

ElectrochemistryDeals energy conversion \rightarrow Chemical \leftrightarrow Electrical.ConductanceElectrolyticMetallic

- | | |
|---|---|
| 1. Temp \uparrow • R \downarrow so conductance \uparrow | \rightarrow T \uparrow R \downarrow so C \uparrow . |
| 2. Conducting power low. | \rightarrow Cond. power comparatively high. |
| 3. Follow Faraday law | \rightarrow X |
- But Both Follow Ohm's Law.
4. due to friction & water transf. \rightarrow Due to free e^- & not molten transf.

1. Conductance

$$C \text{ or } G = \frac{1}{R}$$

R = Ω , Ohm, Volt/metreG = mho, Ω^{-1} or Siemens (S)2. sp. conductance (conductivity) (G, κ)

$$\kappa = \frac{1}{\rho} = \frac{l}{Ra}$$

$$R = \rho \frac{l}{a}$$

 ρ = specific resistance.
or resistivity. ρ unit = (ohm-m) $\kappa = (\text{ohm-m})^{-1}$ or S m^{-1} or S cm^{-1} l = dist b/w electrode & a = dipped surface area of
in cm electrode in cm^2 .3. For cell

$$l/a = \text{cell const (c* or } q^*)$$

$$\kappa = C \times c^*$$

so, conductance of 1 ml / cm^3 is called specific conductance.4. Equivalent conductance (Λ_{eq} or Λ_{eq})

$$\Lambda_{eq} = \kappa \times V$$

Volume of solⁿ in ml contains 1 g eq. electrolyte.

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

$$\frac{\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}}{\text{S cm}^2 \text{eq}^{-1}} =$$

5. Molar conductance

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

$$\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$$

$$\Lambda_m = \kappa \times V$$

Rel? $\Lambda_m = \lambda_{eq} \times v$

⇒ Point to check order of electrolytic conductance:-

1. First check weak or strong electrolyte & compare λ check if all are strong then
 1. Conc more cond. more.
 2. if no. of ion more & more
 3. mobility of ion more & more.

mobility $\propto \frac{1}{\text{hydration}}$ hydⁿ \propto charge size.

Note

But in all ions conductance of H⁺ is highest.

For weak acid

By Ost. dilⁿ law $\alpha \propto \sqrt{v} \propto \frac{1}{\sqrt{c}}$ & if conc same then strength check by eq. concept.

Factor affecting conductance:

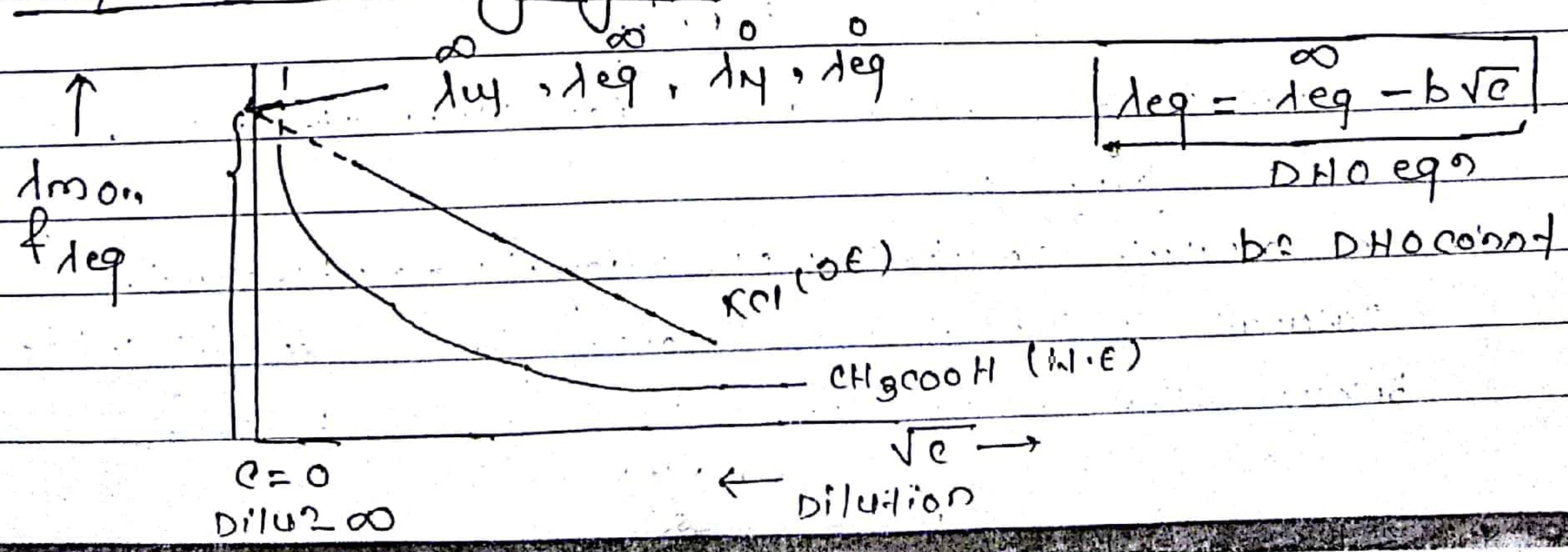
1. Intra ionic interaction force \downarrow so mobility $\uparrow \Rightarrow c \uparrow \Rightarrow \lambda_{eq} \& \Lambda_m \uparrow$.
2. hydⁿ or solvation:-
solⁿ $\uparrow \Rightarrow$ mobility \downarrow so $c \downarrow$.
3. viscosity:- \uparrow so mobility of ions $\downarrow \Rightarrow c \downarrow$.
4. Temp \uparrow , internal R.E \uparrow , & III force \downarrow so mobility rapidly \uparrow & conductance \uparrow .

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Dilution

- A. On Dilⁿ conductance (Weak or strong) Both \uparrow .
 1. For strong \uparrow Dilⁿ \rightarrow III F \downarrow therefore conductance gradually \uparrow .
 2. For weak \uparrow Dilⁿ \rightarrow III F \downarrow & $\alpha \uparrow$ so condⁿ rapidly \uparrow .
- B. on dilⁿ specific conductance (κ) \downarrow b/c no. of ion/cm³ \downarrow .
- C. on dilution Λ_m & λ_{eq} Both \uparrow .

Debye - Huckerl. On graph



- Value of DHO Const (b) depends on
1. Type of electrolyte (nature).
 2. solvent
 - (3) Temp.

Drawback :- We can never obtained max^y value of λ_m for weak electrolyte by extrapolating of curve because for weak α is always less than 1.

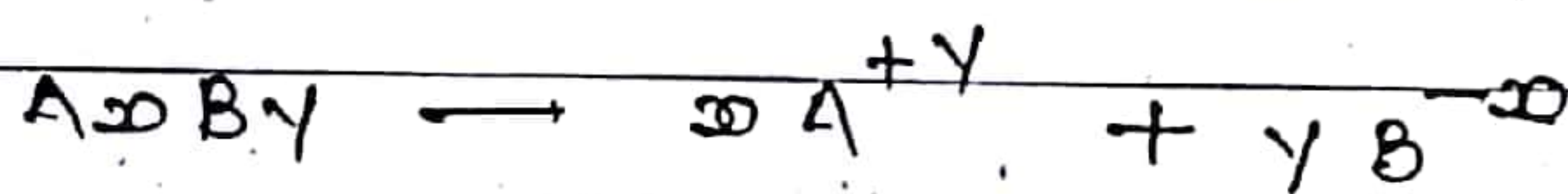
Kohlrausch's law

(App. for both strong & weak electrolyte).

As to it, At ∞ dilⁿ, electrolyte (weak or strong) 100% dissociate then each ion make a definite contribution towards eq. conductance of electrolyte irrespective to nature of other ion of electrolyte.

Dissociate then each ion make a definite contribution towards eq. conductance of electrolyte irrespective to nature of other ion of electrolyte.

$$\lambda_{eq}^{\infty}(AB) = \lambda_{eq}^{\infty} A^{+} + \lambda_{eq}^{\infty} B^{-}$$



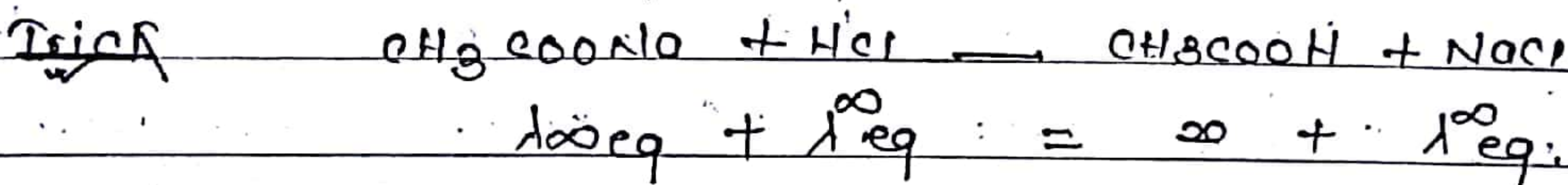
$$\lambda_{eq}^{\infty}(A_{\infty} B_{\infty}) = \frac{\lambda_{m}^{\infty} A^{+y}}{y} + \frac{\lambda_{m}^{\infty} B^{-\infty}}{\infty} \leftarrow \text{charge}$$

$$\lambda_{m}^{\infty}(A_{\infty} B_{\infty}) = \infty \lambda_{m}^{\infty} A^{+y} + y \lambda_{m}^{\infty} B^{-\infty}$$

↑ moles

Appⁿ

1. To calculate max^m value of λ_m / λ_{eq} for weak electrolyte.



2. To calculate α of weak electrolyte.

$$\alpha = \frac{\lambda_{eq/M}^{\infty}}{\lambda_{eq/M}^{\infty}} \cdot \frac{\lambda_{eq/M}^{\infty}}{\lambda_{eq/M}^{\infty}}$$

3. Calculate dissociation const for weak electrolyte

$$K_a = c\alpha^2$$

4. To calculate solubility of sparingly soluble salt.

Saturated solⁿ of this salt consid^r as ∞ diluted solⁿ

because they are very less soluble. so $\lambda_m^{\infty} = \lambda_m^{\infty}$

$$\lambda_m^{\infty} = \frac{R \times 1000}{s}$$

⇒ $K_{sol} = K_{solute} + K_{solvent}$

Part B

1. Electrode potential :- It develop b/w interface of metal and solⁿ.
2. Standard condⁿ :- 1M conc, 1 bar press, 1 atm and if Temp is not given then 25°C (But not standard) at E_p is called S.E.P.
3. Value of Electrode potential (E_p) depends on:
 - i. Nature of electrolytic solⁿ & metal and (ii) conc (iii) Temp.
- A. Oxidⁿ potential :- tendency to get oxidised is called electrolytic solⁿ press & developed potential = O.P.
- B. Redⁿ potential :- Resultant (net) tendency of electrode to get reduced called osmotic press. of solⁿ and dev. potential = R.P.

⇒ A/c IUPAC, Electrode potential is always consider as SRP.

Reference electrode

1. Primary ref. electrode :- S.H. Electrode, cat. cathode or anode depend on with which it coupled.

⇒ SRP & SOP both consider as 0.
2. secondary Ref. electrode (SRP or SOP ≠ 0)
 1. calomel electrode (laboratory use) (Generally act as cathode.)

$$\frac{1}{2} Hg_2Cl_2 + e \rightleftharpoons Hg + Cl^-$$
 2. Ag/AgCl electrode :- (Industrial use) (Generally act as cathode.)

$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$

Electrochemical Series / Electro-motive Series

Best R.A -3.05	→ Li	Co	Ag	↓	SRP increases	1. SRP = -SOP
	R	Fe	Pd ← Br ₂	↓		2. Down the
	Ba	Cd	Pt ← Cl ₂	↓		g ^o . Reactivity
	Sr	Co	Au → Best 0.A Among metal.	↓		of metal ↓
	Ca	Ni	→ F ₂ (+1.5V)	↓		3. But reactivi
	Na	Sn		↓		vity on non
	Mg	Pb		↓		metal ↑.
	Al	H		↓		series in aq. sol ⁿ .
	Mn	Cu		↓		
	Zn	Hg ← I ₂		↓		

app:-

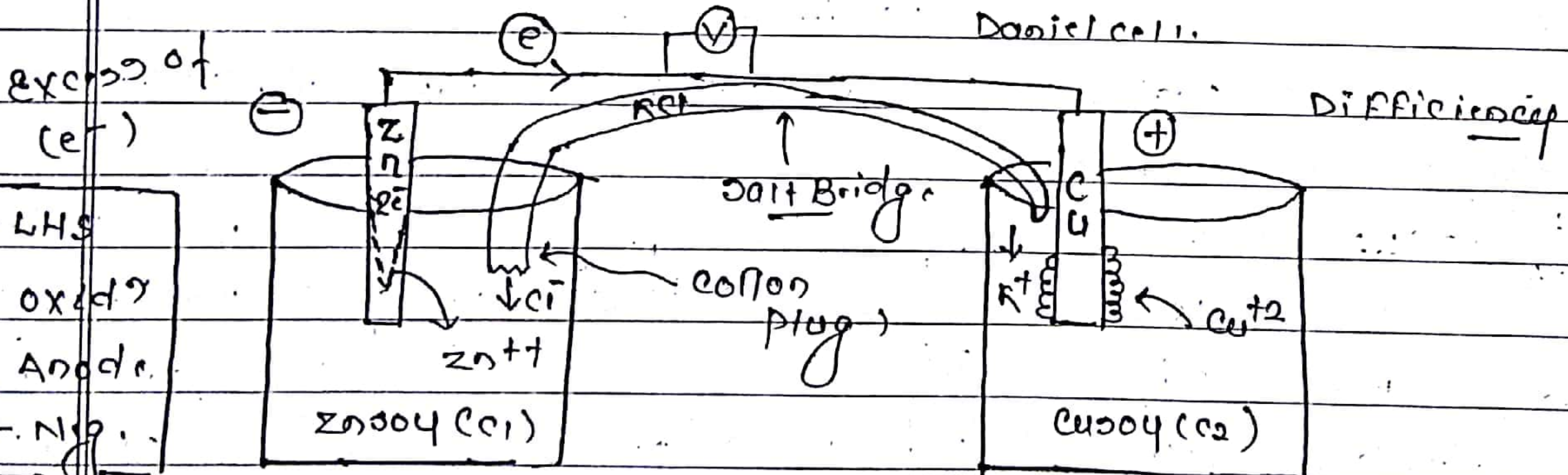
1. Disp of metal ion by metal :- Above ion displac. Below ion from its aq. soln eg - $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$.
2. Disp of H⁺ from acidic soln :- metal placed above H₂ displac. it eg :- $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
3. Disp of H₂ gas from water by metal :-
 1. metal from Li to Na in aq - disp H₂ gas from cold water
 2. metal from Mg to Al - " " " " Hot water
 3. Iron can disp H₂ from steam.
4. solubility of metal oxide :- Electropositive chr. more then stability of metal oxide is more. i.e. Down the series stability of MO $\rightarrow \downarrow$.
5. Disp of Non metal by non metal :- Below displac. upper anion. eg :- $2KI + Cl_2 \rightarrow 2KCl + I_2$

Electrochemical cell

1. Electrolytic cell (Volta meter)
(Electrical \rightarrow chemical)

2. Galvanic cell / Voltaic cell
(chemical energy \rightarrow electrical)
if Zn is anode & Cu is cathode then Galvanic cell is called

Daniel cell.



(Anode) (always oxⁿ)

cathode (redⁿ)

$\Rightarrow \Delta G = -W_{unf} = -W_{elect} = -QV$

$\Delta G = -nFE$ $n = \text{no. of mol. transferred}$
 $F = \text{Faraday const.}$

$E_{cell} = (E_{oxi})_A + (E_{red})_c$

$E_{cell} = (E_{red})_c - (E_{red})_A$

→ If $E_{cell} = +ve$ then then $\Delta G = -ve$ & rxn should be spontaneous.
 - At eqm $\Delta G = 0$ & $E_{cell} = 0$ But ΔG° & $E^{\circ}_{cell} \neq 0$.

Efficiency of cell

$$\eta = \frac{\Delta G}{\Delta H} = \frac{-nFE_{cell}}{\Delta H}$$

Some imp. result

1. Current flow - Cathode to anode (external circuit) but Anode to cathode in internal circuit (Salt bridge).
2. Cell rxn are spontaneous & exothermic so Temp of soln ↑.
3. Salt Bridge (i) maintain electrical neutrality of both electrode.
 (ii) connect different electrolytic soln & complete internal circuit & prevent liq. liq. junction potential (which always oppos. emf of cell)

NOTE

1. E° is intrinsic property. (intensive property)
2. If electrode potential of two half cell rxn given then for 3rd half cell rxn firstly convert $E^{\circ} \rightarrow \Delta G^{\circ}$ then apply Hess's law of thermodynamics.

Nernst's eq
(always write rxn)

use on single electrode as well as cell rxn

At 25°C

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log_{10} \left(\frac{[P]^x [D]^y}{[R]^z [Y]^w} \right) \Rightarrow Q = \frac{[Anode]}{[Cathode]}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log Q$$

n : no. of mol. of e^- transferred
 F : Faraday const

→ $\Delta G = \Delta G^{\circ} + 2.303RT \log Q$ At eqm

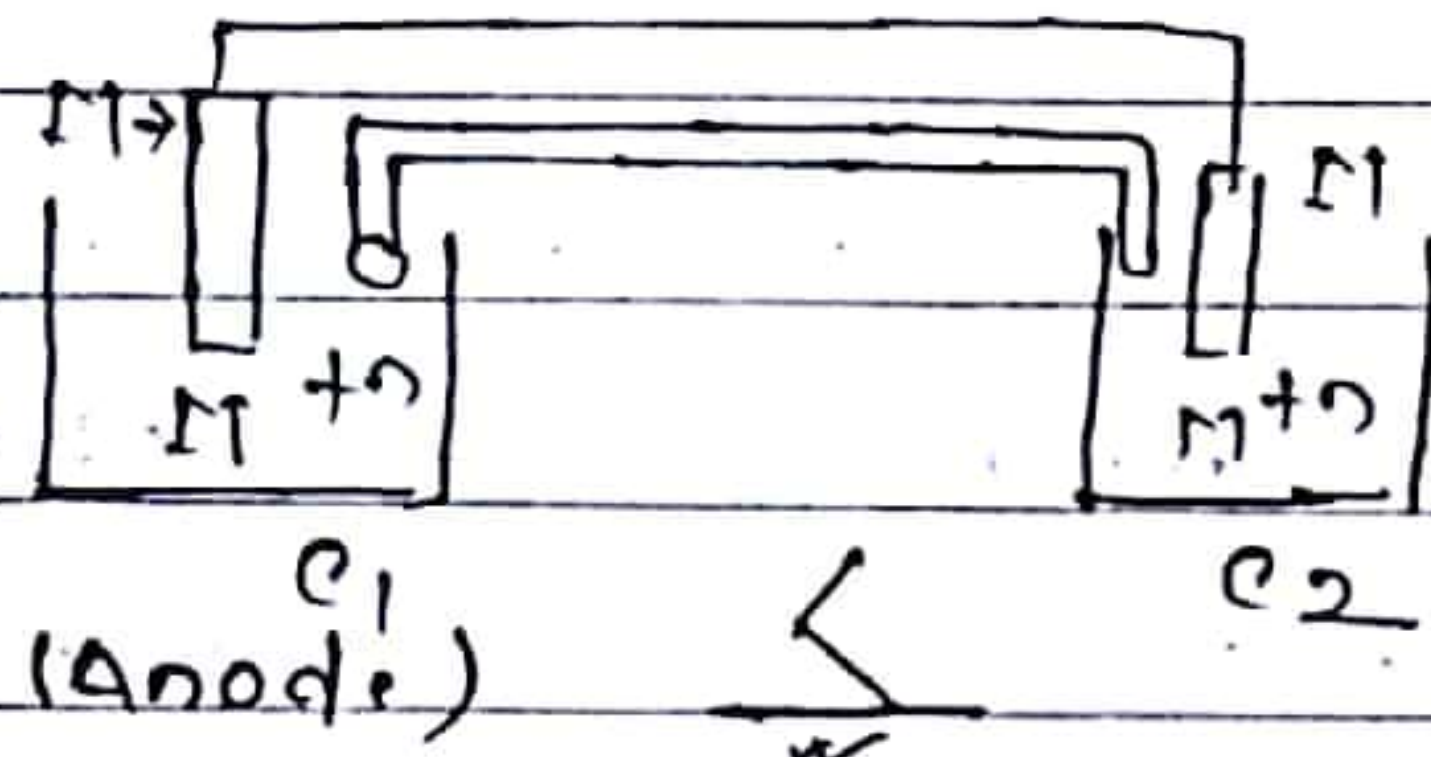
$E_{cell} = 0$ & $Q = K$ $E^{\circ}_{cell} = \frac{0.059}{n} \log K$

$\Delta G = 0$ $\Delta G^{\circ} = -2.303RT \log K$

Concentration cell

- 2 metal rod of same metal are dipping in same electrolyte solⁿ of DIFF conc. & int^{ly} connected through salt bridge formed galvanic cell → conc cell.

for it $E^{\circ}_{cell} = 0$



$c_2 > c_1$, then cell rⁿ

spontaneous & $E_{cell} = +ve.$

if $c_1 = c_2$ then rⁿ stops.

Reversible or Irreversible cell:-

cell rⁿ is reversible when

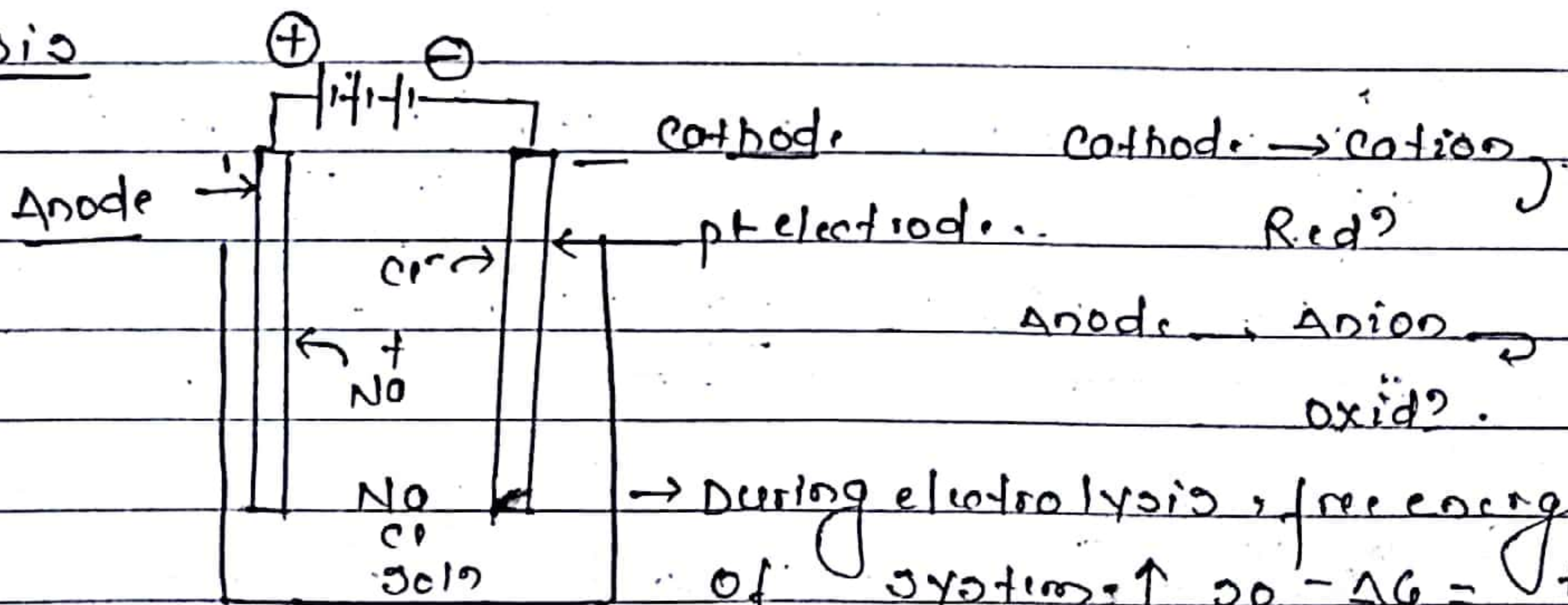
1. cell rⁿ is stops when apply ext. emf equal to cell emf.
2. cell rⁿ is exactly reversed and current will flow in opposite dirⁿ when apply ext. emf is slightly greater than cell emf.
3. if cell emf < ext. emf
 $Zn^{++} + Cu \rightarrow Zn + Cu^{++}$ (reversed)

- Daniel cell is example of reversible cell.

⇒ if above condⁿ is not satisfied then cell is irreversible.

eg. Zn/H₂SO₄/Ag cell.

Electrolysis



→ During electrolysis, free energy of system ↑ so $\Delta G = +ve$ & non spontaneous cell.

ex. pt:-

1. During electrolysis less active element discharge firstly.
2. During electrolysis, electrolytic solⁿ remains electrically neutral.

Product of Electrolysis depends on

1. Nature of Electrode (active or inactive) (2) Nature of electrolytic solⁿ.
3. conc of electrolytic solⁿ (4) charge density of electric current.

Preferential Discharge Theory

- If in electrolysis, more than one ion attracted toward electrode then ion having least value of Discharge potential will discharge firstly.
- At Cathode, redⁿ occurs. Ion greater SRP reduce firstly.
- At Anode, oxdⁿ occurs. Ion greater SOP oxidised firstly.
- For cation → Li^+, K^+, Au^{+3}

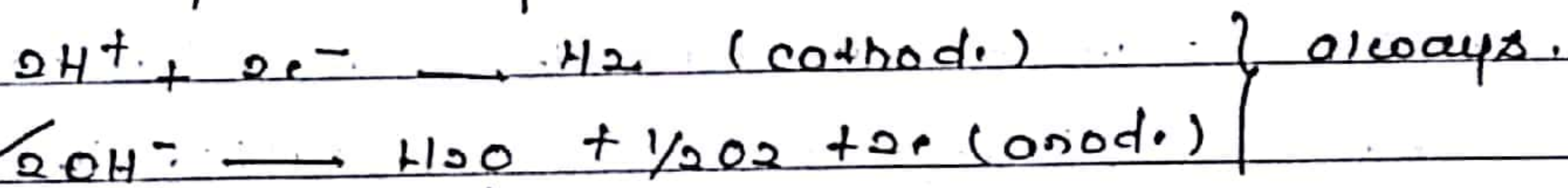
For Anion → $SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$

Tendency to get discharge ↑ ⇒ Discharge potential ↓.

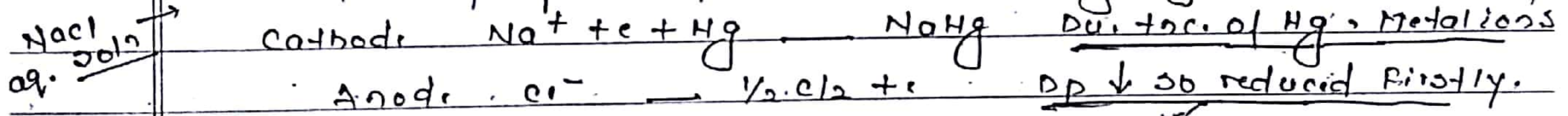
Semi-conc

1. Electrolysis of very dilute solⁿ.

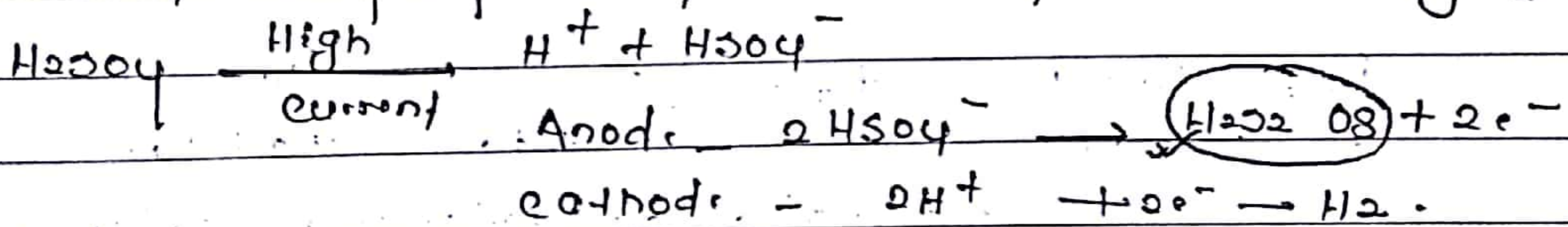
In it excess amount of H^+ & OH^- so they deposit firstly on electrode irrespective of which type solⁿ electrolysed.



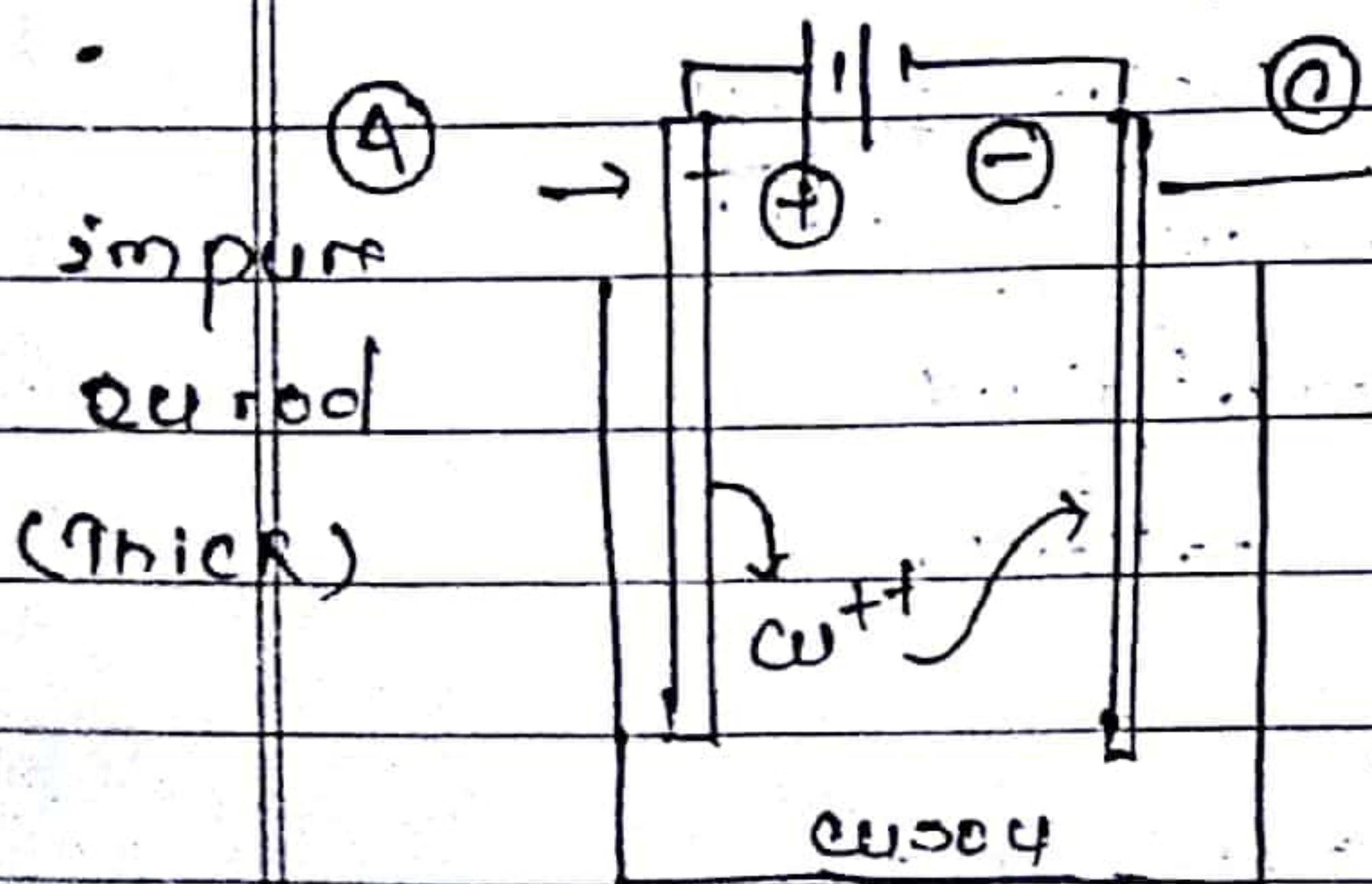
2. Electrolysis of aq. solⁿ of electrolyte having Hg (active electrode)



3. Electrolysis of aq. solⁿ of H_2SO_4 by Pt-electrode & High current.



4. Electrolysis of aq. solⁿ of CuSO₄ by using Cu electrodes (Refining pro^{cess}).



→ Conc of CuSO₄ solⁿ is unaffected.
 → Here decomposition of CuSO₄ solⁿ does not occur.
 Some oxides are produced during electrolysis process.

28. Main features of different cells.

	Names of the cell/Battery	Anode	Cathode	Electrolyte
(i)	Dry cell	Zinc	Graphite	MnO ₂ + C (touching cathode) NH ₄ Cl + ZnCl ₂ (touching anode)
(ii)	Mercury cell	Zinc	Graphite	HgO + KOH (moist)
(iii)	Lead storage battery	Lead	Lead dioxide	H ₂ SO ₄ (38%)
(iv)	Ni-Cd cell	Cadmium	Nickel dioxide	KOH sol.
(v)	H ₂ -O ₂ fuel cell	Porous carbon contg catalysts (H ₂ passed)	Porous carbon contg catalysts (O ₂ passed)	Conc. aq. KOH sol.

are deposited.

f Faraday

nical equivalent.

is same

→ Comparison b/w electrolytic & electrochemical cell

(1)	Electrochemical	Electrolytic
(1)	Anode (-) & cathode (+)	Anode (+) & cathode (-)
(2)	Current flow - C → A	Current flow - A → C
(3)	cell? - spontaneous & separate b/w & salt bridge use.	cell? - non spo. & same b/w & salt bridge X.
(4)	Deposition only at cathode.	Deposition on both.

Some extra point

Relⁿ b/w molar conductance of ion (λ_m) & mobility of ion (u)

$$\lambda_m = F/u = F \cdot z \cdot u$$

= F = Faraday const

2. Transport no. or, Hittorf's no.

$$t_a + t_c = 1 \quad t_c = \frac{\lambda_c}{\lambda_c + \lambda_a} = \frac{u_c}{u_c + u_a}$$

λ_c = molar conductance of cation.

Commercial Batteries

- (1) Primary (non-rechargeable)
 - ↳ Dry cell (Leclanché cell)
 - ↳ Mercury cell (1.35 V)
- (2) Secondary (Rechargeable)
 - ↳ Lead storage battery
 - ↳ NiCd battery
- (3) Fuel cell - pollⁿ free cell.
 - ↳ Used oppolo space ship programme.