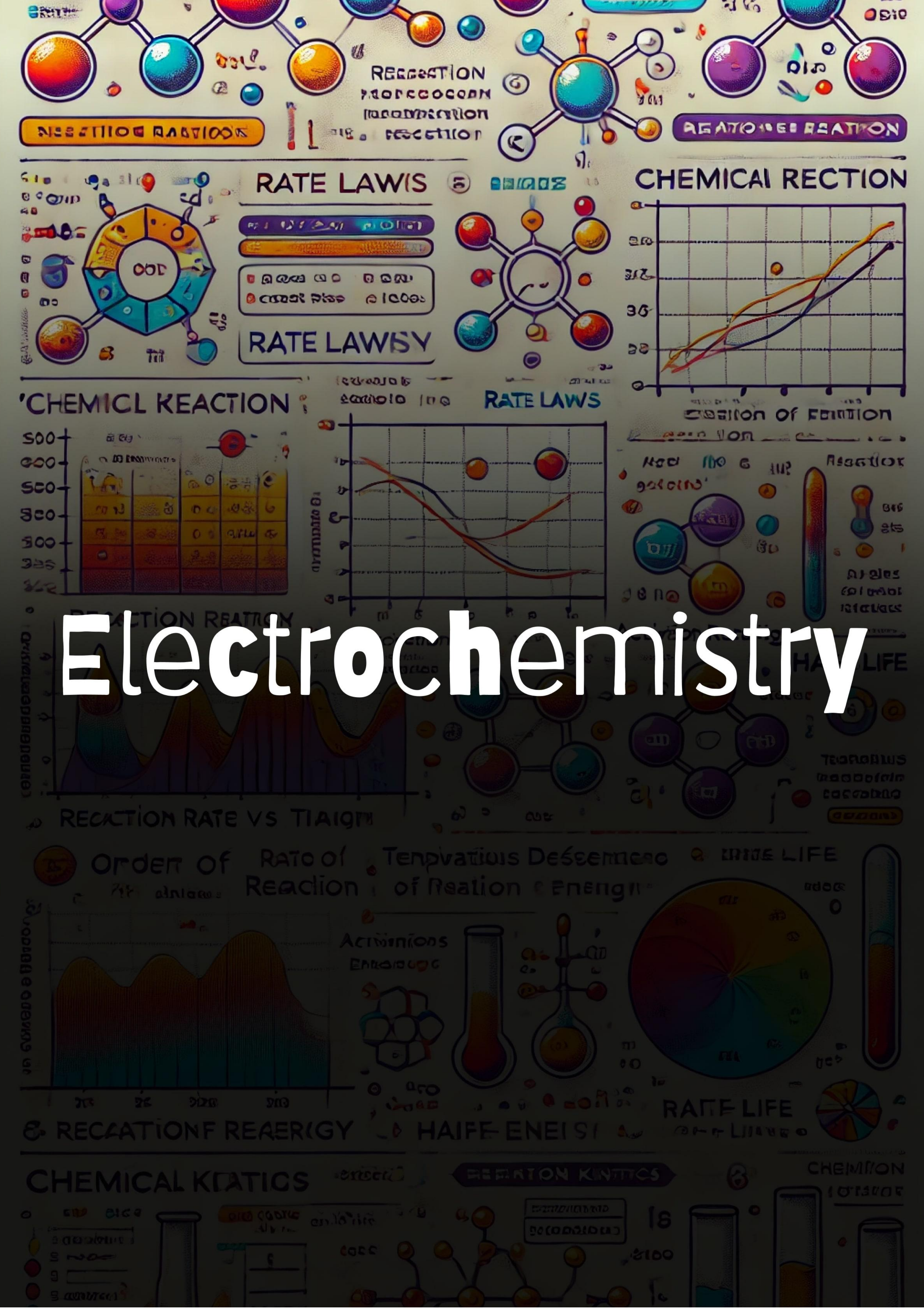
Electrochemistry



Electrochemistry

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Metallic Conductors	Electrolytic conductors
– Metals	solution (aq) — Ionic OR Molten Ionic Liquids
– electrons	Ions (+ or –)
– Reaction ✗	Reaction ✓
– As T↑ R↑	As T↑ R↓

- Part - I :

① Conductance (G)

② Resistance (R)

③ specific conductance or conductivity [κ]

④ Specific Resistance or Resistivity [ρ]

⑤ Molar Conductance Λ_m

⑥ Equivalent conductance Λ_{eq}

⑦ Kolhrausch law – Application

Σ molar conductance of any ion at infinite dilution is same / constant in any Electrolytic solution

① $G = ohm^{-1}$ or Ω^{-1}

② $R = ohm$ or Ω

③ $\kappa = ohm^{-1} cm^{-1}$ / $ohm^{-1} m^{-1}$
$\Omega^{-1} cm^{-1}$ / $\Omega^{-1} m^{-1}$
$S\ cm^{-1}$ / $S m^{-1}$

④ ohm^{-1} = Siemen = S

⑤ $\rho = ohm/cm$ / $ohm\ m$
$\Omega\ cm$ / Ωm

⑥ $\Lambda m = ohm^{-1} cm^2 mol^{-1}$
$\Omega^{-1} cm^2 mol^{-1}$
$S\ cm^2 mol^{-1}$

① $G = \frac{1}{R}$

② $\kappa = \frac{1}{\rho}$

③ $\frac{l}{a}$ = cell constant (b)

④ $R = \rho \frac{l}{a}$

⑤ $\kappa = G \frac{l}{a}$

⑥ $\frac{\Lambda_{eq}}{\Lambda_m} = \frac{M}{N} = \frac{M}{n\text{-factor } M} = \frac{1}{n\text{-factor}}$

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⑦ $\Lambda m = \frac{\kappa \times 1000}{c}$ $\Lambda m = S\,cm^2\,mol^{-1}$

$c = mol\,L^{-1}$

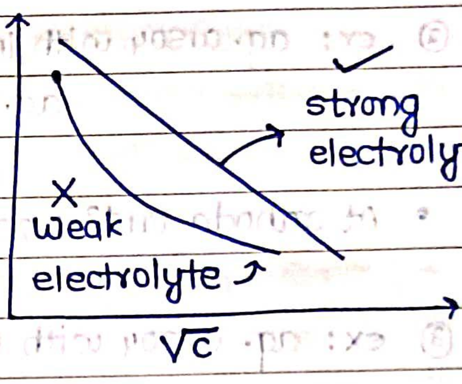
⑧ $\alpha = \frac{\Lambda}{\Lambda^o}$ $\kappa = S\,cm^{-1}$

Λ = molar conductance at some conc 'c'

Λ^o = molar conductance – infinite dilution

α = Degree of Dissociation

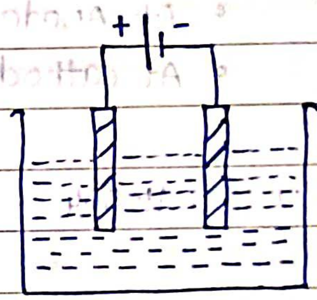
- Upon dilution,
  conc ↓ κ ↓
  conc ↓ Λm ↑
  conc ↓ α of weak electrolyte ↑
  (addition of water)



$\Lambda m = -a\sqrt{c} + \Lambda_0$

– strong electrolyte

- Electrolysis :



cation = cathod

Anion = anode

$NaCl \longrightarrow Na^+$ and Cl^-

At Cathode , $Na^+ + e^- \rightarrow Na$ CCR

(Reduction)

At Anode , $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^{\ominus}$ AAO

(oxidation)

- Discharge potential theory:

Anions : $I^- > Br^- > Cl^- > OH^- > NO_3^- > SO_4^{2-} > F^-$

Cations : $Au^{+3} > Ag^+ > Cu^{+2} > H^+ > Fe^{+2} > Al^{+3} >$
$Zn^{+2} > Mg^{+2} > Na^+ > K^+ > Li^+$

(Discharge hone ka order)

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① ex: aq NaCl ≡ Na^+ H^+ • At cathode $H^+ + e^\ominus \rightarrow \frac{1}{2} H_2 (g) \uparrow$

Cl^- OH^-

• At Anode $Cl^- \rightarrow \frac{1}{2} Cl_2 + e^\ominus$

Dilute — Very Very Dilute — OH^-

Cl^- $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$

② ex: aq. $CuSO_4$ with inert electrode

aq. $CuSO_4 \longrightarrow Cu^{+2}, H^+$

SO_4^{2-}, OH^-

• At cathode $Cu^{+2} + 2e^- \longrightarrow Cu$ • At anode $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$

③ ex: aq. $CuSO_4$ with Cu electrode

• At Anode $Cu \longrightarrow Cu^{+2} + 2e^-$ (Impure) – oxidation

• At cathode $Cu^{+2} + 2e^- \longrightarrow Cu$ (Pure) – Reduction

④ example: H_2SO_4

H_2SO_4 : H^+ — Dilute

OH^- HSO_4^- — 50%

• At cathode

$H^+ + e^- \longrightarrow \frac{1}{2} H_2$ • At anode $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$ (Dilute)

(50%) $HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$

• Faraday First law :

Mass of substance deposited / liberated at electrode is directly proportional to quantity of electric charge (Q).

$W \propto Q$ $W = ZQ$ $Q\,it$ Z = electrochemical equivalent (constant)

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- **Faraday second law :**

When same charge is passed through differt electrolytic cells, then mass of substance deposited / liberated at electrode is directly proportional to its equivalent mass (E). → $\frac{M \cdot M}{n\text{-factor}}$

$W \propto E$ $\quad \frac{W_1}{W_2} = \frac{E_1}{E_2}$

$W = \frac{EQ}{F} \quad \frac{E}{F} = Z \quad E = FZ \quad Q = it$

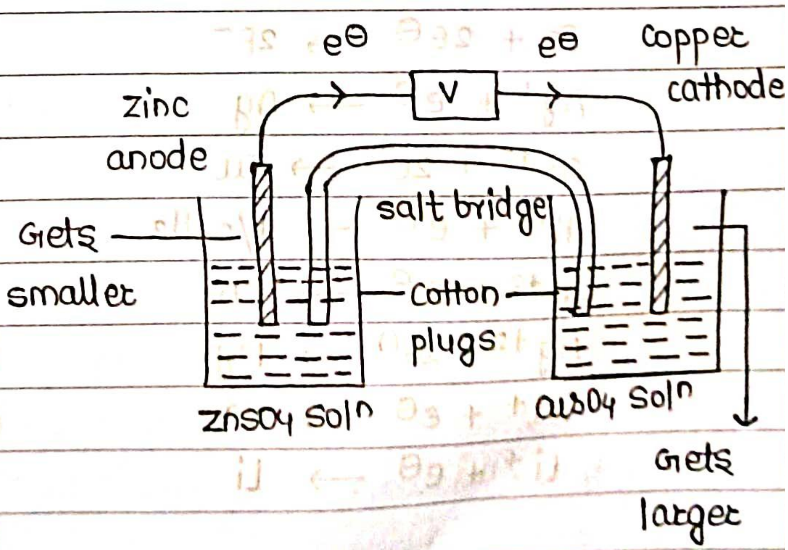
$F = 96500\,C$ = charge of 1 mol of e^-

- **equivalent masses of some Important :**

① $Na = 23$	⑥ $Zn = 65$	⑪ $Au^{+3} = \frac{197}{3}$
② $Mg = 12$	⑦ $H_2 = 1$	
③ $Al = 9$	⑧ $Cl_2 = 35.5$	
④ $Cu^{+1} = 63.5/1$	⑨ $O_2 = 8$	
⑤ $Cu^{+2} = 63.5/2$	⑩ $Ag = 108$	

- Electrochemical cells —— ① Voltaic cells - chemical to electrical
  ② electrolytic cells - Electrical to chemical

- Daniel cell - Zn and Cu Reactions.
(Galvanic cell)



① At anode

$Zn \longrightarrow Zn^{+2} + 2e^{\ominus}$

(oxidation) —— OP

② At cathode

$Cu^{+2} + 2e^{\ominus} \longrightarrow Cu$

(Reduction) —— RP

OP + RP ⟶ cell potential.

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classmate

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- If solution conc. is at 1 molar] temp 298 K ⟶ SOP
- If gas conc is at 1 atm] SRP

SOP + SRP ⟶ standard cell potential

$E^\circ_{cell} = SOP + SRP$ ⟵ (standard emf of cell)

- By IUPAC,

① $E^\circ cell = E^\circ SRP_{cathode} - E^\circ SRP_{anode}$ ② $E^\circ cell = E^\circ SOP_{Anode} - E^\circ SOP_{cathode}$

③ $E^\circ cell = E^\circ SOP_{anode} + E^\circ SRP_{cathode}$

- Electrochemical series —— SRP order based on standard hydrogen electrode.

① More SRP, more tendendy to undergo Reduction — left side
more oxidising power
more strong oxidising agent.

② Low SRP, more tendency to undergo oxidation — Right side
more Reducing power
more strong Reducing agent

$F_2 + 2e^\ominus \longrightarrow 2F^-$
$Ag^+ + e^\ominus \rightleftharpoons Ag$
$Cu^{+2} + 2e^\ominus \longrightarrow Cu$
$H^+ + e^\ominus \longrightarrow 1/2\, H_2$
$Zn^{+2} + 2e^\ominus \longrightarrow Zn$
$Mg^{+2} + 2e^\ominus \longrightarrow Mg$
$Na^+ + e^\ominus \longrightarrow Na$
$Li^+ + e^\ominus \longrightarrow Li$

- Rightside — upar wale ko (Uss) Reduce karta.
- Left side — niche wale ko oxidise karta.

① $\Delta G = -nFE$ / $\Delta G^\circ = -nFE^\circ$

② $\Delta G = \Delta G^\circ + RT\ln(Q)$

③ $E = E^\circ - \frac{RT}{nF}\ln(Q)$ nerst equation

④ $E = E^\circ - \frac{0.059}{n}\log(Q)$

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- At equilibrium $\Delta G = 0$, $K = Q$

① $E^\circ = \frac{RT}{nF} \ln(K)$ ② $E^\circ = \frac{0.059}{n} \log K$

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

Low SRP = Anode = Oxidation

High SRP = Cathode = Reduction

- When two cell half SRP are given then third half cell SRP can be calculated by

$$E^\circ_3 = \frac{n_1E^\circ_1 + n_2E^\circ_2}{n_3}$$