

26/12/17

Electrochemistry

Electrochemistry is the branch of chemistry that deals with interconversion of chemical & electrical energy.

Chemical energy $\xrightleftharpoons[\text{Electrolytic cell}]{\text{Galvanic cell}}$ Electrical Energy

Electrolyte:- Substances which conduct electricity in aq. & molten state through ions called electrolyte.

eg. Acid, Base, Salt.

Strong Electrolyte
complete ionisable
 $\alpha = 1$

Weak Electrolyte
Incomplete ionisable
 $\alpha < 1$

Conductor:- which allow electric current to pass through them.

Metallie

- Charge carrier are free e^-
- Matter does not takes place
- No chemical change takes place
- Conductance is very high.
- $T \uparrow R \uparrow$ conductance $\downarrow$
- Faraday law is not followed

Electrolytic

- Charge carrier are ions.
- Matter transfer takes place.
- Chemical change takes place.
- Very low
- $T \uparrow R \downarrow$ cond $\uparrow$
- Faraday law followed.

Some imp. terms related to Conductance

Resistance : Ohm's law

$$V \propto I$$

$$V = IR$$

$$R = \frac{V}{I}$$

Unit : Ω or ohm

Conductance (G)

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

Unit Ω^{-1} or mho Seimen

Specific Resistance / Resistivity (ρ)

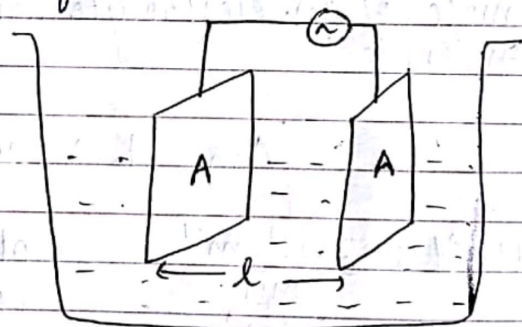
$$R \propto l \quad (\text{length b/w electrodes})$$

$$R \propto \frac{1}{A} \quad (A \rightarrow \text{Area of electrode plate})$$

$$R \propto \frac{l}{A}$$

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

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



Unit : $\Omega \text{ cm}$ or $\Omega \text{ m}$

$$\left. \begin{array}{l} A = 1 \text{ cm}^2 \\ l = 1 \text{ cm} \end{array} \right\} V = 1 \text{ cm}^3 \quad \rho = R$$

Therefore resistivity is the resistance of 1 cm^3 electrolyte.

Sp. Conductance / Conductivity (K) Kappa

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

$$K = \frac{1}{R} \left(\frac{l}{A} \right)$$

$G \rightarrow$ Conductance

$$G^* = \frac{l}{A} \rightarrow \text{cell const}$$

Unit = cm^{-1} or m^{-1}

$$\left. \begin{array}{l} \Omega^{-1} \text{ cm}^{-1} \\ \text{or} \\ \Omega^{-1} \text{ m}^{-1} \end{array} \right\} \leftarrow K = G \cdot G^*$$

$$K = G_1$$

Molar conductance: Conductance of 1 mole of an electrolyte.
(Δ_m) or λ_m

Let

$$\frac{M \text{ mole of an electrolyte}}{1 \text{ mole}} = \frac{+nt \text{ in}}{1 \text{ L}} = \frac{1000 \text{ cm}^3}{M}$$

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

Unit: $\frac{\Omega^{-1} \text{cm}^{-1}}{\frac{\text{mol}}{\text{cm}^3}} = \frac{\text{ohm}^{-1} \text{cm}^{-1} \text{cm}^3 \text{mol}^{-1}}{\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}}$

If unit of K is given in $\text{ohm}^{-1}\text{m}^{-1}$ then $\Lambda_m = (K \times 1000)$

$$\Lambda_m = \left(K \times \frac{1000}{M} \right) \times 10^{-6} \text{ ohm}^{-1} \text{ m}^2 \text{ mol}^{-1}$$

Equivalent Conductance :- Conductance of 1 equivalent of an electrolyte.

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

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

$$\Lambda_m = K \times \frac{1000}{M} \times \frac{V.F.}{V.F.}$$

$$\Lambda_m = K \times \frac{1000}{N} \times V.F.$$

$$\Lambda_m = \Lambda_{eq} \times V.F.$$

$$\Lambda_m \geq \Lambda_{eq}$$

$$V.F. \geq 1$$

Ques A certain conducting cell is filled with 0.05 M K_2SO_4 solⁿ, if it had a resistance of 300Ω then Calculate. (specific conductance = $0.0025 \Omega^{-1} \text{cm}^{-1}$)

$$G^* = \frac{l}{A}$$

$$G^* = \frac{K}{G} = \frac{0.0025}{0.003} \times \frac{1}{2} = \frac{5}{6} = 0.8$$

② Conductance $G = \frac{1}{R} = \frac{1}{300} = 0.003$

③ eq. conductance $\Lambda_{eq} = \frac{K}{G}$

$$\Lambda_{eq} = \frac{0.0025}{0.003} = 0.833$$

$$\Lambda_{eq} = K \times \frac{1000}{N} = 0.0025 \times \frac{1000}{2 \times 0.05}$$

$$= \frac{25}{2 \times 0.05} \times 10^6 = 10$$

④ molar conductance $\Lambda_m = \Lambda_{eq} \times V.F.$

$$= 10 \times 2 = 20$$

Ques The sp. conductance of a 0.1 N KCl solⁿ at $23^\circ C$ is $0.012 \Omega^{-1} \text{cm}^{-1}$. The resistance of containing solⁿ at same Temp. is 55Ω . Then cell constant will be

- ① 0.142 cm^{-1} ② 0.66 cm^{-1} ③ 0.918 cm^{-1} ④ 1.12 cm^{-1}

$$K = G \cdot G^*$$

$$KR = \frac{K}{G} = G^* = 0.012 \times 55$$

$$= 0.66$$

Ques The electrical resistance of a 0.05 mol L⁻¹ NaOH solⁿ of diameter 1 cm & length 50 cm is $5.55 \times 10^3 \text{ ohm}$. Calculate its resistivity & molar conductivity.

$$\rho = \frac{R \cdot A}{l} = \frac{5.55 \times 10^3 \times \frac{\pi}{4} \times (1 \times 10^{-2})^2}{50 \times 10^{-2}}$$

$$= \frac{111 \times 11}{7 \times 2} = \frac{1221}{14} = 87.21$$

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

$$= \frac{1 \times 14}{1221} \times \frac{1000}{0.05} = \frac{28 \times 10^4}{1221} = \frac{280000}{1221} = 229.32$$

$$\begin{array}{r} 1221 \\ 1221 \\ \hline 2442 \\ 3580 \\ 2442 \\ \hline 1138 \end{array}$$

Q.4 The eq. conductance of 0.1 N solⁿ of MgCl₂ is 100 ohm cm² eq⁻¹ at 25°C. A cell with electrode having surface area 1 cm² & 0.5 cm apart is filled with 0.1 N MgCl₂ solⁿ. How much current will flow when potential diff. b/w electrode is 5V

$$V = IR$$

$$\Lambda_{eq} = \frac{l \times 1000}{\rho \cdot N}$$

$$\Lambda_{eq} = \frac{l \cdot 1000}{R \cdot A \cdot N}$$

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

$$R = 50 \Omega$$

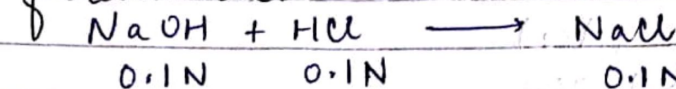
$$V = IR$$

$$I = \frac{V}{R} = \frac{5}{50} = \frac{1}{10} = 0.1 \text{ A}$$

$$\begin{array}{l} N = 0.1 \text{ N} \\ \Lambda_{eq} = 100 \\ A = 1 \text{ cm}^2 \\ l = 0.5 \text{ cm} \\ V = 5 \text{ V} \end{array}$$

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Ques The conductance of 0.1N NaOH solⁿ is 0.022 S cm⁻¹. When equal vol. of 0.1N HCl solⁿ is added. The conductivity of resultant solⁿ is decreased to 0.0055 S cm⁻¹ then calc. eq. conductance of resultant



0.1N

0.1N

0.1N

$$G_1 = 0.22$$

Am

$$N = \frac{0.1}{2} = 0.05$$

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

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

$$= \frac{0.0055 \times 1000}{0.05} \times \frac{\Lambda_m \times 1000}{1000}$$

$$\Lambda_{eq} = 110$$

Factors affecting Electrolytic conductance :-

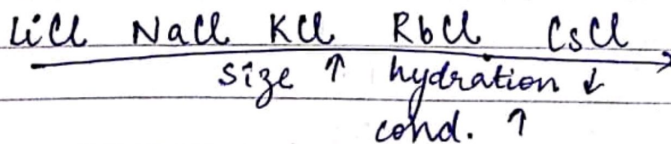
1. Ionic interaction :- Conductance ↓

2. Nature of solvent : Dielectric ↑ ionisation ↑ cond. ↑
const

3. Viscosity of medium Viscosity ↑ cond. ↓

4. Solvation / Hydration of ions :

Hydration ↑ cond ↓



5. Effect of Dilution : As dilution ↑, cond. ↑

For strong electrolyte as dilution ↑ ion interaction ↓ cond. ↑
 $\kappa = 1$

For weak electrolyte as dilution ↑ α ↑ cond. ↑
 $\alpha < 1$

Dilution :

Molar Conductance (Λ_m)

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

dilution $\uparrow$ $V \uparrow$ $M \downarrow$ $\Lambda_m \uparrow$

Eq. conductance (Λ_{eq})

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

dilution $\uparrow$ $V \uparrow$ $N \downarrow$ $\Lambda_{eq} \uparrow$

Sp. conductance

Conductance for $1 \text{ cm}^3 \text{ sol}^n$

dilution $\uparrow$ no. of ions per unit Vol. $\downarrow$ cond $\downarrow$

Molar conductance at infinite dilution & zero concⁿ :-

Debye Huckle Onsgar eqⁿ :-

$$\Lambda_m = \Lambda_m^\circ - b \sqrt{C}$$

$\Lambda_m \rightarrow$ Molar conductance at any conc.

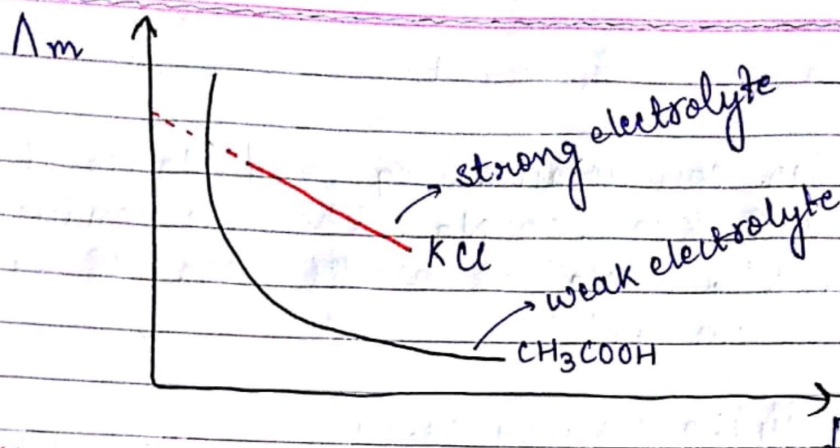
Λ_m° or $\Lambda_m^\infty \rightarrow$ Molar conductance at infinite dilution or zero concⁿ.

$b \rightarrow$ Debye const.

$\hookrightarrow$ at ~~a~~ const temp, it is same for same type of electrolyte.

NaCl	1 : 1	electri ⁿ electrolyte
KCl	1 : 1	
MgCl ₂	2 : 1	
Na ₂ SO ₄	1 : 2	
MgSO ₄	2 : 2	

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Kohlrausch law of Independent migration

It states that molar conductivity of an electrolyte at infinite dilution is sum of individual molar conductance of cation & anion.

$$\Lambda_m^\circ \text{ or } \Lambda_m^\infty = \lambda_+^\circ + \lambda_-^\circ$$

$$\Lambda_m^\circ \text{NaCl} = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ$$

↑
molar cond. of Na^+ at ∞ dil.

generally, If ν_+ cations & ν_- anions are +nt in electrolyte.

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

$$\text{eg } \Lambda_m^\circ \text{MgCl}_2 = \lambda_{\text{Mg}^{2+}}^\circ + 2\lambda_{\text{Cl}^-}^\circ$$

$$\Lambda_{\text{eq}}^\circ = \lambda_{+ \text{eq}}^\circ + \lambda_{- \text{eq}}^\circ$$

$$\Lambda_{\text{eq}}^\circ = \frac{\Lambda_m^\circ}{\text{V.F.}}$$

Ques The ionic conductance of Mg^{2+} & Cl^- at ∞ dilution are 110 & 76 $\text{S cm}^2 \text{mol}^{-1}$. Cal. molar & eq. cond. of MgCl_2 at ∞ dilution?

$$\begin{aligned} \Lambda_m^\circ &= 110 + 2 \times 76 \\ &= 110 + 152 = 262 \end{aligned}$$

$$\Lambda_{eq}^{\circ} = \frac{262}{2} = 131$$

Ques = Calc. molar conductance & eq. conductance at ∞ dil.ⁿ of salt $KOOC.COONa$. The ionic conductance of $C_2O_4^{2-}$, K^+ & Na^+ at ∞ dil.ⁿ are 148.2, 50.2, 73.74 $\Omega^{-1}cm^2mol^{-1}$

$$\Lambda_m = 148.2 + 50.2 + 73.74$$

$$= 272.14$$

$$\Lambda_{eq} = \frac{272.14}{2} = 136.07$$

Application of Kohlrausch Law:

To determine molar conductance for weak electrolyte:

$$\Lambda_{CH_3COOH}^{\circ} = \lambda_{CH_3COO^-}^{\circ} + \lambda_{H^+}^{\circ}$$

$$\Lambda_{CH_3COONa}^{\circ} = \lambda_{CH_3COO^-}^{\circ} + \lambda_{Na^+}^{\circ} \quad \text{--- (1)}$$

$$\Lambda_{HCl}^{\circ} = \lambda_{H^+}^{\circ} + \lambda_{Cl^-}^{\circ} \quad \text{--- (2)}$$

$$\Lambda_{NaCl}^{\circ} = \lambda_{Na^+}^{\circ} + \lambda_{Cl^-}^{\circ} \quad \text{--- (3)}$$

$$\text{--- (1) + (2) - (3)} \quad \Lambda_{CH_3COONa}^{\circ} + \Lambda_{HCl}^{\circ} - \Lambda_{NaCl}^{\circ} = \lambda_{CH_3COO^-}^{\circ} + \lambda_{H^+}^{\circ}$$

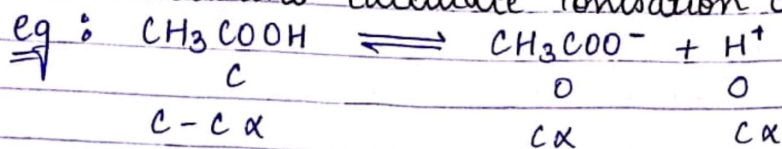
To calculate D.O.D. (α)

$$\alpha = \frac{\text{molar cond. at conc}^n C}{\text{molar cond. at } \infty \text{ dilution or zero conc}^n}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^{\infty}}$$

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

To determine calculate ionisation const :-



$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)}$$

$$K_a \approx C\alpha^2$$

Ques limiting molar conductivity of NH_4OH i.e. $\Lambda_m^\circ(\text{NH}_4\text{OH})$ is equal to

- ① $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NaOH})$
- ② $\Lambda_m^\circ(\text{NaOH}) + \Lambda_m^\circ(\text{NaCl}) - \Lambda_m^\circ(\text{NH}_4\text{Cl})$
- ③ $\Lambda_m^\circ(\text{NH}_4\text{OH}) + \Lambda_m^\circ(\text{NH}_4\text{Cl}) - \Lambda_m^\circ(\text{HCl})$
- ④ $\Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})$

Ques Equivalent conductance of NaCl , HCl & $\text{C}_2\text{H}_5\text{COONa}$ at ∞ dil.ⁿ are 126.45 , 426.16 & $91 \Omega^{-1} \text{cm}^2$ resp.

Calc. eq: cond. of $\text{C}_2\text{H}_5\text{COOH}$

- ① $201.28 \Omega \text{cm}^2$
- ② $390.71 \Omega \text{cm}^2$
- ③ $698.28 \Omega \text{cm}^2$
- ④ $340.48 \Omega \text{cm}^2$

$$\begin{aligned} \Lambda_{\text{eq}} \text{C}_2\text{H}_5\text{COOH} &= -\Lambda_{\text{eq}} \text{NaCl} + \Lambda_{\text{eq}} \text{HCl} + \Lambda_{\text{eq}} \text{C}_2\text{H}_5\text{COONa} \\ &= -126.45 + 426.16 + 91 \\ &= -126.45 + 517.16 \\ &= 390.71 \end{aligned}$$

$$\begin{array}{r} 517.16 \\ 126.45 \\ \hline 390.71 \end{array}$$

Ques The molar conductance of an ∞ dilution solⁿ of NH_4Cl is $150 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ & ionic conductance of $[\text{OH}^-]$ & $[\text{Cl}^-]$ ions 198 & $76 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. What will be the molar cond. of NH_4OH at ∞ dil if conductivity of 0.01M solⁿ of NH_4OH is $9.52 \times 10^{-5} \Omega^{-1} \text{cm}^2$ also cal. D.O.D.

$$\Lambda_m^\circ \text{NH}_4\text{Cl} = 150$$

$$\kappa = 9.52 \times 10^{-5}$$

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

$$\Lambda_{\text{Cl}^-} = 76$$

$$M = 0.01$$

$$\begin{aligned}\Lambda_{\text{NH}_4\text{OH}}^{\infty} &= \Lambda_{\text{NH}_4\text{Cl}} + \Lambda_{\text{OH}^-} - \Lambda_{\text{Cl}^-} \\ &= 150 + 198 - 76 \\ &= 348 - 76 = 272\end{aligned}$$

$$\begin{aligned}\Lambda_{\text{NH}_4\text{OH}}^c &= K \times \frac{1000}{M} \\ &= 9.52 \times 10^{-5} \times \frac{1000 \times 100}{0.01}\end{aligned}$$

$$\begin{aligned}0.02 &= \frac{9.52}{272} \times \frac{100}{100} \\ &= 3.5\%\end{aligned}$$

Ques The eq. conductance of $M/32$ solⁿ of weak monobasic acid is 8 mho cm^2 & at ∞ dilⁿ is 400 mho cm^2 . The dissociation const. of this acid is -
① 1.25×10^{-5} ② 1.25×10^{-6} ③ 6.25×10^{-4} ④ 1.25×10^{-4}

$$\alpha = \frac{8}{400} = 0.02$$

$$\alpha = \frac{8}{400} = 0.02$$

$$K = C \alpha^2$$

$$\begin{aligned}&= \frac{1}{32} \times 0.02 \times 0.02 \times 10^{-4} = 0.1 \times 10^{-4} \times \frac{10}{10} \\ &= 1.25 \times 10^{-5}\end{aligned}$$

To determine solubility of sparingly soluble salt.

eg AgCl , BaSO_4

$\Rightarrow$ Saturated solⁿ of a sparingly solⁿ can be considered as ∞ dilⁿ.

Saturated solⁿ = α diluted solⁿ

$$\Lambda_m^\infty = K \times \frac{1000}{S}$$

M = Solubility
M = S at ∞ dilution

Ques Conductivity of a saturated solⁿ of AgCl is
= $2.2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ & conductivity of water
is $0.8 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. If at ∞ dilⁿ molar conductance
of AgNO_3 , HCl & HNO_3 are 135, 426 & 421
 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ resp. Calculate solubility & solubility
product.

$$K_{\text{AgCl}} = 2.2 \times 10^{-6} \quad K_{\text{H}_2\text{O}} = 0.8 \times 10^{-6}$$

$$\begin{aligned} \Lambda_m \text{ AgCl} &= \Lambda_{\text{AgNO}_3} + \Lambda_{\text{HCl}} - \Lambda_{\text{HNO}_3} \\ &= 135 + 426 - 421 \\ &= 561 - 421 = 140 \end{aligned}$$

$$\begin{aligned} K_{\text{AgCl}} &= K_{\text{AgCl sol}^n} - K_{\text{H}_2\text{O}} \\ &= 2.2 \times 10^{-6} - 0.8 \times 10^{-6} \\ &= 10^{-6} (2.2 - 0.8) \\ &= 10^{-6} (1.4) \\ &= 1.4 \times 10^{-6} \end{aligned}$$

$$\Lambda_m = K \times \frac{1000}{S}$$

$$140 = 1.4 \times 10^{-6} \times \frac{10^3}{S}$$

$$S = \frac{1.4 \times 10^{-3}}{140} = 10^{-5}$$

$$\begin{aligned} K_{\text{sp}} &= S^2 \\ &= 10^{-10} \end{aligned}$$

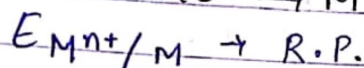
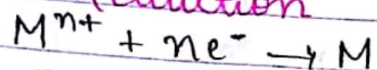
Electrochemical Cell :-

Galvanic cell
Chemical reacⁿ takes place
Δ E. E. is produced.

Electrolytic cell
In this cell chemical reacⁿ
takes place when electricity
is passed.

Galvanic Cell :-

1. Reduction

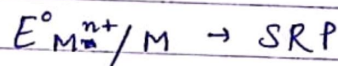
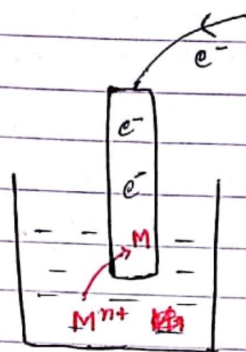


If std. condⁿ :-

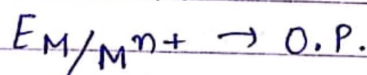
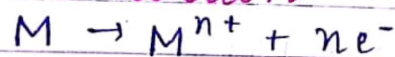
$$P = 1 \text{ atm}$$

$$C = 1 M$$

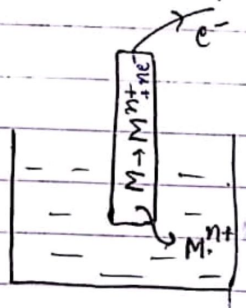
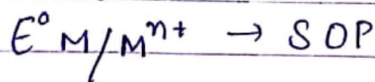
$$T = \text{any (generally } \rightarrow 25^\circ C)$$



Oxidation

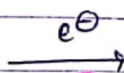


If std. condⁿ



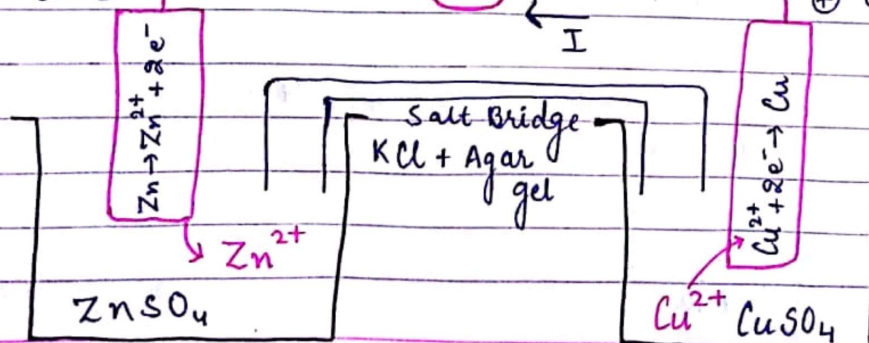
Daniel Cell :-

Anode ⊖



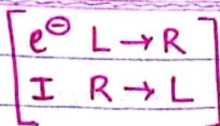
I

Cathode ⊕



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Left $\rightarrow$ anode
charge = -ve



Right = cathode
charge = +ve

Oxidation

Wt. of Zinc Rod $\downarrow$
[Zn²⁺] $\uparrow$ in solⁿ
[SO₄²⁻] same

Reduction

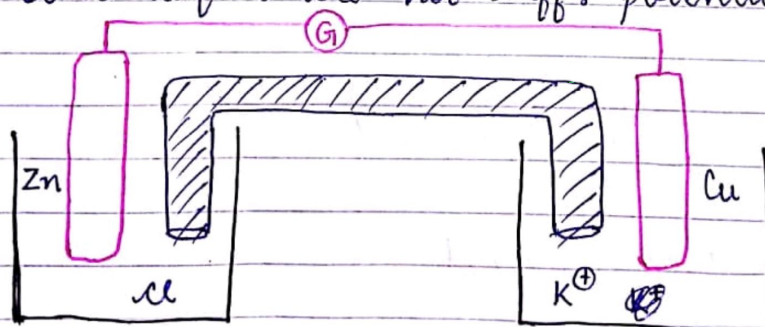
Wt. of Cu Rod $\uparrow$
[Cu²⁺] $\downarrow$
[SO₄²⁻] same

Salt Bridge :- In salt bridge, Agar or gelatin is dissolved in hot & concⁿ inert solvent like KCl, NH₄NO₃ etc. After that we make a paste & fill it in a U-shaped glass tube. This U-shaped glass tube is placed inverted b/w 2 vessels.

$\rightarrow$ In salt bridge, cationic & anionic mobility must be similar

Functions of Salt Bridge :-

- It completes the electric circuit.
- Avoids mechanical mixing.
- Maintain electrical neutrality in both vessels.
- It avoids liquid-liquid Junction Potential ($\because$ both liquid are not diff. potential)



Cell Represented
Zn/Zn²⁺ || Cu²⁺/Cu
 $\downarrow$
Salt Bridge

anode : $Zn \rightarrow Zn^{2+} + 2e^-$

cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

Cell Reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

E.M.F.

$$E_{\text{cell}} = E_{\text{Right}} - E_{\text{Left}}$$

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

$$E_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$$

जिसका red. Potential बड़ा उसका red. होगा (cathode बनेगा)

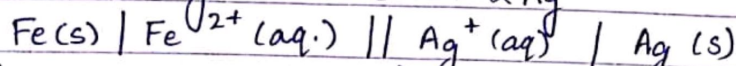
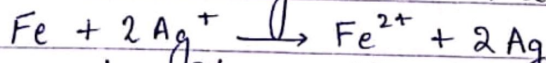
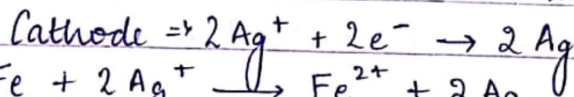
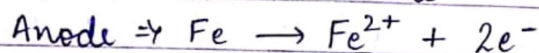
$$\begin{aligned} E_{\text{cell}} &= E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}} \\ &= 0.34 - (-0.76) \\ &= 1.1 \text{ V} \end{aligned}$$

Accⁿ to IUPAC, std. reduction Potential is considered
std. electrode Potential

$$\text{Oxid. Potential} = - \text{red. Potential}$$

ex $E^{\circ}_{\text{cell}} = ?$ $E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$ (oxid) $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = +0.80 \text{ V}$ (red)
red. Potential ज्यादा

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$



$$E^{\circ}_{\text{cell}} = 0.80 - (-0.44) = 1.24 \text{ V}$$

Electrode Potential depend on :-

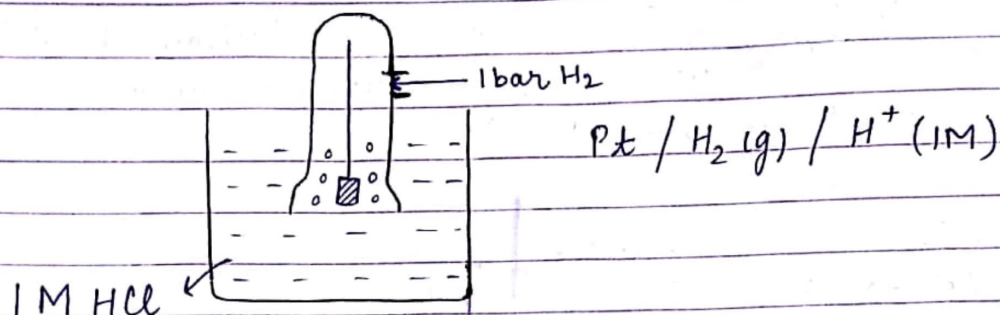
1. Temp.
2. Nature of Electrode
3. Concⁿ of ions.

Imp Ag^+ , F_2 , Br_2 , Ag^+ , Fe^{3+} , Cu^+ , Cu^{2+} , Pb^{2+} , Ni , H_2

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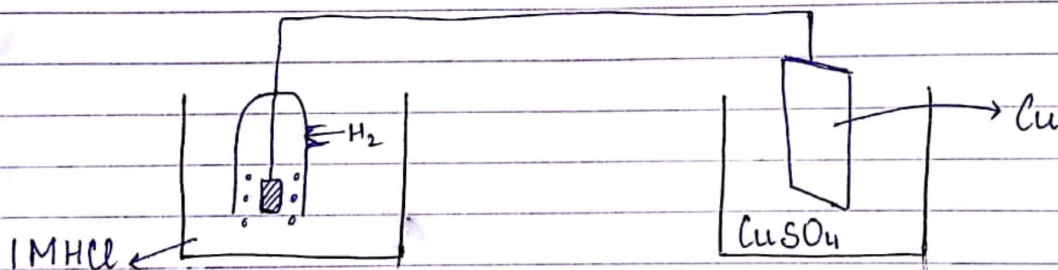
Reference Electrode (Hydrogen Electrode) (SHE)

Accⁿ to IUPAC :- Std. Potential Electrode Potential of Hydrogen electrode is assumed to be zero.



As Anode :- $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ (oxid.)

As Cathode :- $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (red.)

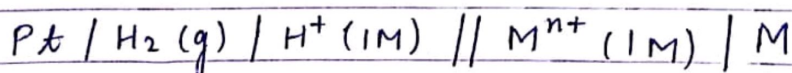


$$E_{\text{cell}}^{\circ} = E_R^{\circ} - E_L^{\circ}$$

$$E_{\text{cell}}^{\circ} = E_R^{\circ} - 0$$

$$E_{\text{cell}}^{\circ} = E_R^{\circ}$$

for $\text{Cu} = 0.34 \text{ V}$
 $\text{Zn} = -0.76 \text{ V}$ } SRP for diff. electrode



*** Element below H_2 work as reducing agent & above element work as oxidising agent in electrochemical series.

* जितना ज्यादा negative electrode Potential or Reduction Potential उतना ही Strong reducing agent.

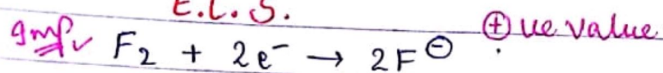
* जितना ज्यादा +ve electrode Potential or oxidation Potential
उतना ही strong oxidising agent.

Strong oxidising Agent = Fe

Strong Reducing Agent = Li

* Electrochemical Series में ऊपर जाने पर Reduction Potential की
Value $\uparrow$ es होती है i.e. metal की Reducing Power $\downarrow$ es
(e^- देने की tendency $\downarrow$ se होती है)

E.C.S.



✓ Au

→ Al

→ O₂

✓ Pt

✓ Ag

→ Br₂

Hg

→ I₂

✓ Cu

✓ H₂

✓ Pb

✓ Sn

✓ Ni

=

✓ Fe

✓ Cr

✓ Zn

-

✓ Al

✓ Mg

✓ Na

Ca

Ba

✓ Li

- ⊖ ⊖ value

Oxidising Power $\downarrow$
Reducing Power $\uparrow$
Reactivity of metal $\uparrow$

Ques Which of following weakest Reducing agent?

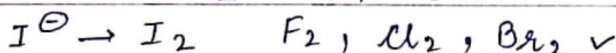
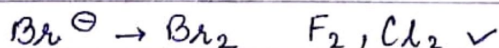
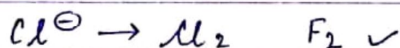
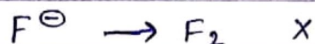
- ① $F^{\ominus}$ ② $Br^{\ominus}$ ③ $Cl^{\ominus}$ ④ $I^{\ominus}$

Accⁿ to Electrochemical Series anode is made up of lower element of (E.C.S.) and cathode is made up of upper element of E.C.S

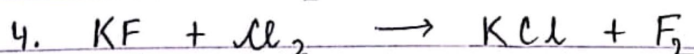
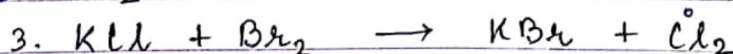
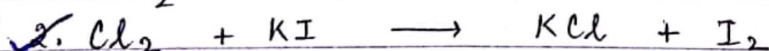
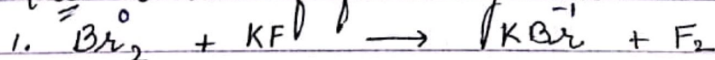
* Oxide of metal which are placed above Cu are unstable and easily reduced to metal when heated.

Oxidising Power Halogens : $F_2 > Cl_2 > Br_2 > I_2$
Reducing Character of Halides = $HF < HCl < HBr < HI$

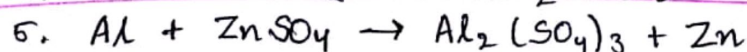
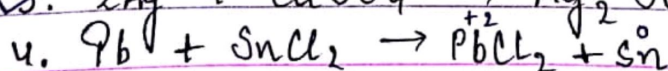
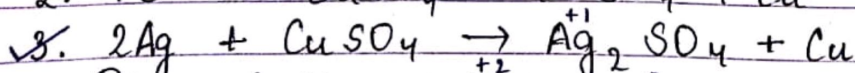
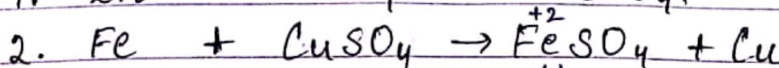
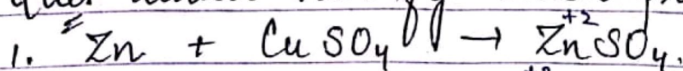
Halide Replacement :-



Ques Which of following reacⁿ is spontaneous?



Ques Identify which process is spontaneous or not.



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Ques Arrange following metal in ↑ order of reducing Power.

	X	Y	Z	W
$E_{M^{n+}/M}$	+0.3	-0.134	-2.05	+2.05

$W < X < Y < Z$

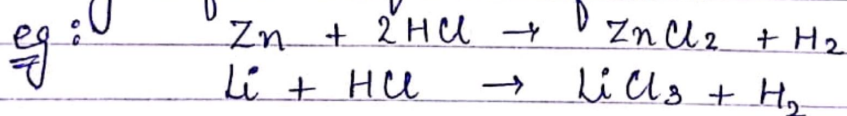
Ques Identify Strongest Oxidising Agent.
① Fe^{2+} ② Cu^{2+} ③ Zn^{2+} ④ Ag^+

Ques Identify strongest oxidising Agent.
① Li^+ ② Zn^{2+} ③ Cu ④ Ag
do not Reactively

Ques Arrange in Torder of S.O.P.
① $2A^{\ominus} + B_2^{\circ} \rightarrow 2B^{\ominus} + A_2^{\circ}$
② $2C^{\ominus} + B_2 \rightarrow 3C$
③ $2D^{\ominus} + A_2^{\circ} \rightarrow 2A^{\ominus} + D_2^{\circ}$
 $B < C < A < D$

Displacement of Hydrogen :-

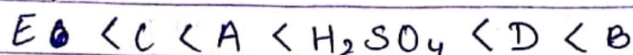
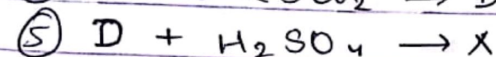
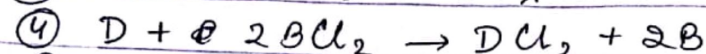
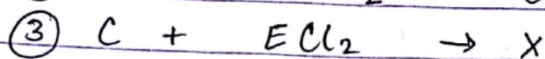
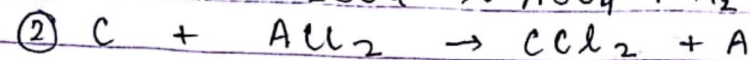
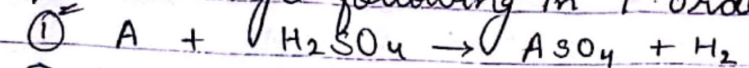
Metal which is placed below Hydrogen can easily displace H_2 gas from aq. solⁿ of acid.



Displacement of Hydrogen from water :-

- * Metal which are placed below Mg can easily displace H_2 gas from water. Metal from Mg to Cr can displace H_2 from hot water.
- * Fe can displace H_2 from water steam.

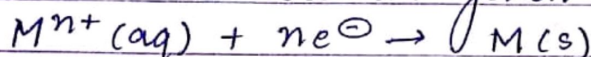
Ques Arrange following in $\uparrow$ order of SRP.



Nerst Equation:- It is use to calculate electrode potential or emf of cell.

We calculate std. Electrode Potential (E°)
at std. condⁿ $\Rightarrow 25^\circ C / 1 \text{ bar} / 1 \text{ M}$

If std. condⁿ are not given :-



$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$[M] = 1 \text{ solid}$

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

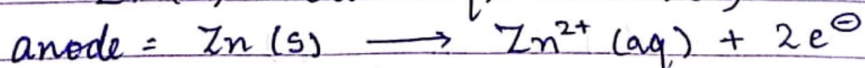
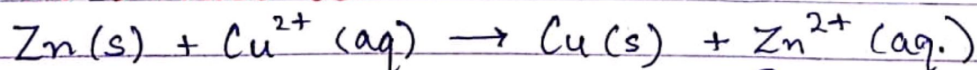
$R = \text{Universal gas const.} = 8.314 \text{ J/K/mol}$

$T = \text{Temp. (K)}$

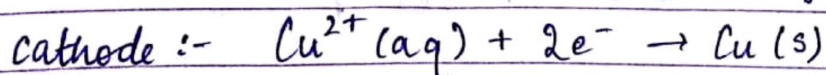
$n = \text{no. of } e^-$

$F = \text{Faraday const.} = 96487 \text{ C mol}^{-1}$
 $\approx 96500 \text{ C mol}^{-1}$

For Daniel Cell :-



$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{2.303RT}{2F} \log \frac{1}{[Zn^{2+}]}$$



$$E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} - \frac{2.303RT}{2F} \log \frac{1}{[Cu^{2+}]}$$

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

$$E_{\text{cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}}$$

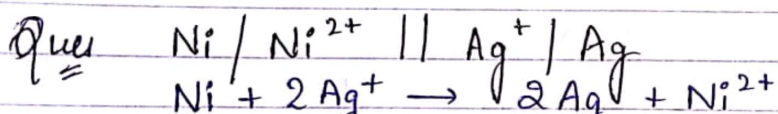
$$E_{\text{cell}} = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - \frac{2 \cdot 303 RT}{2F} \log \frac{1}{[\text{Cu}^{2+}]}$$

$$= E_{\text{Zn}^{2+}/\text{Zn}} + \frac{2 \cdot 303 RT}{2F} \log \frac{1}{[\text{Zn}^{2+}]}$$

$$E_{\text{cell}} = (E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}})$$

$$= -\frac{2 \cdot 303 RT}{2F} \log \frac{1}{[\text{Cu}^{2+}]} + \frac{2 \cdot 303 RT}{2F} \log \frac{1}{[\text{Zn}^{2+}]}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2 \cdot 303 RT}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2 \cdot 303 RT}{2F} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^{+}]^2}$$

For a reacⁿ $\Rightarrow aA + bB \rightarrow cC + dD$

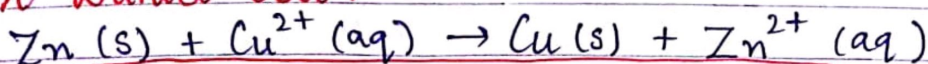
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2 \cdot 303 RT}{nF} \log a$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2 \cdot 303 RT}{nF} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

at 298 K R, F

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

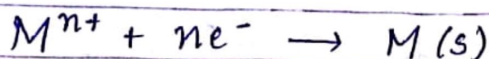
For Daniel Cell :-



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Application of Nernst Equation :-

1. To calculate electrode Potential.



$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

Ques Calculate electrode potential of Cu if Cu electrode is dipped to 0.1 M CuSO_4 at 25°C .
The std. electrode Potential of Cu^{2+}/Cu is 0.34 V

Ques A piece of Zn metal is dipped in 0.1 M solⁿ of ZnSO_4 . The salt is dissociated to the extent of 20%. Calculate that electrode Potential of Zn if $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$.

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Ques Calculate change in electrode Potential of Zn/Zn^{2+} if solⁿ is diluted up to 10 times?

Let initial concⁿ of $[Zn^{2+}] = 1$

$$\text{then } (E_{Zn^{2+}/Zn})_1 = E_{Zn^{2+}/Zn}^{\circ} - \frac{0.0591}{2} \log \frac{1}{1}$$

$$(E_{Zn^{2+}/Zn})_1 = E_{Zn^{2+}/Zn}^{\circ} \Rightarrow E_{Zn/Zn^{2+}} = -E_{Zn^{2+}/Zn}^{\circ}$$

diluted upto 10 times

$$[Zn^{2+}] = \frac{1}{10} M$$

$$E_{(Zn^{2+}/Zn)}_2 = -E_{Zn^{2+}/Zn}^{\circ} - \frac{0.0591}{2} \log \frac{1}{1/10}$$

$$= E_{Zn^{2+}/Zn}^{\circ} - \frac{0.0591}{2}$$

$$(E_{Zn/Zn^{2+}})_2 = -E_{Zn^{2+}/Zn}^{\circ} + \frac{0.0591}{2}$$

$$(E_{Zn/Zn^{2+}})_2 = (E_{Zn/Zn^{2+}})_1 = \frac{0.0591}{2}$$

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2. To calculate Electrode Potential of Hydrogen electrode:-

$$2H^+ + 2e^- \rightarrow H_2$$

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{2} \log \frac{P_{H_2}}{[H^+]^2}$$

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

at atm. press. = 1 atm

$$E_{H^+/H_2} = -\frac{0.0591}{2} \log \frac{1}{[H^+]^2}$$

$$E_{H^+/H_2} = 0.0591 \log [H^+]_{10}$$

$$E_{H_2/H^+} = -0.0591 \log [H^+]$$

Ques Calc. electrode Potential of Hydrogen electrode when pH of acidic solⁿ is 3 HCl/H₂ (10 atm)
Pt

$$pH = 3 \quad [H^+] = 10^{-3}$$

$$E_{H^+/H_2} = -\frac{0.0591}{2} \log \frac{10}{[10^{-3}]^2}$$

$$= -\frac{0.0591}{2} \times 7 = -\frac{0.4137}{2} = -0.2068$$

Ques A Hydrogen gas electrode is made by dipping Platinum wire in a solⁿ of HCl of pH 10 & passing H₂ gas around the Pt wire at 1 atm Pr. The ox. potential of electrode would be -

(a) 0.059 V (b) 0.59 V (c) 0.118 V (d) -0.591 V

$$pH = 10 \quad [H^+] = 10^{-10}$$

$$E_{H_2/H^+} = -0.0591 \log_{10} 10^{-10}$$

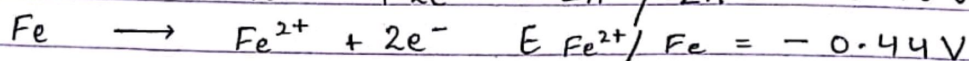
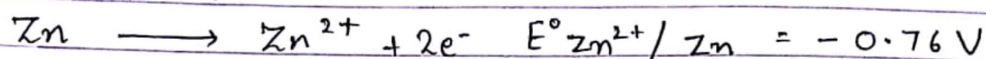
$$= +0.0591 \times 10$$

$$= 0.59$$

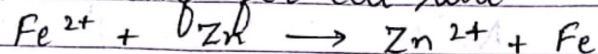
3. To calculate E_{cell}

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

Ques The red. Potential for the following half cell reaction are



find the emf for cell reaction



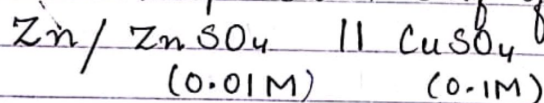
$$E^\circ_{Zn/Zn^{2+}} = 0.76V$$

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

$$= 0.76 - (-0.44) = 0.76 + 0.44 = 1.20$$

Ques The std. oxi. potential of Zn & Cu are 0.76V & -0.34V resp. calc. emf of following cell

1.39V



$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[anode]}{[cathode]}$$

$$0.76 + 0.34$$

$$1.10$$

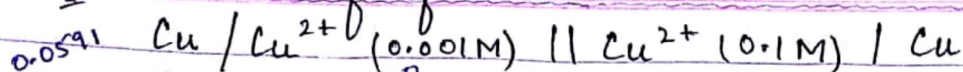
$$= 1.10 - \frac{0.0591}{2} \log \frac{10^{-2}}{10^{-1}}$$

$$= 1.10 + \frac{0.0591}{2} \log 10$$

$$= 1.10 + 0.029$$

Ques Calc. emf of cell

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$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-1}}$$

$$= + \frac{0.0591 \times 2}{2} \log 10$$

$$= 0.0591$$

Ques Calc. emf of cell $\text{Ni} / \text{Ni}^{2+} (0.1\text{M}) \parallel \text{Ag}^{+} (0.1\text{M}) / \text{Ag}$

given $E_{\text{Ag}^{+}/\text{Ag}} = 0.80\text{V}$

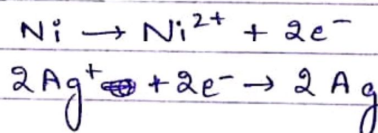
$E_{\text{Ni}^{2+}/\text{Ni}} = -0.25\text{V}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{10^{-1}}{(10^{-1})^2}$$

$$= 1.05 - \frac{0.0591}{2} \log 10$$

$$= 1.05 + 0.0295$$

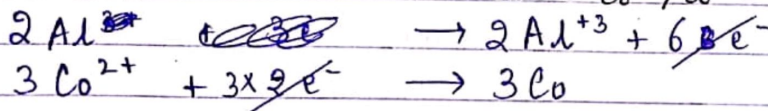
$$= 1.0795$$



Ques Calculate emf $\text{Al} / \text{Al}^{3+} (10^{-2}\text{M}) \parallel \text{Co}^{2+} (10^{-1}\text{M}) / \text{Co}$

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

$E^{\circ}_{\text{Co}^{2+}/\text{Co}} = -0.20\text{V}$



Ques $\text{Pt}(s) / \text{Br}_2(l) \parallel \text{Br}^{-} (0.01\text{M}) \parallel \text{H}^{+} (0.01\text{M}) / \text{H}_2(g) / \text{Pt}$

$E_{\text{Pt}/\text{Br}_2/\text{Br}^{-}} = 1.09\text{V}$ $E_{\text{cell}} = ?$

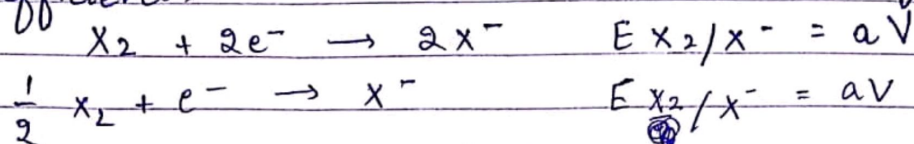
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{H}^+/\text{H}_2} - E^{\circ}_{\text{Br}_2/\text{Br}^-} \quad \begin{array}{l} 2\text{Br}^- \rightarrow \text{Br}_2 + 2e^- \\ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \end{array}$$

$$= 0 - 1.09 = -1.09 \text{ V}$$

$$E^{\circ}_{\text{cell}} = - \frac{0.0591}{2} \log \frac{[\text{Br}_2] [\text{P}_{\text{H}_2}]}{[\text{Br}^-]^2 [\text{H}^+]^2}$$

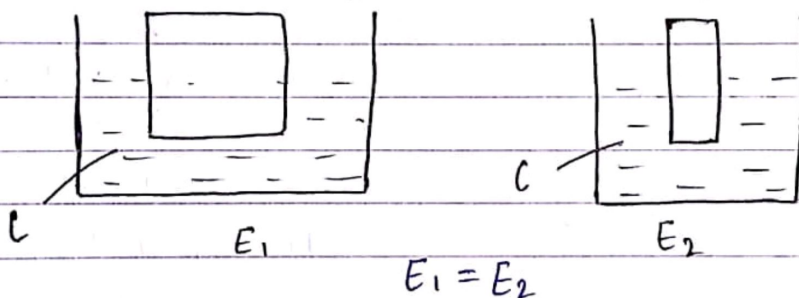
Note:

1. For a given electrode, Electrode Potential does not change when reacⁿ is multiplied or divided by coefficient.



2. Value of Electrode Potential does not depend upon size of electrode and amt. of solⁿ but depends upon concⁿ of solⁿ.

3. Electrode Potential is an intensive property.



Eq^m constant for Nernst Eqⁿ :-

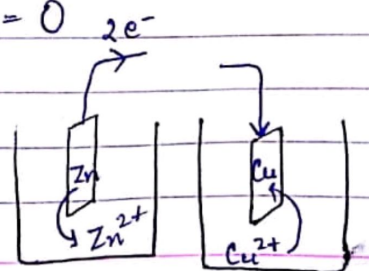
eg In Daniell Cell :- $[\text{Zn}^{2+}] \uparrow$ & $[\text{Cu}^{2+}] \downarrow$ continuous
After some $[\text{Zn}^{2+}] = \text{const.}$] state of
 $[\text{Cu}^{2+}] = \text{const}$] eqⁿ.

no flow of e^-

emf of cell = 0

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$0 = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

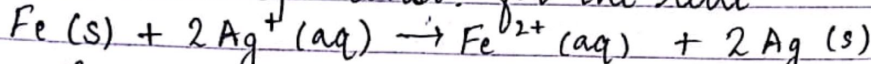


Reduction Potential $\rightarrow$ Cathode

$$E^\circ_{\text{cell}} = \frac{0.0591}{2} \log_{10} K_c \quad \left| \quad \begin{array}{l} \text{Zn (s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Cu (s)} + \text{Zn}^{2+}(\text{aq}) \\ K_c = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \end{array} \right.$$

In Generally $E^\circ_{\text{cell}} = \frac{0.0591}{n} \log_{10} K_c$

Ques Calc. the eq^m const. for the reacⁿ



$$E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V} \quad \& \quad E^\circ_{\text{Fe}/\text{Fe}^{2+}} = 0.44 \text{ V}$$

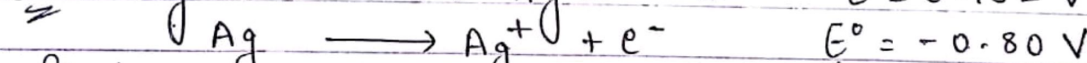
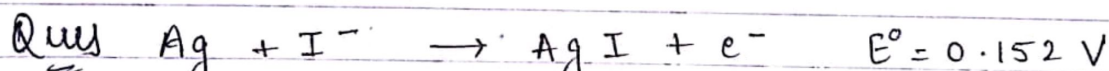
$$E^\circ_{\text{cell}} = 0.80 - (-0.44) = 1.24$$

$$E^\circ_{\text{cell}} = \frac{0.0591}{2} \log_{10} K_c$$

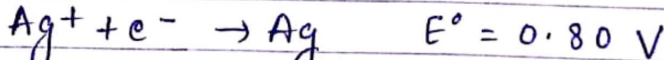
$$\frac{1.24 \times 2}{0.06} = \log_{10} K_c$$

$$\frac{2.48}{0.06} \times 100 = \frac{248}{6} = \log_{10} K_c = 41$$

$$K_c = 10^{41}$$



Find K_{sp} of AgI



$$E^\circ_{\text{cell}} = 0.80 - 0.152 = \frac{0.0591}{1} \log \frac{[\text{Ag}^+][\text{I}^-]}{[\text{AgI}]}$$

$$\frac{0.648}{0.06} = \log [\text{Ag}^+][\text{I}^-]$$

$$\frac{108 \times 648 \times 10^2}{6 \times 10^3} = 10.8 = \log_{10} K_c$$

$$K_c = 10^{10.8}$$

Electrochemical Cell & Gibbs free Energy :-

Useful work
(electrical work done)

non useful work
(mechanical)

W_{electrical} = Charge × Potential

$$= q \times E_{\text{cell}}$$

$$W_{\text{electrical}} = n F E_{\text{cell}}$$

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

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

$$\Delta G^\circ = -n F E^\circ_{\text{cell}}$$

$$1e^- = 1.6 \times 10^{-19} \text{ C}$$

$$1 \text{ mole } e^- = 6.022 \times 10^{23} \times 1.6 \times 10^{-19} \text{ C}$$

$$= 96487 \text{ C}$$

$$1F \approx 96500 \text{ C}$$

$$n \text{ mole } e^- = nF$$

$$\text{charge of 'n' mole } e^- = q = nF$$

$$\Delta G = \Delta G^\circ + 2.303 RT \log Q$$

$$-n F E_{\text{cell}} = -n F E^\circ_{\text{cell}} + 2.303 RT \log Q$$

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

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

spont. $\Delta G < 0$

$$\Delta E_{\text{cell}} > 0$$

non spont. $\Delta G > 0$

$$\Delta E_{\text{cell}} < 0$$

at $\rightleftharpoons$

$$\Delta G = 0$$

$$E_{\text{cell}} = 0$$

$$0 = E^\circ_{\text{cell}} - \frac{2.303 RT \log K_c}{nF}$$

$$E^\circ_{\text{cell}} = \frac{2.303 RT \log K_c}{nF}$$

$$\Delta G^\circ = -n F E^\circ_{\text{cell}}$$

$$\Delta G^\circ = -2.303 RT \log K_c$$

$$\Delta G^\circ < 0$$

$$\log K_c > 0$$

$$K_c > 1$$

$$\Delta G^\circ > 0$$

$$\log K_c < 0$$

$$K_c < 1$$

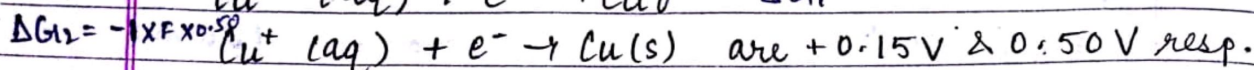
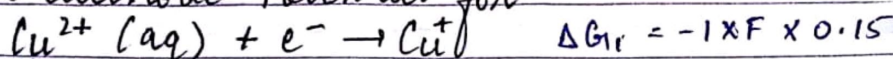
$$\Delta G^\circ = 0$$

$$\log K_c = 0$$

$$K_c = 1$$

AIPMT-11

Ques The electrode Potential for



Then value of $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}}$ will be

- ① 0.325 V ② 0.650 V ③ 0.150 V ④ 0.500 V

$$\Delta G_1 + \Delta G_2 = \Delta G_3$$

$$E_{\text{Cu}^{2+}/\text{Cu}^{+}} = 0.15$$

$$E_{\text{Cu}^{+}/\text{Cu}} = 0.50$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.15 + 0.50 = 0.65$$

$$-1 \times F \times 0.15 + 1 \times F \times 0.5 = -2 \times F \times E_{\text{Cu}^{2+}/\text{Cu}}$$

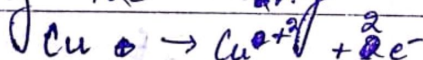
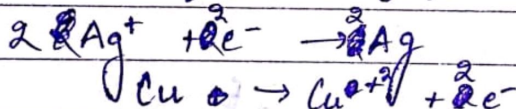
$$0.65 = 2 E_{\text{Cu}^{2+}/\text{Cu}}$$

AIPMT-10

Ques For the reduction of silver ions with copper metal, the std. cell potential was found to be +0.46 V at 25°C. find the value of ΔG° ? $F = 96500 \text{ C mol}^{-1}$

- ① -0.89 KJ ② -89.0 J ③ -44.5 KJ ④ -98.0 KJ

$$E_{\text{cell}} = 0.46$$



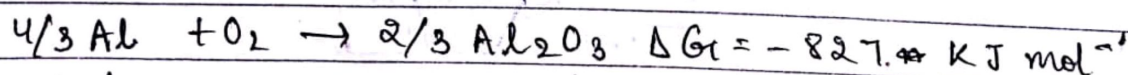
$$\Delta G^{\circ} = -n F E_{\text{cell}}$$

$$= -2 \times 96500 \times 0.46$$

$$= -89000$$

$$\begin{array}{r} 3 \times 3 \\ 96500 \\ 46 \\ \hline 579000 \end{array}$$

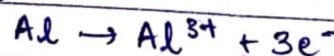
Ques



Find the min^m emf req^d to carry the electrolysis of Al_2O_3 ? ($F = 96500 \text{ C mol}^{-1}$)

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

$$-827000 = -4 \times 96500 \times E_{\text{cell}}$$



$$n = \frac{4}{3} \times 3 = 4$$

AIPMT - 1974

Date _____ Page 3/

Ques $\text{Zn} / \text{Zn}^{2+} \parallel \text{Cu}^{2+} (\text{aq}) / \text{Cu}$ $E^\circ_{\text{cell}} = 1.10 \text{ V}$ at 25°C
The eq^m const. for the reactⁿ
 $\text{Zn} (\text{s}) + \text{Cu}^{2+} (\text{aq}) \rightleftharpoons \text{Cu} (\text{s}) + \text{Zn}^{2+} (\text{aq})$ is of the order.

- (1) 10^{37} (2) 10^{28} (3) 10^{18} (4) 10^{17}

$$E^\circ_{\text{cell}} = \frac{2.303 RT}{nF} \log_{10} K_c$$

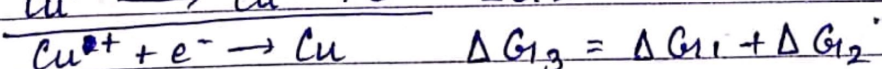
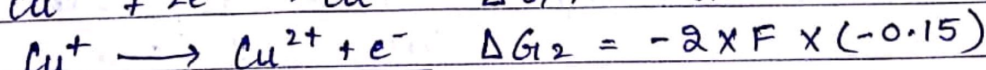
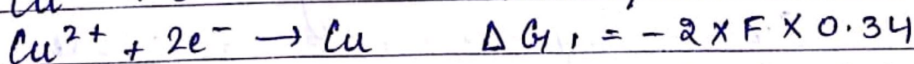
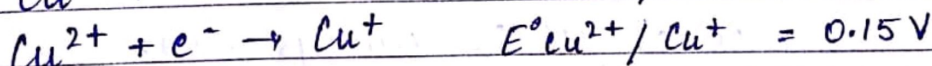
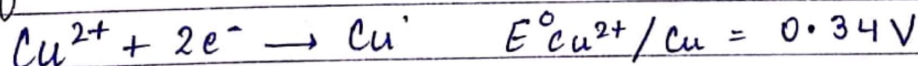
$$1.10 = \frac{2.303 \times 0.08 \times 300}{2 \times 96500} \log_{10} K_c$$

$$\frac{1.10 \times 2 \times 96500}{2.303 \times 0.08 \times 300} = \log_{10} K_c$$

$$\frac{1 \times 1 \times 100 \times 965}{2 \times 4 \times 3} = \log_{10} K_c$$

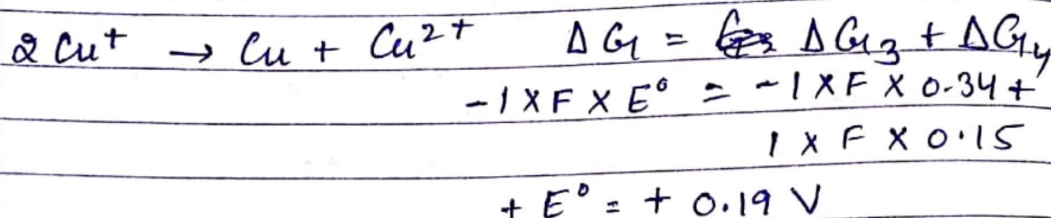
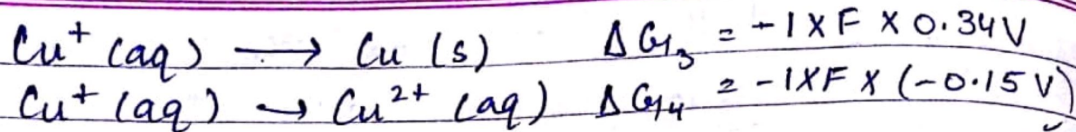
Ques $\text{Cu}^+ (\text{aq})$ is unstable in solⁿ undergoes simultaneous oxidation & reduction accⁿ to the reactⁿ
 $2 \text{Cu}^+ (\text{aq}) \rightleftharpoons \text{Cu}^{2+} (\text{aq}) + \text{Cu} (\text{s})$
Find E°_{cell}

If $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$ & $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15 \text{ V}$



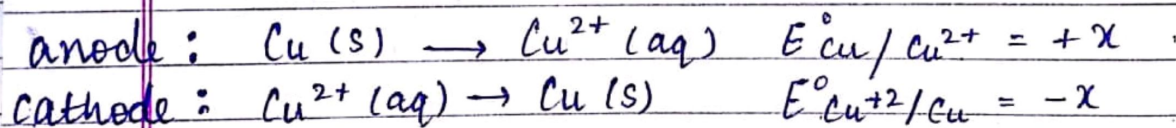
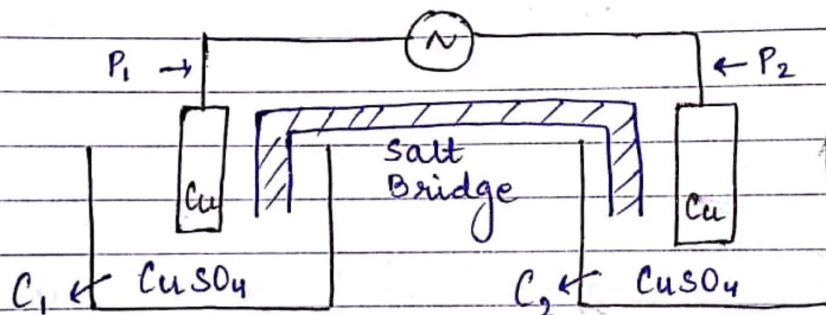
$$-1 \times F \times E^\circ_{\text{Cu}^+/\text{Cu}} = -2 \times F \times 0.34 + 2 \times F \times 0.15$$

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



Concentration Cell :-

When 2 similar electrode with different concⁿ of electrolyte solⁿ are connected then cell is called concⁿ cell.



$$\begin{aligned} E^\circ_{\text{cell}} &= C - a \\ &= -x - (-x) = 0 \end{aligned}$$

E°_{cell} for concⁿ cell is always zero.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303 RT}{nF} \log \frac{(\text{anode})}{(\text{cathode})}$$

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

$$E_{\text{cell}} = +\frac{0.0591}{2} \log \frac{C_2}{C_1}$$

$$\begin{aligned} E_{\text{cell}} > 0 & \quad \log \frac{C_2}{C_1} > 0 & \quad \frac{C_2}{C_1} > 1 \\ & & & C_2 > C_1 \end{aligned}$$

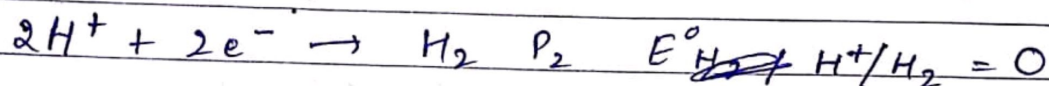
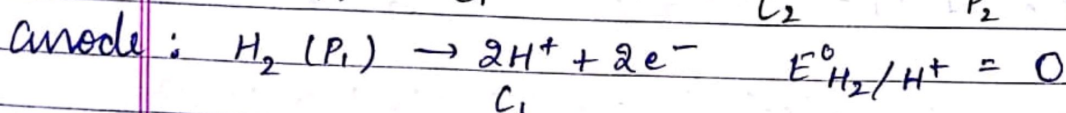
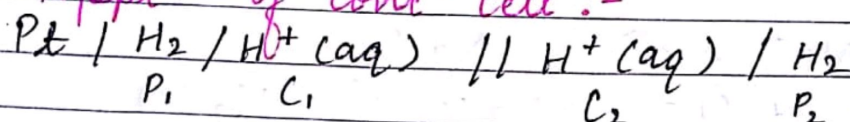
at $t = t$
$$E_{cell} = \frac{0.0591}{2} \log \frac{C_2 - x}{C_1 + x}$$

if $E_{cell} = 0$
$$\frac{C_2 - x}{C_1 + x} = 1$$

$$C_2 - x = C_1 + x$$

$$x = \frac{C_2 - C_1}{2}$$

Applⁿ of Concⁿ Cell :-



$$E_{cell} = E_{cell}^0 - \frac{0.0591}{2} \log \frac{(C_1)^2 P_2}{P_1 (C_2)^2}$$

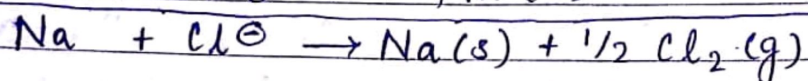
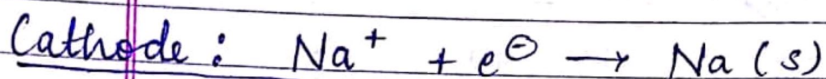
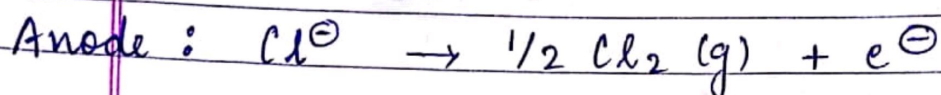
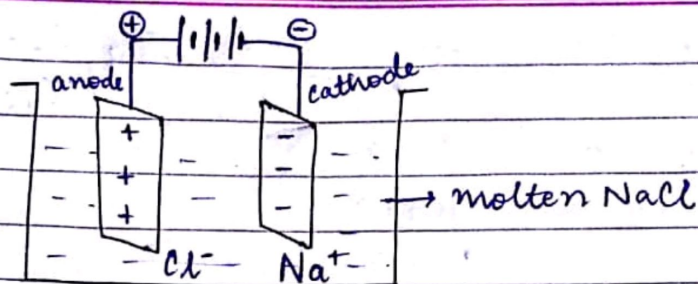
$$E_{cell} = \frac{0.0591}{2} \log \frac{P_1}{P_2} \left(\frac{C_2}{C_1} \right)^2$$

If $P_1 = P_2$
$$E_{cell} = \frac{0.0591}{2} \log \frac{C_2}{C_1}$$

If $C_1 = C_2$
$$E_{cell} = \frac{0.0591}{2} \log \frac{P_1}{P_2}$$

Electrolysis :- The process of chemical decomposition of electrolytes by passage of electricity.
→ Device in which electrolysis takes place is known as Electrolytic Cell or Voltmeter.

Electrolytic cell : Electrical energy is converted into chemical energy.



Prod. of Electrolysis of Molten NaCl :-

Anode : Cl_2 gas is liberate

Cathode : $\text{Na} (\text{s})$ is obtained

Electrolysis of aq. NaCl

anode

Cl^-

OH^-

H_2O

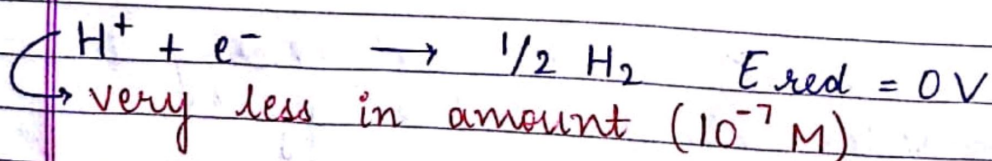
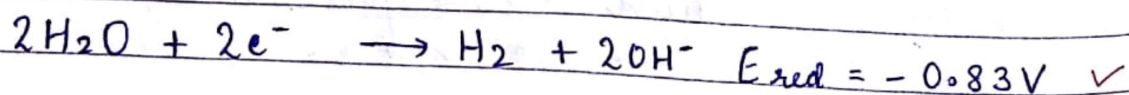
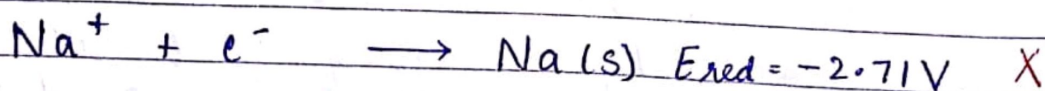
Cathode

Na^+

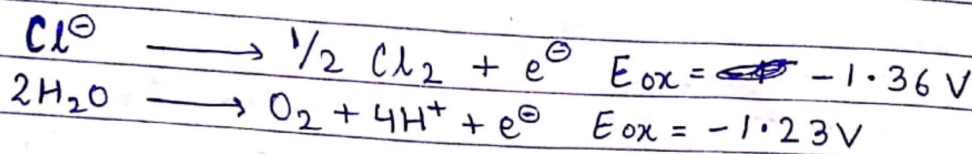
H^+

H_2O

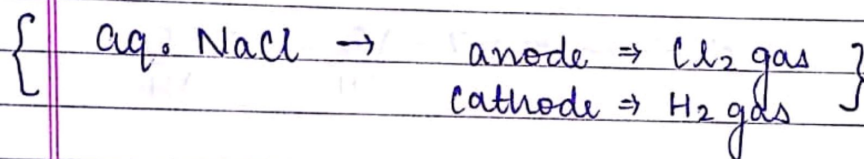
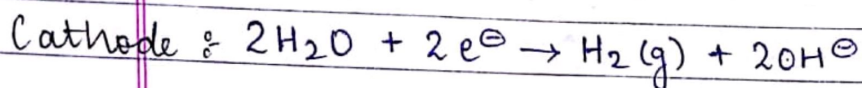
Cathode :- जिसका red. Potential ज्यादा उसका Cathode पर red. होगा।



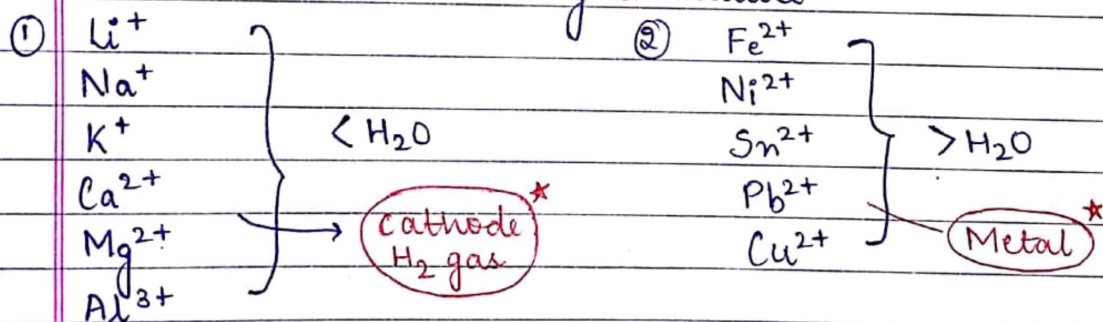
Anode : जिसका Ox. Potential ज्यादा होगा उसका Oxidation होगा।



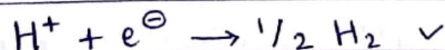
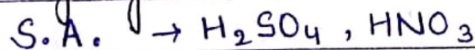
Nearly same but देखो Cl की conc. बहुत ज्यादा होगा इसलिए Ox. Cl का होगा।
Very less in amount (10^{-1} M)



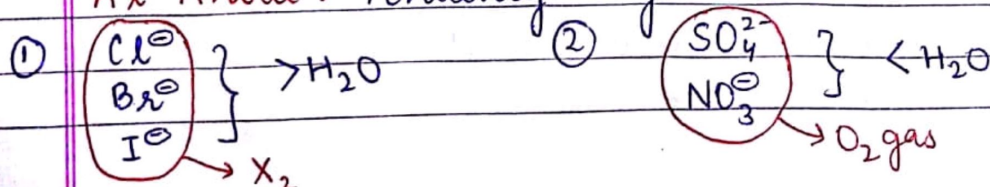
At Cathode : Tendency to reduce



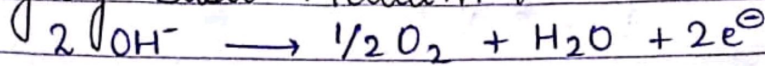
③ Highly acid Medium :



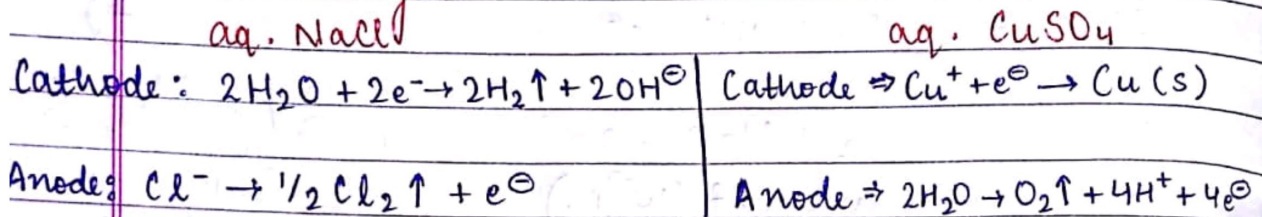
At Anode : Tendency to get oxidise



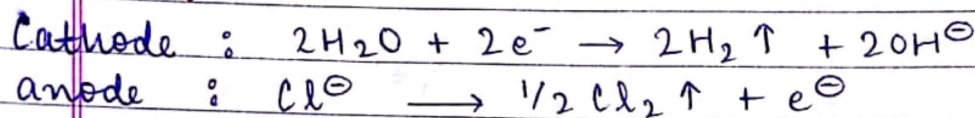
3. Highly Basic Medium :-



Summary :-

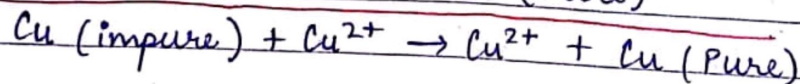
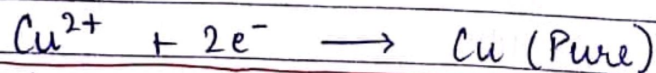
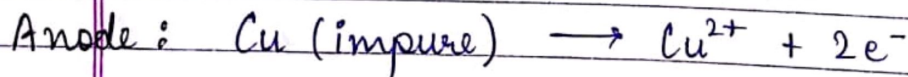
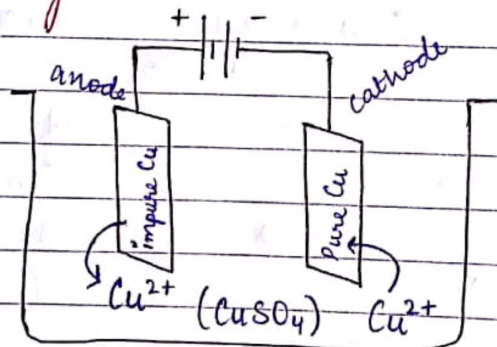


aq. LiCl



Thermodynamic efficiency of cell = $\frac{\Delta G}{\Delta H} = -\frac{nFE_{\text{cell}}}{\Delta H}$

Electroplating :-



Electroplating :

Anode = Impure Metal

Cathode = Pure Metal

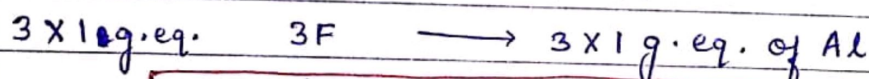
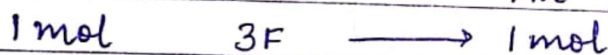
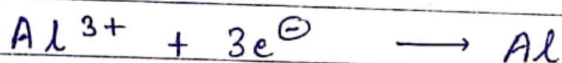
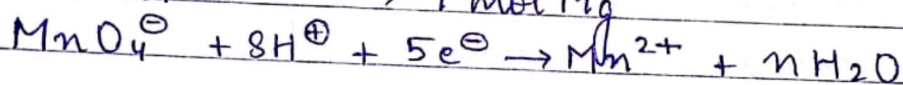
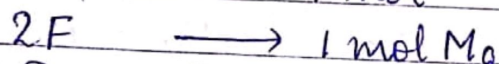
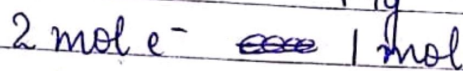
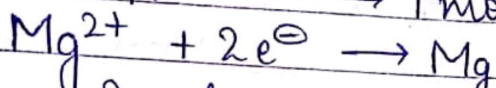
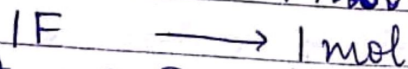
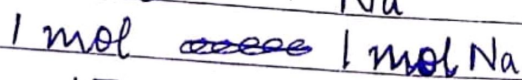
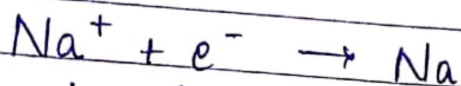
Quantitative Analysis :-

$$1 e^- = 1.6 \times 10^{-19} C$$

$$1 \text{ mole } e^- = 6.022 \times 10^{23} \times 1.6 \times 10^{-19} C$$

$$= 96487 C$$

$$1 \text{ mole } e^- = 1 F \approx 96500 C$$



$$n \text{ mole } e^- = n F = n \text{ g.eq. metal}$$

Law of Faraday :-

1st Law : The amount of substances deposited or liberated at an electrode is directly proportional to current pass through it.

$$W \propto Q$$

$$\text{weight} \leftarrow \boxed{W = ZQ}$$

$Z = \text{Electrochemical equivalent}$

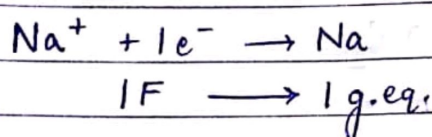
$$Q = 1 \quad W = 2$$

Electrochemical Equivalent is the amount of substance deposited or liberated when 1 C charge is passed through the Electrolytic solⁿ.

$$Q = it$$

$$W = Z it$$

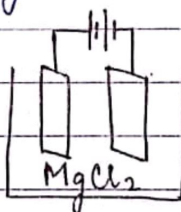
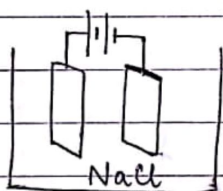
$$Z = \frac{E}{96500}$$



$$E = \frac{\text{Molar Mass}}{n\text{-factor}}$$

IInd Law :-

When same amount of charge is pass through 2 different Electrolytic solⁿ (connected in series) then amount of substance deposited at Electrode will be directly proportional to their equivalent weight.



$$W \propto E$$

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

$$\frac{W_1}{E_1} = \frac{W_2}{E_2}$$

$$W = ZQ$$

$$W \propto Z = \frac{E}{96500}$$

$$W \propto E$$

More Cells in Series :-

$$\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}$$

Ques =

Calculate amount of Al deposited when 9.65×10^3 C charge is passed through molten AlCl_3

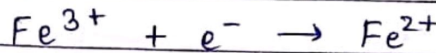
$$W = ZQ$$

$$= \frac{9}{96500} \times \frac{9650 \times 10^3}{1000} = \frac{9}{10} = 0.9$$

$$Z = \frac{279}{2 \times 96500}$$

$$2 \times 96500$$

Ques Calculate amt. & wt. of Fe^{2+} & Fe^{3+} ions reduced by 1.5 F Given Mol. wt. of Fe = 56 g/mol



1 F

1 mol Fe^{2+}

APMT-05
Ques

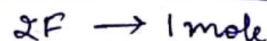
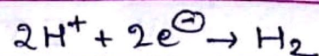
How much Electricity is required to prepare 5.12 kg of Al by Electrolysis

IIT-08

Ques Electrolysis of dil. aq. NaCl solⁿ was carried out by passing 10 mA current. Find time req^d to liberate 0.01 mole of H_2 gas at cathode
(1 F = 96500 mol⁻¹)

$$I = 10 \times 10^{-3} \text{ A}$$

$$Q = it$$



1 mol H_2 is obtain by pass = 2F

$$0.01 \text{ mol} \rightarrow = 0.02 \text{ F}$$

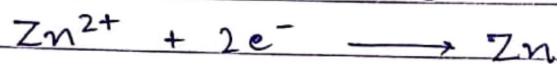
$$Q = 0.02 \times 96500 \text{ C} = 10 \times 10^{-3} \times t$$

$$t = \frac{0.02 \times 96500}{10 \times 10^{-3}}$$

Ques A 5 A current is passed through a solⁿ of Zinc sulphate for 40 min? Find amount of Zinc deposited at cathode (At. mass of Zn = 63)

$$Q = 5 \times 40 \times 60$$

$$= 12000 \text{ C}$$

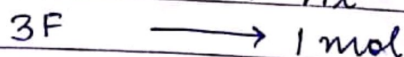
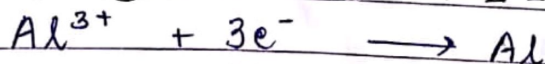


$$\approx 63 \text{ g}$$

$$1 \rightarrow \frac{63}{2} \times \frac{12000}{96500}$$

Ques 4.5 g Al is deposited at Cathode from Al^{3+} solⁿ by certain electric charge. The vol^m of H_2 produced at STP from H^+ ions in solⁿ by the same quantity of Electric Charge will be

- ① 44.8 L ② 22.4 L ③ 11.2 L ④ 5.6 L

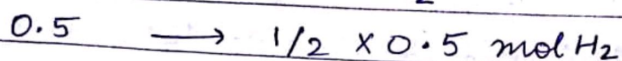
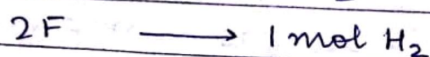
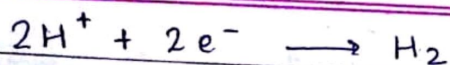


$$27 \text{ g}$$

27 g is obtain = 3F

$$1 \text{ g} \rightarrow = 3/27$$

$$4.5 \text{ g} \rightarrow = \frac{3}{27} \times \frac{4.5}{10} = 0.5 \text{ F}$$



$$= 0.25 \text{ mol } H_2$$

$$= 0.25 \times 22.4 \text{ L}$$

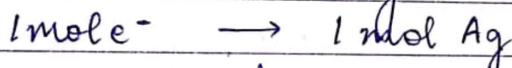
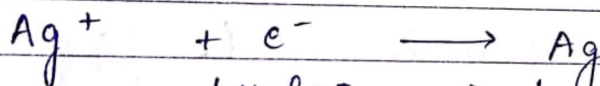
$$= 5.600 \text{ L} = 5.6 \text{ L}$$

Ques How long a current of 3A should be passed through $AgNO_3$ solⁿ to coat a metal surface 80 cm^2 of 0.005 mm thick layer density of this layer is 10.5 g/cm^3 ($Ag = 108 \text{ g/mol}$)

$$d = \frac{M}{V} \Rightarrow M = d \times V = 10.5 \times 80 \times 0.005 \times 10^{-1}$$

$$= 10.5 \times 0.04 = 0.420 \text{ gm}$$

$$V = 80 \times 0.005 \times 10^{-1} \text{ cm}^3$$



1F charge produced = 108 g Ag
 108 g is produced by from = 1F = 96500 C
 $1 \text{ g} \longrightarrow \frac{96500}{108}$

$$0.42 \text{ g} \longrightarrow \frac{96500}{108} \times 0.42 \text{ C}$$

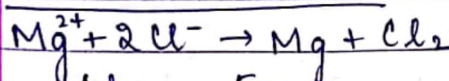
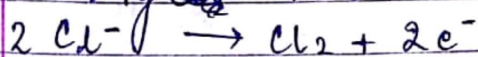
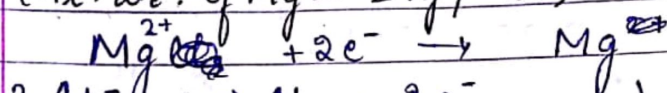
$$\frac{96500 \times 0.42}{108} = it = 3 \times t$$

$$t = \frac{96500 \times 0.42}{54 \times 108 \times 3 \times 100}$$

$$= \frac{965 \times 7}{54}$$

Ques: How long $\rightarrow$ eq. of $\text{Cl}_2 = \text{eq. of Mg}$

Ques Calculate vol. of chlorine gas at NTP produced during electrolysis of MgCl_2 which produce 8g Magnesium (At. wt. of $\text{Mg} = 24 \text{ g/mol}$)



$$\frac{W_{\text{Cl}_2}}{E_{\text{Cl}_2}} = \frac{E_{\text{Mg}}}{W_{\text{Mg}}}$$

$$\frac{W_{\text{Cl}_2}}{8} = \frac{71/2}{3 \times 24/2} = \frac{71}{3}$$

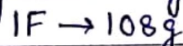
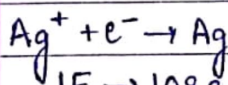
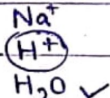
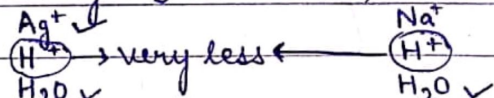
$$n_{\text{Cl}_2} = \frac{71}{71} = \frac{1}{3} \text{ mol}$$

$$\text{Vol.} = \frac{1}{3} \times 22.4$$

$$= \frac{22.4}{3} \text{ L}$$

Ques 5 L of 1M AgNO_3 solⁿ & 2 L of 1M NaCl solⁿ are connected in series when electricity is passed, 54 g of Ag deposited on cathode in AgNO_3 solⁿ. Then calculate vol. of H_2 gas at STP produced in NaCl solⁿ (Mw. of Ag = 108 g/mol)

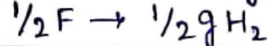
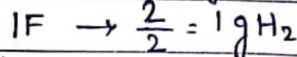
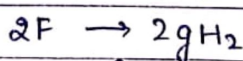
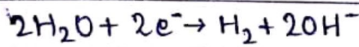
5 L 1M AgNO_3 solⁿ 2 L, 1M NaCl solⁿ



108 g is obtained from 1F

$$1 \text{ g} \rightarrow \frac{1}{108} F$$

$$54 \text{ g} \rightarrow \frac{1}{108} \times 54 F = \frac{1}{2} F$$



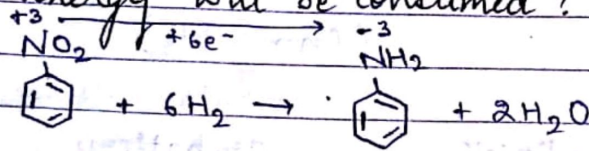
$$= \frac{1}{4} \text{ mol H}_2$$

$$= \frac{22.4}{4} = 5.6 \text{ L}$$

Series same
same current
i.e. same charge

Ques Calculate the electricity that would be required to reduce 12.3 g of nitrobenzene to aniline. If current efficiency is 50%.

If the potential drop across the cell is 3.0 V How much energy will be consumed?



$$6\text{F} \rightarrow 12.3\text{g}$$

12.3 g is obtained by Passing = 6F

$$1\text{g} \rightarrow \frac{6}{12.3}$$

$$12.3\text{g} \rightarrow \frac{6}{12.3} \times 12.3$$

$$= 0.6\text{F}$$

$$= 0.6 \times 96500\text{C}$$

Current efficiency = 50% = $\frac{i_{\text{used}}}{i_{\text{supplied}}} \times 100$

$Q = it$

Charge efficiency = 50%

Total charge required =

$$0.6 \times 96500 \times \frac{100}{50}$$

$Q_{\text{supplied}} = 115800\text{C}$

$E = Q \times V$

$$= 115800 \times 3 = 347400\text{J}$$

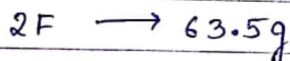
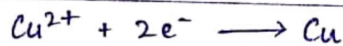
$$= 347.4\text{KJ}$$

$Q_{\text{supplied}} = Q_{\text{used}} \times \frac{100}{50}$

Ques

A current of 3A was passed for 2h through a solⁿ of CuSO_4 . 3g of Cu^{2+} ions were discharged at cathode. Calculate current efficiency for this process.

$I = 3\text{A}$ $t = 2\text{h}$ $M = 3\text{g of Cu}^{2+}$



63.5g is obtained $\rightarrow 2\text{F}$

$$3\text{g} \rightarrow \frac{2}{63.5} \times 3\text{F}$$

$$Q_{\text{used}} = \frac{2}{63.5} \times 3 \times 96500\text{C}$$

$Q_{\text{supplied}} = it = 3 \times 2 \times 60 \times 60$

$$\text{efficiency} = \frac{\frac{2}{63.5} \times 3 \times 96500}{3 \times 2 \times 60 \times 60} = \frac{3}{7} \times 100$$

Battery :- redox reacⁿ C.E. $\rightarrow$ E.E.

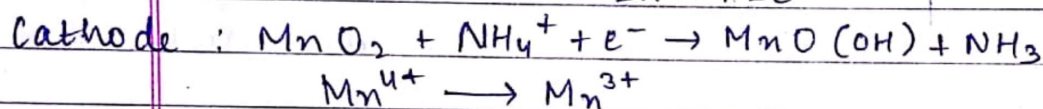
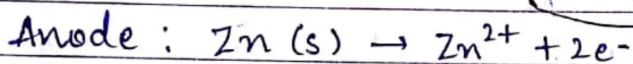
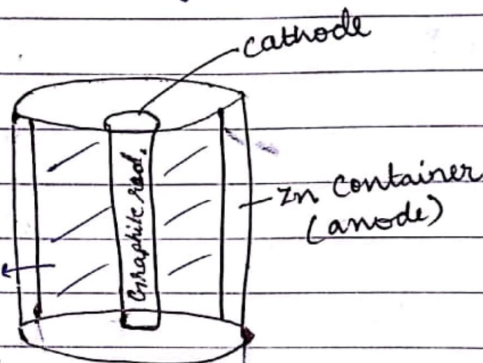
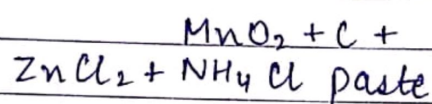
Primary
(non-chargable)
dead after use

eg: remote cell, clock cell, radio cell

Secondary
(Chargable)
 $\rightarrow$ inverter battery
car battery

Primary Batteries :- Reacⁿ occur only once & after use over a period of time battery is dead & can not be used

eg Leclanche Cell / Dry Cell

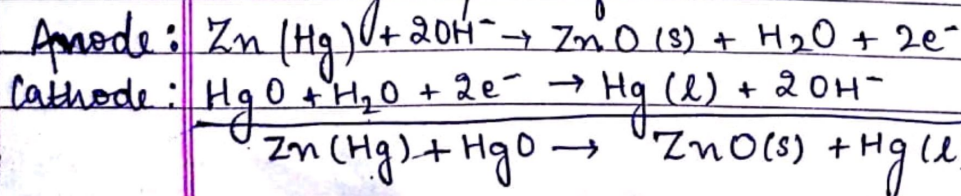
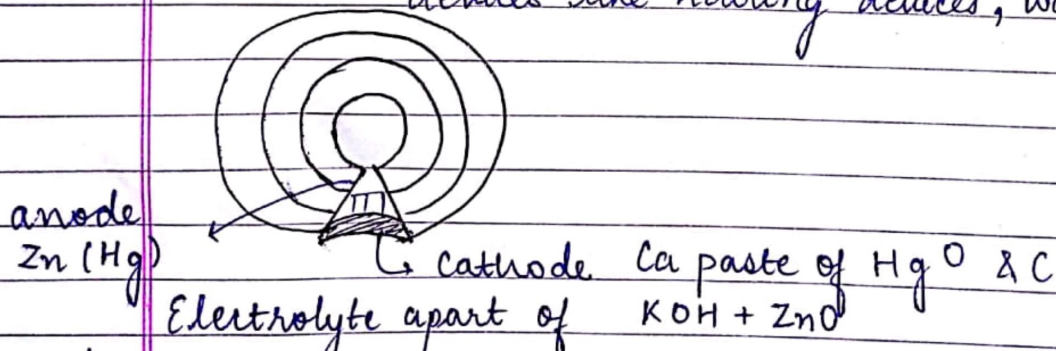


NH_3 produced in reacⁿ forms a complex with Zn^{2+}
 $\rightarrow [Zn(NH_3)_2]^{2+}$

$E_{cell} = 1.5V$

Use $\rightarrow$ in transistor & clocks.

Mercury Cell :- Suitable for low current devices like hearing devices, watches etc.

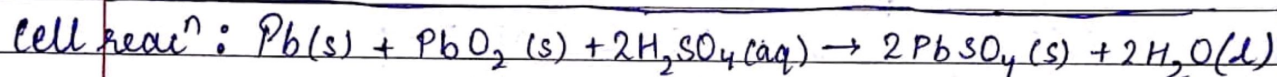
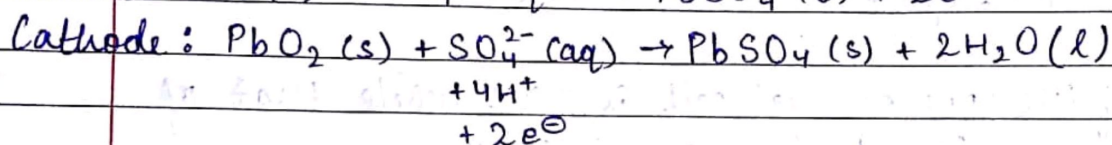
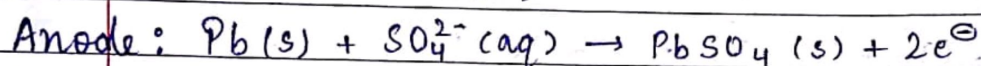


$E_{\text{cell}} = 1.35 \text{ V}$

remains const. during its life as overall reacⁿ does not involve any ion in solⁿ whose concⁿ can change during its concⁿ.

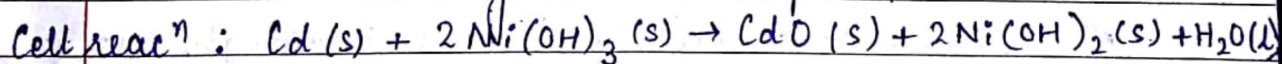
Secondary Batteries :- A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again.

eg: Lead storage Battery: used in automobiles, inverters.
 $\text{Pb} / \text{PbSO}_4 / \text{H}_2\text{SO}_4 / \text{PbO}_2 / \text{PbSO}_4$
(38%)

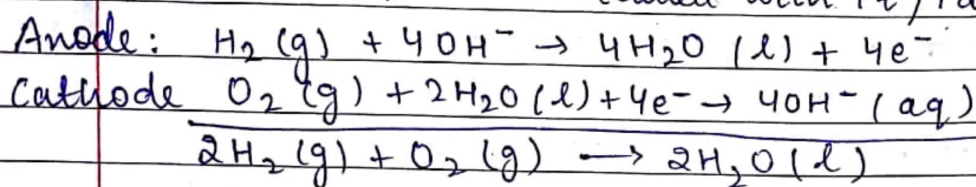
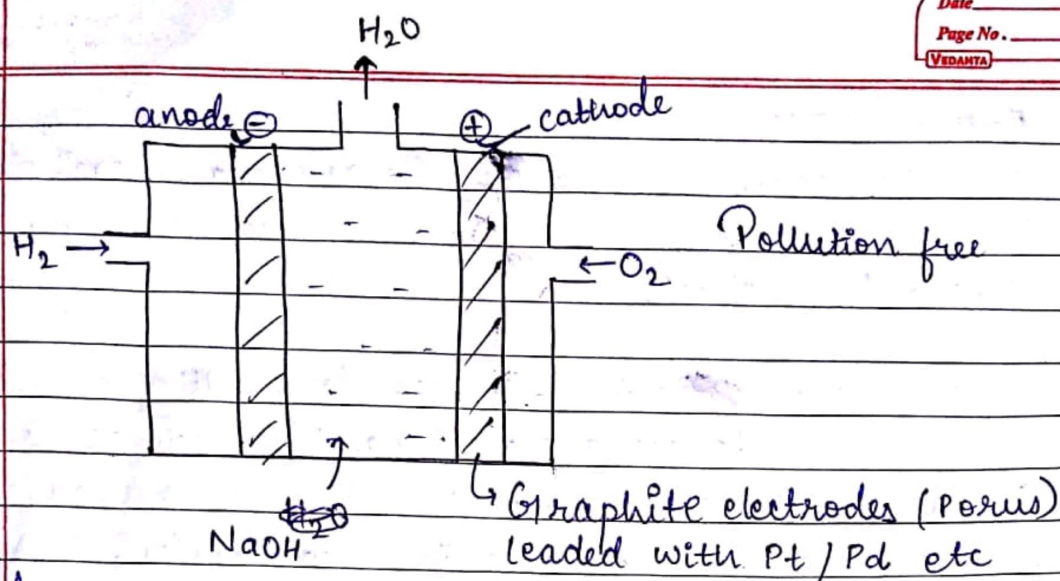


On charging the battery, the reacⁿ is reversed & $\text{PbSO}_4(s)$ on anode & cathode & converted into Pb & PbO_2 respectively.

Nickel-Cadmium cell: longer life than lead storage Battery but it is expensive.



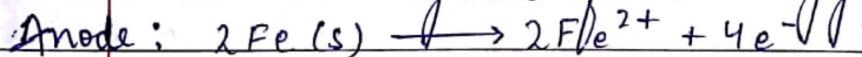
Fuel Cell :- Galvanic cell that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc directly into electrical energy are c/a fuel cells.



Efficiency of fuel cell is 70% while that of thermal plant is about 40%.

$$\text{Cell efficiency} = \frac{\Delta G}{\Delta H} = \frac{-nFE_{\text{cell}}}{\Delta H}$$

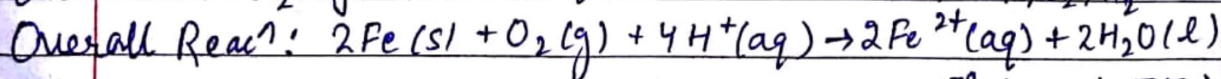
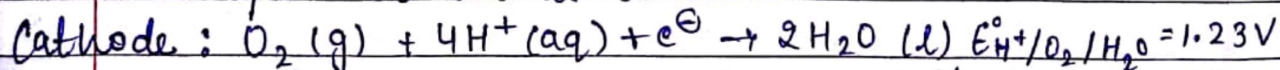
Corrosion :- Rusting of iron, green coating on copper & bronze. In corrosion a metal is oxidised by loss of e^- to oxygen & forms its oxide.



$$E^\circ_{Fe^{2+}/Fe} = -0.44V$$

→ e^- released at anodic spot move through the metal to another spot & react with oxygen in presence of H^+ (from acids which are formed in atmosphere due to reaction of acidic oxides & atmospheric water eg H_2CO_3)

This spot behave as cathode



$$E^\circ_{\text{cell}} = 1.57V$$

⇒ Ferrous ions are further oxidised by atmospheric oxygen to ferric ions which comes out as rust in the form of hydrated ferric oxide.
($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) & Further H^+ ions are produced.

Prevention of Corrosion :-

1. By covering surface of metal with paint or some chemical like Bisphenol.
2. By covering metal with inert metal like Sn, Zn.
3. By Electroplating of Mg, Zn etc.