

ELECTROCHEMISTRY

Electrochemistry is the branch of physical chemistry which deals with the study of conversion of

- * chemical energy into electrical energy (Galvanic cell)
- * Electrical energy into chemical energy (Electrolytic cell)

PART - ONE - GENERAL POINTS

1. CONDUCTANCE

Those substances which can conduct electricity are called Conductors. Conductors are of two types

- * Metallic Conductors (electronic conductors)
 - * Electrolytic conductors (Ionic conductors)
- BOTH FOLLOW OHM'S LAW

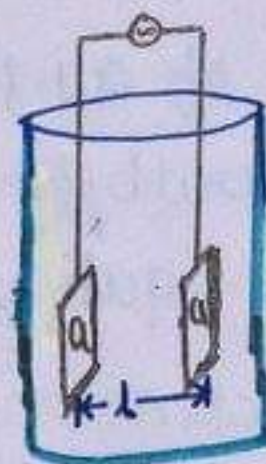
METALLIC CONDUCTOR	ELECTROLYTIC CONDUCTOR
Flow of current due to movement of free electrons	Flow of current due to movement of ions
Doesnot involves transfer of matters	Involves transfer of matters
Does not involve any chemical changes	Involves chemical changes
conducting Power is usually very High	conducting Power is comparatively less
Doesnot follow faraday's law of electrolysis	follows faradays' Law of electrolysis
on increasing Temperature Resistance increases Conductivity decreases	on increasing Temperature Resistance decreases Conductivity increases



IN CHEMISTRY CONCEPT OF [K]

* l = distance between electrode
(generally in cm)

Battery कोई metre या दो मीटर का generally नहीं होता है।



* a = Dipped surface area

ये surface area लेते वक्त दिमाग और आँख का बनी जला लो वरना सामने wrong answer खड़ा है।

* l and a don't depend upon nature of electrolysis.

* for a given cell l and a always remain same
therefore $\frac{l}{a}$ is also called cell constant $[C^*/G^*]$

Reason ये है कि Battery का size एक बार जो बन गया सो बन गया अब Battery थोड़े ना अपना length और area increase या decrease करेगा that's why $\frac{l}{a}$ is constant and called cell constant $[C^*/G^*]$

$$K = \frac{l}{R} \cdot \frac{l}{a}$$

$$K = G \times G^*$$

K = conductance $\times$ cell constant

if $l = 1\text{cm}$
 $a = 1\text{cm}$

then $K = G$ so we can say that conductance of $1\text{cm}^3/1\text{M}$ solution is called as specific conductance or conductivity

2.C. EQUIVALENT CONDUCTANCE [λ_{eq} OR Λ_{eq}]

Conductance of all the ions produced by **1 gm equivalent** of an electrolyte **in given volume** of solution is called as equivalent conductance

$\therefore$ conductance of 1 cm^3 solution = K

$\therefore$ conductance of $V \text{ cm}^3$ solution = $K \times V$

$$\boxed{\lambda_{eq} = K \times V}$$

$\downarrow$
vol^m of solution (ml) which contain **1 gm eq** of an electrolyte

Suppose concentration is $N \text{ eq/lit}$

$\therefore$ vol^m of solution containing $N \text{ gm eq} = 1000 \text{ ml}$

$\therefore$ vol^m of solution containing $1 \text{ gm eq} = \frac{1000}{N}$

$$\lambda_{eq} = K \times V$$

$$\boxed{\lambda_{eq} = K \times \left(\frac{1000}{N}\right)}$$

$\rightarrow$ vol^m of solution (ml) which contain **1 gm eq** of an electrolyte

$$\text{UNIT } [\lambda_{eq} / \Lambda_{eq}] = \Omega^{-1} \text{ cm}^{-1} \times \text{cm}^3 \text{ eq}^{-1}$$

$$= \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

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

2.D- MOLAR CONDUCTANCE [λ_M OR Λ_M OR μ_M]

Conductance of all the ions produced by **1 mol** of an electrolyte in **given volume** of solution is called as **MOLAR CONDUCTANCE**

$$\therefore \text{conductance of } 1 \text{ cm}^3 \text{ solution} = K$$

$$\therefore \text{conductance of } V \text{ cm}^3 \text{ solution} = K \times V$$

$$\boxed{\lambda_M = K \times V}$$

$\downarrow$
vol^m of solution (ml) which contain **1 mol** of electrolyte

$$\therefore \text{volume of solution containing } M \text{ molar} = 1000 \text{ ml}$$

$$\therefore \text{ " " " " " } 1 \text{ molar} = \frac{1000}{M} \text{ ml}$$

$$\boxed{\lambda_M = K \times V}$$

$$\boxed{\lambda_M = K \times \left(\frac{1000}{M} \right)}$$

$\rightarrow$ vol^m of solution (ml) which contain **1 mol** of electrolyte

$$\text{UNIT } [\lambda_M / \Lambda_M / \mu_M] = \Omega^{-1} \text{ cm}^{-1} \times \text{cm}^3 \text{ eq}^{-1}$$

$$= \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$= \text{S cm}^2 \text{ mol}^{-1}$$

RELATION BETWEEN λ_M AND λ_{eq}

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

$$\lambda_{eq} = K \times \frac{1000}{M \times v \cdot f}$$

$$\lambda_{eq} = \frac{\lambda_M}{v \cdot f}$$

$$\boxed{\lambda_{eq} \times v \cdot f = \lambda_M}$$

Min^m value of $v \cdot f$ 1 तो होगा ही होगा so

$$\boxed{\lambda_M \geq \lambda_{eq}}$$

conductance and conductivity are additive property
 जैसे कि अगर कोई electrolytic solution में several electrolytic
 ions हैं तो total conductance of solution will be

$$C_{\text{TOTAL}} = \sum C_{\text{ION}} + \sum C_{\text{WATER}}$$

FORMULAE

$$1. \quad G = \frac{1}{R}$$

$$2. \quad K = \frac{1}{R} \cdot \frac{L}{A} = G \times G^* = \frac{G}{R}$$

$$3. \quad \lambda_{eq} = K \times V = K \times \frac{1000}{N}$$

$$4. \quad \lambda_{eq} = K \times V = K \times \frac{1000}{M}$$

$$5. \quad \lambda_M = \lambda_{eq} \times V \cdot f$$

Qsn The resistance of 0.005M K_2SO_4 at 25°C is 200Ω . Cell constant (K) of conducting cell is 1cm^{-1} then find equivalent conductance

Ans

$$\begin{aligned}\lambda_{eq} &= K \times \frac{1000}{N} \\ &= K \times \frac{1000}{M \times v \cdot f} \\ &= \frac{1}{R} \times G^{\#} \times \frac{1000}{M \times v \cdot f} \\ &= \frac{1}{200} \times (1) \times \frac{1000}{0.005 \times 2} \\ &= \underline{500 \Omega^{-1}\text{cm}^2\text{eq}^{-1}}\end{aligned}$$

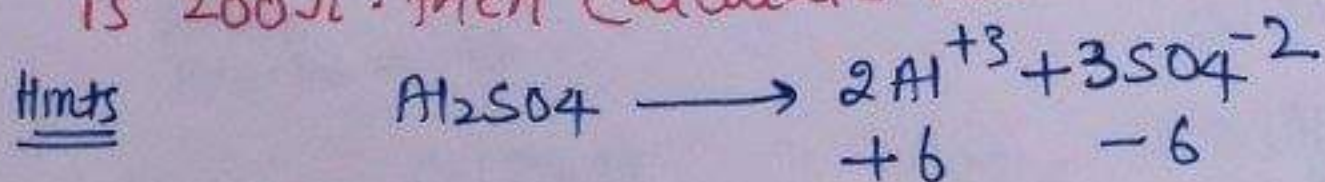
Qsn Resistance of Decinormal solution present between two platinum electrode that are 1.8cm apart dipped and 5.4cm^2 are found to be 50Ω then calculate λ_{eq} of solution

Ans

$$\begin{aligned}\lambda_{eq} &= K \times \frac{1000}{N} \\ &= \frac{1}{R} \times \frac{l}{a} \times \frac{1000}{N} \\ &= \frac{1}{50} \times \frac{1.8}{5.4} \times \frac{1000}{1/10} \\ &= 66.67 \Omega^{-1}\text{cm}^2\text{eq}^{-1}\end{aligned}$$

Qsn. HOME WORK

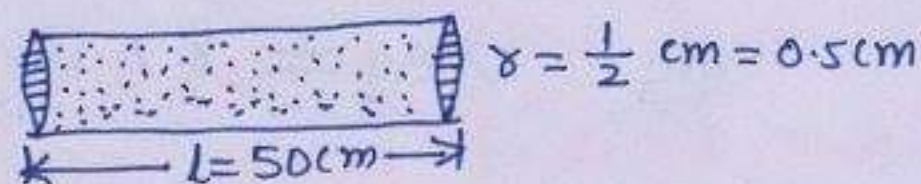
0.5N $\text{Al}_2(\text{SO}_4)_3$ solution is present between two platinum electrode that are $2\text{cm} \times 4\text{cm}$ the resistance of solution is 200Ω . then calculate molar conductance of solution



$$\lambda_M = \frac{K \times 1000 \times v \cdot f}{N}$$

Ques Resistance of a column of 0.5 mole per litre NaOH solution of diameter 1cm and length 50cm is $5.5 \times 10^3 \Omega$. calculate its Resistivity, Conductivity and molar conductivity

Ans $R = \rho \cdot \frac{l}{A}$



$$\rho = \frac{RA}{l} = \frac{R(\pi r^2)}{l}$$

$$\rho = \frac{5.5 \times 10^3 \times 3.14 \times (0.5)^2}{50}$$

$$\boxed{\rho = 87.135 \Omega\text{-cm}}$$

$$K = \frac{1}{\rho} = \frac{1}{87.135 \Omega\text{-cm}} = 0.01148 \Omega^{-1}\text{cm}^{-1}$$

$$\Lambda_M = K \times \frac{1000}{M} = 0.01148 \Omega^{-1}\text{cm}^{-1} \times \frac{1000}{0.5}$$

OPTION में ये तीनों
में से कोई एक
रहेगा. जैसे
नीचे दिया है।

$$\left[\begin{aligned} \Lambda_M &= 229.6 \Omega^{-1}(\text{cm}^2) \text{mol}^{-1} \\ &= 229.6 \Omega^{-1}(10^{-4} \text{m}^2) \text{mol}^{-1} \\ &= 229.6 \times 10^{-4} \Omega^{-1} \text{m}^2 \text{mol}^{-1} \end{aligned} \right.$$

(i) $\Lambda_M = 229.6 \Omega^{-1}(\text{cm}^2) \text{mol}^{-1}$

(ii) $\Lambda_M = 229.6 \Omega^{-1}(10^{-4} \text{m}^2) \text{mol}^{-1}$

(iii) $\Lambda_M = 229.6 \times 10^{-4} \Omega^{-1} \text{m}^2 \text{mol}^{-1}$

(iv) All are correct

Ans = (iv)

Qsn Equivalent conductance of 0.1M solution of MgCl_2 is $100 \text{ mho cm}^2 \text{ eq}^{-1}$ at 25°C . A cell with electrode that are 1.5 cm is surface area and 0.5 cm apart is filled with 0.1N MgCl_2 solution. How much current will flow when the potential difference between electrode is 5V.

Ans $V = IR$ $I = \frac{V}{R}$ [V तो है But R find करना है]

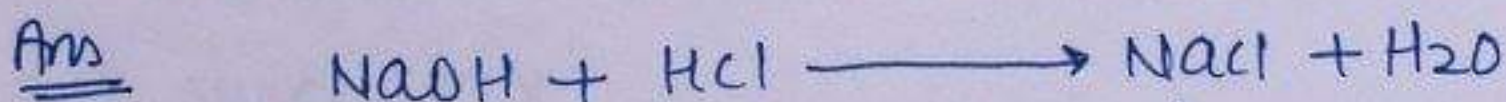
$$\Lambda_{\text{eq}} = K \times \frac{1000}{N}$$

$$100 = \frac{1}{R} \times \frac{l}{a} \times \frac{1000}{N}$$

$$100 = \frac{1}{R} \times \frac{0.5}{1.5} \times \frac{1000}{0.1}$$

$$\boxed{R = \frac{100}{3}}$$
 $I = \frac{V}{R} = \frac{5 \times 3}{100} = \frac{15}{100} = \boxed{0.15 \text{ Amp}}$

Qsn The conductivity of 0.1N NaOH solution is 0.022 scm^{-1} . When equal volume of 0.1N HCl solution is added. The conductivity of resultant solution decreases to 0.0055 scm^{-1} . Then calculate equivalent conductivity of resultant solution



0.1N 0.1N

let vol^m = 1 lit 1 lit

gm eq = N x V N x V
= 0.1 gm eq 0.1 gm eq

After Reaction = 0 0 0.1 gm eq

$$N_{\text{NaCl}} = \frac{0.1 \text{ gm eq}}{(1+1) \text{ lit}} \\ = 0.05 \text{ N}$$

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

$$\Lambda_{\text{eq}} = 0.0055 \times \frac{1000}{0.050}$$

$$\boxed{\Lambda_{\text{eq}} = 110}$$

Qsn
HOME
WORK When a certain conductance was filled with 0.05 M KCl solution it had resistance of 400Ω at 25°C when it is filled with CaCl_2 solution (11.1 gm in 500 ml solution). it had resistance of 900Ω if conductivity of 0.05 N KCl solution is $0.00189 \text{ S cm}^{-1}$ calculate (Ans = 0.756)

- (a) cell constant (Ans = 0.756)
- (b) Conductivity of CaCl_2 solution (Ans = $8.4 \times 10^{-4} \text{ S cm}^{-1}$)
- (c) molar conductivity of CaCl_2 solution (Ans = $4.2 \text{ S cm}^2 \text{ mol}^{-1}$)
- (d) equivalent conductivity of CaCl_2 solution (Ans = 2.1 S cm)

FACTOR EFFECTING ELECTROLYTIC CONDUCTANCE

- [I] INTER IONIC INTERACTION
- [II] SOLVENT OR HYDRATION OF IONS
- [III] VISCOSITY
- [IV] TEMPERATURE
- [V] DILUTION

[I] INTER IONIC INTERACTION

If inter ionic interaction is more then mobility of ions will be decreases and thus conductance will decreases

[II] SOLVATION OR HYDRATION

* Solvent molecule का ION से जुड़ना solvation कहलाता है। अब जब ION को solvent पकड़ कर रखेगा तो ION move ही नहीं कर पाएगा या अगर move करेगा तो slowly move करेगा so conductance decreases.

* जो ion जितना छोटा होता है पानी में उतना ही ज्यादा मोटा हो जाता है पानी पीकर नहीं बल्कि H_2O को जोड़कर

* Size of ION = $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

* HYDRATED size = $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

[III] VISCOSITY

VISCOSITY बढ़ेगा तो IONS easily move नहीं कर पाएगा
so VISCOSITY OF MEDIUM increases, conductance decreases

[IV] TEMPERATURE

on increasing Temp K.E of ions increases and force of attraction become weak therefore mobility of ions increases. that's why -

Temperature increases $(T) \uparrow = \text{conductance } (G) \uparrow$



(iv) DILUTION

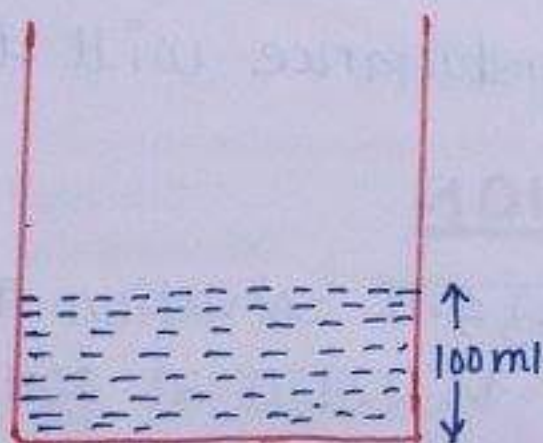
अब तक जो तीन effect था interionic interaction, solvation and temperature से तीनो common concept था. But effect of dilution on conductance is so important concept.

DILUTION INCREASES = CONDUCTANCE INCREASES (G)

DILUTION INCREASES = CONDUCTIVITY DECREASES (K)

BEFORE DILUTION

1 mol present in 100 ml



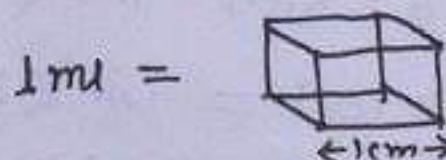
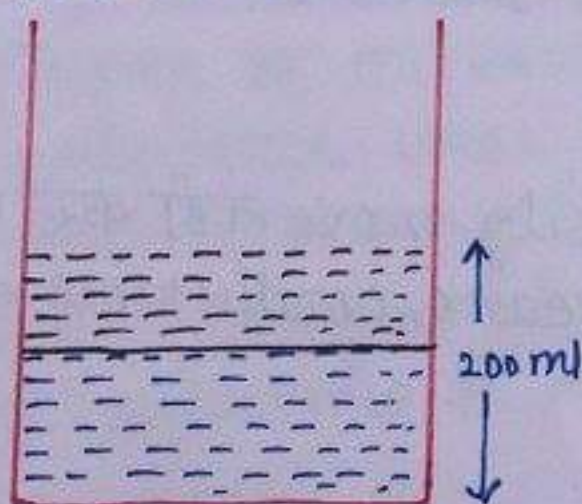
Let

100 ml solⁿ have = 50,00,000 ions = $G_1 = \Lambda M_1$

1 ml solⁿ have = 50,00,000 ions = K_1 [K Always 1ml के लिए होता है]

AFTER DILUTION

1 mol in 200 ml



$G_2 > G_1$ $K_1 > K_2$

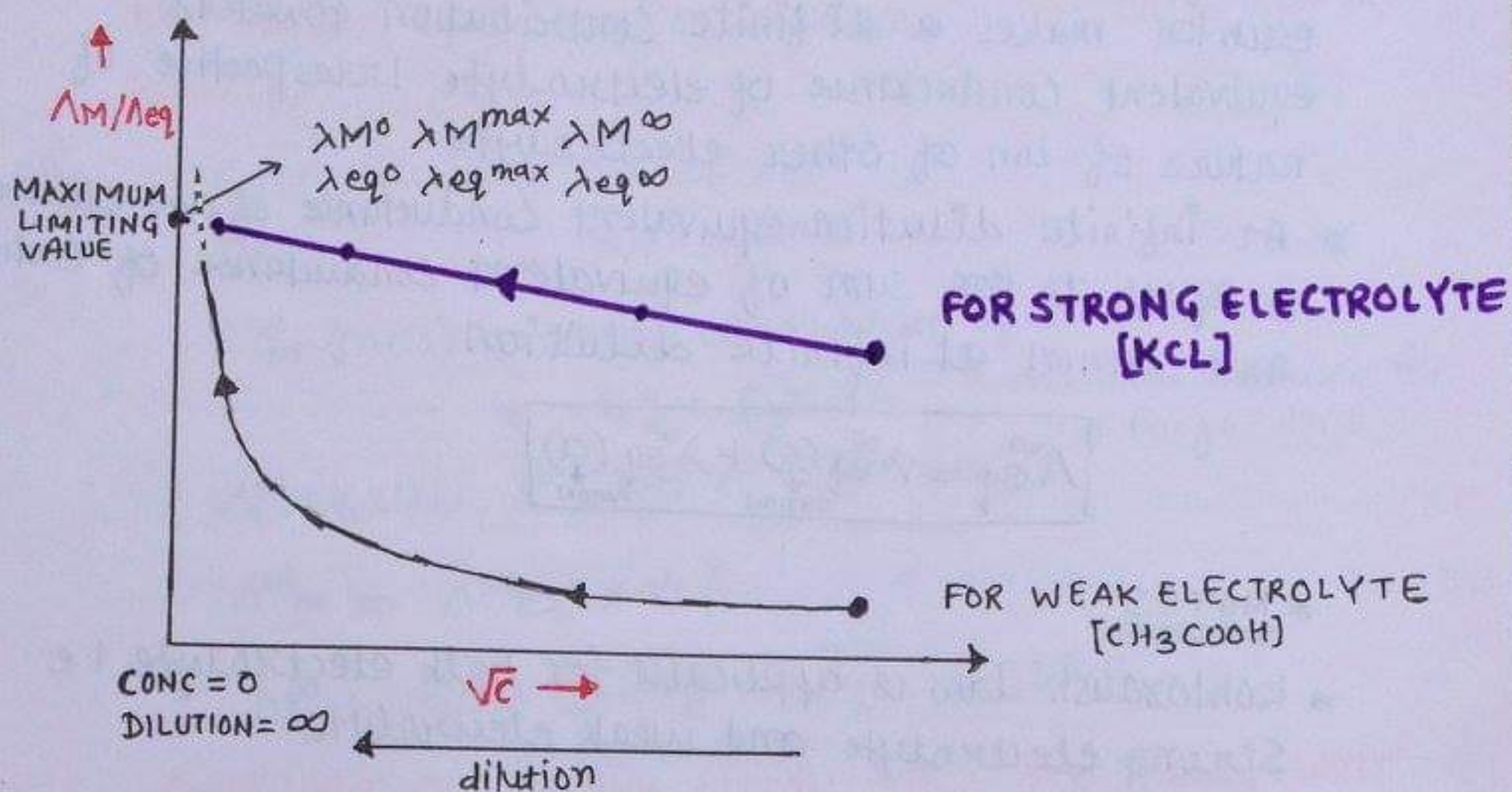
200 ml solⁿ contains 60,00,000 ions = $G_2 = \Lambda M_2$

1 ml solⁿ contains 30,00,000 ions = K_2

* ON DILUTION $\Rightarrow G \uparrow$ BUT $K \downarrow$

* ON DILUTION $\Rightarrow \Lambda_{eq} \uparrow$ AND $\Lambda_M \uparrow$ [दोनों INCREASES]

DEBYE-HUCKEL-ONSAGAR GRAPH



FOR STRONG ELECTROLYTE

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{c}$$

OR

$$\Lambda_{eq} = \Lambda_{eq}^\infty - b\sqrt{c}$$

DEBYE-HUCKEL-ONSAGAR EQUATION

→ b = DHO constant

→ b depends upon - Nature of electrolyte
- Nature of solvent
- Temperature

OBSERVATION OF DHO-GRAPH

- * Dilution ko increase करने पर strong electrolyte की molar conductance weak electrolyte की molar conductance के जितना increase नहीं होता.
BUT strong electrolyte की conductance to weak electrolyte की conductance से Always greater ही होगा.
- * on increase dilution conduction of strong electrolyte तो gradually increase होती है। But conduction of weak electrolyte rapidly increase करती है।
- * अगर Graph को extrapolate किया जाए तो strong electrolyte की Λ_m obtain किया जा सकता है। But weak electrolyte की maximum Λ_m obtain नहीं किया जा सकता है, क्योंकि weak electrolyte की α is always less than 1

KOHLRAUSCH'S LAW

- * At infinite dilution when dissociation is completed each ion makes a definite contribution towards equivalent conductance of electrolyte irrespective of nature of ion of other electrolyte
- * At infinite dilution equivalent conductance of an electrolyte is equal to the sum of equivalent conductance of cation and anion at infinite dilution

$$\Lambda_{eq}^{\infty} = \lambda_{eq}^{\infty}(c) + \lambda_{eq}^{\infty}(a)$$

$\downarrow$
CATION
 $\downarrow$
ANION

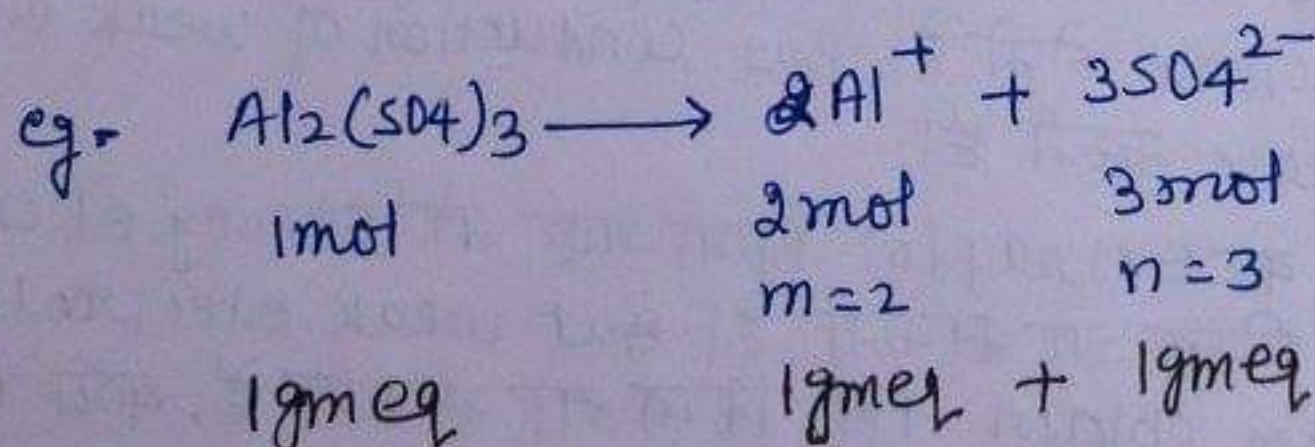
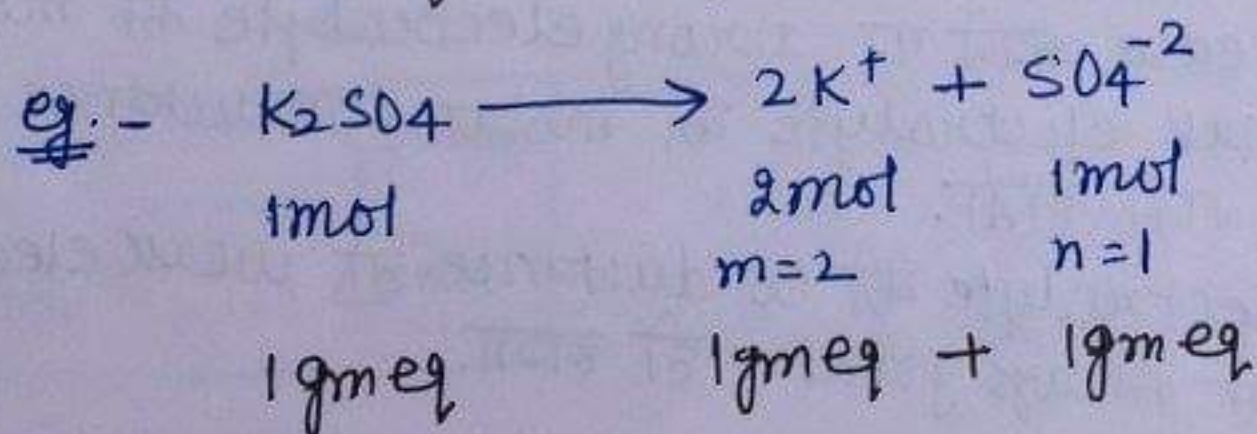
* NOTES

- ⇒ Kohlrausch law is applicable for both electrolyte i.e. strong electrolyte and weak electrolyte
- ⇒ Kohlrausch's original statement was in terms of equivalent conductance but according to I.U.P.A.C. convention now Kohlrausch law is expressed in terms of molar conductance

$$\Lambda_M^{\infty} = m \lambda_M^{\infty}(c) + n \lambda_M^{\infty}(a)$$

m = No of moles of cation in 1 mol of electrolyte

n = No of moles of anion in 1 mol of electrolyte



Qsn ionic conductance at infinite dilution of Ca^{2+} and Cl^- are 119 and 76 $\text{cm}^2 \text{mol}^{-1}$ respectively. Calculate the molar equivalent conductance of CaCl_2 at infinite dilution



$$\Lambda_M^\infty(\text{CaCl}_2) = \text{molar conductance of Cation} + \text{Anion}$$

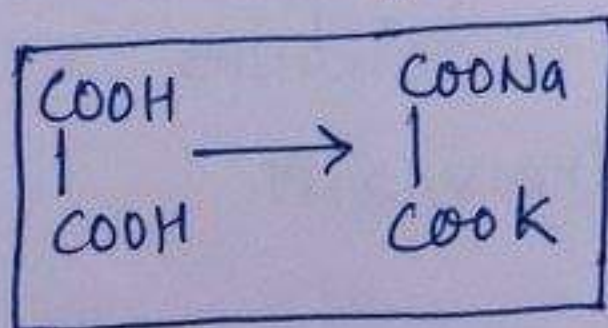
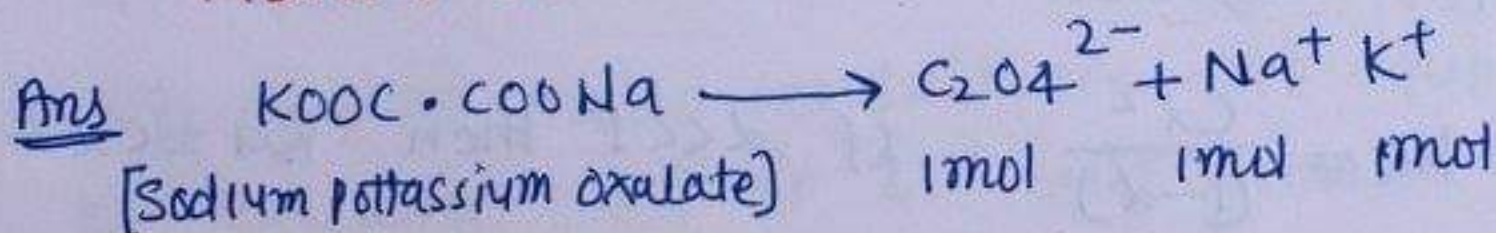
$$= 119 + 2 \times 76 \quad \text{maximum mistake we forget this}$$

$$\Lambda_M^\infty(\text{CaCl}_2) = 271 \text{ } \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

$$\Lambda_M^\infty = \Lambda_{eq}^\infty \times v.f$$

$$\Lambda_{eq}^\infty(\text{CaCl}_2) = \frac{\Lambda_M^\infty}{v.f} = \frac{271}{2} = 135.5$$

Qsn Calculate the molar conductance and equivalent conductance at infinite dilution of the salt $\text{KOOx} \cdot \text{COONa}$. Given the ionic conductance is at infinite dilution O^{2-} (oxalate ion), K^+ and Na^+ are 148.2, 50.1 and 73.5 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$



$$\Lambda_M^\infty = \Lambda_M^\infty(\text{Ox}^{2-}) + \Lambda_M^\infty \text{Na}^+ + \Lambda_M^\infty \text{K}^+$$

$$\Lambda_M^\infty = 148.2 + 50.1 + 73.5$$

$$\Lambda_M^\infty = 271.8 \text{ } \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

$$\Lambda_{eq}^\infty = \frac{\Lambda_M^\infty}{v.f} = \frac{271.8}{2} = 135.9$$

APPLICATION OF KOHLRAUSH LAW

- [i] To determine degree of ionisation (α)
- [ii] To determine dissociation constant [K]
- [iii] To determine Λ_M^∞ OR λ_{eq}^∞ for weak electrolyte
- [iv] To determine solubility of sparingly soluble salt

[I] TO DETERMINE DEGREE OF IONISATION

$$\alpha = \frac{\text{Dissociated moles}}{\text{Total moles}} = \frac{\text{ions obtained by dissociation of electrolyte}}{\text{Total ions present in electrolyte}}$$

At constant "concentration c"

$$\alpha = \frac{\lambda_{eq} c}{\lambda_{eq}^\infty} \text{ or } \frac{\Lambda_M c}{\Lambda_M^\infty}$$

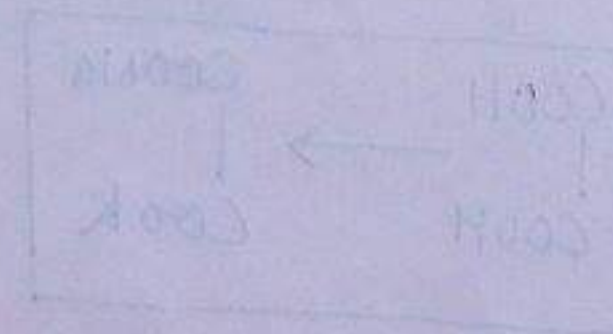
[II] TO DETERMINE DISSOCIATION CONSTANT [K]

eg- for CH_3COOH

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \quad \text{if } \alpha \ll 1 \text{ then } K_a = c\alpha^2$$

$$[\text{H}^+] = c\alpha$$

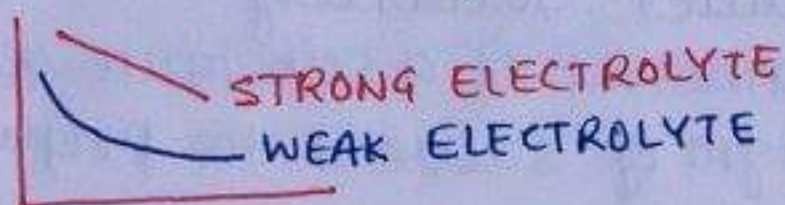
$$i = 1 - \alpha + n\alpha$$



[III] TO DETERMINE Λ_M^∞ OR Λ_{eq}^∞ FOR A WEAK ELECTROLYTE

Q.51: $\Lambda_M^\infty (\text{CH}_3\text{COOH}) = ?$

- * यहाँ CH_3COOH एक weak electrolyte है। और graph से weak electrolyte का Λ_M^∞ find नहीं कर सकते हैं।
Graph से तो सिर्फ strong electrolyte का ही Λ_M^∞ find कर सकते हैं।



- * But we can use Kohlrausch law because Kohlrausch law is applicable for both strong and weak electrolyte

$$\Lambda_M^\infty (\text{CH}_3\text{COOH}) = \Lambda_M^\infty (\text{CH}_3\text{COO}^-) + \Lambda_M^\infty (\text{H}^+) \quad \text{--- (i)}$$

$$\Lambda_M^\infty (\text{CH}_3\text{COONa}) = \Lambda_M^\infty (\text{CH}_3\text{COO}^-) + \Lambda_M^\infty (\text{Na}^+) \quad \text{--- (ii)}$$

$$\Lambda_M^\infty (\text{HCl}) = \Lambda_M^\infty (\text{H}^+) + \Lambda_M^\infty (\text{Cl}^-) \quad \text{--- (iii)}$$

$$\Lambda_M^\infty (\text{NaCl}) = \Lambda_M^\infty (\text{Na}^+) + \Lambda_M^\infty (\text{Cl}^-) \quad \text{--- (iv)}$$

- * $\Lambda_M^\infty (\text{CH}_3\text{COO}^-)$ की molar conductance चाहे equation (i) में हो या equation (ii) में हो दोनों जगह same ही होगी

- * $\Lambda_M^\infty (\text{H}^+)$ की molar conductance चाहे equation (i) में हो या equation (iii) में हो दोनों जगह same ही होगी

- * equation (i) = equation (ii) + equation (iii) - equation (iv)

$$\Lambda_M^\infty (\text{CH}_3\text{COOH}) = \Lambda_M^\infty (\text{CH}_3\text{COO}^-) + \Lambda_M^\infty (\text{H}^+) - \Lambda_M^\infty (\text{NaCl})$$

$$\Lambda_M^\infty (\text{CH}_3\text{COOH}) = \Lambda_M^\infty (\text{CH}_3\text{COONa}) + \Lambda_M^\infty (\text{HCl}) - \Lambda_M^\infty (\text{NaCl})$$

[IV] TO DETERMINE SOLUBILITY OF SPARINGLY SOLUBLE SALT

Eg - AgCl , BaSO_4 , PbSO_4

Solubility

- Concentration of saturated solution at constant temperature called solubility
- The maximum amount of a substance which can be dissolved in 100 gm of solvent to prepare its saturated solution

FUNDA:

- Saturated solution of sparingly soluble salt can be considered as infinitely diluted solution because these salt dissolve very less therefore

Saturated solution = infinitely diluted solution

$$\Lambda_M = \Lambda_M^\infty = k \times \frac{1000}{M}$$

↓
By Kohlrausch law

यहाँ पर $M=S$

* if we add 500 gm AgCl in 1 litre of H_2O then only upto 5g AgCl is dissolved.

* 495 gm AgCl remain undissolved. So actual solubility = 5g/l

Qsn At a certain temperature the saturated solution of AgCl has conductivity (κ) $1.8 \times 10^{-6} \text{ mho cm}^{-1}$. The ionic conductance of Ag^+ and Cl^- at infinite dilution are 54.5 and 65.5 $\text{mho cm}^2 \text{ mol}^{-1}$. Find the solubility of AgCl at this temperature.

Ans $\Lambda_M^\infty \text{AgCl} = 54.5 + 65.5$
 $= 120$

$$\Lambda_M^\infty = 1.8 \times 10^{-6} \times \frac{1000}{S}$$

$$120 = 1.8 \times 10^{-6} \times \frac{1000}{S}$$

$$S = \frac{1.8 \times 10^{-6} \times 1000}{120}$$

$$S = 1.5 \times 10^{-5} \text{ mol/litre}$$

$$K_{sp} = S^2 = 2.25 \times 10^{-10}$$

Qsn The molar conductance for acetic acid at 0.2 M molar conductance at infinite dilute are 4.8 and $400 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively. Calculate degree of dissociation and dissociation constant of CH_3COOH .

Ans $C = 0.2 \text{ M } \text{CH}_3\text{COOH}$

$$\Lambda_M^c = 4.8$$

$$\Lambda_M^\infty = 400 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_M^c}{\Lambda_M^\infty} = \frac{4.8}{400} \times 100 = 1.2\% = 1.2 \times 10^{-2}$$

$$K_a = C\alpha^2$$

$$= 0.2 (1.2 \times 10^{-2})^2$$

$$= 2.88 \times 10^{-5}$$

Qsn The molar conductance of an infinitely diluted solution of Ammonium chloride (NH_4Cl) is $150 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ and ionic conductance is ($\text{OH}^- = 198$), ($\text{Cl}^- = 76 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) What will be the molar conductance of the solution of NH_4OH (Ammonium hydroxide) at infinite dilution. If the conductivity of 0.01M solution of NH_4OH is $9.52 \times 10^{-5} \Omega^{-1} \text{cm}^2$ what will be its degree of dissociation.

Ans $\text{NH}_4\text{Cl} = 150 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$

$$\text{OH}^- = 198$$

$$\text{Cl}^- = 76 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

$$\Lambda^\infty_{\text{M}} (\text{NH}_4\text{OH}) = \Lambda^\infty_{\text{M}} (\text{NH}_4\text{Cl} + \text{OH}^- - \text{Cl}^-)$$

$$\Lambda^\infty_{\text{M}} (\text{NH}_4\text{OH}) = \Lambda^\infty_{\text{M}} (150 + 198 - 76)$$

$$\Lambda^\infty_{\text{M}} (\text{NH}_4\text{OH}) = 272 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

$$C = 0.01 \text{M}$$

$$K = 9.52 \times 10^{-5} \Omega^{-1} \text{cm}^2$$

$$\Lambda^c_{\text{M}} = K \times \frac{1000}{M}$$

$$\Lambda^c_{\text{M}} = \frac{9.52 \times 10^{-5} \times 1000}{0.01} = 9.52$$

$$\alpha = \frac{\Lambda^c_{\text{M}}}{\Lambda^\infty_{\text{M}}} = \frac{9.52}{272} \times 100$$

$$\alpha = 3.5\%$$



Qsn Conductivity of saturated solution of AgCl is $2.2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ and conductivity of water is $0.8 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. Molar conductance at infinite dilution of AgNO_3 , HCl and HNO_3 are 135, 426 and 421 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ respectively calculate solubility product of AgCl

Ans

$$\begin{aligned}\text{AgNO}_3 &= 135 \\ \text{HCl} &= 426 \\ \text{HNO}_3 &= 421\end{aligned}$$

$$\begin{aligned}\Lambda_m^\infty(\text{AgCl}) &= \Lambda_m^\infty(\text{AgNO}_3 + \text{HCl} - \text{HNO}_3) \\ &= \Lambda_m^\infty(135 + 426 - 421)\end{aligned}$$

$$\Lambda_m^\infty(\text{AgCl}) = 140 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

$$K_{\text{AgCl solution}} = 2.2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$$

$$K_{\text{H}_2\text{O solution}} = 0.8 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$$

$$K_{\text{solution of electrolyte}} = K_{\text{electrolyte}} + K_{\text{H}_2\text{O}}$$

$$= K_{\text{solute electrolyte}} + K_{\text{H}_2\text{O}}$$

$$= 2.2 \times 10^{-6} - 0.8 \times 10^{-6}$$

$$K_{\text{AgCl}} = 1.4 \times 10^{-6}$$

it should neglect

Qsn specific conductance of 0.03M aqueous solution of weak base BOH is $1.5 \times 10^{-4} \text{Scm}^{-1}$. also the molar conductance at infinite dilution is $250 \text{Scm}^2 \text{mol}^{-1}$ find ionisation constant of weak base

Ans

$$\begin{aligned}C &= 0.03 \text{M} \\ K &= 1.5 \times 10^{-4} \text{Scm}^{-1} \\ \Lambda_m^\infty &= 250 \text{Scm}^2 \text{mol}^{-1}\end{aligned}$$

$$\Lambda_m^c = K \times \frac{1000}{M}$$

$$\Lambda_m^c = 1.5 \times 10^{-4} \times \frac{1000}{0.03}$$

$$\Lambda_m^c = 5$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{5}{250} = 0.02$$

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

$$K_b = 0.03 (0.02)^2$$

$$K_b = 1.2 \times 10^{-5}$$

AIMS

ELECTROLYTE	KCl	KNO ₃	HCl	NaOAc	NaCl
Λ^∞ ($\text{Scm}^2\text{mol}^{-1}$)	149.9	145.0	426.2	91.0	126.5

calculate $\Lambda^\infty_{\text{HOAc}}$ using appropriate molar conductance of electrolyte listed above at infinite dilution in H_2O at 25°C

Ans

$$\begin{aligned}\Lambda^\infty_{\text{HOAc}} &= \Lambda^\infty_{\text{NaOAc}} + \Lambda^\infty_{\text{HCl}} - \Lambda^\infty_{\text{NaCl}} \\ &= 91.0 + 426.2 - 126.5 \text{ Scm}^2\text{mol}^{-1} \\ &= 390.7 \text{ Scm}^2\text{mol}^{-1}\end{aligned}$$

Qsn
AIMS

Hydrofluoric acid is weak acid. At 25°C the molar conductivity of 0.002 M HF is $176.2 \text{ S}^{-1}\text{cm}^2\text{mol}^{-1}$ if its $\Lambda^\infty_m = 405.2 \text{ S}^{-1}\text{cm}^2\text{mol}^{-1}$. Equilibrium constant at the given concentration is

Ans

$$\alpha = \frac{\Lambda_c}{\Lambda^\infty_m} = \frac{176.2 \text{ S}^{-1}\text{cm}^2\text{mol}^{-1}}{405.2 \text{ S}^{-1}\text{cm}^2\text{mol}^{-1}} = 0.435$$

$$K = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{C\alpha^2}{1-\alpha} = \frac{(0.002 \text{ M})(0.435)^2}{1-0.435}$$

$$K = 6.70 \times 10^{-4} \text{ M}$$



ELECTROCHEMISTRY - PART TWO

ELECTRODE POTENTIAL

When a metal is placed in aqueous solution of its ion it acquires either negative or positive charge with respect to solution and potential is developed between metal and solution which is called electrode potential of metal.

Explanation:

* अगर Cu को उसके aqueous solution CuSO_4 में डुबाया जाए तो potential developed हो जाएगा.

* अगर Zn को उसके aqueous solution ZnSO_4 में डुबाया जाए तो potential developed हो जाएगा.

Electrode potential mainly depends upon

- (a) Nature of electrode
- (b) Concentration of ions in solution
- (c) Temperature

NCERT

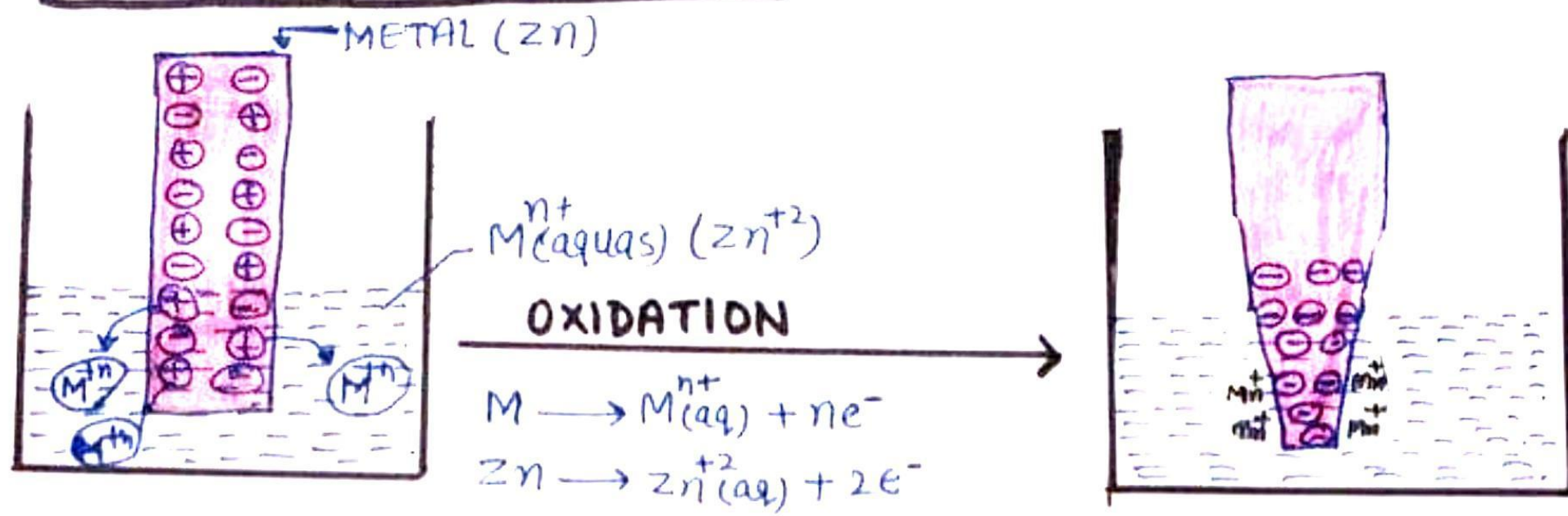
A large number of $\left\{ \begin{array}{l} \text{Metals} \\ \text{Sodium hydroxide} \\ \text{Fluorine} \\ \text{Chlorine} \\ \text{and many other chemicals} \end{array} \right.$

are produced by electrochemical method.

ELECTRODE POTENTIAL ARE OF TWO TYPES:

- (i) OXIDATION POTENTIAL
- (ii) REDUCTION POTENTIAL

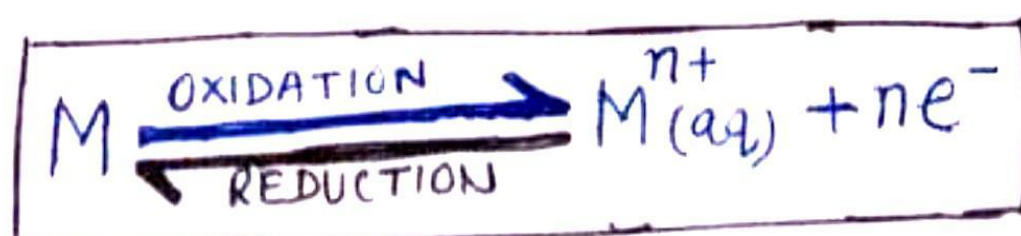
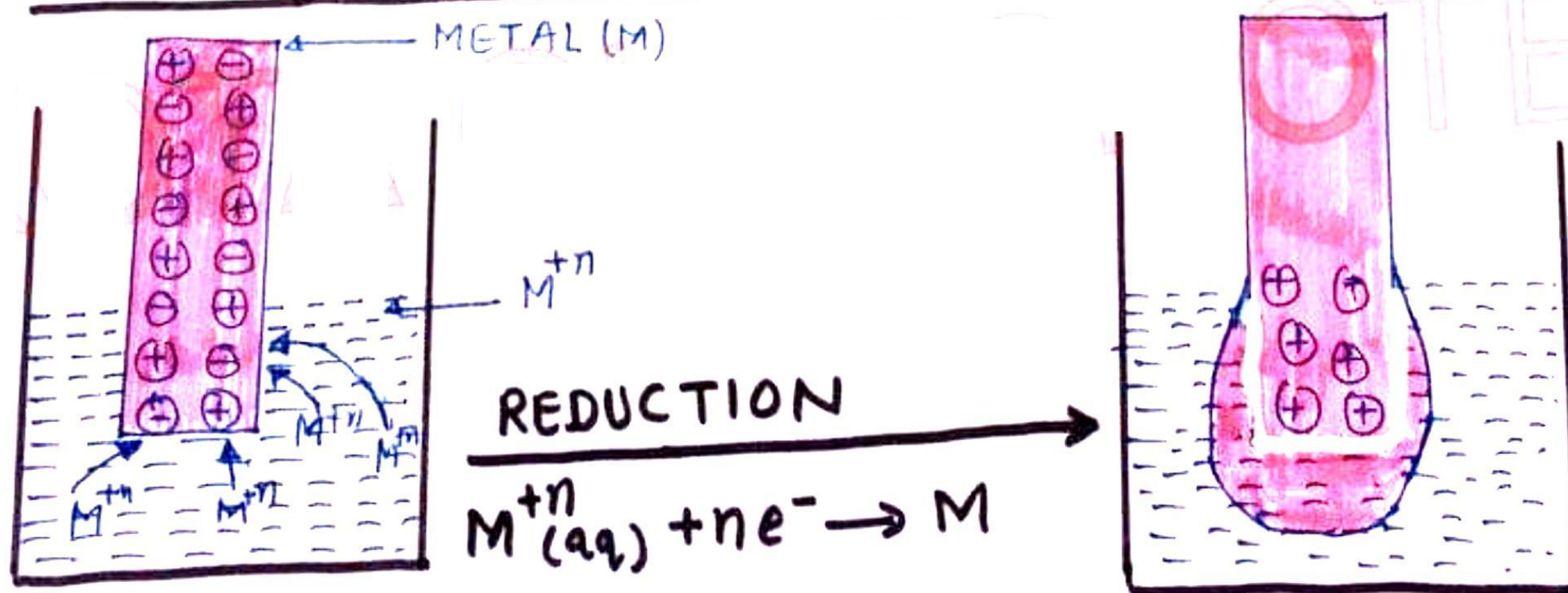
(i) OXIDATION POTENTIAL



* Metal atom of electrode have tendency to go into the solution as ions. and leave behind the electrons at the electrode trying make it negatively charged.

* यहाँ electrode की oxidation हो रहा है। और potential develop हो रहा है। so called oxidation potential

(ii) REDUCTION POTENTIAL



IF OXID > RED THEN OXID-POTENTIAL
IF RED > OXID THEN RED-POTENTIAL

CE ELECTRODE

attery at least दो Half cell की
we want measure potential
measure नहीं कर पाएंगे इसके
की requirement होगी

REFERENCE ELECTRODE [SH

standard Hydrogen electrode

electrode represented by = P
ned to ZERO POTENTIAL at all te
action



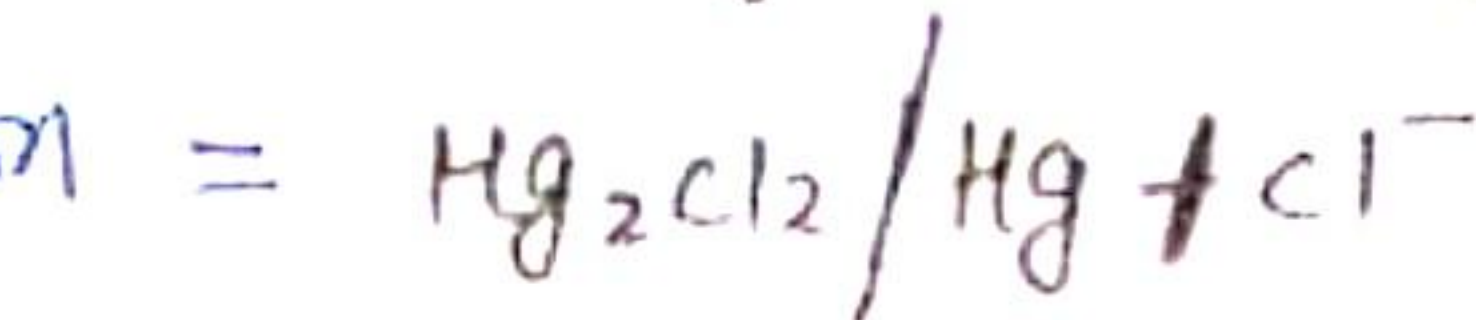
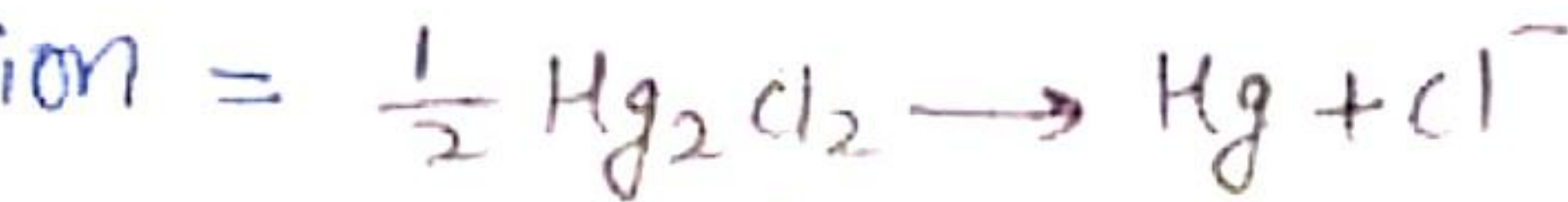
REFERENCE ELECTRODE

ELECTRODE

Connected to
Salt Bridge

Electrode is commonly acts as
reference electrode as it is situated at very
low electrochemical potential.

When it acts as cathode then its



SILVER CHLORIDE ELECTRODE

Connected to
Salt Bridge

Electrode generally

ELECTROCHEMICAL SERIES

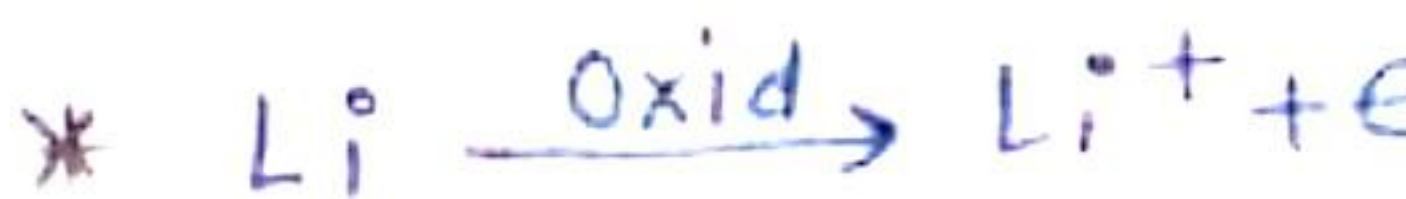
Best reducing agent

$$\underline{SRP = -3.04V}$$

* As we go down +

Reactivity of non-metals

Reactivity of metals



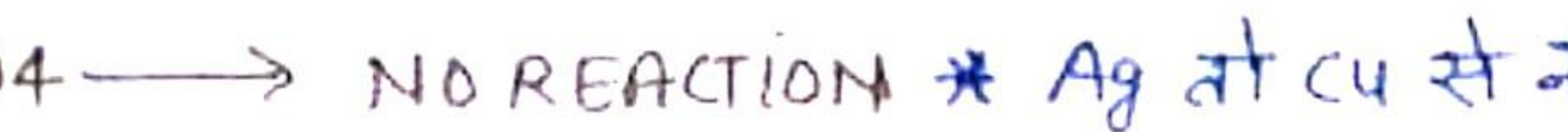
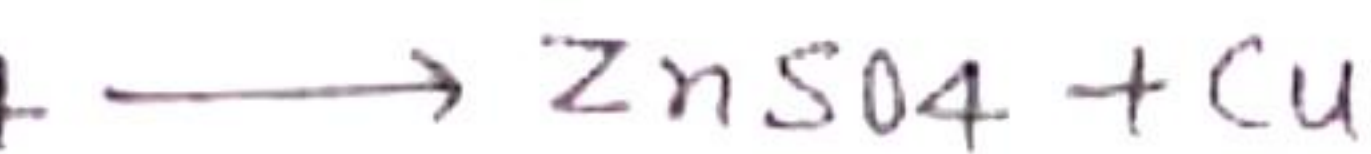
$$= -0.76V$$

* As we go from
strength of oxidising

CONCLUSION FROM E.C.S

DISPLACEMENT OF METAL IONS BY METAL

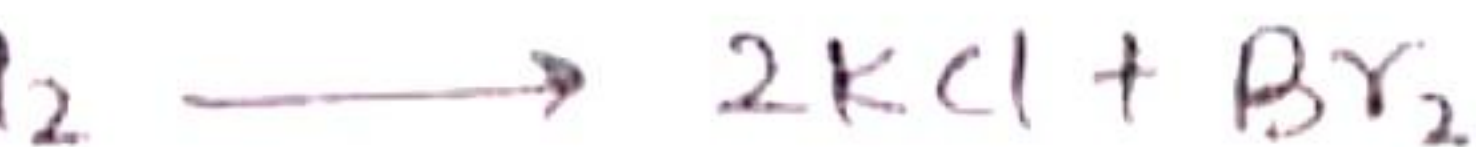
metal higher in E.C.S displaces metal lower than them in E.C.S from their solution



Zn तो Cu से ऊपर है इसलिए Zn व Cu के घोल में डालने तो वो Cu को displace कर देगा

DISPLACEMENT OF NON-METAL ION BY NON-METAL

non-metal higher in E.C.S displaces the anion of non-metal lower than them in electrochemical series from their solution



basis of following chemical reactions
of metal A B C D E and H₂ in order



E
C
A
H₂
D
B
↓

Rank these metals in increasing
reducing power

METAL	E° (SRP/SEP)
	-1.5V

ELECTROCHEMICAL CELL

two types of electrochemical
Galvanic cell OR VOLTALIC CELL
ELECTROLYTIC CELL

GALVANIC CELL OR VOLTALIC CELL

which convert chemical energy
called galvanic cell.

Galvanic cell में Anode को Zn
और cathode को Copper से
cell DANIEL CELL कहलाएगा
को cell बनाया था उससे Dani
नाया और dripped किगा था

Observations are observed during

cell reaction electric current
anode in external circuit
flows from anode to cathode

cell reaction weight of anode
whereas weight of cathode

cell reaction concentration
solution increases whereas
in cathodic solution de
reactions are spontaneous a

Liquid-liquid junction potential
different electrolytic solutions in
direct contact with each other
of potential is developed
liquid-liquid junction potential
is always such that it
of cell

to thermodynamics ΔG is
by the system

Useful = - W electrical

$$Q dv = - n F \times E_{\text{cell}}$$

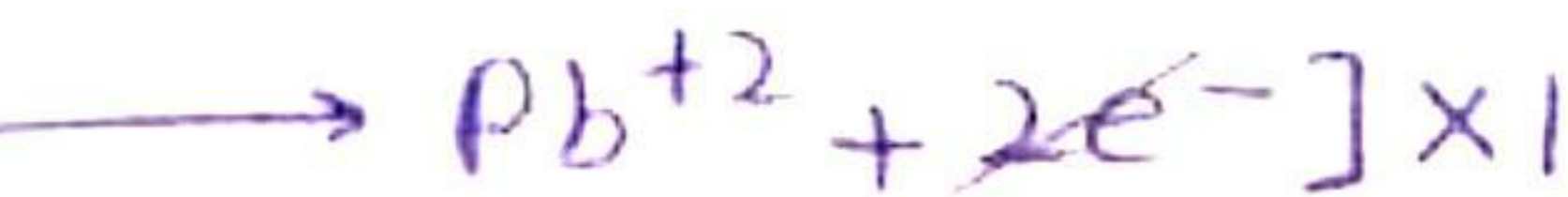
$$n F E_{\text{cell}}$$

n = no of moles of
 F = Faraday constant

It was dipped in $Pb(NO_3)_2$ solution
dipped in $AgNO_3$ solution then
reaction and cell representation

→ $Pb(NO_3)_2 = \text{cathode}$

→ $AgNO_3 = \text{anode}$



cell representation = $Pb/Pb^{+2} // Ag^+/Ag$

cell $Al/Al^{+3} // Ni^{+2}/Ni$

ES

electrode potential does not
depend/divided by a coefficient
potential is an intrinsic

electrode potential does not depend on
metallic rod

for two different electrodes
want to calculate E° for $3Zn$

these two electrodes then to
 ΔG° and then apply Nernst

$$1/Cl^- = x$$

$$1/1/2 Cl_2 = y$$

$$1/1/2 Cl_2 = z$$

$$Fe^{+2}/Fe = 0.26 V$$

$$Fe^{+3}/Fe = 0.76 V$$

$$Fe^{+2}/Fe^{+3} = ?$$



$$(1) - eq (2) = eq (3)$$

$$-\Delta G_2^\circ = \Delta G_3^\circ$$

$$-F + 2 \cdot 2.8 = -F \times E_3$$

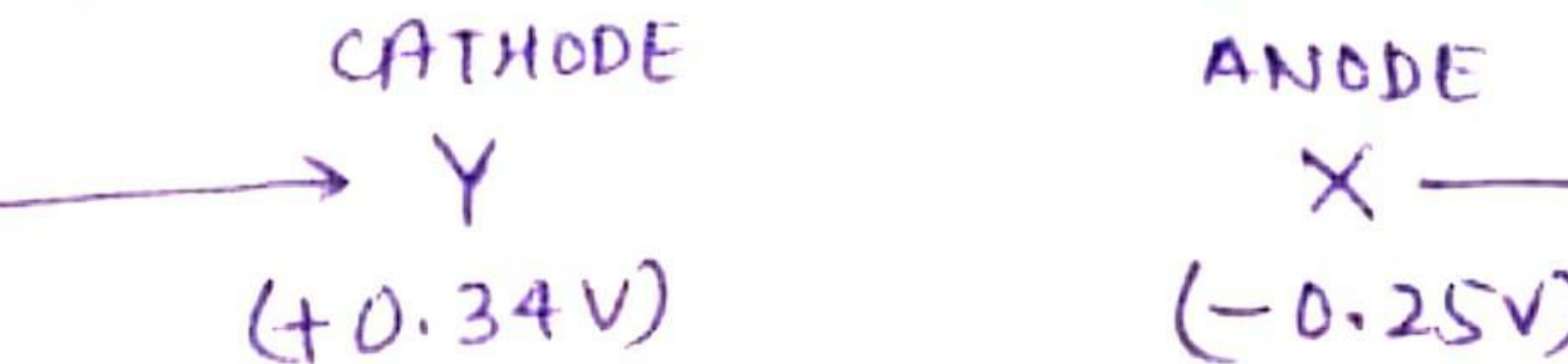
$$+1.76 = -E_3$$

$$E_3 = -1.76 V$$

Standard Reduction Potentials (SRP) of two metals



and Y are connected then
to Y and if X is connected
crossed from X to SHE then
the cell made up by X and



$$E_{\text{cell}} = (E^\circ_{\text{red}})_C - (E^\circ_{\text{red}})_A$$

HERST EQUATION

assumed in the previous section
reduction of the species involve

• This need not be always
showed that for the electro



trude potential at any conc
with respect SHE can be

$$E = \frac{RT}{nF} \log_e \frac{[Product]}{[Reactant]}$$

OF NERST EQUATION

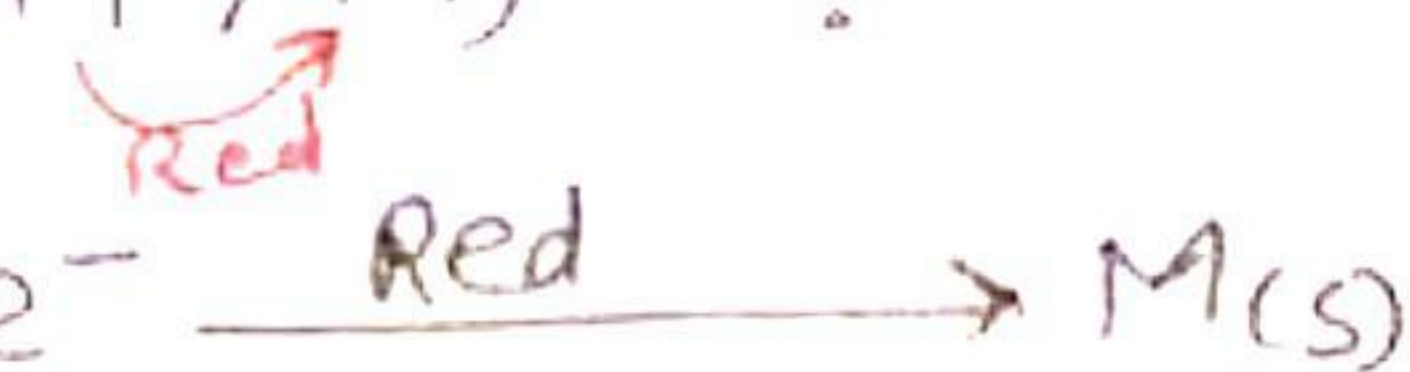
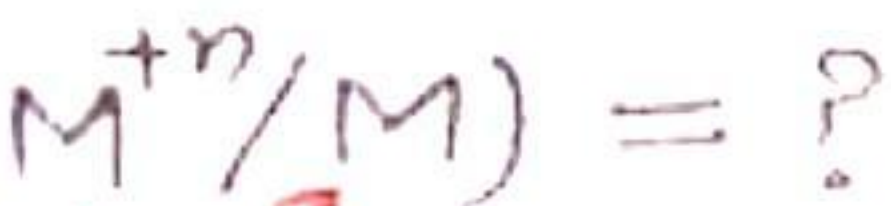
Calculate electrode potential

Calculate electrode potential of H

Calculate e.m.f of cell

CALCULATE ELECTRODE POTENTIAL

Electrode potential given then



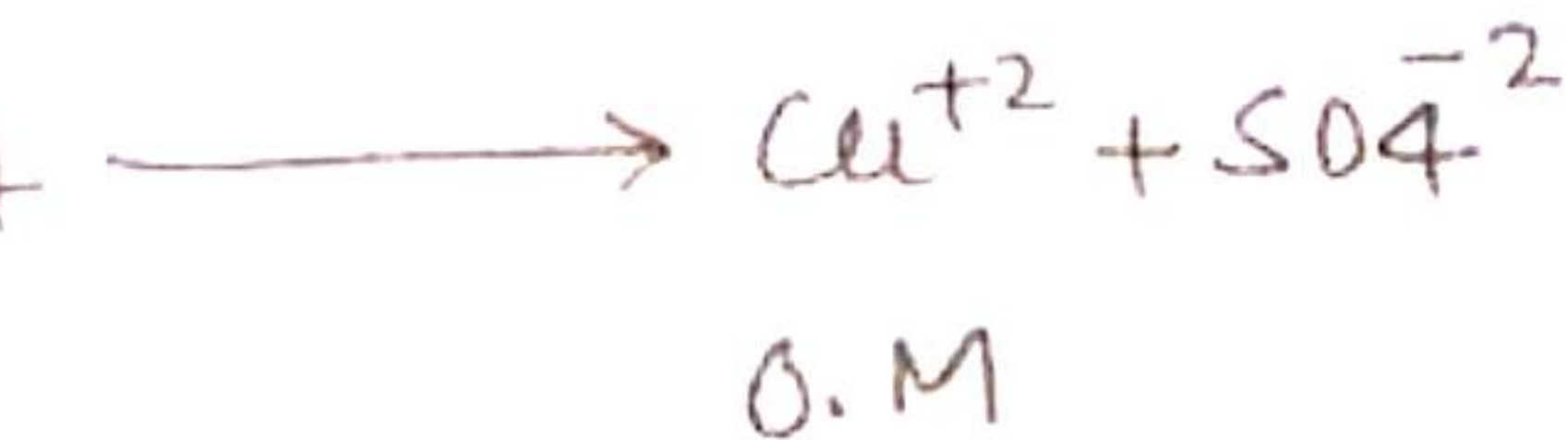
$$E^{\circ}_{\text{red}} - \frac{0.591}{n} \log_{10} \frac{[M]}{[M^{n+}]}$$

1 B

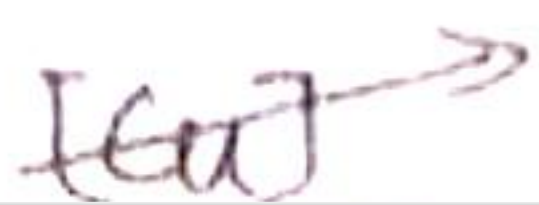
$$E_{\text{red}} + \frac{0.591}{n} \log [M^{n+}]$$

ate electrode potential of a
 in a 0.1M solution of CuSO_4
 reduced electrode potential Cu^{2+}
 K

is a salt and α is not given
 tion occur



$$\alpha = 0.1 \times \frac{100}{100} = 0.1$$



CULATE ELECT. POTENTIAL



$$E^{\circ}_{\text{red}} - \frac{0.0591}{2} \log \frac{[P_{\text{H}_2}]}{[\text{H}^+]^2}$$

equation concentration term
pressure of gas (Atmosphere)

of $[P_{\text{H}_2}]$ is pressure while

tion मगर ये गलत नहीं है। ये
एक unitless है। इसे replace

electrode potential of follow
acidic solution is 2

pH of following Half cell
($E_{oxi} = 0.25V$)

$H_2(g) / HCl$



~~$E_{oxi} = \frac{0.0591}{2} \log \frac{[H^+]^2}{[PH_2]}$~~

~~$= \frac{0.0591}{2} \times 2 \log [H^+]$~~

~~$= - \log [H^+]$~~

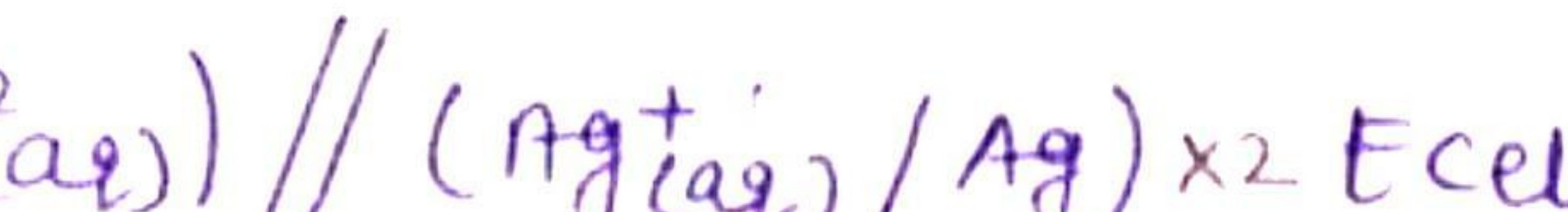
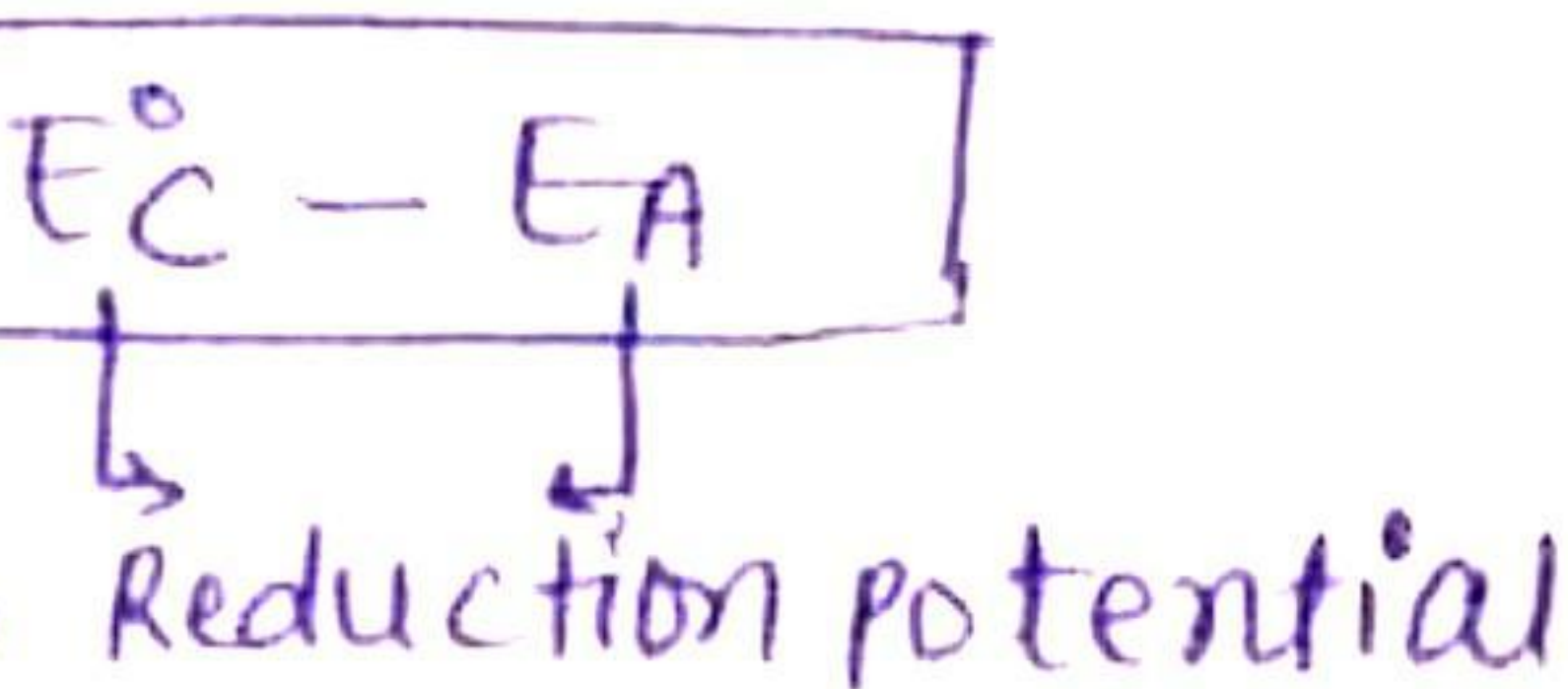
E_{oxi} $= \frac{-E_{red}}{0.0591}$

CALCULATE e.m.f OF THE CELL

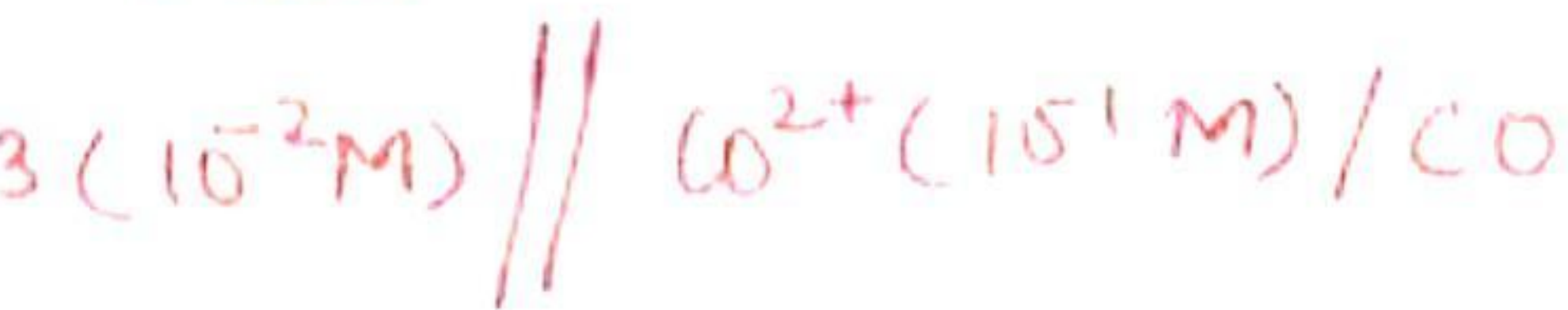
Cell potential = Potential of Anode + Red Pot

$$E_{\text{cathode}} - E_{\text{anode}}$$

Standard condition

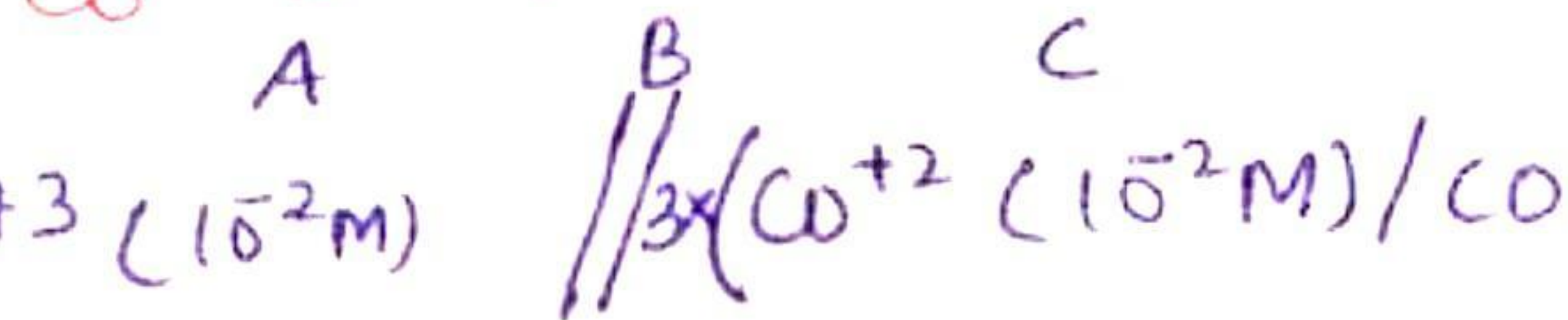


$$E_{\text{cell}} = ?$$



$$A_1 = -1.66\text{V}$$

$$\text{Co} = -0.28\text{V}$$



$$e^- = 6e^- \quad 3 \times 2e^- = 6e^-$$

$$A_1 = -1.66\text{V},$$

anode)

(Bridge)

(Cathode)

A

B

C



$E_{\text{cell}} = ?$

$$E^\circ \text{Pt} / \text{Br}_2 / \text{Br}^- = 1.09 \text{ V}$$

anod पर Br^- को absorb करा
मे dipped किया

anod पर H_2 absorb कर कर
किया

$- E^\circ_A$

$- 1.09$

of a system = $\downarrow$ in Free energy of

obtained by cell = in the form of

$$W = Q \times V$$

$$\boxed{W = n F \times E_{\text{cell}}}$$

$$E_{\text{cell}} = -\Delta G$$

$$\boxed{n F E}$$

n = no of moles of tra

and condition

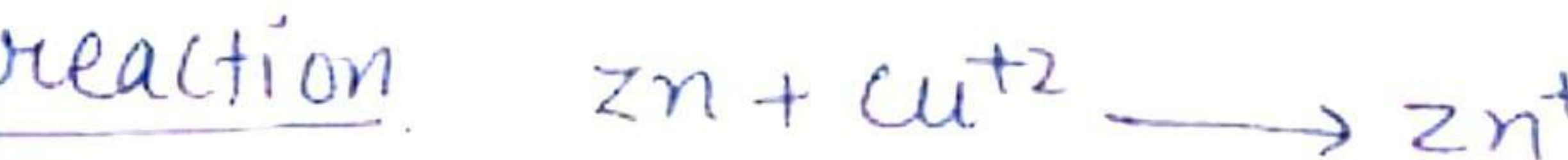
$$\boxed{F E^{\circ}_{\text{cell}}}$$

spontaneity of reaction in Dan



$$E^\circ_{\text{Zn}^{+2}/\text{Zn}} = -0.76 \text{ volt}$$

$$E^\circ_{\text{Cu}^{+2}/\text{Cu}} = 0.34 \text{ volt}$$



$$E = E^\circ_c - E^\circ_a$$

$$= (E^\circ_c) - (E^\circ_a)$$

$$= 0.34 - (-0.76 \text{ v})$$

$$E = +1.1 \text{ volt} \quad \text{OR} \quad \Delta G = -nFE$$

EQUILLIBRIUM

Reaction occurs concentration decreases therefore its also decreases but concentration increases therefore it also increases.

cathode



Anode

* E°_{cell}

E°_{cell}

ΔG

* $\Delta G = 0$

the Equilibrium constant for



$$E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.45\text{V}$$

$$E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.67\text{V}$$

$$= E^\circ_c - E^\circ_a$$

$$= (\text{Ce}) - (\text{Fe})$$

$$= 1.45 - 0.67$$

$$= 0.78\text{V}$$

$$\frac{0.0591}{1} \log_{10} K$$

standard electrode potential

$$E^\circ(\text{Fe}) = -0.4\text{V}$$

$$E^\circ(\text{Fe}^{2+}) = 0.8\text{V}$$

$$E^\circ(\text{Mn}) = -1.2\text{V}$$

$$E^\circ(\text{Mn}^{2+}) = 1.5\text{V}$$

It on relative stability of +2 state of Iron and manganese of the two metal is more (+2) state.

$$E^\circ(\text{Fe}) = -0.4\text{V}$$

$(Fe^{2+}) = ?$

$$Fe^{3+}/Fe) = -0.036V$$

$$Fe^{2+}/Fe) = -0.440V$$



an intrinsic property इसलिए
मे convert करेंगे क्योंकि ΔG°
property means ΔG° is additive

$$/ \text{MnO}_2) = ?$$

$$(\text{MnO}_4^- / \text{Mn}^{+2}) = 1.51 \text{ V}$$

$$(\text{MnO}_2 / \text{Mn}^{+2}) = 1.23 \text{ V}$$

$$\xrightarrow{n_1 = 5} \text{Mn}^{+2} ; E_1^\circ = 1.51 \text{ V}$$

$$\xrightarrow{n_2 = 2} \text{Mn}^{+2} ; E_2^\circ = 1.23 \text{ V}$$

$$\xrightarrow{n_3 = 3} \text{MnO}_2 ; E^\circ = ?$$

$$\text{Eqn (2)} = \text{Eqn (3)}$$

$$n_2 E_2^\circ = n_3 E_3^\circ$$

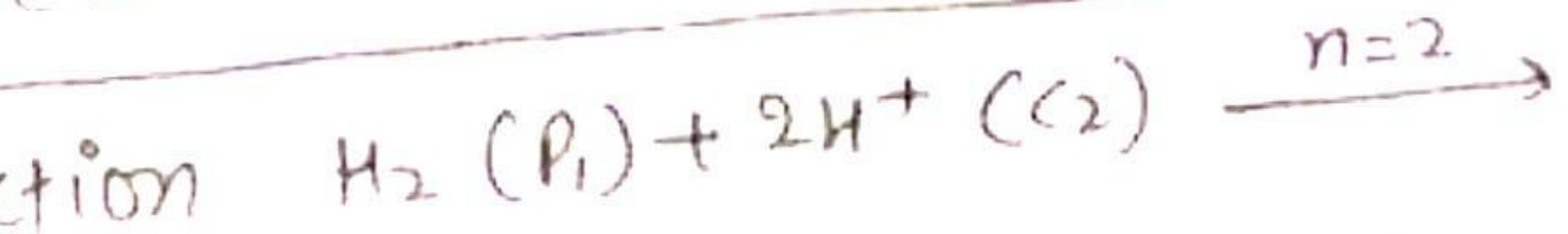
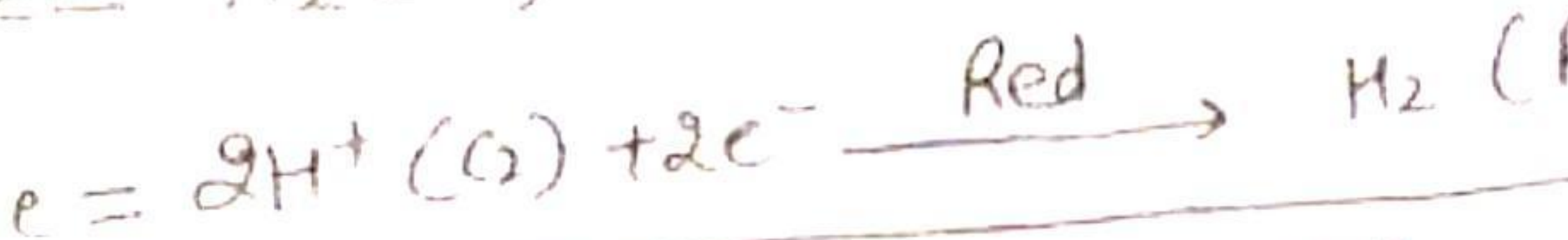
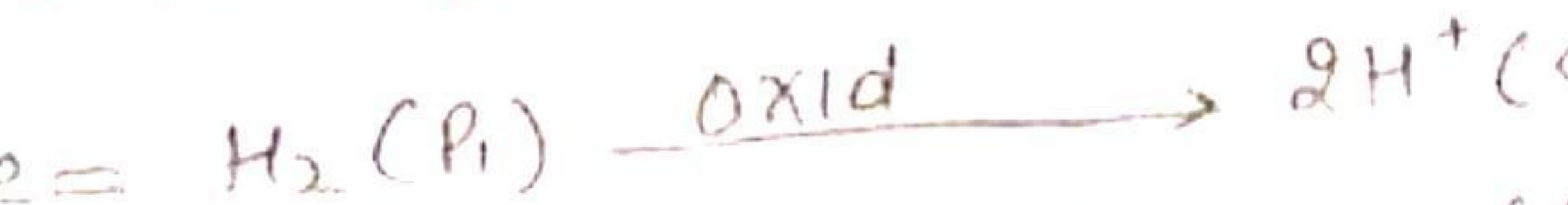
CONCENTRATION CELL

Similar electrode having different concentrations of ion in solution are connected which is called concentration cell.



$$E = 0.0591 \log_{10} \left(\frac{C_1}{C_2} \right)$$

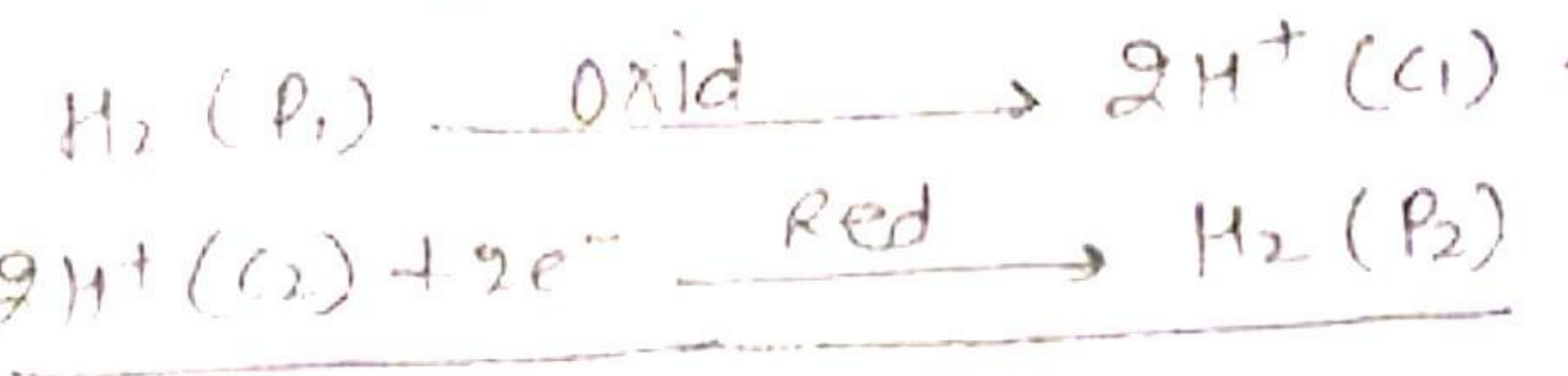
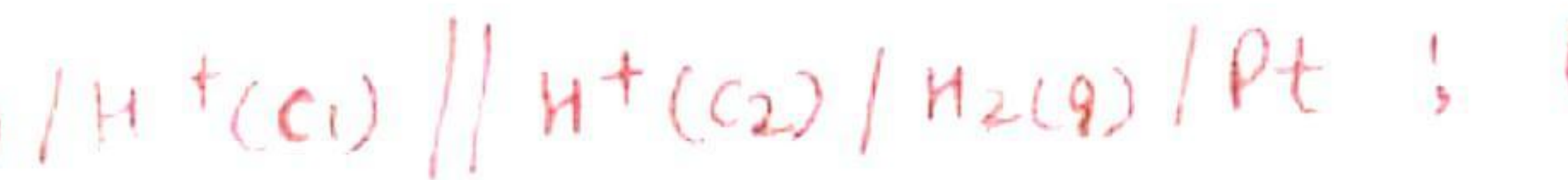
1 bar) / HA₁ // HA₂ / H₂ (1 bar) / Pt ;



$$E_{\text{cell}} = \frac{0.0591}{2} \log_{10} \frac{(\text{C}_1)^2}{(\text{C}_2)^2}$$

u for concentration cell = 0

$$= \frac{0.0591}{2} \log \left(\frac{\text{C}_1}{\text{C}_2} \right)$$



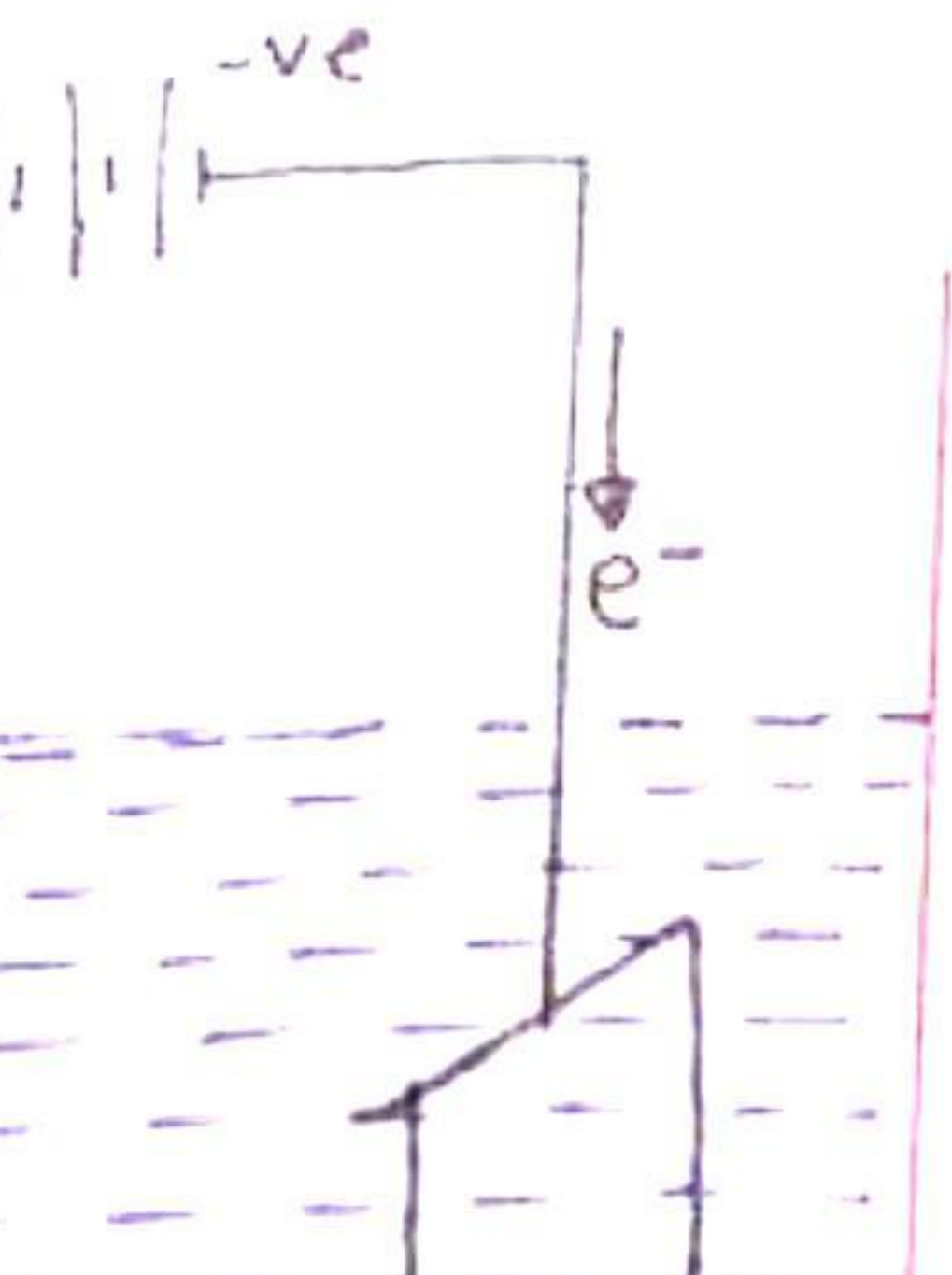
$$E = 0 - \frac{0.0591}{2} \log \frac{(c_1)^2 (P_2)}{(c_2)^2 (P_1)}$$

$$P_1 = P_2 = 1 \text{ bar} \quad \text{but} \quad c_1 \neq c_2$$

$$E = 0 - \frac{0.0591}{2} \log \frac{c_1^2}{c_2^2}$$

THREE - ELECTROLYSIS

of decomposition of an electrolyte
passed through its aqueous solution
ed electrolysis
in which electrolysis is carried out
electrolytic cell



Electrolysis

↓

CATION (+ve)

↓

CATHODE (-ve)

↓

Reduction

Electrolysis mainly depends upon

ELECTROLYTE (STRONG OR WEAK)

ELECTRODE

- inert (not attacked) electrode

Electrode does not react with solution
or with product of electrolysis
Electrodes are used for electrolysis

PPA, C (graphite)

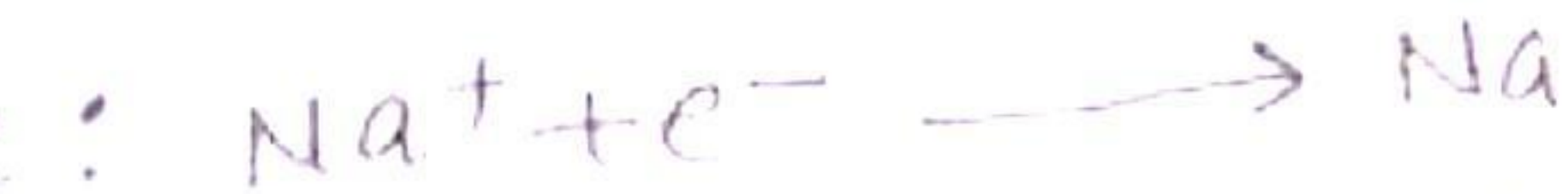
Electrodes

Electrodes are not used in electrolysis

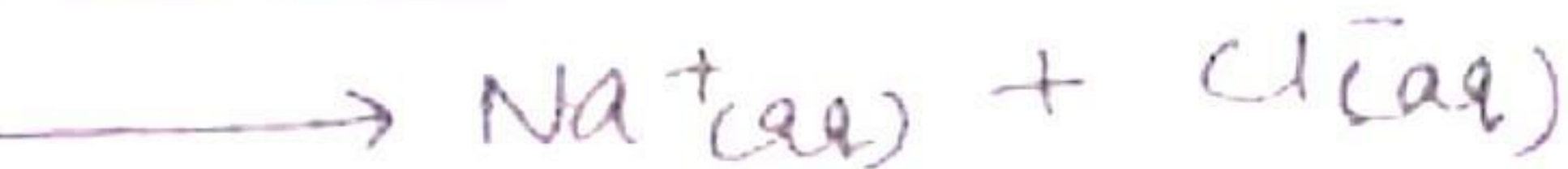
CONCENTRATION OF SOLUTION

TEMPERATURE

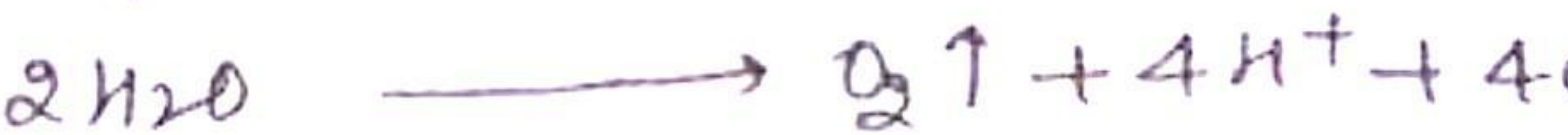
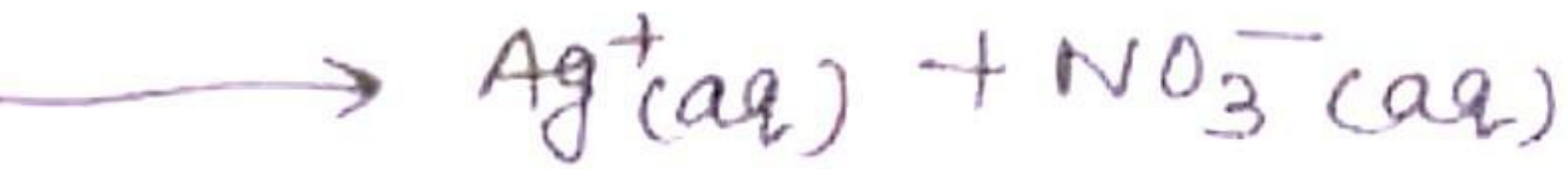
of fused (molten) NaCl using



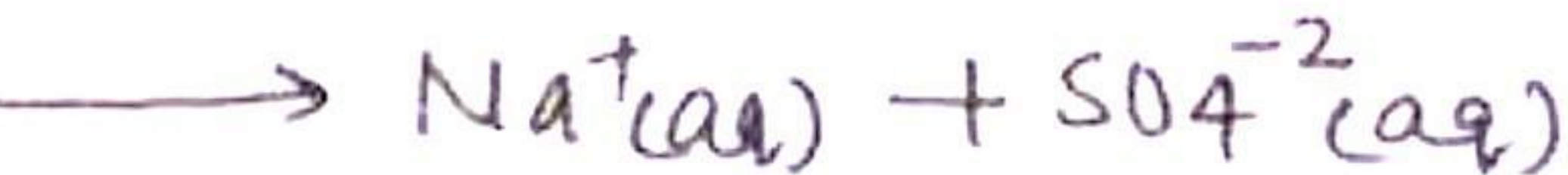
of Aq. soln of NaCl using



s of aq solution of AgNO_3



s of aqueous solution of Na_2SO_4



X

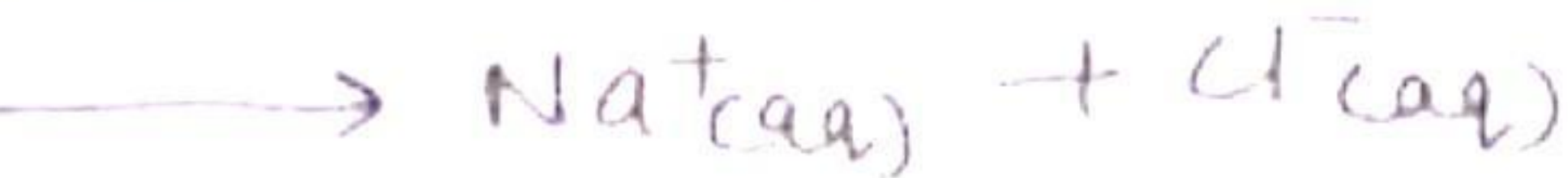
X



and water

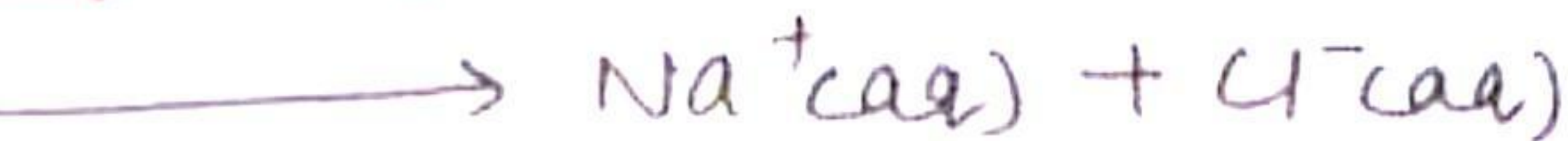
EXAMPLE OF ELECTROLYSIS

lysis of very dil aq NaCl using

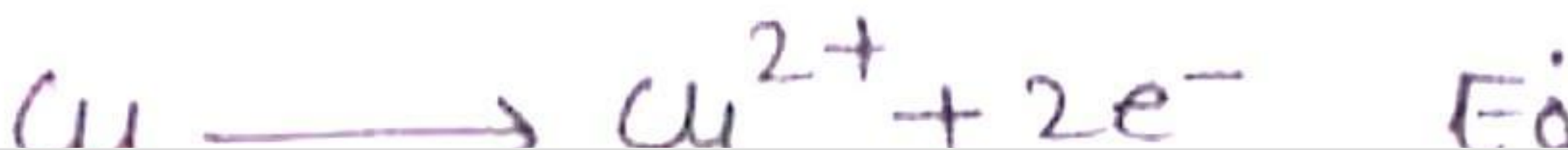
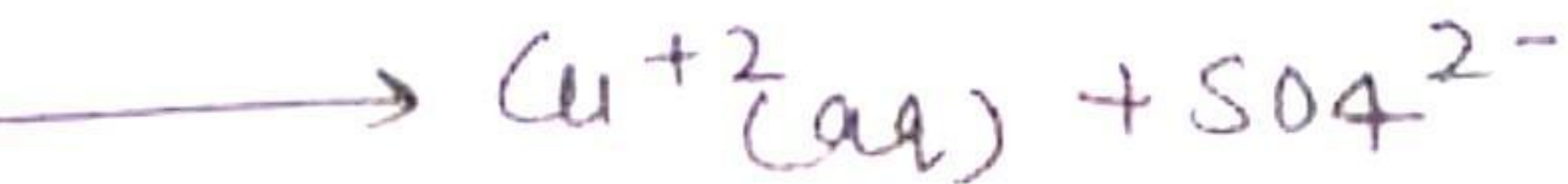
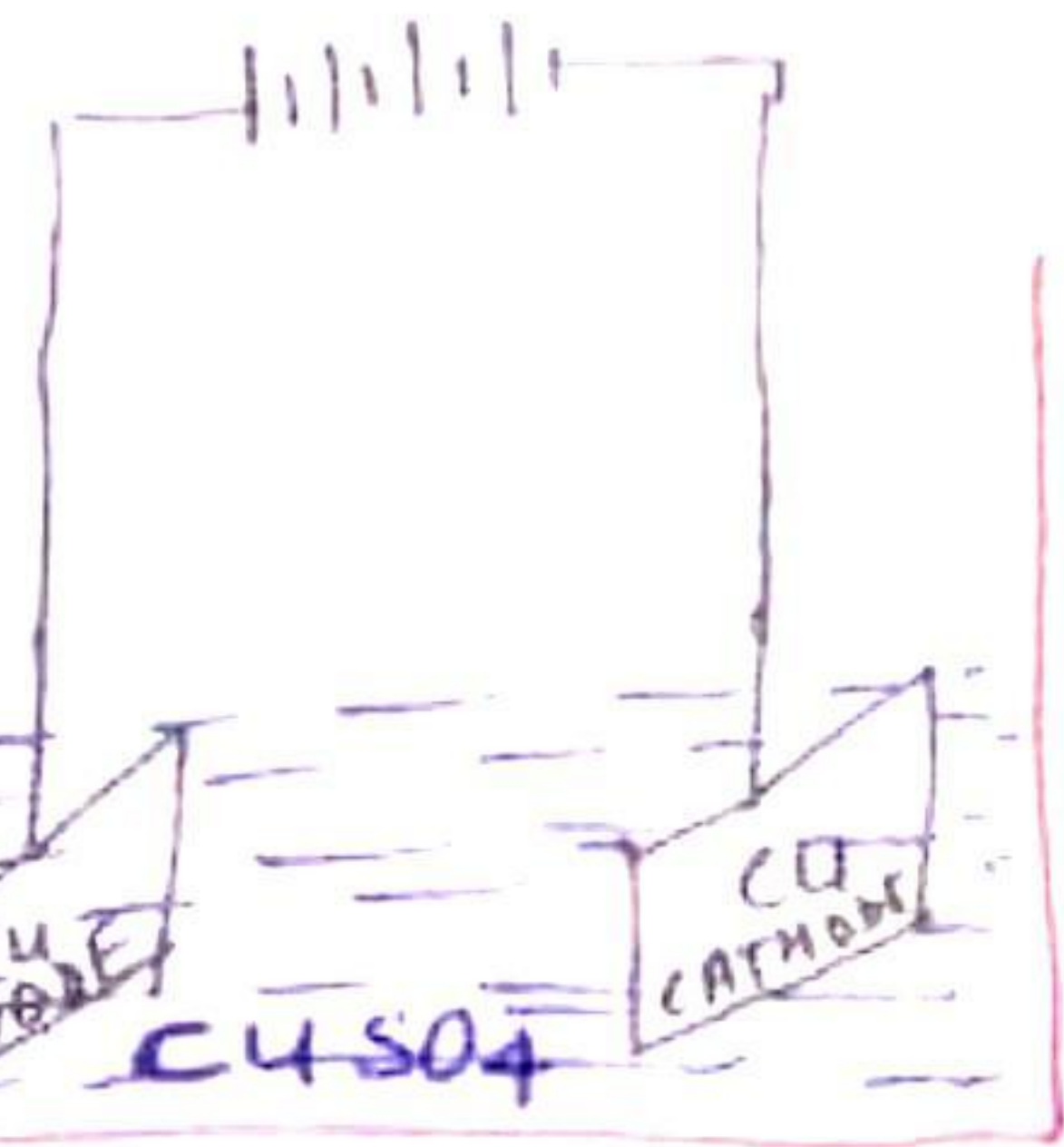


के कम concentration पर di
से ज्यादा चाहिए

lysis of aq solution of NaCl



Electrolysis of aqueous solution of copper sulfate



LAW OF ELECTROLYSIS

LAW OF FARADAY'S LAW OF

Electricity is passed through electrolyte substance discharged on electrode proportional to the quantity of electricity passed through electrolyte

$$W \propto Q$$

$$W \propto It$$

$$\boxed{W = ZIt}$$

$Z =$ electrochem

1cb then

$$\boxed{W = Z} \text{ gm}$$

... equivalence

LAW OF FARADAY'S LAW OF ELECTROLYSIS

If a quantity of charge is passed through an electrolyte then the amount of substance deposited at an electrode will be proportional to its equivalent weight

$$\boxed{\frac{w_1}{E_1} = \frac{w_2}{E_2} = \frac{w_3}{E_3} \dots \dots C}$$

the weight of Cu deposited when a quantity of charge is passed through a solution of CuSO₄.
Atomic weight of Cu = 63.5

→ Q

current is necessary
at the rate of 1ml/sec

1ml

1 sec

$$\frac{1}{22400} \times 32 \text{ gm}$$

$$\frac{E_{O_2}}{96500} \times i t$$

$$= \frac{8}{96500} \times i \times 1 \text{ sec}$$

$$7.23 \text{ amp}$$

Gas	MW
O_2	32
H_2	2
Cl_2	71

of 1 M AgNO_3 solution and
 and solution are connected
 electricity is passed 54
 osited on cathode in AgNO_3
 calculate volume of H_2 gas Ca
 ed at cathode in NaCl sol

54 gm of Ag

$$\frac{W}{g} = \frac{E_{\text{H}_2}}{E_{\text{Ag}}}$$

$$\frac{12}{4} = \frac{1}{108} \Rightarrow W_{\text{H}_2} = \frac{1}{2} =$$

$$0.5 \times 22.4 = 11.2 \text{ litre}$$

of electricity producing
 x . What is the cost of
 electricity of producing x
 ss of Al = 27) (At mass of
 of deposition $\propto$ charge (Q)

$$W = \frac{E}{96500} \times Q$$

$$\frac{W_{mg}}{W_{Al}} = \frac{E_{mg} \times Q_{mg}}{E_{Al} \times Q_{Al}}$$

$$\frac{W_{mg}}{W_{Al}} = \frac{E_{mg} \times (\text{cost})}{E_{Al} \times (\text{cost})}$$

$$x \quad 24/2 \quad (\text{cost})$$

ent of 3 Amp was passed
 a solution of CuSO_4 . 3
 e discharged at cathode - c
 efficiency for this process (

$$\frac{E_{\text{ext}}}{96500}$$

$$96500$$

$$\frac{63.5}{2 \times 96500} \times i_{\text{used}} \times 2 \times 60 \times 60$$

$$= 1.266 \text{ Amp}$$

$$\text{Efficiency} = \frac{i_{\text{used}}}{i_{\text{passed}}} \times 100$$

$$= 1.266$$

the charge require for ox

FeO to Fe_2O_3

Fe_2O_3 to FeO

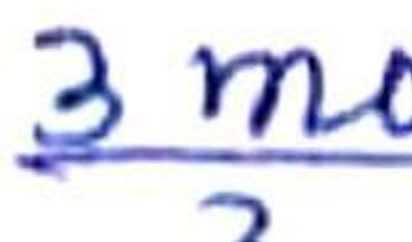
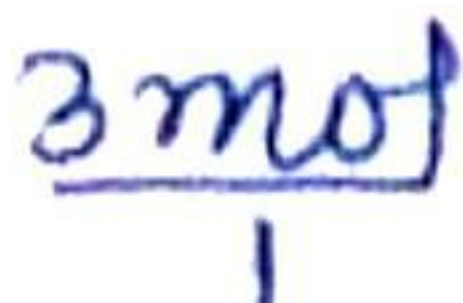
H_2O to O_2



changed in oxl. no = (1)

solution of AuCl_3 , AgNO_3 ,
 in series when 3F charge
 calculate the ratio of mole
 d on electrode

Method



between ionic Conductance

$$\gamma_c \propto v_c$$
$$\gamma_a v_a$$

$$\chi_c = F v_c$$
$$\chi_a = F v_a$$

$n(u)$.

velocity of ion (v)
potential gradient

⇓

GALVANIC CELL	ELECTROLYTIC CELL
Chemical energy is converted into electrical energy	* Converts electrical energy into chemical energy
Cell reaction is spontaneous	* Cell reaction is Non-spontaneous
Anode is negative Cathode is positive	* Anode = +ve Cathode = -ve
Deposition of substance occurs at cathode	* Deposition of substance occurs at both electrodes
Salt bridge is not used	* Salt bridge is used

	ANODE	CATHODE
CELL (EABLE)	Zn	Carbon Rod Coated with MnO_2
2	Pb	Pb Rod Coated With PbO_2
e	Cd	Ni Rod Coated With Nickel Powder
u cell	H_2 gas Passing through	O_2 Passing through Porous Carbon