \times K$

Same cell ⇒ $R_1 k_1 = R_2 k_2$

Molar Conductivity (Λ_m) $= \frac{K}{C}$

if (K) is in Scm^{-1}

then

$$\Lambda_m = \frac{K \times 1000}{C}$$

Λ_m → $S\,cm^2\,mol^{-1}$

if (K) is in Sm^{-1}

then

$$\Lambda_m = \frac{K}{C \times 1000}$$

Λ_m → $Sm^2\,mol^{-1}$

equivalent conductivity = $\Lambda_{eq} = \frac{K}{N}$

if (K) → Scm^{-1}

then

$$\Lambda_{eq} = \frac{K \times 1000}{N}$$

if (K) → Sm^{-1}

then

$$\Lambda_{eq} = \frac{K}{N \times 1000}$$

$$\Lambda_{eq} = \frac{\Lambda_m}{\text{n-factor}}$$

Concentration decreases (On dilution)

Conductance increases ⇒ IMF decreases

Conductivity decreases ⇒ no. of ions/volume decreases

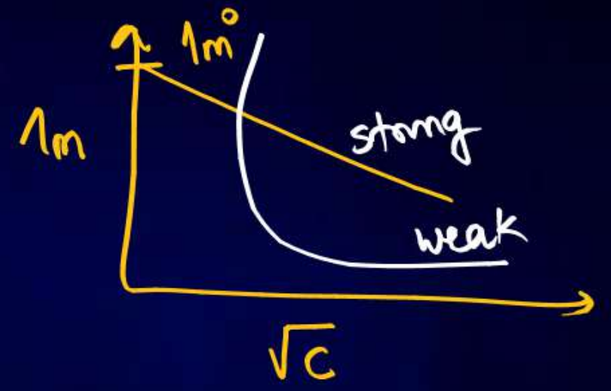
Molar Conductivity increases ⇒ total vol. increases

Conc ↓ Λ_m ↑

Concentration approaches to zero (infinite dilution) → Λ_m → $(\Lambda_m)_{maximum} = \Lambda_m^\circ$ → limiting molar Conductivity

For strong electrolyte $\Lambda_m = \Lambda_m^\circ - B\sqrt{C}$

For weak electrolyte $\Lambda_m \propto \frac{1}{\sqrt{C}}$



Kohlaursch's law

$$(\Lambda_m^\circ)_{AB} = \lambda^\circ_{mA^\oplus} + \lambda^\circ_{mB^\ominus}$$

$$(\Lambda_m^\circ)_{A_2B} = 2(\lambda^\circ_m)_{A^{+}} + \lambda^\circ_{B^{-2}}$$

$$(\Lambda_{eq}^\circ)_{AB} = (\lambda^\circ_{eq})_{A^\oplus} + (\lambda^\circ_{eq})_{B^\ominus}$$

Λ_m° $\begin{cases} H^\oplus >> OH^\ominus \\ Na^\oplus < K^\oplus \\ Ca^{+2} > Mg^{+2} \\ Cl^\ominus < Br^\ominus \end{cases}$

Applications of Kohlaursch's law

① $\left\{\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}\right\}$ or $\left\{\alpha = \frac{\Lambda_{eq}}{\Lambda_{eq}^\circ}\right\}$

(2) $K_a = \frac{C\alpha^2}{1-\alpha}$ $K_b = \frac{C\alpha^2}{1-\alpha}$

dissociation constant of acid & Base.

(3) Saturated solution

$\Lambda_m = \Lambda_m^\circ = \frac{K \times 1000}{C/S}$

electrolysis → Quantitative Analysis = amount of products at electrode.

→ Qualitative Analysis ⇒ products formed by electrolysis

Quantitative analysis ⇒ Faraday's Ist law ⇒ mass deposited ∝ amount of electricity passed (Charge)

$m \propto Q$

$m = ZQ$

$Q = \frac{\text{Current (I)}}{\text{time (s)}}$

electrochemical equivalent = $\frac{\text{Molar mass}}{n \cdot F}$

$m = \frac{MIt}{nF}$

Faraday's 2nd law ⇒ (Same charge), mass deposited ∝ Equivalent mass.

$$\frac{m_A}{m_B} = \frac{E_A}{E_B}$$

≠ Qualitative Analysis or Product of electrolysis → depends on

① electrode → Active electrode (participate)

→ inert electrode (don't participate)

② Anode → Best O.P

Oxidation

Anions

→ Preference discharge theory

$Cl^{\ominus} > OH^{\ominus} > SO_4^{-2}$ or $NO_3^{\ominus}$

③ Cathode → high R.P

↓

Preference is decided by electrochemical series

H_2O

→ Anode

$H_2O \longrightarrow O_2$

$E^\circ = -1.23V$

Kinetically slow

$E = -1.23 - 0.23V$

$\Rightarrow -1.46V$

→ overpotential

→ Cathode

$H_2O \longrightarrow H_2$

$E = -0.83V$

Product of electrolysis

Aqueous NaCl → $Na^{\oplus}$, $Cl^{\ominus}$

H_2O, $OH^{\ominus}$

Cathode ⇒ $H_2O \longrightarrow H_2(g)$

anode ⇒ $Cl^{\ominus} \longrightarrow Cl_2(g)$

H_2O — Cathode; $OH^{\ominus}$ — anode

electrolysis of Molten NaCl

cathode	anode
$Na^{\oplus}$	$2Cl^{\ominus}$
↓	↓
$Na_{(s)}$	$Cl_2 + 2e^{\ominus}$

Batteries → Primary Battery

(non-rechargeable)

(non-reusable)

- → leclanche cell
- → Mercury cell

Construction: Cathode, Anode, Electrolyte

Rxn: Cathode, Anode, Overall

Secondary Batteries

Rechargeable

Reusable

- → lead storage Battery
- → Ni-Cd cell

Fuel cell ⇒ combustion of H_2, CH_4 etc

H_2-O_2 fuel cell

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Corrosion

$Fe_2O_3 \cdot xH_2O$ → Rust

Homework

- NCERT
  - exercise
  - examplar
- PYQs
  - NEET
  - jee-mains (last 5-years)


Thank you