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

2. CONDUCTANCE TERMS

2.A- CONDUCTANCE [C / G]

NCERT ने conductance के लिए [G] use किया हुआ है।

Reciprocal of Resistance is called as conductance

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

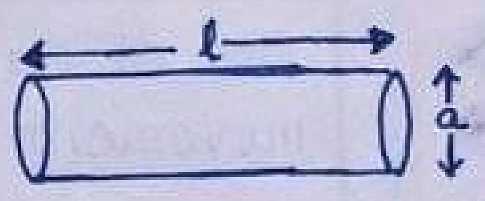
Unit = Ω^{-1} = ohm^{-1} = mho = siemens (S)

2.B- SPECIFIC CONDUCTANCE / CONDUCTIVITY [σ/K]

PHYSICS USES SIGN = σ
CHEMISTRY USES SIGN = K

IN PHYSICS CONCEPT OF [σ]

$$R = \rho \times \frac{l}{a} \Rightarrow \underset{\substack{\downarrow \\ \text{SPECIFIC RESISTANCE} \\ \text{OR} \\ \text{RESISTIVITY}}}{\rho} = \frac{Ra}{l}$$



Reciprocal of Resistivity OR SPECIFIC RESISTANCE is called Conductivity OR SPECIFIC CONDUCTANCE

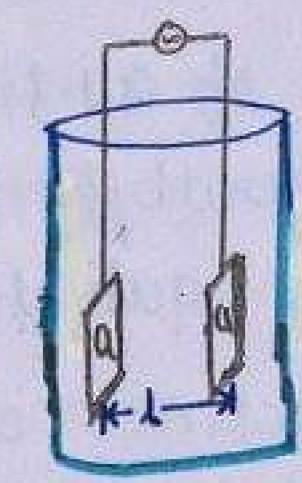
$$\sigma = \frac{1}{\rho}$$

$$\boxed{\sigma = \frac{1}{R} \times \frac{l}{a}}$$

unit = ρ (Resistivity) = Ωm OR Ωcm

σ (conductivity) = $\Omega^{-1} m^{-1}$ OR $\Omega^{-1} cm^{-1}$ OR $S m^{-1}$ OR $S cm^{-1}$

IN CHEMISTRY CONCEPT OF [K]



- * l = distance between electrode (generally in cm)

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

- * a = Dipped surface area

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

- * (l) and (a) donot depends 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 thats why $\frac{l}{a}$ is constant and called cell constant [C^* / G^*]

$$K = \frac{1}{R} \cdot \frac{l}{a}$$

$$\boxed{K = G \times G^*}$$

K = conductance x cell constant

if $l = 1cm$
$a = 1cm$

then $\boxed{K = G}$ so we can say that conductance of $1cm^3$/1ml 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

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

$\therefore$ conductance of V cm^3 solution = K × V

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

volm of solution (ml) which contain **1 gmeq** of an electrolyte

suppose concentration is N eq/lit

$\because$ volm of solution containing N gmeq = 1000 ml

$\therefore$ volm of solution containing 1 gmeq = $\frac{1000}{N}$

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

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

volm of solution (ml) which contain **1 gm eq** of an electrolyte

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

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

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

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

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

$\therefore$ conductance of V cm^3 solution = K × V

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

volm of solution (ml) which contain **1 mol** of electrolyte

$\because$ volume of solution containing M molar = 1000 ml

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

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

$$\boxed{\lambda_M = K \times \frac{1000}{M}}$$

volm of solution (ml) which contain **1 mol** of electrolyte

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

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

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

RELATION BETWEEN λ_M AND λ_{eq}

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

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

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

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

Min^m value of v.f 1 तो होगा ही होगा so

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

conductance and conductivity are additive property
जैसे कि अगर कोइ electrolytic solutionमे several electrolytic
ions है तो total conductance of solution willbe

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

FORMULAE

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

2. $K = \frac{1}{R} \cdot \frac{l}{a} = G \times G^{*} = \frac{G}{R}$

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

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

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

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

Ans

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

$$= K \times \frac{1000}{M \times v.f}$$

$$= \frac{1}{R} \times G^{*} \times \frac{1000}{M \times v.f}$$

$$= \frac{1}{200} \times (1) \times \frac{1000}{0.005 \times 2}$$

$$= \underline{500\ \Omega^{-1}\,cm^2\,equi^{-1}}$$

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

Ans

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

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

$$= \frac{1}{50} \times \frac{1.8}{5.4} \times \frac{1000}{\text{[illegible]}/10}$$

$$= 66.67\ \Omega^{-1}\,cm^2\,eq^{-1}$$

Qsn. HOME WORK

0.5 N $Al_2(SO_4)_3$ solution is present between two platinum electrode that are 2cm × 4 cm the resistance of solution is 200Ω. then calculate molar conductance of solution

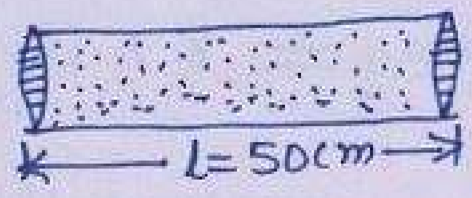
Hints

$$Al_2SO_4 \longrightarrow \underset{+6}{2Al^{+3}} + \underset{-6}{3SO_4^{-2}}$$

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

[redacted]

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



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

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

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

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

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

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

OPTION मे ये तीनो मे से कोई एक रहेगा. जैसे नीचे दिया है।

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

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

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

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

~~(iv)~~ All are correct

Ans = (iv)

Qsn Equivalent conductance of 0.1M solution of $MgCl_2$ is 100 mho $cm^2 eq^{-1}$ 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 $V = IR$ $\quad I = \frac{V}{R}$ [V तो है But R find करना है]

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

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

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

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

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

Ans

	$NaOH$ +	HCl $\longrightarrow$	$NaCl + H_2O$
	0.1N	0.1N	
let vol^m =	1Lit	1lit	
gm eq =	N×V	N×V	
	= 0.1 gmeq	0.1 gmeq	
After Reaction =	0	0	0.1 gm eq

$$N_{NaCl} = \frac{0.1\,gmeq}{(1+1)\,lit} \qquad \Lambda eq = \frac{K \times 1000}{N}$$

$$= 0.05N \qquad \Lambda eq = 0.0055 \times \frac{1000}{0.050}$$

$$\boxed{\Lambda eq = 110}$$

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

(a) cell constant (Ans = 0.756)

(b) Conductivity of $CaCl_2$ solution (Ans = $8.4 \times 10^{-4} S\,cm^{-1}$)

(c) Molar conductivity of $CaCl_2$ solution (Ans = $4.2\ S\,cm^2 mol^{-1}$)

(d) equivalent conductivity of $CaCl_2$ solution (Ans = 2.1 Scm

FACTOR EFFECTING ELECTROLYTIC CONDUCTANCE

[I] INTERIONIC INTERACTION

[II] SOLVENT OR HYDRATION OF IONS

[III] VISCOCITY

[IV] TEMPERATURE

[V] DILUTION

[I] INTERIONIC INTERACTION

if interionic i [illegible] 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 नही कर पाएगा या अगर move करेगा तो slowly move करेगा so conductance decreases.
- जो ion जितना छोटा होता है पानी मे उतना ही ज्यादा मोटा हो जाता है पानी पीकर नही But 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 नही कर पाएगा so VISCOCITY 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. thats why –

Temperature increases $(T)\uparrow$ = conductance $(G)\uparrow$

[iv] DILUTION

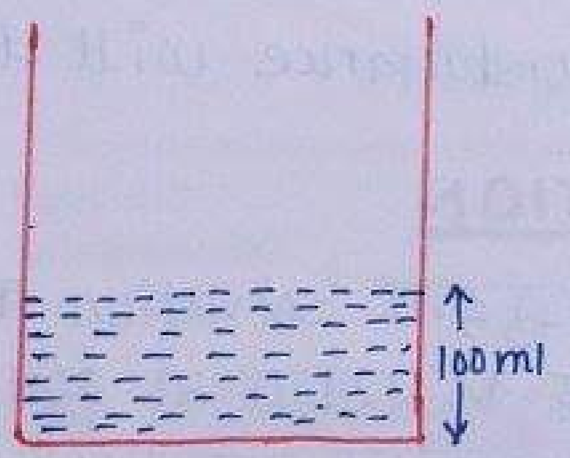
अब तक जो तीन effect था interionic interaction, solvation and temperature ये तीनों common concept था. But effect of dilution on conductance is so important concept.

DILUTION INCREASES = CONDUCTANCE INCREASES (G)

DILUTION INCREASES = CONDUCTIVITY DECRESES (K)

BEFORE DILUTION

1mol present in 100ml



Let

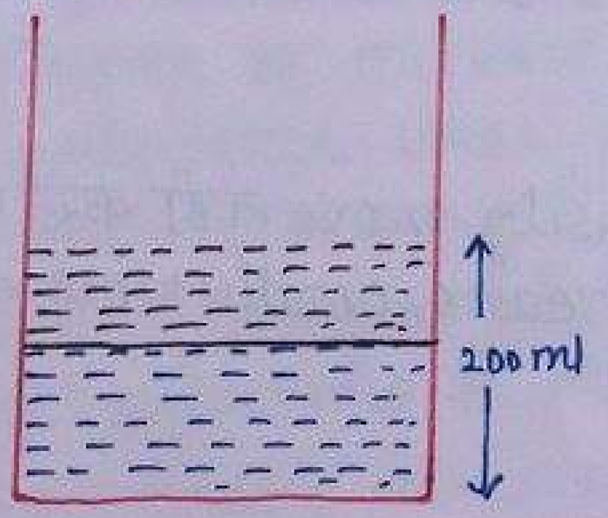
100ml sol^n have = 50,00000 ions = G_1 = ΛM_1

1ml sol^n have = 50,00000 ions = K_1 [K Always 1ml के लिए होता है]

AFTER DILUTION

1 mol in 200 ml

1ml = 



$G_2 > G_1$

$K_1 > K_2$

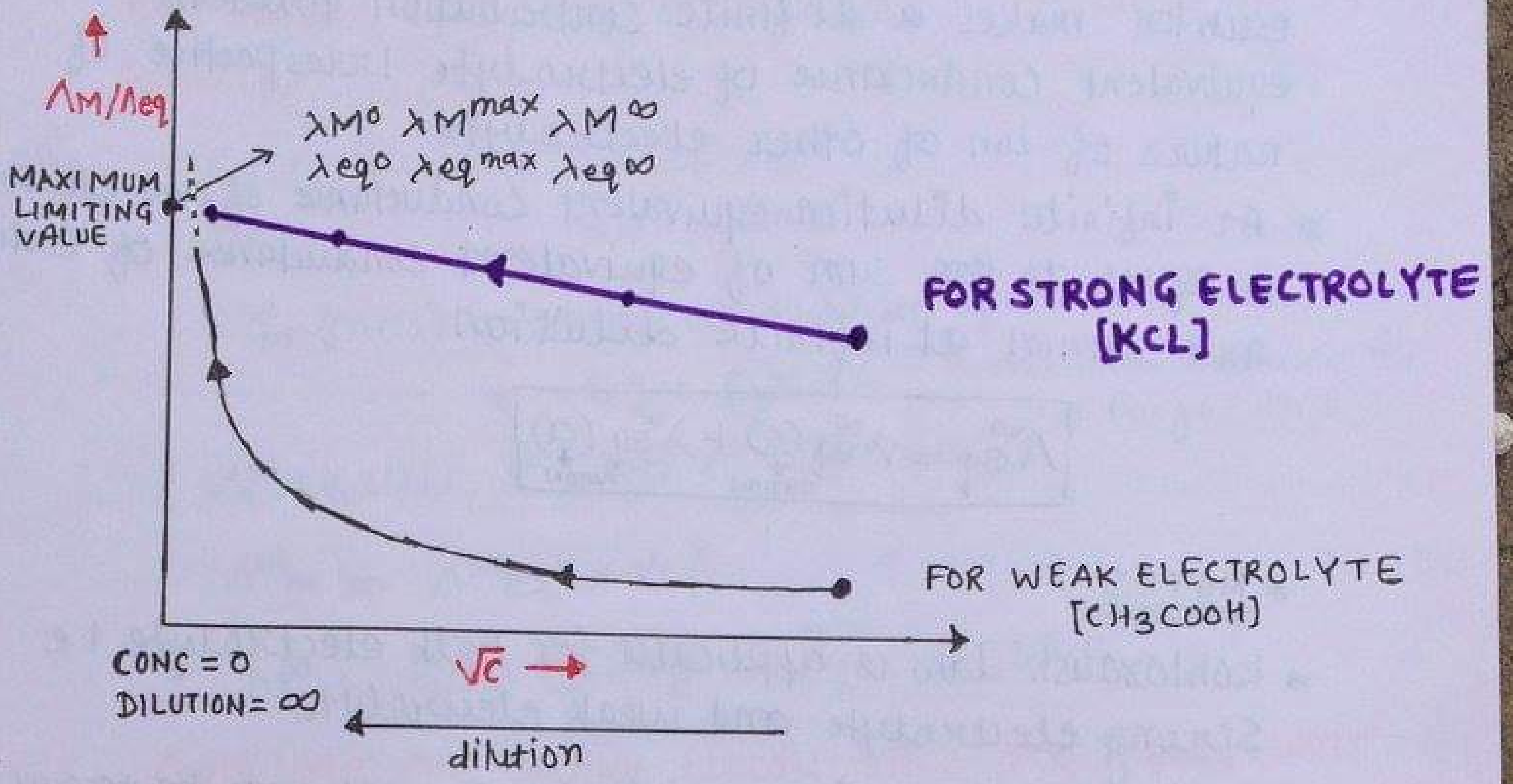
200 ml so^n contains 60,00000 ions = G_2 = ΛM_2

1 ml sol^n Contains 30.00000 ions = K_2

*** ON DILUTION ⇒ G↑ BUT K↓**

*** ON DILUTION ⇒ Λeq↑ AND ΛM↑ [दोनों INCREASES]**

DEBYE-HUCKEL-ONSAGAR GRAPH



FOR STRONG ELECTROLYTE

$$\boxed{\Lambda m = \Lambda M^{\infty} - b\sqrt{c}}$$

OR

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

→ DEBY-HUCKLE-ONSAGAR EQUATION

→ b = DHO constant

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

OBSERVATION OF DHO-GRAPH

* Dilution को increase करने पर strong electrolyte की molar Conductance weak electrolyte की molar conductance के जितना increase नही होता.
BUT strong electrolyte की conductance तो 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 extraplot किया जाए तो strong electrolyte की λM obtain किया जा सकता है! But weak electrolyte की maxmym λM obtain नही किया जा सकता है, क्यों कि weak electrolyte की α is always less than 1

KOHLRAUSCH'S LAW

* At infinite dilution when dissociation is completed each ion makes a difinite 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

$$\boxed{\Lambda^{\infty}_{eq} = \lambda^{\infty}_{eq}\underset{\text{CATION}}{\underset{\downarrow}{(c)}} + \lambda^{\infty}_{eq}\underset{\text{ANION}}{\underset{\downarrow}{(a)}}}$$

* NOTES

⇒ kohlaraush law is applicable for both electrolyte i.e Strong electrolyte and weak electrolyte

⇒ kohlraush has given original statement was in terms of equivalent conductance but according to I.U.P.A.c Convention now Kohlraush law is expressed interms of molar conductanc

$$\boxed{\Lambda^{\infty}_{M} = m\lambda^{\infty}_{M}(c) + n\lambda^{\infty}_{M}(a)}$$

m = NO of moles of cation in 1 mol of electrolyte
n = NO of moles of anion in 1 mol of electrolyte

eg.- $K_2SO_4 \longrightarrow 2K^+ + SO_4^{-2}$
1mol   2mol   1mol
m=2   n=1
1gmeq   1gmeq + 1gmeq

eg. $Al_2(SO_4)_3 \longrightarrow 2Al^+ + 3SO_4^{2-}$
1mol   2mol   3mol
m=2   n=3
1gmeq   1gmeq + 1gmeq

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

Ans $CaCl_2 \longrightarrow Ca^{+2} + 2Cl^-$

1mol 1mol 1mol

$\Lambda^\infty_M (CaCl_2) =$ molar conductance of Cation + Anion

$= 119 + \textcircled{2} \times 76$ → maximum mistake ~~th~~ we forget this

$\Lambda^\infty_M (CaCl_2) = 271\ \Omega^{-1} cm^2 mol^{-1}$

$\Lambda^\infty_M = \Lambda^\infty_{eq} \times v.f$

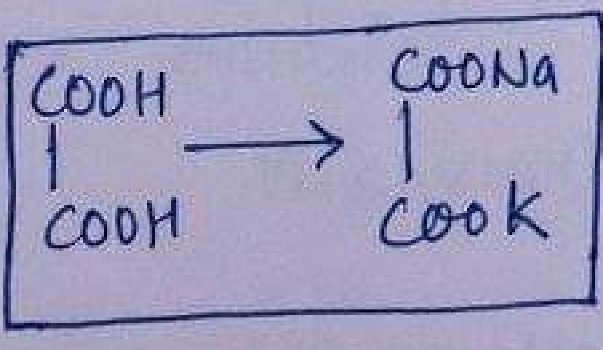
$\Lambda^\infty_{eq} (CaCl_2) = \frac{\Lambda^\infty_M}{v.f} = \frac{271}{2} = 135.5$

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

Ans $KOOC.COONa \longrightarrow C_2O_4^{2-} + Na^+\ K^+$

[Sodium pottassium oxalate] 1mol 1mol 1mol

↓



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow \begin{matrix} COONa \\ | \\ COOK \end{matrix}$$

$\Lambda^\infty_M = \lambda^\infty_M (Ox^{-2}) + \lambda^\infty_M Na^+ + \lambda^\infty_M K^+$

$\Lambda^\infty_M = 148.2 + 50.1 + 73.5$

$\Lambda^\infty_M = 271.8\ \Omega^{-1} cm^2 mol^{-1}$

$\Lambda^\infty_{eq} = \frac{\Lambda^\infty_M}{v.f} = \frac{271.8}{2} = 135.9$

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

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

At constan "concentration c"

$$\boxed{\alpha = \frac{\Lambda_{eq}^{c}}{\Lambda_{eq}^{\infty}} \text{ or } \frac{\Lambda_{M}^{c}}{\Lambda_{M}^{\infty}}}$$

[II] TO DETERMINE DISSOCIATION CONSTANT [K]

eg- for CH_3COOH

$$Ka = \frac{C\alpha^2}{(1-\alpha)} \quad \text{if } \alpha << 1 \text{ then } Ka = C\alpha^2$$

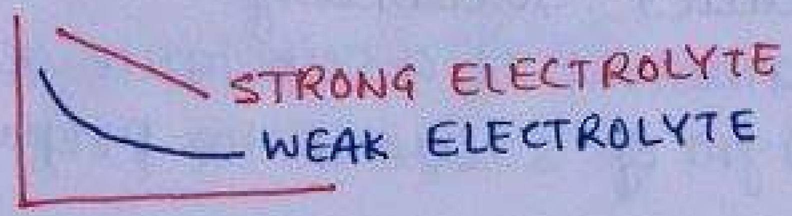
$$[H^+] = C\alpha$$

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

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

Qsn: $\Lambda_M^\infty (CH_3COOH) = ?$

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



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

$$\Lambda_M^\infty (CH_3COOH) = \boxed{\lambda_M^\infty (CH_3COO^-)} + \boxed{\lambda_M^\infty (H^+)} \text{ ----- (i)}$$

$$\Lambda_M^\infty (CH_3COONa) = \boxed{\lambda_M^\infty (CH_3COO^-)} + \lambda_M^\infty (Na^+) \text{ ----- (ii)}$$

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

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

* $\lambda_M^\infty (CH_3COO^-)$ की molar conductance चाहे equation (i) मे हो या equation (ii) मे हो दोनो जगह same ही होगी

* $\lambda_M^\infty (H^+)$ की molar conductance चाहे equation (i) मे हो या equation (iii) मे हो दोनो जगह same ही होगी

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

$$\Lambda_M^\infty (CH_3COOH) = \Lambda_M^\infty (CH_3COO^-) + \lambda_M^\infty (H^+) - \Lambda_M^\infty (NaCl)$$

$$\Lambda_M^\infty (CH_3COOH) = \Lambda_M^\infty (\underline{CH_3COO}Na + \underline{H}Cl + NaCl)$$

[IV] TO DETERMINE SOLUBILITY OF SPARINGLY SOLUBLESALT

Eg- Alcl, $BaSO_4$, $PbSO_4$

Solubility

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

FUNDA:

- saturated solution of sparingly soluble salt canbe considered as infinitely diluted solution because these salt dissolve very less therefore

saturated solution = infinitely diluted solution

$$\Lambda_M = \Lambda^{\infty}_M = K \times \frac{1000}{M}$$

↓

By Kohlraush law

$$\boxed{\text{यहाँ पर } M = S}$$

* if we add 500 gm AgCl in 1 litre of H_2O then only upto 5g AgCl is dissolve.
* 495 gm AgCl remain undissolve. so actual solubility = 5g/L

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

Ans Λ^{∞}_{M} AgCl $= 54.5 + 65.5$

$= 120$

$$\Lambda^{\infty}_{M} = 1.8 \times 10^{-6} \times \frac{1000}{S}$$

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

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

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

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

Qsn The molar conductance for acetic acid at 0.2M Molar conductance at infinite dilute are 4.8 and 400 Ω^{-1} cm^2 mol^{-1} respectively. calculate degree of dissociation and dissociation constant of CH_3COOH.

Ans $C = 0.2$ M CH_3COOH

$\Lambda^{c}_{M} = 4.8$

$\Lambda^{\infty}_{M} = 400\ \Omega^{-1}$ cm^2 mol^{-1}

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

$$Ka = C\alpha^2$$

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

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

Qsn The molar conductance of an infinitely diluted solution of Ammonium chloride (NH_4Cl) is $150\,\Omega^{-1}cm^2mol^{-1}$ and Ionic conductance is ($OH^- = 198$), ($Cl^- = 76\,\Omega^{-1}cm^2mol^{-1}$) 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 $9.52 \times 10^{-5}\,\Omega^{-1}cm^2$ what will be its degree of dissociatio

Ans. $NH_4Cl = 150\ Ohm^{-1}\,cm^2\,mol^{-1}$

$OH^- = 198$

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

$$\Lambda^\infty_M(NH_4OH) = \Lambda^\infty_M(\underline{NH_4Cl} + \underline{OH^-} - Cl^-)$$

$$\Lambda^\infty M(NH_4OH) = \Lambda^\infty_M(150 + 198 - 76)$$

$$\Lambda^\infty_M(NH_4OH) = 272\ \Omega^{-1}cm^2\,mol^{-1}$$

$C = 0.01M$

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

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

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

$$\alpha = \frac{\Lambda^c M}{\Lambda^\infty M} = \frac{9.52}{272} \times 100$$

$$\underline{\alpha = 3.5\%}$$

Qsn Conductivity of saturated solution of AgCl is $2.2\times10^{-6}\,\Omega^{-1}\,cm^{-1}$ and conductivity of water is $0.8\times10^{-6}\,\Omega^{-1}\,cm^{-1}$. Molar conductance at infinite dilution of $AgNO_3$, HCl and HNO_3 are 135, 426 and 421 $\Omega^{-1}\,cm^2\,mol^{-1}$ respectiv calculate solubility product of AgCl

Ans

$AgNO_3 = 135$

$HCl = 426$

$HNO_3 = 421$

$$\Lambda_M^\infty(AgCl) = \Lambda_M^\infty(AgNO_3 + HCl - HNO_3)$$
$$= \Lambda_M^\infty(135 + 426 - 421)$$

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

K_{AgCl} solution $= 2.2\times10^{-6}\,\Omega^{-1}\,cm^{-1}$

K_{H_2O} Solution $= 0.8\times10^{-6}\,\Omega^{-1}\,cm^{-1}$

It should neglect

$K_{\text{solution of electrolyte}} = K_{electrolyte} + K_{H_2O}$

$= K_{\text{solute electrolyte}} + \boxed{K_{H_2O}}$

$= 2.2\times10^{-6} - 0.8\times10^{-6}$

$$\underline{K_{AgCl} = 1.4\times10^{-6}}$$

Qsn specific conductance of 0.03M aquas solution of weak base BOH is $1.5\times10^{-4}\,S\,cm^{-1}$. also the molar conductance at infinite dilution is $250\,S\,cm^2\,mol^{-1}$ find ionisation constant of weak base

Ans

$C = 0.03M$

$K = 1.5\times10^{-4}\,S\,cm^{-1}$

$\Lambda_M^\infty = 250\,S\,cm^2\,mol^{-1}$

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

$$\Lambda_M^c = 1.5\times10^{-4}\times\frac{1000}{0.03}$$

$$\Lambda_M^c = 5$$

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

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

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

$$\underline{K_b = 1.2\times10^{-5}}$$

AIIMS

ELECTROLYTE	KCl	KNO3	HCl	NaOAc	NaCl
Λ^{∞} $(S cm^2 mol^{-1})$	149.9	145.0	426.2	91.0	126.5

calculate Λ^{∞}_{HOAc} using appropriate molar conductance of electrolyte listed above at infinite dilution in H_2O at 25°C

Ans $\Lambda^{\infty}_{HOAc} = \Lambda^{\infty}_{NaOAc} + \Lambda^{\infty}_{HCl} - \Lambda^{\infty}_{NaCl}$

$= 91.0 + 426.2 - 126.5 \ S cm^2 mol^{-1}$

$= 390.7 \ S cm^2 mol^{-1}$

Qsn
AIIMS

Hydro Fluoride acid is weak acid. At 25°C the molar conductivity of 0.002 M HF is $176.2 \ \Omega^{-1} cm^2 mol^{-1}$ if its $\Lambda^{\circ}_{m} = 405.2 \ \Omega^{-1} cm^2 mol^{-1}$, Equillibrium constant at the given concentration is

Ans $\alpha = \frac{\Lambda_c}{\Lambda^{\infty}_{m}} = \frac{176.2 \ \Omega^{-1} cm^2 mol^{-1}}{405.2 \ \Omega^{-1} cm^2 mol^{-1}} = 0.435$

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

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

ELECTROCHEMISTRY – PART TWO

ELECTRODE POTENTIAL

when a metal is placed in aquas solution of its ion Its 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 aquas solution $CuSO_4$ मे डुबाया जाए तो Potential developed हो जाएगा.
* अगर Zn को उसके aquas solution $ZnSO_4$ मे 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

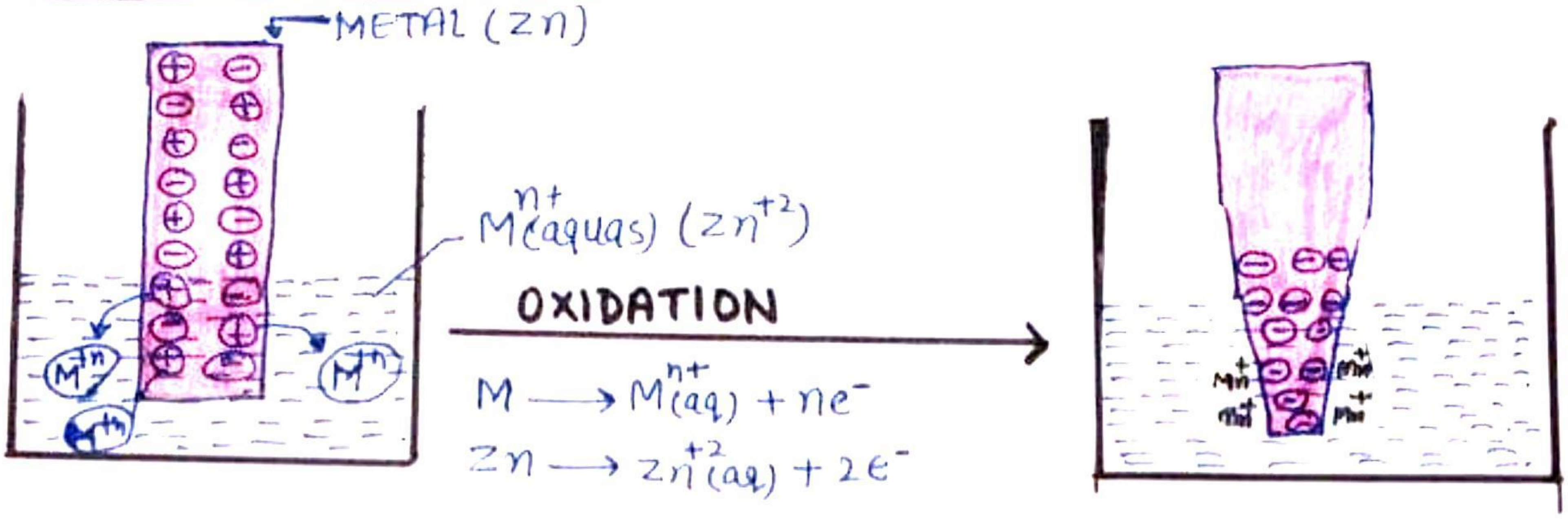
A large number of
- Metals
- Sodium hydroxide
- Fluorine
- Chlorine
- and many other chemicals

are produced by electrochemical method.

ELECTRODE POTENTIAL ARE OF TWO TYPES:

(I) OXIDATION POTENTIAL
(II) REDUCTION POTENTIAL

(I) OXIDATION POTENTIAL



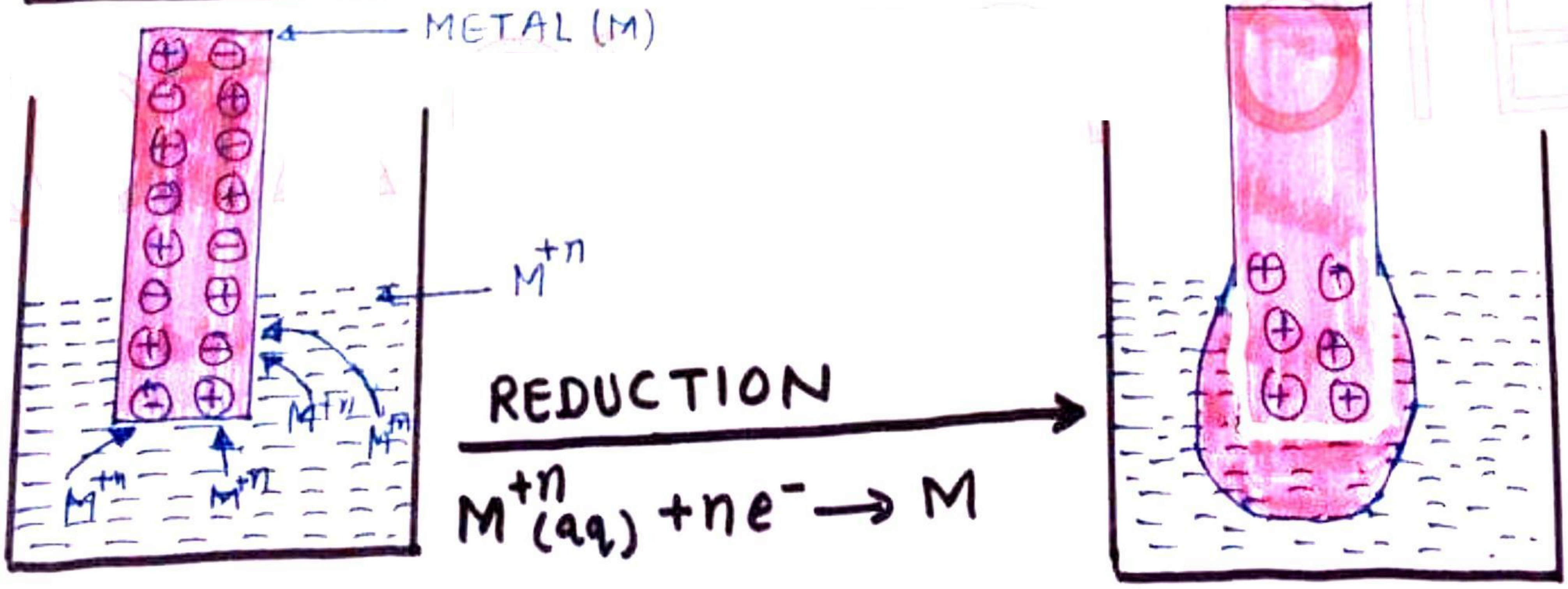
$M \longrightarrow M^{n+}_{(aq)} + ne^-$

$Zn \longrightarrow Zn^{+2}_{(aq)} + 2e^-$

* 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 का oxidation हो रहा है। और potential develop हो रहा है। so called oxidation potential

(II) REDUCTION POTENTIAL



$M^{+n}_{(aq)} + ne^- \longrightarrow M$

$$\boxed{M \underset{\text{REDUCTION}}{\overset{\text{OXIDATION}}{\rightleftharpoons}} M^{n+}_{(aq)} + ne^-}$$

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

REFERENCE ELECTRODE

कोई भी Battery at least दो Half cell की बनी होती है। But when we want measure potential of single half cell हम measure नहीं कर पाएगे इसके लिए reference electrode की requirement होगी

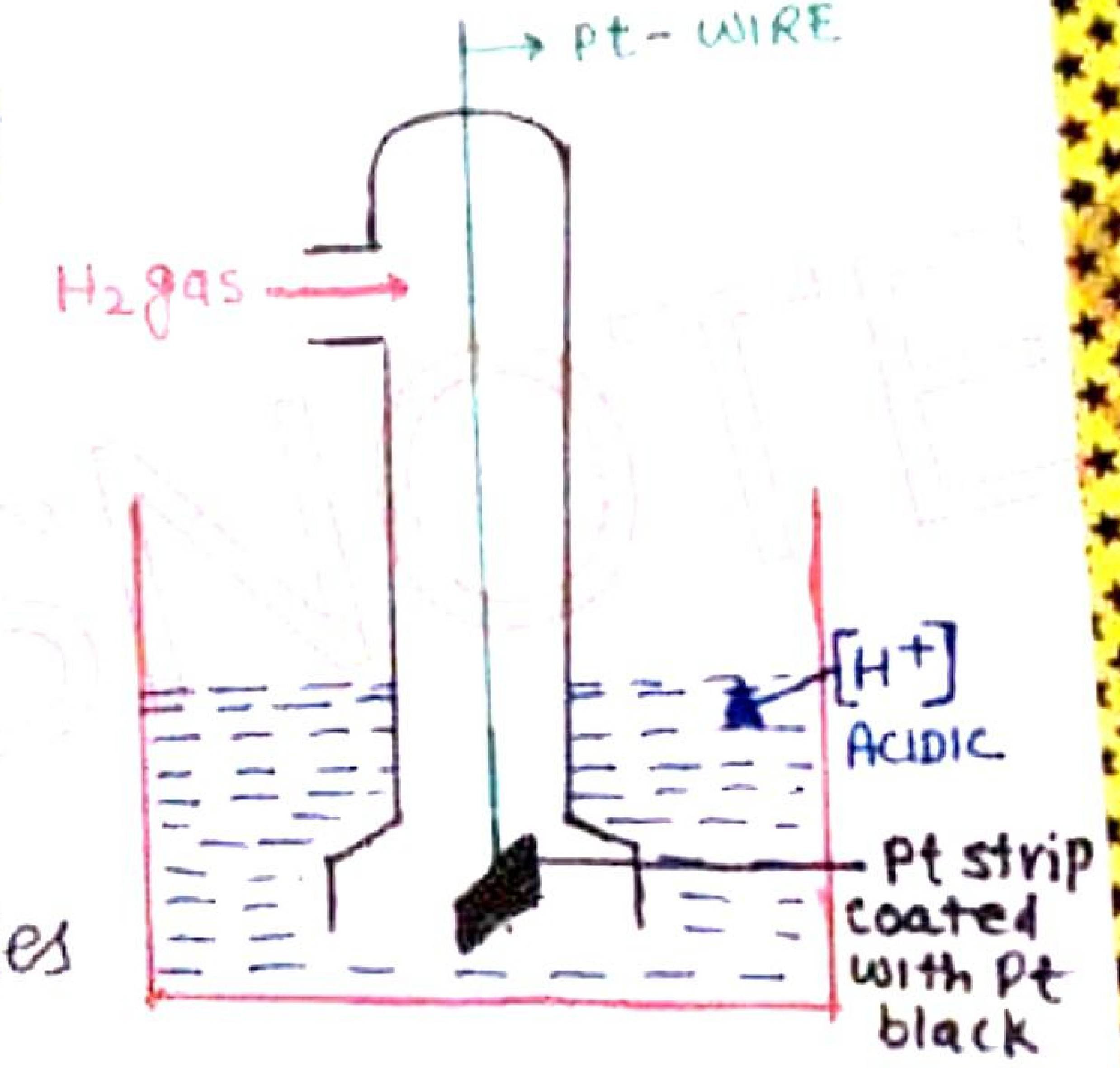
PRIMAR REFERENCE ELECTRODE [SHE/NHE]

SHE = Standard Hydrogen electrode

Hydrogen electrode represented by = $Pt(s)|H_2(g)/H^+(aq)$

It is assigned to ZERO POTENTIAL at all temp corresponding to this reaction

$$H^+(aq) + e^- \longrightarrow \underline{\tfrac{1}{2}\,H_2\,g}$$



- H_2 is a gas so gas wants free and to hold gas Pt-strip is coated with Pt-black (Powder)
- Pt is black powder which increases surface area.
- Pt is less reactive and cannot react with H+ (Acid)

SHE AS ANODE (OXIDATION)

H_2 (gas) $\longrightarrow 2H^+(aq) + 2e^-$ (Half cell reaction)

$Pt/H_2(g)\,/\,H^+(aq)$ – Representation

Oxidation

SHE AS CATHODE (REDUCTION)

$2H^+_{(aq)} + 2e^- \longrightarrow H_2(g)$ (Half cell reaction)

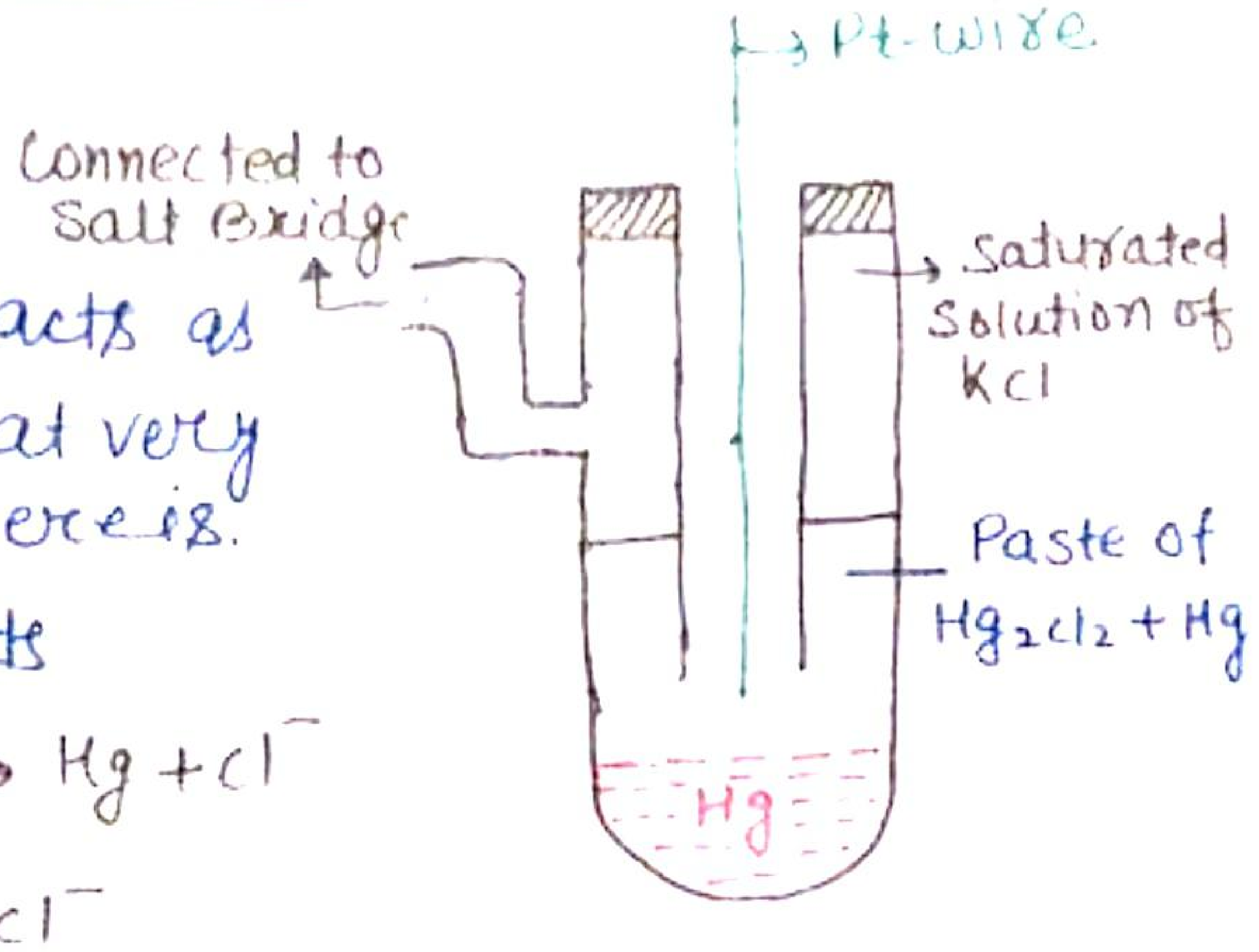
$[H^+(aq)/H_2(g)\,/\,Pt]$ – Representation

Reduction

SECONDARY REFERENCE ELECTRODE

[A] CALOMEL ELECTRODE

Hg_2Cl_2

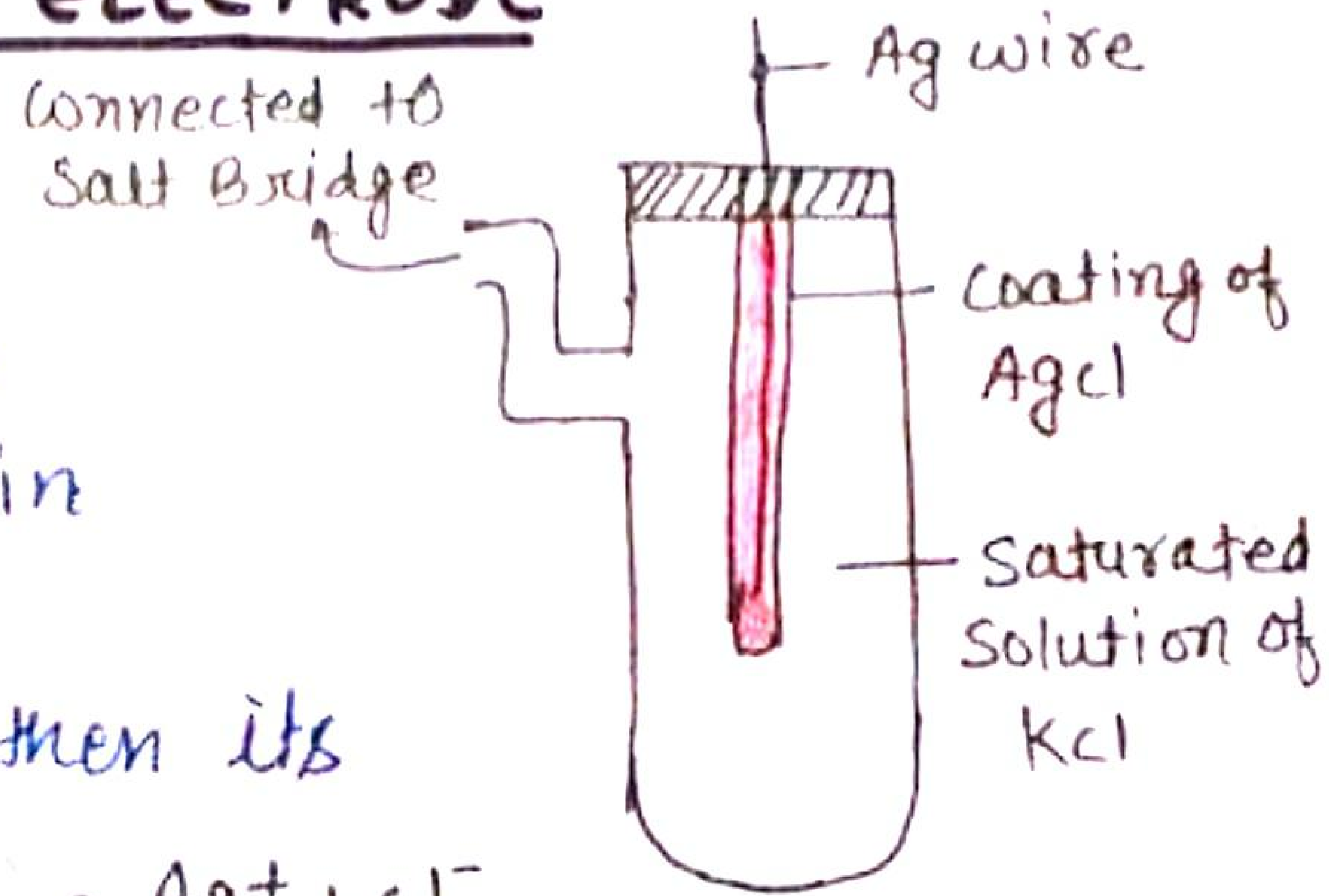


* Calomel electrode is commonly acts as Cathode because it is situated at very low position in Electro chemical sereis.

* when it acts as cathode then its

- Half cell reaction = $\frac{1}{2} Hg_2Cl_2 \rightarrow Hg + Cl^-$
- Representation = $Hg_2Cl_2 / Hg + Cl^-$

[B] SILVER-SILVER CHLORIDE ELECTRODE



* Ag-AgCl electrode generally acts as Cathode because it is Situated at very low position in electro-chemical Sereis

* when it acts as cathode then its

- Half cell reaction- $AgCl + e^- \rightarrow Ag^+ + Cl^-$
- Representation - $AgCl / Ag / Cl^-$

NOTE

⇒ For secondary referrance electrode SRP (standard reduction Potential) and SOP (standard oxidation potential) not zero

⇒ According to IUPAC

SRP ⟷ standard electrode potential (E°)

$$Li^{\circ} \xrightarrow[Red \uparrow]{oxid \uparrow\uparrow\uparrow} Li^+_{(aq)} + e^- = E^{\circ}_{ox} = 3.05V$$

(S.O.P)

$$Li^+_{(aq)} + e^- \xrightarrow[Oxid \uparrow]{Red \uparrow\uparrow\uparrow} Li = E^{\circ}_{red} = -3.05V$$

(SRP)

ELECTROCHEMICAL SEREIS

Best reducing agent

लीथम	Li	= SRP = −3.04V
के	K	
बाप	Ba	
से	Sr	
काका	Ca	
ने	Na	
माँगी	Mg	
अलमारी	Al	
मनी	M	
जमीन	Zn	= −0.76 V
कार	Cr	
फ्रिज	Fe	
कड़े	Cd	
को	Co	
नी	Ni	
स्नेह	Sn	
प्रभा	Pb	
ही	H_2	0 volt
कुटेगी	Cu	
होगी	Hg	I_2
आगे	Ag	Br_2
पड़े	Pd	Cl_2
पिटाई	Pt	
आउ	Au	= +1.5V
	F_2	= +2.87

CHAPPA element

Best oxidising agent

* As we go down the group

Reactivity of Non-metal increases

Reactivity of metal decreases

* $Li \xrightarrow{Oxid} Li^+ + e^-$ $E^\circ ox = 3.04V$

$Li^+ + e^- \xrightarrow{Red} Li$ $E^\circ red = -3.04V$ (SRP)

* As we go from Li to F

strength of oxidising agent increases

→* H_2 से पहले वाली को जब SHE के साथ connect करते है तो :-

oxidation > reduction

Thats why oxidation potential लिखा जाएगा।

* But जब S.R.P लिखा जाएगा तो −ve sign लगेगा

eg Li = S.O.P = +3.04V

S.R.P = −3.04V

* H_2 से नीचे वाली को जब SHE के साथ connect करते है तो :-

Reduction > oxidation

Thats why

$Cu^{2+} + 2e^- \xrightarrow{Red} Cu$ $E^\circ red = 0.34V$

$Cu \longrightarrow Cu^{2+} + 2e^-$ $E ox = -0.34$

IMPORTAN CONCLUSION FROM E.C.S

(I) DISPLACEMENT OF METAL IONS BY METAL

Metal placed higher in E.C.S displaces metal ion (cation) Placed below them in E.C.S from their solution

$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

$Ag + CuSO_4 \longrightarrow$ NO REACTION * Ag तो Cu से नीचे है so can't displace

E.C.S मे Zn तो Cu से उपर है इसलिए Zn को जब Cu के solution CuSO4 मे डाले तो वो Cu को displace कर दिया

(II) DISPLACEMENT OF NON-METAL ION BY NON-METAL

Non-metal displaces the anion of non-metal placed above it in electrochemical sereis from their solution

$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$

$2KBr + I_2 \longrightarrow$ No reaction

(III) DISPLACEMENT OF H_2 GAS FROM H_2O BY METAL

* Metal placed above Mg in E.C.S can displace H_2 gas from cold water

* Metal from Mg to Cr can displace H_2 gas from Hot water

* Iron can displace H_2 gas from steam

(IV) DISPLACEMENT OF H^+ ION FROM ACIDIC SOLUTION OF METAL

Metal placed above Hydrogen in E.C.S displaces H^+ ion from acidic solution

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

$Ag + H_2SO_4 \longrightarrow$ No reaction

(V) STABILITY OF METAL-OXIDE DECREASES DOWN THE SEREIS

If electropositive character of metal is more then the stability of metal oxide will be more so we can say that Down the sereis stability of metal oxide decreases

(VI) oxides of metals which are placed below (Cu) are unstable and easily reduces to metal when heated

$[CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow]$

Qsn On the basis of following chemical reaction decide position of Metal ABCDE and H2 in E.C.S

(a) $A + H_2SO_4 \longrightarrow ASO_4 + H_2$

(b) $C + ACl_2 \longrightarrow CCl_2 + A$

displaced

(c) $C + ECl_2 \longrightarrow$ NO RXN

donot displace

(d) $D + H_2SO_4 \longrightarrow$ NO RXN

(E) $D + 2BCl \longrightarrow DCl_2 + 2B$

E
C
A
H_2
D
B
$\downarrow$

SRP↑

Qsn Arrange these metals in increasing order of their reducing power

METAL	E°(SRP/SCP)
A	−1.5V
B	−2.3V
C	+1.5V
D	+0.1V
E	−0.1V

* Lowest value of SRP will having highest Reducing Power and weakest oxidising agent

$C < D < E < A < B$

Qsn W.O.F is strongest oxidising agent and reducing agent

(a) Li Ag Cu Zn SR.A = Li Best O.A = Ag

(b) Li^+ Ag Cu^{+2} Zn^{+2} S.R.A = Ag Best O.A = Cu^{+2}

ELECTROCHEMICAL CELL

There are two types of electrochemical cell

(I) Galvanic cell OR VOLTAIC CELL

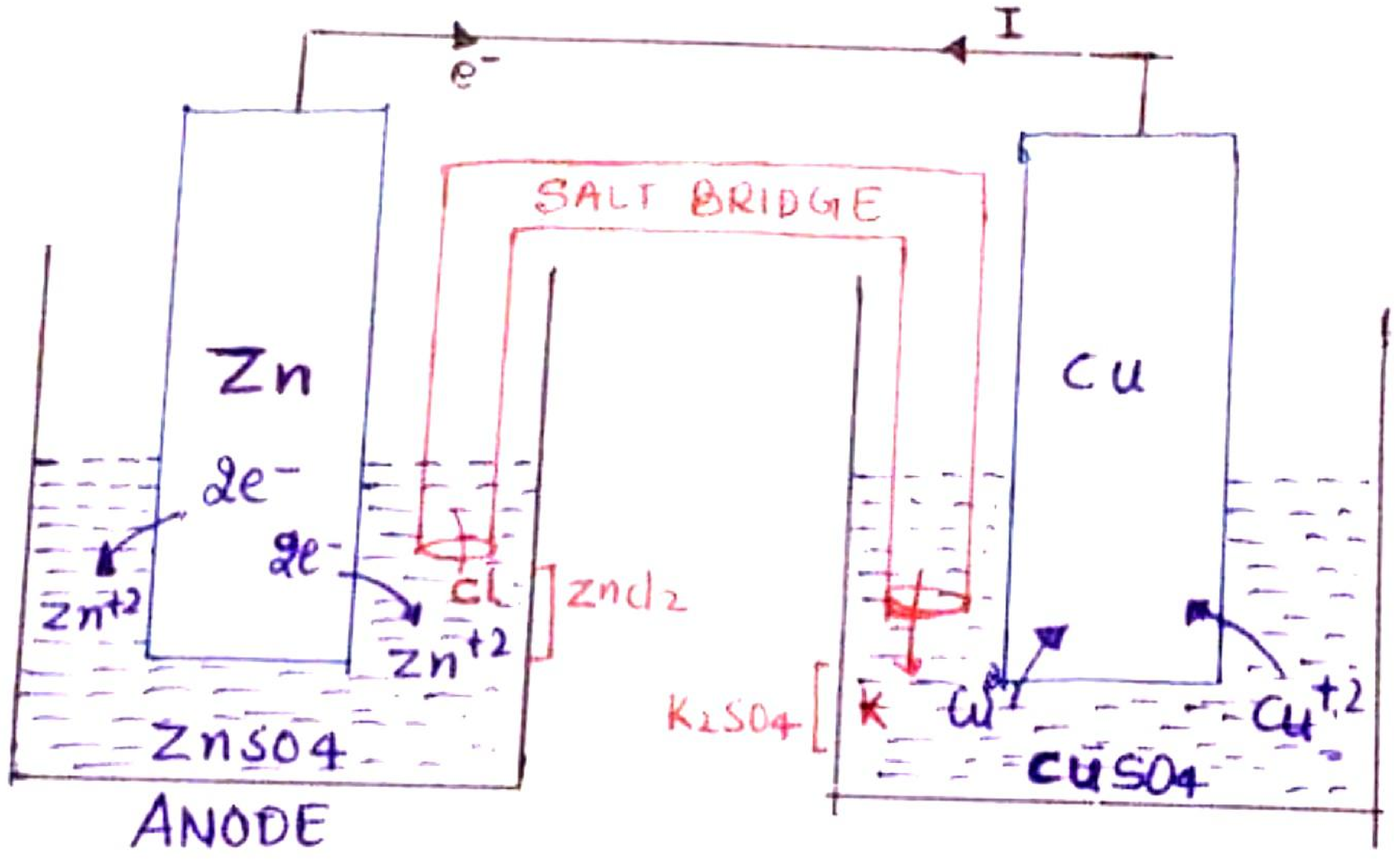
(ii) ELECTROLYTIC CELL

(I) GALVANIC CELL OR VOLTAIC CELL

* A device which convert chemical energy into electrical energy is called galvanic cell.

* अगर Galvanic cell मे Anode को Zn electrode से बनाया जाए और cathode को copper से बनाया जाए तब galvanic cell DANIEL CELL कहलाएगा।

* Daniel ने जो cell बनाया था उसमे Daniel ने Cu को Cathode बनाया और dipped किया था $CuSO_4(aq)$ solⁿ मे Zn को anode बनाया और dipped किया था $ZnSO_4(aq)$ में



OXIDATION HALF CELL REACTION

$$Zn \longrightarrow Zn^{+2} + 2e^- \quad \text{—(i)}$$

REDUCTION HALF CELL REACTION

$$Cu^{+2} + 2e^- \longrightarrow Cu \quad \text{—(ii)}$$

COMPLETE CELL REACTION

Reduction because Cu की S.R.P ज्यादा

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$$

Oxidation

CELL REPRESENTATION = $Zn_{(s)}/Zn^{+2}_{(aq)} // Cu^{+2}_{(aq)}/Cu_{(s)}$

Following observations are observed during cell Reaction

(i) During cell reaction electric current flow from Cathode to anode in external circuit whereas current flows from anode to cathode in internal circuit

(ii) During cell reaction weight of anodic terminal decreases whereas weight of cathodic terminal increases

(iii) During cell reaction concentration of ion in anodic solution increases whereas concentration of Cu^{+2} ion in cathodic solution decreases

(iv) cell reactions are spontaneous and exothermic therefore during cell reaction temperature of Cell is increase.

SALT-BRIDGE

(i) it is a glassed U-tube which is filled by inert Compound like KCl, KNO_3, NH_4NO_3 etc with gelating or agar-agar to convert into semi-solid form or past form by which rate of diffusion of ion decreases. Cotton plug is also plugged at the end of salt bridge

(ii) It connect two different electrolytic solution and Completes the cell circuit

(iii) it mentain electrolytical neutrality of both electrolytic solution by supplying Cl^- in anodic and K^+ in cathodic

(iv) it prevents liquid-liquid junction potential asn. what is liquid-liquid junction potential

Ans when two different electrolytic solutions are placed in direct contact with each other then a junction of potential is developed which is called as liquid-liquid junction potential and its nature is always such that it opposses the e.m.f of cell

⇒ According to thermodynamics ΔG is equal to useful work by the system

$$\Delta G = -W_{useful} = -W_{electrical}$$

$$\Delta G = -Q\,dv = -nF \times E_{cell}$$

$$\boxed{\Delta G = -nFE_{cell}}$$

n = no of moles of transferred e^-
F = Faraday constant = 96500 Cb

$$\Delta G_{Cell} = (\Delta G_{oxidation})_{Anode} + (\Delta G_{reduction})_{cathode}$$

$$-nFE_{cell} = (-nFE_{oxi})_{Anode} + (-nFE_{red})_c$$

$$-nFE_{cell} = -nF(E_{ox})_A + (-nFE_{red})_c$$

$$-\cancel{nF}E_{cell} = -\cancel{nF}(E_{ox})_A + (E_{red})_c$$

$$\boxed{\begin{aligned} E_{cell} &= (E_{oxid})_A - (E_{red})_c \\ E_{cell} &= (E_{red})_c - (E_{red})_A \\ E_{cell} &= (E_{ox})_A - (E_{ox})_c \end{aligned}} \rightarrow \because SRP = -SOP$$

IMPORTANT

⇒ if conditions are standard

$$E^\circ_{cell} = (E^\circ_{red})_c - (E^\circ_{oxi})_A$$

$$\Delta G^\circ = -nFE_{cell}$$

⇒ If cell reaction is spontaneous = $\Delta G = -ve$ $E_{cell} = +ve$

⇒ If cell reaction is in equillibrium = $\Delta G = 0$ $E_{cell} = 0$

$\Delta G \neq 0$ $E_{cell} \neq 0$

Qsn Pb rod was dipped in $Pb(NO_3)_2$ solution and Ag rod was dipped in $AgNO_3$ solution then write down Cell reaction and cell representation

Ans $Pb \longrightarrow Pb(NO_3)$ = cathode

$Ag \longrightarrow Ag(NO_3)$ = Anode

$$Pb \longrightarrow Pb^{+2} + \cancel{2e^-}\ ] \times 1$$

$$Ag^+ \cancel{+e^-} (2)\rightarrow Ag \quad] \times 2$$

$$\underline{\overline{Pb + 2Ag^+ \longrightarrow Pb^{+2} + 2Ag}}$$

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

Qsn For the cell $Al/Al^{+3} // Ni^{+2}/Ni$

$E^\circ Ni/Ni^{+2} = +0.25\,V$

$E^\circ Al^{+3}/Al = -1.66\,V$

Then find out (i) cell reaction (ii) E°cell (iii) ΔG°cell

(i) $Al \longrightarrow Al^{+3} + 3e^-\ ] \times 2$

$Ni^{+2} + 2e \rightarrow Ni \quad] \times 3$

$$\underline{\overline{2Al + 3Ni^{+2} \longrightarrow 2Al^{+3} + 3Ni}}$$

(ii) $E^\circ_{cell} = (E^\circ red)_C - (E^\circ red)_A$

$= -.25 - (-1.66)$

$= +1.41$ volt

(iii) $\Delta G^\circ = -nF E^\circ_{cell}$

$\Delta G^\circ = -6 \times 96500\,Cb \times 1.41\,J$

$\Delta G^\circ = -816390\,J$

-ve sign of ΔG° shows that reaction is spontaneous

SPECIAL NOTES

- Value of electrode potential doesnot change when it is multiplied/devided by a co-efficient because electrode potential is an intrinsic property
- value of electrode potential doesnot depends on size of metallic rod
- if E° for two different electrode are given and we want to calculate E° for 3rd electrode by using these two electrode then firstly convert E° into ΔG° and then apply HEISS law of energetics

Qsn $E^\circ_{OCl^-/Cl^-} = x$

$E^\circ_{Cl^-/\frac{1}{2}Cl_2} = y$

$E^\circ_{OCl^-/\frac{1}{2}Cl_2} = ?$

Ans $OCl^+ + 2e \longrightarrow Cl^- \qquad \Delta G^\circ = -2Fx$

$-2+x=-1$

$x=+1$

$Cl^- \longrightarrow \frac{1}{2}Cl_2^0 + e^- \qquad \Delta G_2^\circ = -Fy$

$OCl^- + e \longrightarrow \frac{1}{2}Cl_2^0 \qquad \Delta G_3^\circ = -1F \times E_3^\circ$

Eqn (1) + Eqn (2) = Eqn (3)

$\Delta G^\circ + \Delta G_2^\circ = \Delta G_3^\circ$

$-2Fx - Fy = -F \times E_3^\circ$

$-(2x+y) = -2x-y = -E_3^\circ$

$$\underline{E^\circ = 2x+y}$$

Qsn E° $Fe^{+2}/Fe = 0.26\,V$

E° $Fe^{+3}/Fe = 0.76\,V$

E° $Fe^{+2}/Fe^{+3} = ?$

Ans $Fe^{+2} + 2e^- \longrightarrow Fe \quad \Delta G_1^\circ = -2F \times 0.26$

$Fe^{+3} + 3e^- \longrightarrow Fe \quad \Delta G_2^\circ = -3F \times 0.76$

$Fe^{+2} \longrightarrow Fe^{+3} + e \quad \Delta G_3^\circ = -1F \times E_3$

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

$\Delta G_1^\circ - \Delta G_2^\circ = \Delta G_3^\circ$

$-0.52F + 2.28 = -F \times E_3$

$+1.76 = -E_3$

$\boxed{E_3 = -1.76}$

HOME WORK

VVI

E° $Cu^{+2}/Cu^{+} = +0.15V$

E° $Cu^{+2}/Cu = +0.34V$

E° for disproportion of $Cu^{+} = ?$

Qsn Magnitude of SRP of two metals x and y are

$Y^{+2} + 2e^- \longrightarrow Y$ $|E^\circ| = 0.34$ volt

$X^{+2} + 2e^- \longrightarrow X$ $|E^\circ| = 0.25$ volt

When x and Y are connected then electron crossed from x to Y and if x is connected to SHE then electron crossed from x to SHE then calculate E°cell for the cell made up by x and y

Ans

$$\underset{(-0.25)}{\overset{\text{ANODE}}{X}} \longrightarrow \underset{(+0.34\,V)}{\overset{\text{CATHODE}}{Y}} \qquad \underset{(-0.25\,V)}{\overset{\text{ANODE}}{X}} \longrightarrow \overset{\text{CATHODE}}{\text{SHE}}$$

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

$$E^\circ_{cell} = 0.34 + 0.25$$

$$\boxed{E^\circ_{cell} = 0.59}$$

Qsn The Efficiency of a hypothetical cell is 84%. which involves the reaction

$$A_{(s)} + B^{+2}_{(aq)} \longrightarrow A^{+2}_{(aq)} + B_{(s)} \qquad \Delta H = -285\,KJ$$

Then calculate E° of cell

Ans

$$\text{Efficiency} = \frac{\Delta G^\circ}{\Delta H^\circ} = \frac{-nFE_{cell}}{\Delta H}$$

$$0.84 = \frac{-2 \times 96500 \times E^\circ_{cell}}{-285 \times 10^3}$$

$$E^\circ_{cell} = \frac{0.84 \times -285 \times 10^3}{-2 \times 96500}$$

NERST EQUATION

- We have assumed in the previous section that the concentration of the species involved in the reaction is unity. This need not be always true
- Nerst showed that for the electrode reaction

$$M^{n+}_{(aq)} + ne^- \longrightarrow M(s)$$

- The electrode potential at any concentration measured with respect SHE canbe represented by

$$\boxed{E = E^\circ - \frac{RT}{nF} \log_e \frac{[\text{Product}]}{[\text{Reactant}]}}$$

E = Electrode potential (volt)
E° = Standard electrode potential
R = Gas constant ($8.314\ J mol^{-1} K^{-1}$)
T = Temperature (kelvin)
n = number of moles of e^- transferred
F = Faraday (96500 cb/mole)
$[\ ]$ = Active mass or concentration

$$\frac{[P]}{[R]} = Q$$

Generally in question ($T = 298$ K) given then:-

$$\frac{2.303\,RT}{F} = \frac{2.303 \times 8.314\,J\,mol^{-1}K^{-1} \times 298}{96500} = 0.591$$

$$\boxed{E = E^\circ - \frac{0.591}{n} \log_{10} \frac{[P]}{[R]}}$$

This formula valid only at 298 K

APPLICATION OF NERST EQUATION

(I) To calculate electrode potential
(II) To calculate electrode potential of H_2 electrode
(III) To calculate e.m.f of cell

[I] TO CALCULATE ELECTRODE POTENTIAL

if only electrode potential given then take SRP

eg :- $E(M^{+n}/M) = ?$ Red

$$M^{n+}_{(aq)} + ne^- \xrightarrow{Red} M_{(s)}$$

$$E_{red} = E^\circ_{red} - \frac{0.591}{n} \log_{10} \frac{[M] \rightarrow 1}{[M^{n+}]}$$ 1 Because solid

$$E_{red} = E^\circ_{red} + \frac{0.591}{n} \log [M^{n+}]$$

for Metal electrode

if $[M^{+n}] \uparrow \Rightarrow E_{red} \uparrow \Rightarrow E_{oxi} \downarrow$

if $[M^{n+}] \downarrow \Rightarrow E_{red} \downarrow \Rightarrow E_{oxi} \uparrow$

Qsn $E(M/M^{n+}) = ?$ oxi

$$M \longrightarrow M^{n+} + ne^-$$

Here oxidation so take formula of oxidation

$$E_{oxi} = E^\circ_{oxi} - \frac{0.0591}{n} \log_{10} \frac{[M^{n+}]}{[M] \rightarrow 1}$$ ∵ for solid active mass = 1

Qsn Calculate electrode potential of at copper electrode dipped in a 0.1M solution of $CuSO_4$ at 25°c. The standard electrode potential Cu^{2+}/Cu is 0.34 volt at 298 K

Ans $CuSO_4$ is a salt and α is not given means 100% ionisation occur

$$\underset{0.1M}{CuSO_4} \longrightarrow \underset{0.M}{Cu^{+2}} + SO_4^{-2}$$

$$[Cu^{+2}] = C\alpha = 0.1 \times \frac{100}{100} = 0.1$$

$$Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu(s)$$

$$E_{red} = E^\circ_{red} - \frac{0.591}{2} \log_{10} \frac{[Cu] \rightarrow 1}{[Cu^{+2}]}$$

(∵ for solid active mass is 1)

$$= 0.34 - \frac{0.6}{2} \log_{10} \frac{1}{0.1} = 0.34 - 0.03 = 0.31 \text{ volt}$$

Qsn A piece of Zn metal is dipped in a 0.1M solution of Zn salt. The salt is dissociated to the extent of 20%. Calculate the electrode potential of Zn^{+2}/Zn.
(Given $E^\circ(Zn^{+2}/Zn) = -0.76$ volt)

Here α is given so salt will not dissociate 100% it will dissociate only upto 20%.

$C = 0.1M \quad [Zn^{2+}] = C\alpha$

$$[Zn^{+2}] = 0.1 \times 20\% = 0.1 \times \frac{20}{100} = 0.02M$$

$$Zn^{+2}(aq) + 2e^- \longrightarrow Zn$$

$$E_{red} = E^\circ_{red} - \frac{0.0591}{n} \log_{10} \frac{[Product]}{[reactant]}$$

$$= -0.76 - \frac{0.0591}{2} \log_{10} \frac{[Zn] \rightarrow 1}{[Zn^{+2}]}$$

(∵ for solid active mass=1)

$$= -0.76 - 0.03 \log_{10} \frac{1}{0.02}$$

$$= -0.76 - 0.03 \log_{10} \boxed{\frac{100}{2}} \Rightarrow 50 \quad \Rightarrow \underline{-0.811 \text{ volt}}$$

[II] TO CALCULATE ELECT. POTENTIAL OF H_2 ELECTR.

$$2H^+ + 2e^- \longrightarrow H_2(g)$$

$$E_{red} = E^\circ_{red} - \frac{0.0591}{2} \log \frac{[P_{H_2}]}{[H^+]^2}$$

* In Nerst equation concentration term is replaced by partial pressure of gas (Atmospheric)

* Here log $[P_{H_2}]$ is Pressure while log $\frac{1}{[H^+]^2}$ is Concentration मगर ये गलत नहीं है। ये फिर भी सही है क्यों कि log एक unitless है। इसे replace किया जा सकता है।

Qsn Calculate electrode potential of following electrode when pH of acidic solution is 2

$$HCl / H_2(10\,atm) / Pt$$

$$\downarrow$$

$$Cl^- + H^+ / H_2(10\,atm) / Pt \qquad [H^+] = 10^{-pH} = [10^{-2}]$$

Reduction

$$2H^+ + 2e^- \longrightarrow H_2(gas)$$

$$E_{red} = E^\circ_{red} - \frac{0.0591}{2} \log \frac{[P_{H_2}]}{[H^+]^2}$$

$$E_{red} = 0 - \frac{0.06}{2} \log \boxed{\frac{[10]}{[10^{-2}]^2}} \; 10^5$$

$$= -0.03 \times 5$$

$$= \underline{-0.15 \text{ volt}}$$

Qsn calculate pH of following Half cell reaction Given (Eoxi = 0.25V)

$$Pt / H_2(g) / HCl$$

Ans $$H_2 \xrightarrow{oxid} 2H^+ + 2e^-$$

$$E_{oxi} = \underset{0}{\cancel{E_{oxi}}} - \frac{0.0591}{2} \log \frac{[H^+]^2}{\cancel{[PH_2]} \to 2}$$

$$E_{oxi} = - \frac{0.0591}{\cancel{2}} \times \cancel{2} \log [H^+]$$

$$\frac{E_{oxi}}{0.0591} = - \log [H^+]$$

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

$$pH = \frac{0.25}{0.6} = 4.16$$

NOTE :

(i) Value of electrode potential for a given electrode doesnot change when reaction is multiplied or devided by co-efficient

$$A_2 + 2e^- \longrightarrow 2A^- \qquad E = x \text{ volt}$$

$$\frac{1}{2} A_2 + e^- \longrightarrow A^- \qquad E = ?$$

Ans = x volt (∵ No change)

(ii) Value of electrode potential doesnot depends on size of electrode and amount of solution but depends on concentration of solution. It is an intensive property

[III] TO CALCULATE e.m.f OF THE CELL

$$\boxed{E_{cell} = \text{OXI Potential of Anode} + \text{Red Pote of cathode}}$$

$$\boxed{E_{cell} = E_{cathode} - E_{anode}}$$

At Standard condition

$$\boxed{E^\circ_{cell} = E^\circ_C - E_A}$$

Stand. Reduction potential

eg $1 \times (Cu/Cu^{+2}_{(aq)}) // (Ag^+_{(aq)}/Ag) \times 2$ $E_{cell} = ?$

Anode $Cu \longrightarrow Cu^{+2} + 2e \,] \times 1$

Cathode $Ag^+ + e^- \longrightarrow Ag \quad] \times 2$

Cell reaction

$$Cu + 2Ag^+ \xrightarrow{n=2} Cu^{+2} + 2Ag$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[Cu^{+2}][Ag]^2}{[Ag^+]^2 [Cu]}$$

when cell is formed by two metal electrodes

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[\text{Anode}]^x}{[\text{Cathode}]^y}$$

Qsn Calculate Ecell = ?

$Al/Al^{+3}(10^{-2}M) \| Co^{2+}(10^{-1}M)/Co$

Given

$E^\circ\ Al^{+3}/Al = -1.66V$

$E^\circ\ Co^{+2}/Co = -0.28V$

Ans $2\times(\overset{A}{Al}/\overset{B}{A^{+3}}(10^{-2}M) \| 3\times(Co^{+2}\overset{C}{(}10^{-2}M)/Co$

$2\times3e^- = 6e$ $\quad 3\times2e^- = 6e^-$ $\quad n = 6e^-$

$E^\circ\ \underset{\text{Red}}{\overset{\frown}{Al^{+3}/Al}} = -1.66V$,

$E^\circ\ \underset{\text{Red}}{\overset{\frown}{Co^{+2}/Co}} = -0.28V$

$E^\circ cell = E^\circ_C - E^\circ_A$ Anode हो या cathode हो दोनो की SRP put करनी है।

$E^\circ cell = (Co) - (Al)$

$E^\circ cell = -0.28 - (-1.66)$

$E^\circ cell = 1.38V$

$$Ecell = E^\circ cell - \frac{0.0591}{6}\log\frac{[Al^{+3}]^2}{[Co^{2+}]^3}$$

$$= 1.38 - 0.01\log\frac{[10^{-2}]^2}{[10^{-1}]^3}$$

$$= 1.38 - 0.01\log 10^{-1}$$

$$= 1.38 + 0.01$$

$$= 1.39\ \text{volt}$$

(Anode) A — (Bridge) B — (Cathode) C

Qsn $Pt_{(s)} / Br_2(l) / Br^- (0.01M) \,||\, H^+ (0.01M) / H_2(g) (1 bar) / Pt_{(s)}$

what is Ecell = ?

Given - ($E^\circ Pt / Br_2 / Br^- = 1.09 V$)

Ans * $Pt(s)$ के rod पर Br^- को absorb करा कर Br^- के solution मे dipped किया

* $Pt(s)$ के rod पर H_2 absorb कर कर H^+ के solution मे dipped किया

$$E^\circ cell = E^\circ_C - E^\circ_A$$
$$= 0 - 1.09$$
$$= -1.09 \text{ Volt}$$

Anode $2Br^- \xrightarrow{oxi} Br_2 + 2e^-$

Cathode $2H^+ + 2e^- \xrightarrow{Red} H_2$

cell reaction $2HBr^- + 2H^+ \longrightarrow Br_2 + H_2$

$$E\,cell = E^\circ cell - \frac{0.0591}{2} \log \frac{[Br_2]\,[PH_2]}{[Br^-]^2\,[H^+]^2}$$

$$= -1.09 - 0.03 \log \boxed{\frac{1}{[10^{-2}]^2\,[10^{-2}]^2}} \to 10^{-8}$$

$$= -1.09 - 0.03 \times 8$$

$$= -1.33V$$

⇒ Work done by a system = ↓ in Free energy of system ($-\Delta G$)

⇒ Useful work obtained by cell = in the form of electrical energy

$$W = Q \times V$$

$$\boxed{W = nF \times E_{cell}}$$

⇒ $W = nF E_{cell} = -\Delta G$

⇒ $\boxed{\Delta G = -nFE}$ n = no of moles of transferred electrons

* At Standard condition

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

CASE - I

if $E_{cell} = +ve$ OR $\Delta G = -ve$

then given cell reaction is spontaneous

CASE - II

if $E_{cell} = -ve$ OR $\Delta G = +ve$

Then given cell reaction is non-spontaneous But It will be spontaneous in reverse condition

CASE - III

if $E_{cell} = 0$ OR $\Delta G = 0$

Then given cell reaction will be in equillibrium

Qsn Find spontaneoty of reaction in Daniel cell reaction

Ⓐ Ⓑ Ⓒ

$Zn / Zn^{+2}(1M) \, || \, Cu^{+2}(1M) / Cu$

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

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

Ans Cell reaction $Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$

$$E^\circ cell = E^\circ_C - E^\circ_A$$

$$= (Cu) - (Zn)$$

$$= 0.34 - (-0.76V)$$

$E^\circ cell = +1.1$ volt OR $\Delta G = -ve$

$E^\circ cell = +ve$ means spontaneous

Ⓐ Ⓑ Ⓒ

Qsn $Cu / Cu^{2+}(1M) \, || \, Zn^{2+}(1M) / Zn$

Ans Cell reaction : $Cu + Zn^{+2} \longrightarrow Cu^{2+} + Zn$

$$E^\circ cell = \underset{(Zn)}{E^\circ_C} - \underset{(Cu)}{E^\circ_A}$$

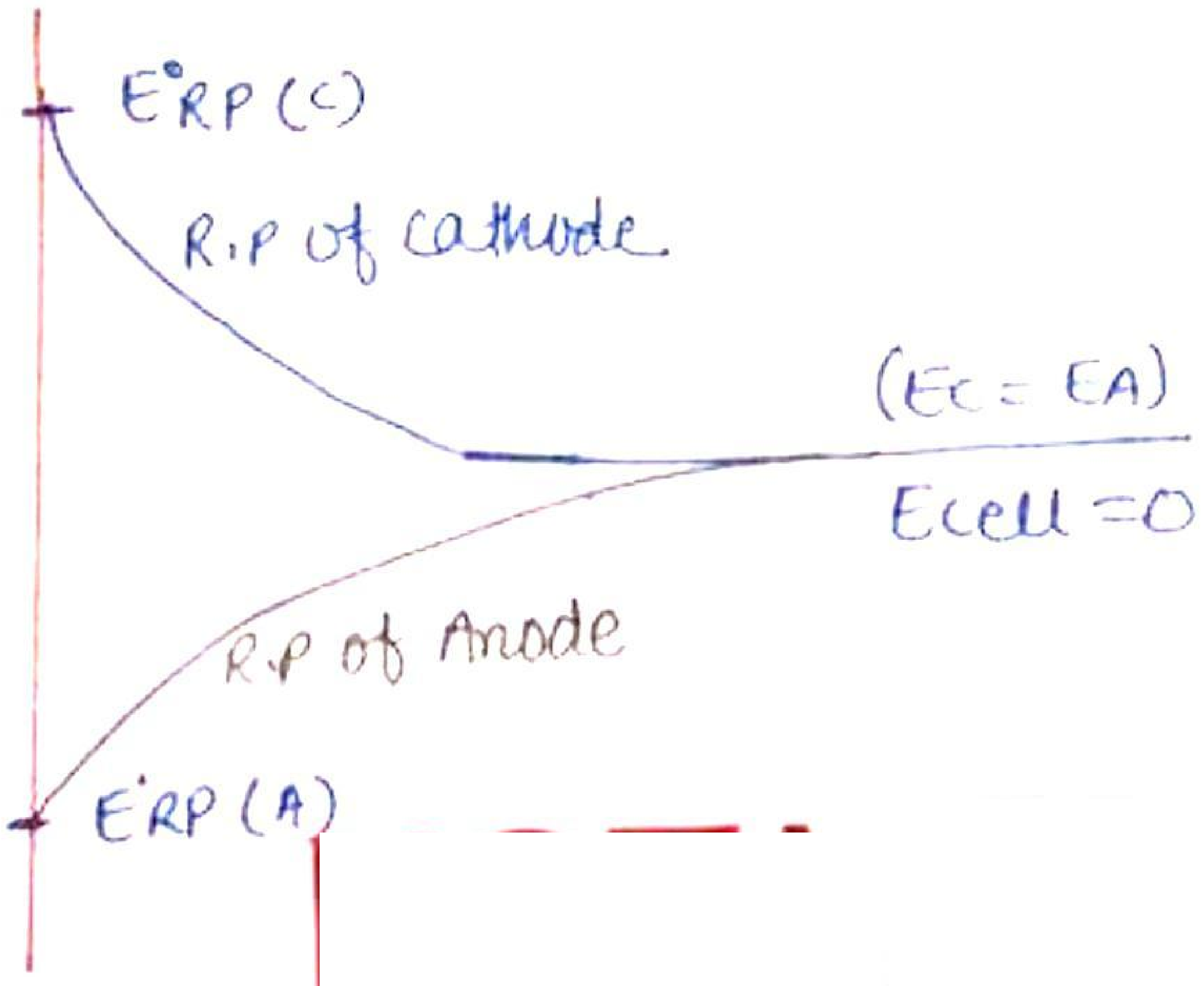
$$= -0.76 - (+0.34)$$

$E^\circ cell = -1.1$ volt OR $\Delta G = +ve$

$E^\circ cell = -ve$ means non-spontaneous.

CONCEPT OF EQUILLIBRIUM

When cell reaction occurs concentration of ions in Cathode solution decreases therefore its reduction Potential also decreases but concentration of ions in Anode solution increases therefore its reduction Potential also increases.



* $E^\circ_{cell} = E_{cath} - E_{Anode}$

$E^\circ_{cell} = 0$

$\Delta G = 0$

* $\Delta G = 0$ cell rxn is equillib

According Nerst equation

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[P]}{[R]} = \frac{[\text{Anode}]\uparrow}{[\text{Cathode}]\downarrow} \Rightarrow Q$$

At equillibrium $E_{cell} = 0$, $Q = K$ (eq^m constt for cell Rxn)

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln K$$

$$0 = E^\circ_{cell} - \frac{RT}{nF} \ln K$$

VVI

$$\boxed{E^\circ_{cell} = \frac{RT}{nF} \log_e K} \qquad \boxed{E^\circ_{cell} = \frac{0.0591}{n} \log_{10} K}$$

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

$$\Delta G^\circ = -nF \left\{ \frac{RT}{nF} \log_e K \right\}$$

$$\boxed{\Delta G^\circ = -2.303\, RT \log_{10} K}$$

Qsn. Calculate equillibrium constant for the reaction

$Fe^{+2} + Ce^{+4} \longrightarrow Ce^{+3} + Fe^{+3}$

Given ⇒ $E^\circ_{Ce^{4+}/Ce^{3+}} = 1.45V$ RED

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

RED

Ans

$E^\circ cell = E^\circ_C - E^\circ_A$

$= (Ce) - (Fe)$

$= 1.45 - 0.67$

$= 0.78V$

$E^\circ cell = \frac{0.0591}{1} \log_{10} K$

$0.78 = 0.06 \log_{10} K$

$\log_{10} K = 13$ $\boxed{K = 10^{13}}$

Qsn In which direction the reaction is proceed spontaneous at following concentration of Ion participating in rxn

$2Hg(l) + 2Ag^{+}(aq) \rightleftharpoons 2Ag(s) + Hg_2^{+2}(aq)$

(I) $[Ag^{+}] = 10^{-4} M$; $[Ag^{+2}] = 10^{-1} M$

(II) $[Ag^{+}] = 10^{-1} M$; $[Hg_2^{2+}] = 10^{-4} M$

Given

$E^\circ_{Hg_2^{+2}/Hg} = 0.79V$

$E^\circ_{Ag/Ag} = 0.80V$

Ans

$E^\circ cell = E^\circ_C - E_A$

$E^\circ cell = 0.80 - 0.79$

$E^\circ cell = 0.1V$

$$\boxed{\begin{aligned} Ecell &= E^\circ cell - \frac{0.591}{2} \log \frac{[Hg_2^{+2}]}{[Ag^{+}]^2} \\ &= 0.01 - 0.03 \log \left(\frac{[10^{-1}]}{(10^{-4})^2}\right) \Rightarrow 10^{+7} \\ &= 0.01 - 0.03 \times 7 = -0.20 \text{ Volt} \end{aligned}}$$

(I) $Ecell = -0.20V$; $\Delta G = +ve$ (Right to Left)

(II) $Ecell = 0.07V$; $\Delta G = -ve$ (Left to Right)

Qsn Given standard electrode potential in 1M acidic soln

$E^\circ(Fe^{2+}/Fe) = -0.4V$

$E^\circ(Fe^{3+}/Fe^{2+}) = 0.8V$

$E^\circ(Mn^{2+}/Mn) = -1.2V$

$E^\circ(Mn^{3+}/Mn^{+2}) = 1.5V$

(i) Comment on relative stability of +2 and +3 oxidation state of Iron and mangnese

(ii) which of the two metal is more easily to oxidise (+2) state

Ans * $E^\circ(\underset{\curvearrowright}{Fe^{2+}/}Fe) = -0.4V$

$E^\circ = -ve$ and $\Delta G = +ve$ thats why

Fe^{+2} को Fe मे नही जाना चाहेगी बल्कि Fe को Fe^{2+} मे जाना चाहेगी

* $E^\circ(Mn^{+2}/Mn) = -1.2V$

$E^\circ = -ve$ and $\Delta G = +ve$ thats why

Mn^{+2} को Mn मे नही जाना चाहेगी But Mn तो Mn^{+2} मे जाना चाहेगी

$\Rightarrow$ Fe(II) > Fe(III)

Mn (II) > Mn (III)

* $Fe \xrightarrow{oxi} Fe^{+2} + 2e$ $\left.\begin{array}{l} E^\circ_{ox} = +0.4 \\ \Delta G^\circ_{ox} = -ve \end{array}\right]$ spontaneous

$Fe^{+3} \xrightarrow{Red} Fe^{+2} + 2e$

$Mn \xrightarrow{oxi} Mn^{2+}$

$Mn^{3+} + e \xrightarrow{Red} Mn^{2+}$

Qsn $E^\circ(Fe^{3+}/Fe^{2+}) = ?$

Given $E^\circ(Fe^{3+}/Fe) = -0.036V$

$E^\circ(Fe^{+2}/Fe) = -0.440V$

Ans $Fe^{+3} + 3e^- \longrightarrow Fe \quad E_1^\circ = -0.036V$

$Fe^{2+} + 2e^- \longrightarrow Fe \quad E_2^\circ = -0.440V$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}; \quad E_3 = ?$

Funda:

Since E° is an intrinsic property इसलिए पहले हम E° को ΔG° मे convert करेगे क्यो कि ΔG° is an extensive property means ΔG° is additive. now Solve the equation

$Fe^{3+} + 3e^- \longrightarrow Fe \quad E_1^\circ = -0.036V \qquad \Delta G_1^\circ = -n_1FE_1^\circ$

$Fe^{2+} + 2e^- \longrightarrow Fe \quad E_2^\circ = -0.440V \qquad \Delta G_2^\circ = -n_2FE_2^\circ$

$Fe^{3+} + e^- \longrightarrow Fe^{+2} \quad E_3 = ? \qquad \Delta G_3^\circ = -n_3FE_3^\circ$

equation ① − equation ② = equation ③

$E_1^\circ - E_2^\circ = E_3^\circ \Rightarrow$ × Because E° is an intensive (Non-additive)

$$\Delta G_1^\circ - \Delta G_2^\circ = \Delta G_3$$

$$-nFE_1^\circ - (-n_2FE_2^\circ) = -n_3FE_3^0$$

$$-\cancel{F}(n_1E_1^\circ - n_2E_2) = -\cancel{F}(n_3E_3)$$

$$n_1E_1^\circ - n_2E_2^\circ = n_3E_3^\circ$$

$$3 \times 0.036 - 2(-0.440) = 1 \times E_3^\circ$$

$$\underline{E_3^\circ = 0.772 \text{ volt}}$$

Qsn $E^\circ (MnO_4^- / MnO_2) = ?$

Given $E^\circ (MnO_4^- / Mn^{+2}) = 1.51V$

$E^\circ (MnO_2 / Mn^{+2}) = 1.23V$

Ans $\overset{+7}{MnO_4^-} \xrightarrow{n_1=5} \overset{+2}{Mn^{2+}}$; $E_1^\circ = 1.51V$

$\overset{+4}{MnO_2} \xrightarrow{n_2=2} \overset{+2}{Mn^{2+}}$; $E_2^\circ = 1.23V$

$\overset{+7}{MnO_4^-} \xrightarrow{n_3=3} \overset{+4}{MnO_2}$; $E^\circ = ?$

Eqn ① − eqn ② = Eqn ③

$n_1 E_1^\circ - n_2 E_2^\circ = n_3 E_3^\circ$

$E_3 = 1.69$ volt

Qsn Cu^+ ion not stable in aquas solution because of disproportion reaction. calculate E° for dispropo reaction.

Given $E^\circ (Cu^{2+}/ Cu^+) = 0.15V$

$E^\circ (Cu^{2+}/ Cu) = 0.34V$

Ans Disproportion of Cu

$Cu^+ + \cancel{e^-} \xrightarrow{Red} Cu$

$Cu^+ \longrightarrow Cu^{2+} + \cancel{e^-}$

$2Cu^+ \xrightarrow{n=1} Cu + Cu^{2+}$ $E^\circ = ?$

$-2 \times$ eqn ① + eqn ② = eqn ③

$-2 \times n_1 E_1^\circ + n_2 E_2^\circ = n_3 E_3^\circ$

$E_3^\circ = 0.38V$

CONCENTRATION CELL

When two similar electrode having difference in Concentration of Ion in solution are combined then a cell is formed which is called concentration cell.

$M / M^{+n} (C_1) // M^{+n} (C_2) / M$ $\quad$ $E_{cell} = ?$

Anode = $M \longrightarrow M^{+n} + ne^-$

cathode = $M^{+n} + ne^- \longrightarrow M$

Cell Rxn = $M + M^{n+} (C_2) \longrightarrow M^{+n} (C_1) + M$

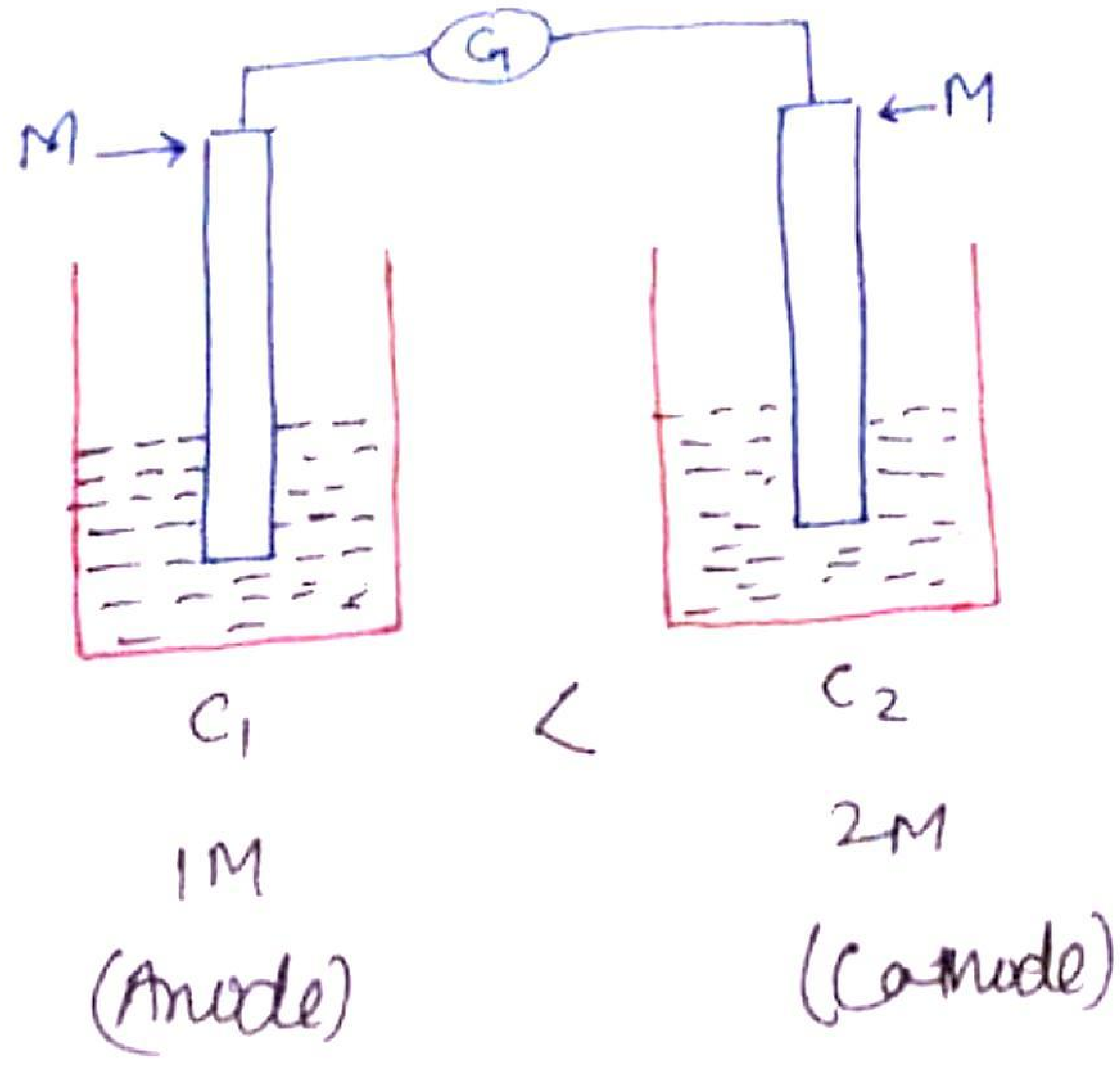
$$E_{cell} = \underset{\substack{\downarrow \\ 0}}{E^\circ_{cell}} - \frac{0.0591}{n} \log_{10} \left(\frac{C_1}{C_2} \right)$$

$(E^\circ_{cell} = E_C - E_A)$

E°_{cell} is always zero (0) for concentration cell

$$E_{cell} = \frac{+0.0591}{n} \log_{10} \left(\frac{C_2}{C_1} \right)$$

If $C_2 > C_1$ then $\left. \begin{array}{l} E_{cell} = +ve \\ \Delta G = -ve \end{array} \right]$ spontaneous reaction



Qsn $Pt / H_2 (1bar) / HA_1 || HA_2 / H_2 (1bar) / Pt$; $E_{cell} = ?$

Ans Anode = $H_2 (P_1) \xrightarrow{oxid} 2H^+ (c_1) + 2e^-$

Anode = $2H^+ (c_2) + 2e^- \xrightarrow{Red} H_2 (P_2)$

cell reaction $H_2 (P_1) + 2H^+ (c_2) \xrightarrow{n=2} 2H^+ (c_1) + H_2 (P_2)$

$$E_{cell} = \underset{0}{\cancel{E^\circ_{cell}}} - \frac{0.0591}{2} \log_{10} \frac{(c_1)^2}{(c_2)^2}$$

E°_{cell} for concentration cell = 0

$$E_{cell} = \frac{-0.0591}{2} \log\left(\frac{c_1}{c_2}\right)$$

$$E_{cell} = -0.0591 \log \boxed{\frac{(10^{-5})}{(10^{-3})}} \Rightarrow 10^{-2}$$

$$E_{cell} = +2 \times 0.0591$$

$$\boxed{E_{cell} = 0.1182V}$$

AIIMS Qsn H.W $Cu / Cu^{+2} (0.001M) || Cu^{+2} (0.1M) / Cu$

Hints concentration cell so $E^\circ_{cell} = 0$

$$E_{cell} = \underset{0}{\cancel{E^\circ_{cell}}} - \frac{0.0591}{n} \log\left(\frac{c_1}{c_2}\right)$$

$$E_{cell} = -\frac{RT}{2F} \ln \boxed{\frac{10^{-3}}{10^{-1}}} \Rightarrow 10^{-2}$$

$$\boxed{E_{cell} = \frac{-RT}{F} \ln 0.1}$$

Qsn $Pt / H_2(g) / H^+(C_1) || H^+(C_2) / H_2(g) / Pt$; $E_{cell} = ?$

Ans Anode $H_2(P_1) \xrightarrow{Oxid} 2H^+(C_1) + 2e^-$

$2H^+(C_2) + 2e^- \xrightarrow{Red} H_2(P_2)$

Cell rxn = $H_2(P_1) + 2H^+(C_2) \xrightarrow{n=2} 2H^+(C_1) + H_2(P_2)$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{(C_1)^2 (P_2)}{(C_2)^2 (P_1)} \quad \text{—— (1)}$$

CASE - I $P_1 = P_2 = 1$ bar but $C_1 \neq C_2$

$$E_{cell} = 0 - \frac{0.0591}{2} \log \frac{C_1^2}{C_2^2}$$

CASE - II if $C_1 = C_2 = 1M$ but $P_1 \neq P_2$

$$E_{cell} = 0 - \frac{0.0591}{2} \log \left(\frac{P_1}{P_2}\right)$$

if $P_1 > P_2$ then $E_{cell} = +ve$

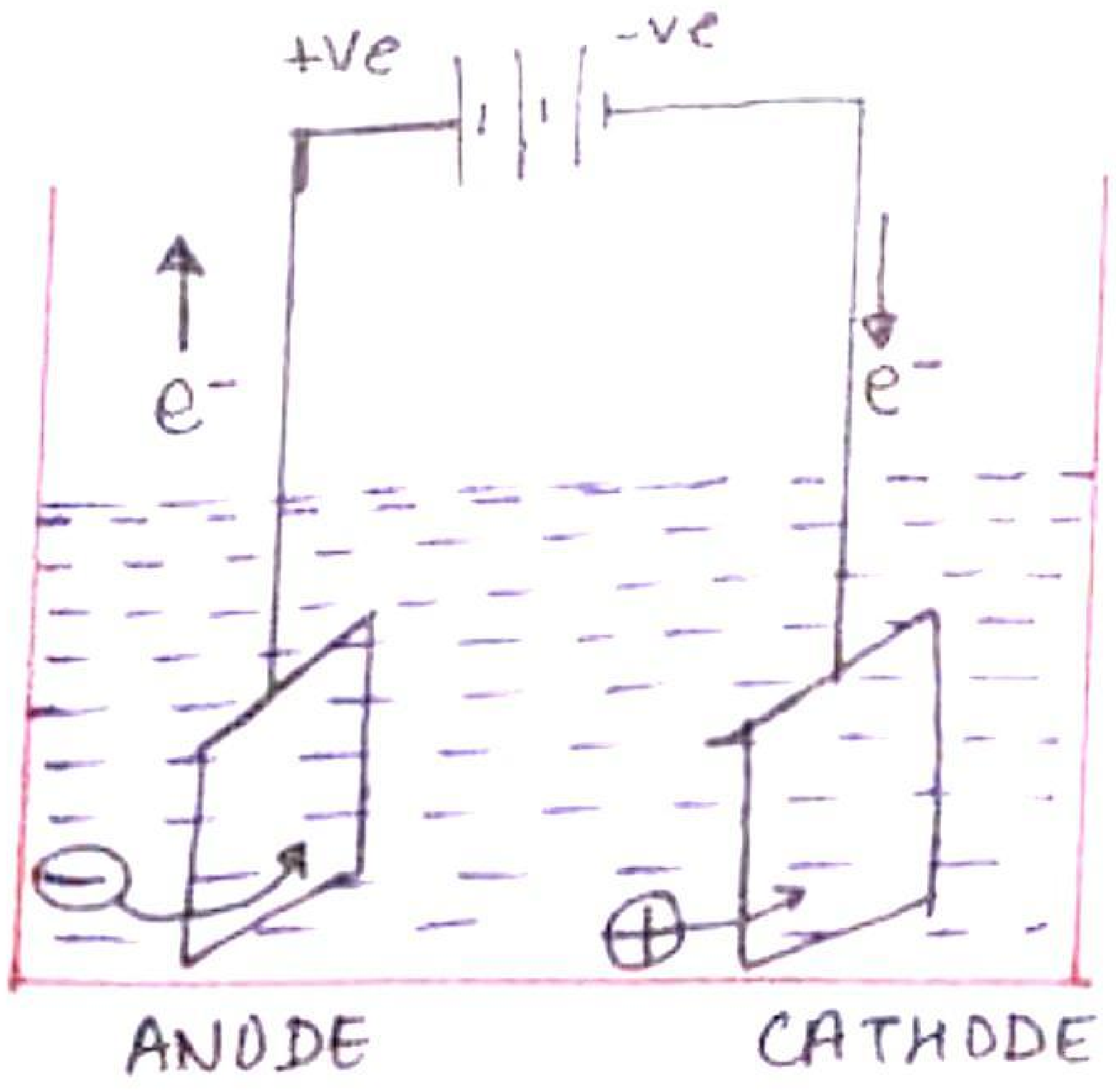
$\Delta G = -ve$ spontaneous

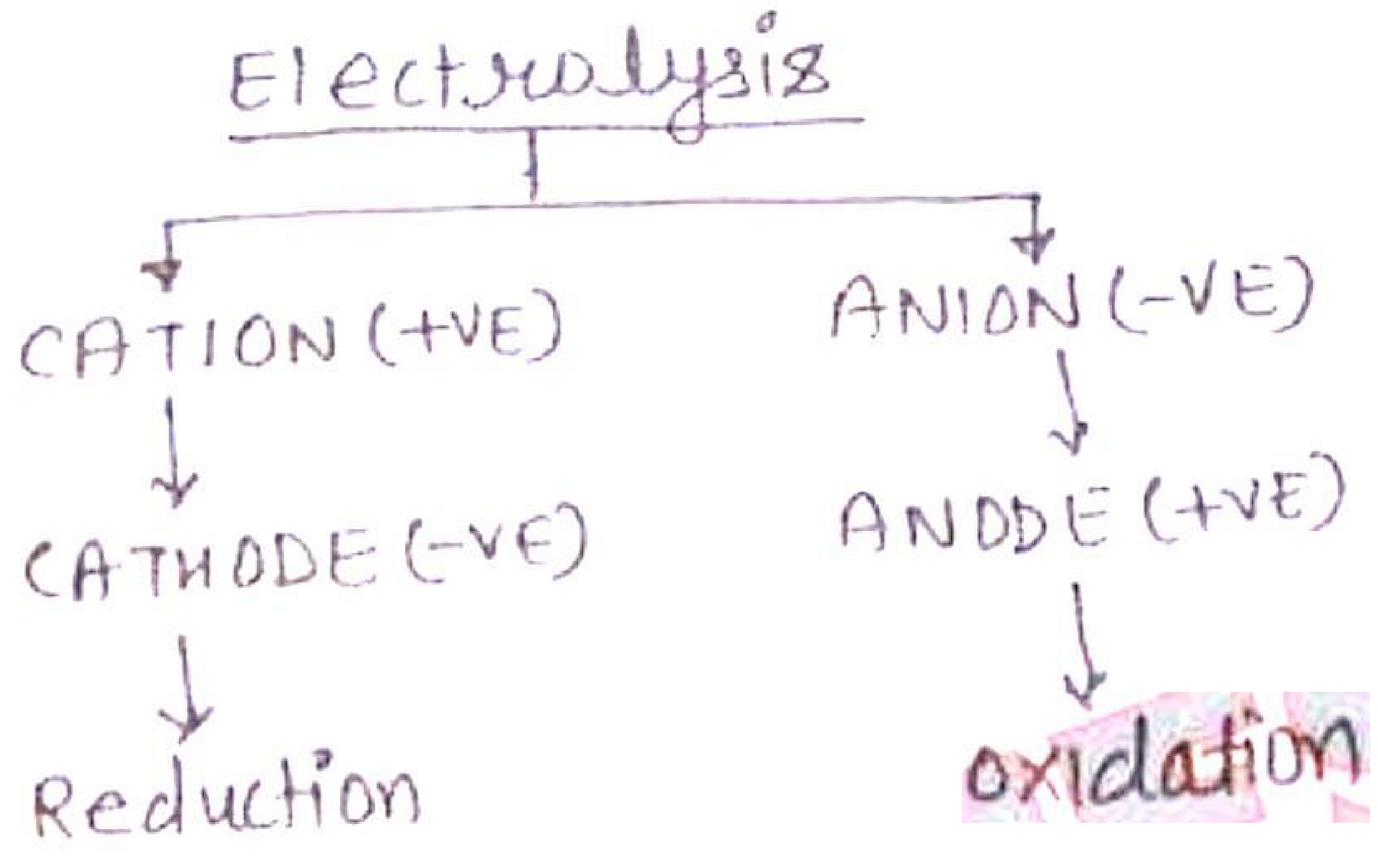
PART TWO COMPLETES HERE

PART- THREE - ELECTROLYSIS

* The process of decomposition of an electrolysis when electricity passed through its aquas solution or in molten state called electrolysis

* The device in which electrolysis is carried out is called electrolytic cell





TRICK An Ox (एक बैल)
Red Cat (लाल बिल्ली)

* Sign of Anode and Cathode तो Galvanic cell के opposite है।

* For Galvanic cell	For electrolytic cell
$\Delta G = -ve$ (spontaneous)	$\Delta G = +ve$ (Non-spontaneous)
Chem. energy → elect. energy	elect. energy → chemical ener

* For electrolysis D.C is used क्यों कि जब A.C Pass करेगे तो Electrode की Polarity change होता रहेगा. और Ion confuse हो जाएगा कि cathode पर जाए कि ANODE पर जाए

* To measure resistance of electrochemical cell we will use A.C क्यो कि D.C जब Pass करेगे तो electrolysis होगा और अगर NaCl electrolysis करेगा तो NaOH बन जाएगा

* A.C Pass करने पर Ion confusion मे रहेगा और cathode and anode के बीच combine हो जाएगा और हम easily electrolytic cell की resistance measure कर लेगे.

Product of electrolysis mainly depends upon

(i) NATURE OF ELECTROLYTE (STRONG OR WEAK)

(ii) NATURE OF ELECTRODE

(A) inert (non-attacked) electrode

Inert electrode doesnot react with solution of electrolytes or with product of electrolysis. Such electrodes are used for electrolysis.

eg CHAPPA , C(graphite)

(B) Reactive electrodes

Reactive electrodes are not used in electrolysis

(iii) CONCENTRATION OF SOLUTION

(iv) OVER POTENTIAL OF GASES

Eg OF ELECTROLYSIS (COMMON)

1. Electrolysis of fused (MOLTEN) NaCl using Pt electrode
2. Electrolysis of Aquas solution of NaCl using Pt electrod
3. Electrolysis of Aquas solution of $CuSO_4$ using Pt electrod
4. Electrolysis of Aquas solution of $AgNO_3$ using Pt electro
5. Electrolysis of Aquas solution of Na_2SO_4 using Pt electr
6. Electrolysis of Aquas solution of $NiSO_4$ using Pt electr

Eg OF ELECTROLYSIS (SPECIAL)

1. Electrolysis of very dil aquas NaCl using Pt electrode
2. Electrolysis of aquas solution NaCl using Hg electrode
3. Electrolysis of H_2SO_4 using Pt electrode
4. Electrolysis of aq. solution of $CuSO_4$ using Cu electr

1. Electrolysis of Fused (MOLTEN) NaCl using Pt electrode

Cathode : $Na^+ + e^- \longrightarrow Na$

Anode ; $2Cl^- \longrightarrow Cl_2\uparrow + 2e^-$

2. Electrolysis of Aq. soln of NaCl using Pt electrode

$NaCl \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

Cathode × $Na^+ + e^- \longrightarrow Na$, $E^\circ_{red} = -2.71$ volt

✓ $2H_2O + 2e^- \longrightarrow H_2\uparrow + 2OH^-$, $E^\circ_{red} = -0.83$ volt

× $H^+ + e^- \longrightarrow H_2$; $E_{red} = 0$

Anode ✓ $2Cl^- \longrightarrow Cl_2\uparrow + 2e^-$ $E^\circ_{oxi} = -1.36$ volt

× $2H_2O \longrightarrow O_2 + 4H^+ + 4e$ $E^\circ_{oxi} = -1.23$ volt

NOTE:

- S.O.P तो water का Cl से ज्यादा है इसलिए water should be oxidised at anode
- But it is kinetically slow at that lower potential So some extrapotential supply करना पड़ता है। इसे OVER POTENTIAL या BUBBLE POTENTIAL कहते है।

3. ELECTROLYSIS OF Aq SOLUTION OF CUSO4 USING Pt ELECTRODE

$CuSO_4 \longrightarrow Cu^{+2}_{(aq)} + SO_4^{-2}{}_{(aq)}$

Cathode ⇒ ✓ $Cu^{+2} + 2e^- \longrightarrow Cu$ $E^\circ_{red} = 0.34$ Volt

× $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ $E^\circ_{red} = -0.83$ volt

Anode ⇒ × $2SO_4^{-2} \longrightarrow S_2O_8^{-2} + 2e^-$. $E^\circ_{oxi} = -2.01$ volt

$2H_2O \longrightarrow O_2\uparrow + 4H^+ + 2e^-$ $E^\circ_{oxi} = -1.23$ volt

NOTE: Cathode पर Higher SRP वाला reaction will preferred
Anode पर Higher SOP वाला reaction will preferred

4. Electrolysis of aq solution of $AgNO_3$ using Pt electrod

$AgNO_3 \longrightarrow Ag^+(aq) + NO_3^-(aq)$

H_2O

Cathode; $Ag^+ + e^- \longrightarrow Ag$

Anode; $2H_2O \longrightarrow O_2\uparrow + 4H^+ + 4e^-$

5. Electrolysis of aquas solution of Na_2SO_4 using Pt ele

$NaSO_4 \longrightarrow Na^+(aq) + SO_4^{-2}(aq)$

H_2O × ×

Cathode : $H_2O \longrightarrow H_2\uparrow$

Anode : $H_2O \longrightarrow O_2\uparrow$

only electrolysis of water

6. Electrolysis of aquas solution of $NiSO_4$ using Pt ele

$NiSO_4 \longrightarrow Ni^+(aq) + SO_4^{-2}(aq)$

H_2O

Cathode : $Ni^{+2} + 2e^- \longrightarrow Ni$

Anode ; $H_2O \longrightarrow O_2\uparrow$

SPECIAL EXAMPLE OF ELECTROLYSIS

1. Electrolysis of very dil aq NaCl using Pt electrode ;

$\mathrm{NaCl} \xrightarrow[H_2O]{} Na^+_{(aq)} + Cl^-_{(aq)}$

Cathode. $H_2O \longrightarrow H_2\uparrow$

Anode $H_2O \longrightarrow O_2\uparrow$

⇒ Cl^- ions के कम concentration पर discharged Potential water से ज्यादा चाहिए

2. Electrolysis of aq solution of NaCl using Hg electro

$\mathrm{NaCl} \xrightarrow[H_2O]{} Na^+_{(aq)} + Cl^-_{(aq)}$

Cathode ; $Na^+ + e^- \longrightarrow Na$

$Na + Hg \longrightarrow Na-Hg$ (sodium amulgum)

$NaHg + 2H_2O \longrightarrow 2NaOH + 2Hg + H_2\uparrow$

Anode ; $Cl_2\uparrow$

⇒ At Hg electrode discharge potential of Na^+ is lesser than H_2O

3. Electrolysis of H_2SO_4 solution using Pt electrode

$H_2SO_4 \xrightarrow[H_2O]{} H^+ + SO_4^{-2}$

Cathode $2H^+ + 2e^- \longrightarrow H_2$

Anode $2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$ $E^\circ_{ox} = -2.01V$

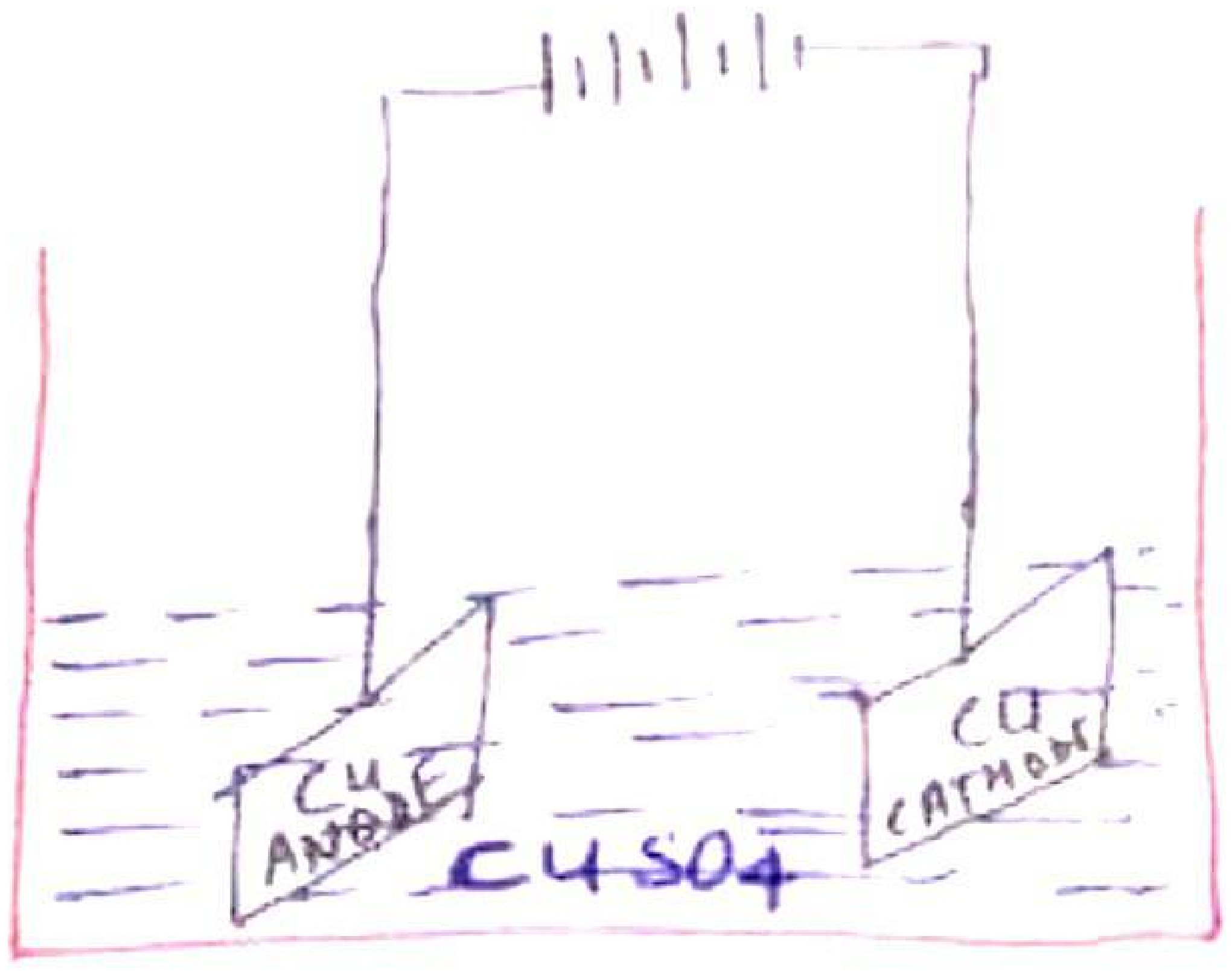
$2H_2O \longrightarrow O_2\uparrow + 4H^+ + 4e^-$ $E^\circ_{ox} = -1.23V$

Note:

At lower concn second reaction is prefforred

At higher concn first reaction is Preferrred

4. Electrolysis of aquas solution of copper sulphate using Pt electrode



$CuSO_4(aq) \xrightarrow[H_2O]{} Cu^{+2}(aq) + SO_4^{2-}$

Anode = $Cu \longrightarrow Cu^{2+} + 2e^-$ $E^\circ_{oxid} = -0.34V$

$2H_2O \longrightarrow O_2\uparrow + 4H^+ + 4e^-$ $E^\circ_{oxi} = -1.23V$

Cathode = $Cu^{+2} + 2e^- \longrightarrow Cu$

NOTE

- * In this process concⁿ of solution remains same
- * It is not considered as an example of electrolysis
- * This process canbe used for purification of Cu
- * Purification जब करते हैं तब :-

  Cathode को pure metal से बनाते है।

  Anode को impure metal से बनाते है।

Similar case

- * Electrolysis of Aq solution of $CuCl_2$ using Cu electrode
- * ———————— $AgNO_3$ —— Ag ——
- * ———————— $Ni(NO_3)_2$ —— Ni ——

FARADAY'S LAW OF ELECTROLYSIS

⇒ FIRST LAW OF FARADAY'S LAW OF ELECTROLYSIS

When electricity is passed through electrolyte then amount of substance discharged on electrode is directly proportional to the quantity of charge passed through electrolyte

$$W \propto Q$$

$$W \propto it$$

$$\boxed{W = Zit}$$ Z = electrochemical equivalent

if $Q = it = 1\,cb$ then

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

Electrochemical equivalence

The weight of substance (in gm) discharged by 1 Coloumb of charge is called electrochemical equivalence of that substance

∵ 1 Faraday charge discharges (W) = E gm
(96500 cb)

∴ 1 cb charge discharge $\frac{E}{96500} = Z$

$$W = Zit$$

$$\boxed{W = \frac{E}{96500} \times it}$$

If $Q = it$ is constant then

$$W \propto E$$

$$\frac{W}{E} = \text{Constant}$$

⇒ SECOND LAW OF FARADAY'S LAW OF ELECTROLYSIS

if same quantity of charge is passed through different solution of electrolyte then amount of substance discharged on electrode will be in the ratio of their equivalent weight

$$\boxed{\frac{W_1}{W_2} = \frac{E_1}{E_2}} \qquad \boxed{\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3} \cdots \text{Constt}}$$

Qsn Calculate the weight of Cu deposited when 2×10^3 coloumb of charge is passed through $CuSO_4$ solution (Atomic weight of Cu = 63.5)

Ans

$$\frac{W_{Cu}}{E_{Cu}} = \frac{\overset{\rightarrow Q}{\boxed{it}}}{96500}$$

$$W_{Cu} = \frac{it \times E_{Cu}}{96500} = \frac{63.5 \times 2 \times 10^3}{2 \times 96500} = 0.658 \text{ gm}$$

Qsn 0.36 gm of metal is deposited on the electrode when 1.2 amp current is passed for 15 minute through its salt. Atomic weight of the metal is 96. what will be its vacancy

Ans

$$W = \frac{E \times Q}{96500} = \frac{w \times i \times t}{\text{valency} \times 96500} = \frac{96 \times 1.2 \times 15 \times 60}{x \times 96500}$$

$$0.36 = \frac{96 \times 1.2 \times 15 \times 60}{x \times 96500}$$

$$x = \frac{96 \times 1.2 \times 15 \times 60}{96500 \times 0.36}$$

$$x = 2.98$$

$$\underline{x = 3}$$

[क्यो कि x होगा एक whole number होता है।]

Qsn How much current is necessary to produce O_2 gas at the rate of 1ml/sec at STP.

GAS	Mw	Ew
O_2	32	8
H_2	2	1
Cl_2	71	35.5

Ans: $V_{O_2} = 1 ml$

$t = 1 sec$

$$W_{O_2} = \frac{1}{22400} \times 32 \, gm$$

$$W_{O_2} = \frac{E_{O_2}}{96500} \times it$$

$$\frac{32}{22400} = \frac{8}{96500} \times i \times 1 sec$$

$$\boxed{i = 17.23 \, amp}$$

Qsn How long a current of 3 amp has to be passed through a silver nitrate solution to coat a metal surface of 80 cm² with 0.005 mm thick layer. $\rho_{silver} = 10.5 \, gm/cm^3$

Ans weight of Ag deposited on metal $= V \times d$

$= (\text{Area} \times \text{thick}) \times d$

$= \frac{80 \times 0.005}{10} \times 10.5$

$= 0.42 \, gm$

$$W_{Ag} = E_{Ag} \times \frac{it}{96500}$$

$$0.42 = \frac{108}{96500} \times 3 \times t$$

$$\boxed{t = 129.09 \, sec}$$

Qsn 5 lit of 1 M $AgNO_3$ solution and 2 lit of 1M Nacl solution are connected in sereis when electricity is passed 54 gm of silver is deposited on cathode in $AgNO_3$ solution then calculate volume of H_2 gas (at STP) produced at cathode in Nacl solution (Ag = 108)

Ans W = 54 gm of Ag

$$\frac{W_{H_2}}{W_{Ag}} = \frac{E_{H_2}}{E_{Ag}}$$

$$\frac{W_{H_2}}{54} = \frac{1}{108} \Rightarrow W_{H_2} = \frac{1}{2} = 0.5 \text{ gm}$$

$$V_{H_2} = \frac{0.5}{2} \times 22.4 = 5.6 \text{ litr}$$

$$V_{H_2} = 5.6 \text{ lit}$$

Qsn Calculate the time required to deposit 40% Cu from 200 ml of 0.5 M $CuSO_4$ solution when 0.2 amp current is passed through it

Ans $M \times (V)_L$ = mole of solute

$$0.5 \times \frac{200}{100} = 0.1 \text{ mol of } CuSO_4$$

$$\downarrow$$

$$0.1 \text{ mol of } Cu^{+2}$$

$$\downarrow$$

$$(0.1 \times 63.5) g \; Cu^{+2}$$

$$\text{wt of Cu deposited} = \frac{0.1 \times 63.5 \times 40}{100} \text{ gm}$$

$$W_{Cu} = \frac{E_{Cu} \times i t}{96500}$$

$$\frac{0.1 \times 63.5 \times 40}{100} = \frac{63.5 \times 0.2 \times t}{2 \times 96500}$$

$$t = 38600 \text{ sec.}$$

Qsn If cost of electricity producing x gm of Al is Rs x. What is the cost of electricity of electricity of producing x gm of mg (At mass of Al = 27) (At mass of mg = 24)

Ans cost of deposition ∝ charge (Q)

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

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

$$\frac{W_{mg}}{W_{Al}} = \frac{E_{mg} \times (\text{Cost})_{Mg}}{E_{Al} \times (\text{Cost})_{Al}}$$

$$\frac{x}{x} = \frac{24/2}{27/3} \times \frac{(\text{Cost})_{mg}}{x}$$

$$1 = \frac{12}{9} \times \frac{(\text{Cost})_{mg}}{x}$$

$$(\text{Cost})_{Mg} = x \times \frac{3}{4} = 0.75x \text{ Rs}$$

Qsn 100 gm concentration solution of $AgNO_3$ is electrolysed using 0.1 Faraday of electricity by Pt electrodes. Find the weight of resulting solution (At mass of Ag = 108)

Ans

$$1F \longrightarrow W = E\,gm$$

$$0.1\,F \longrightarrow W = (0.1 \times E) = 0.1 \times 108$$

$$\text{Cathode} \longrightarrow W_{Ag} = 10.8\,gm$$

$$\text{Anode} \longrightarrow W_{O_2} = 0.1 \times 8 = 0.8\,gm$$

$$\text{Remaining wt of solution} = 100 - (10.8 + 0.8)$$

$$= 88.4\,gm$$

Qsn A current of 3 Amp was passed for 2 hours through a solution of $CuSO_4$. 3 gm of Cu^{+2} ions were discharged at cathode. calculate current efficiency for this process ($Cu = 63.5$)

Ans $W = \frac{E \times i \times t}{96500}$

$3 = \frac{63.5}{2 \times 96500} \times i_{used} \times 2 \times 60 \times 60$

$i_{used} = 1.266$ Amp

Current efficiency $= \frac{i_{used}}{i_{passed}} \times 100$

$= \frac{1.266}{3} \times 100$

$= 42.2\%$

Qsn Calculate charge require for oxidation of

(I) 1 mol FeO to Fe_2O_3

(II) 1 mol Fe_2O_3 to FeO

(III) 1 mol H_2O to O_2

Ans (I) $FeO \longrightarrow \frac{1}{2} Fe_2O_3 + \underset{(1F)}{e^-}$

$\downarrow$

1mol

$\downarrow$

$Fe^{+2} \longrightarrow Fe^{+3}$

$\underbrace{x^{+2} \longrightarrow x = +3}_{\text{Increased in oxi. no} = ①}$

Ans = 1F , $Q = 96500$ Cb

(ii) 1mol $\underline{Fe_2O_3}$ to FeO

$\downarrow$

$2Fe^{+3}$

$\underbrace{Fe^{+3} + e^- \longrightarrow Fe^{+2}}_{\Delta oxid = 1}$

1mol = 1 Faraday

2mol = 2 Faraday

(III) $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

2mol 4F

1mol 2F

$Q = 2 \times 96500$

$= 193000$ cb

Qsn Aquas solution of $AuCl_3$, $AgNO_3$, $CuSO_4$ are Connected in sereis when 3F charge is passed then calculate the ratio of moles of metal deposited on electrode

Ans 1st method

	$AuCl_3$	$AgNO_3$	$CuSO_4$
	↓	↓	↓
	Au^{+3}	Ag^{+}	Cu^{+2}
	↓	↓	↓
3F ⇒	3gm eq	3gm eq	3gm eq
v.f ⇒	$\frac{3\,mol}{3}$	$\frac{3\,mol}{1}$	$\frac{3\,mol}{2}$
v.f ⇒	1	3	$\frac{3}{2}$
v.f ⇒	2	6	3

Relation between ionic Conductance (λ) and mobility of ion (u)

$\lambda \propto u$

for cation $\lambda_c \propto u_c$

for Anion λ_a u_a

$$\boxed{\begin{array}{l}\lambda_c = F u_c \\ \lambda_a = F u_a\end{array}}$$

$F = 96500$ /mol.

mobility of ion (u).

$$\boxed{u = \frac{\text{Velocity of ion } (v)}{\text{potential gradient}}}$$

$$\Downarrow$$

transport No(t).

* The Current flowing through an electrolytic Solution is Carried by the ions (Cation anion) both.

× The fraction of total current carried by an anion is called its transport number

$$\boxed{t_c = \frac{\lambda_c}{\lambda_c + \lambda_a} \text{ or } \frac{U_c}{U_c + U_a} \text{ or } \frac{V_c}{V_c + V_a}}$$

$$\boxed{t_a = \frac{\lambda_a}{\lambda_c + \lambda_a} \text{ or } \frac{U_a}{U_c + U_a} \text{ or } \frac{V_a}{V_c + V_a}}$$

$$\boxed{t_c + t_a = 1}$$

GALVANIC CELL	ELECTROLYTIC CELL
* Convert chemical energy into electrical energy	* Converts electrical energy into chemical energy
* Cell reaction is spontaneous	* cell reaction is Non-spontaneous
* Anode = -ve Cathode = +ve	* Anode = +ve cathode = -ve
* Deposition of substances only at cathode	* Deposition of substance on both electrode cathode and anode
* Salt Bridge is used	* salt Bridge is not used
* Both electrodes are separated	* Both electrodes are placed in same compartment
* Current flows from cathode to anode	* current flows from anode to cathode

BATTERY	ANODE	CATHODE	ELECTROLYTE
DRY CELL/PRI CELL (NON-RECHARGEABLE)	Zn	Carbon Rod Coated with MnO_2	NH_4Cl with $ZnCl_2$
Lead storage Battery	Pb	Pb rod Coated with PbO_2	38% By mass of H_2SO_4
Ni-Cd Cell (secondary cell) Rechargeable	Cd	Ni rod Coated with Nickel Powder	Aquas solution of KOH/NaOH
H_2O_2 Fuel cell Pollution free cell	H_2 gas Passing through Porus Carbon	O_2 Passing through Porus Carbon	Aquas solution of KOH/NaOH