Electrochemistry

Metallic Conductors	Electrolytic Conductors
Metals	solution (aq) → Ionic
	OR
	Molten Ionic Liquids
electrons	Ions (+ or −)
Reaction X	Reaction ✓
As T↑ R↑	As T↑ $\left(R↓\right)$

- **Part – I :**

①	Conductance (G)	⑤	Molar Conductance Λ_m
②	Resistance (R)	⑥	Equivalent conductance Λ_{eq}
③	specific conductance or conductivity [κ]	⑦	Kohlrausch law – Application molar conductance of any ion at infinite dilution is same /constant in any Electrolytic solution
④	specific Resistance or Resistivity [ρ]		

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

⑥ $\Lambda_m = ohm^{-1} cm^2 mol^{-1}$
$\Omega^{-1} cm^2 mol^{-1}$
$s\ cm^2 mol^{-1}$

① $G = \dfrac{1}{R}$ ② $\kappa = \dfrac{1}{\rho}$ ③ $\dfrac{l}{a} = $ cell constant (b)

④ $R = \rho \dfrac{l}{a}$

⑤ $\kappa = G \dfrac{l}{a}$

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

⑦ $\Lambda m = \dfrac{K \times 1000}{C}$ $\Lambda m = S\,cm^2\,mol^{-1}$

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

⑧ $\alpha = \dfrac{\Lambda}{\Lambda^o}$ $K = S\,cm^{-1}$

   Λ = molar conductance at some conc 'c'

   Λ^o = molar conductance – infinite dilution

- Upon dilution, α = Degree of Dissociation

  conc ↓ K ↓

  conc ↓ Λm ↑

  conc ↓ α of weak electrolyte ↑

  (addition of water)

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

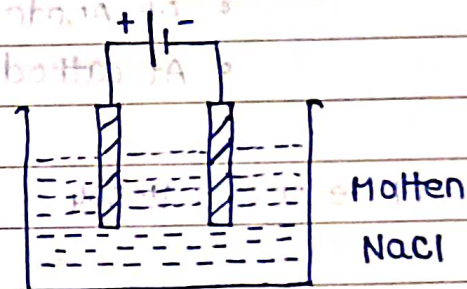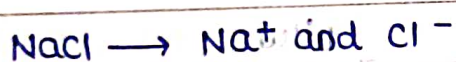 – strong electrolyte
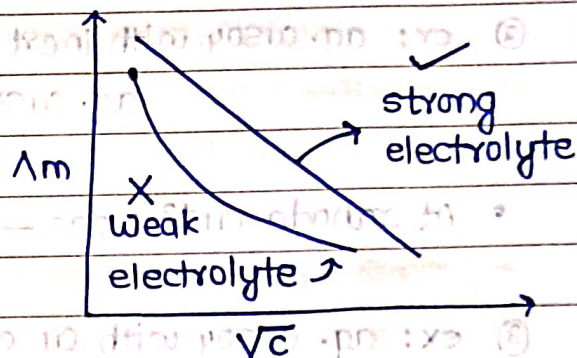
- Electrolysis :

  cation = cathod

  Anion = anode

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

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

  (Reduction)

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

  (oxidation)
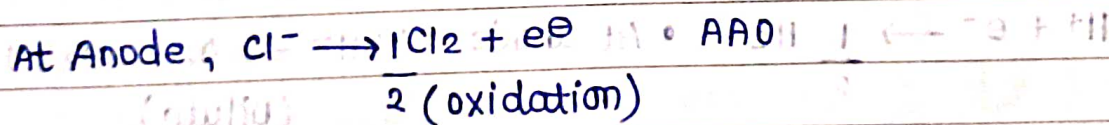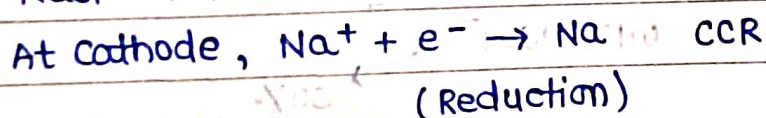
- Discharge potential theory :

  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)

classmate

① ex: aq NaCl $\equiv$ Na$^+$ H$^+$ • At cathode   H$^+$ + e$^\ominus$ ⟶ $\frac{1}{2}$ H$_2$ (g) ↑

      Cl$^-$ OH$^-$

          • At Anode   Cl$^-$ ⟶ $\frac{1}{2}$ Cl$_2$ + e$^\ominus$

Dilute   Very Very

     Dilute ⟶ OH$^-$

Cl$^-$ 4OH$^-$ ⟶ O$_2$ + 2H$_2$O + 4e$^-$

② ex: aq. CuSO$_4$ with inert electrode

     aq. CuSO$_4$ ⟶ Cu^{+2}, H$^+$

       SO$_4{}^{2-}$, OH$^-$

• At cathode Cu^{+2} + 2e$^-$ ⟶ Cu   • At anode   4OH$^-$ ⟶ O$_2$ + 2H$_2$O + 4e$^-$

③ ex: aq. CuSO$_4$ with Cu electrode

   • At Anode   Cu ⟶ Cu^{+2} + 2e$^-$ (Impure) – oxidation
   • At cathode   Cu^{+2} + 2e$^-$ ⟶ Cu   (Pure) – Reduction

④ example: H$_2$SO$_4$

      H$_2$SO$_4$:   H$^+$ Dilute

        4OH$^-$ HSO$_4{}^-$

• At cathode   50%

   H$^+$ + e$^-$ ⟶ $\frac{1}{2}$ H$_2$ • At anode   4OH$^-$ ⟶ O$_2$ + 2H$_2$O + 4e$^-$

          (oxidation)   (Dilute)

     (50%)   HSO$_4{}^-$ ⟶ H$_2$S$_2$O$_8$ + 2e$^-$

• Faraday First law :

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

            z = electrochemical

W $\propto$ q   W = zq   q it   equivalent (constant)

- **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).

$$W \propto E \qquad \frac{W_1}{W_2} = \frac{E_1}{E_2} \qquad\qquad \frac{M \cdot M}{n\text{-factor}}$$

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

F = 96500 C = charge of 1 mol of e⁻

- **equivalent masses of some Important :**

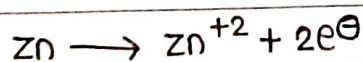|					
①	Na = 23	⑥	Zn = 65	⑪	$Au^{+3} = \dfrac{197}{3}$
②	Mg = 12	⑦	H₂ = 1		
③	Al = 9	⑧	Cl₂ = 35·5		
④	Cu⁺¹ = 63·5/1	⑨	O₂ = 8		
⑤	Cu⁺² = 63·5/2	⑩	Ag = 108		

- **Electrochemical cells** —— ① Voltaic cells – chemical to electrical

② electrolytic cells – Electrical to chemical
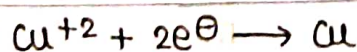
- **Daniel cell** – Zn and Cu Reactions.
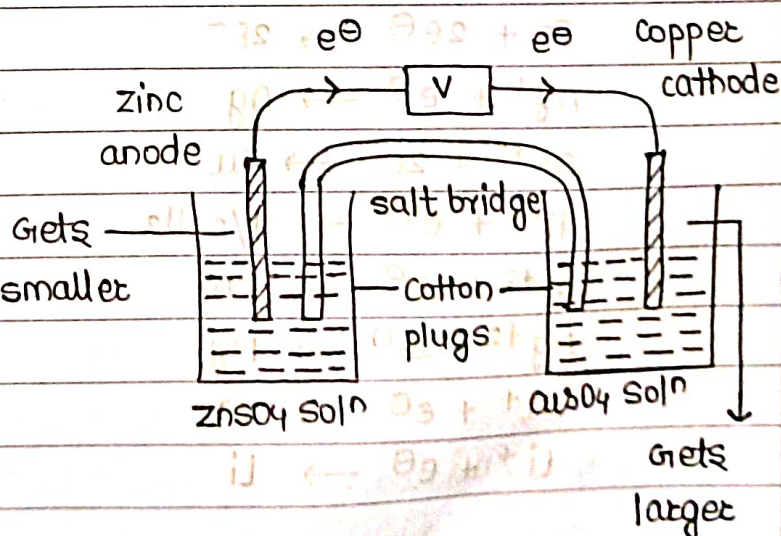 (Galvanic cell)

① At anode

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

(oxidation) —— OP ① smaller

② At cathode

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

(Reduction) —— RP

zinc anode Gets smaller

copper cathode Gets larger

ZnSO₄ sol^n   CuSO₄ sol^n

salt bridge Cotton plugs

OP + RP ⟶ cell potential.

– If solution conc. is at 1 molar ⎤
– If gas conc is at 1 atm ⎦ → temp 298 k ——→ SOP
SRP

SOP + SRP ——→ standard cell potential

1 M | $E^{o}cell = SOP + SRP$ | ←——— (standard emf of cell)

– By IUPAC,

① $E^{o}cell = E^{o}SRP - E^{o}SRP$ ② $E^{o}cell = E^{o}SOP - E^{o}SOP$
      cathode   anode   Anode   cathode

③ $E^{o}cell = E^{o}SOP + E^{o}SRP$
     anode   cathode

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

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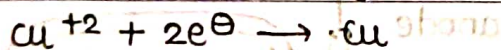   more oxidising power
            more strong oxidising agent.

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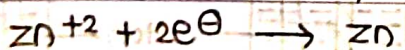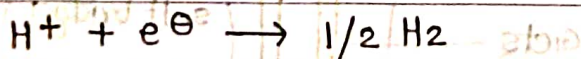   more strong Reducing agent

• Rightside — upar wale ko Reduce karta. (cell)

$F_2 + 2e^{\ominus} \longrightarrow 2F^-$

$Ag^+ + e^{\ominus} \longrightarrow Ag$

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

$H^+ + e^{\ominus} \longrightarrow 1/2\, H_2$

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

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

$Na^+ + e^{\ominus} \longrightarrow Na$

$Li^+ + e^{\ominus} \longrightarrow Li$
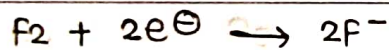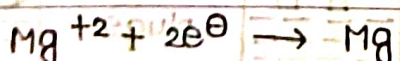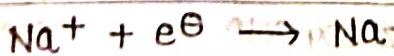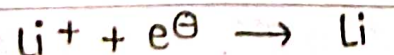
• left side — niche wale ko oxidise karta.

① $\Delta G = -nFE$ (/ $\Delta G^{o} = -nFE^{o}$

② $\Delta G = \Delta G^{o} + RT\ln(Q)$

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

④ $E = E^{o} - \dfrac{0.059}{n}\log(Q)$

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

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

- 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

$$E^\circ_3 = \dfrac{n_1 E^\circ_1 + n_2 E^\circ_2}{n_3}$$

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