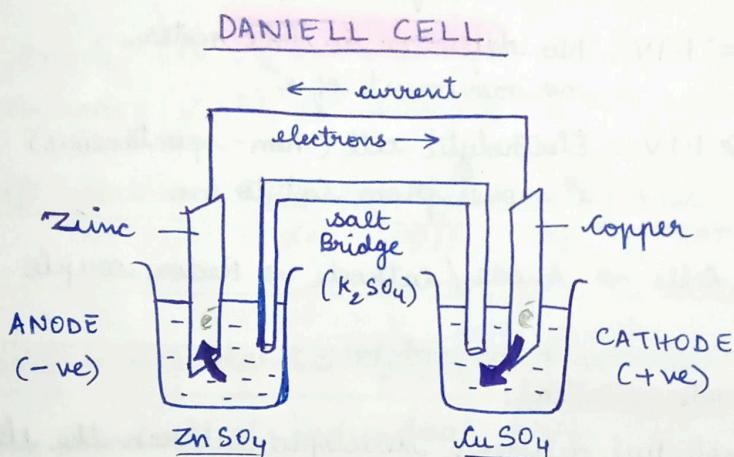


Chapter 4 : ELECTROCHEMISTRY

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

Galvanic / Voltaic cell:

An electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy.



→ Electron flow from Zn to Cu

→ Current flow from Cu to Zn

$$\rightarrow E_{cell}^{\circ} = 1.1 \text{ V}$$

- Electrode potential \Rightarrow Reduction potential (By default)

Oxidation potential = - (Reduction potential)

(SOP = -SRP) \Rightarrow not used here

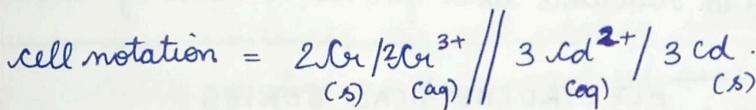
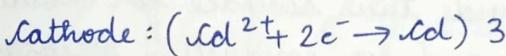
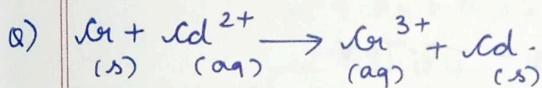
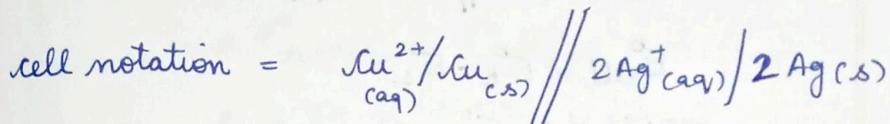
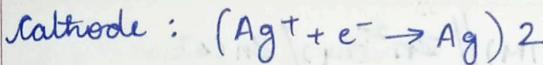
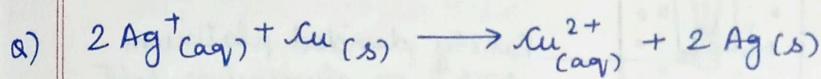
$$\Rightarrow E_{cell}^{\circ} = E_{right}^{\circ} - E_{left}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$$

$$\Rightarrow E_{cell}^{\circ} = E_{Cu^{2+}/Cu}^{\circ} - E_{Zn^{2+}/Zn}^{\circ} = 0.34 - (-0.76)$$

$$\Rightarrow emf \text{ of cell} = E_{cell}^{\circ} = 1.1 \text{ V}$$

- Electrochemical cell : LOAN.
 - Left Oxidation Anode Negative
(For electrolytic cell, Anode = +ve).
- ALWAYS Left - anode
Right - cathode For cell notation (x)
- An Ox, Red Cat → for electrochemical cell only.
 ↓
 Anode, Oxidation Reduction, Cathode .
- If the potential provided by the external battery is
 - $< 1.1V$: Electrochemical cell (spontaneous)
 e^- moves from An to Cat
 - = $1.1V$: No deflection in volt meter,
no movement of e^- .
 - $> 1.1V$: Electrolytic cell (non-spontaneous)
 e^- moves from Cat to An
- Half Cells \Rightarrow Anode / Cathode \Rightarrow Redox couple.
- Electrode potential :
The potential difference developed between the electrode and the electrolyte.
- Standard Electrode Potential :
When the concentrations of all the species involved in the half cell is unity, then the electrode potential is known as standard Electrode Potential (SRP)
- Cell potential :
The difference between the electrode potentials (reduction potentials) of the cathode and the anode.
- Cell electromotive force or EMF of a cell (E_{cell}°)

Cell potential of the cell when no current is drawn through the cell is called the cell's EMF or E°_{cell} .



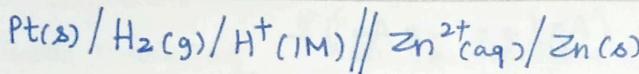
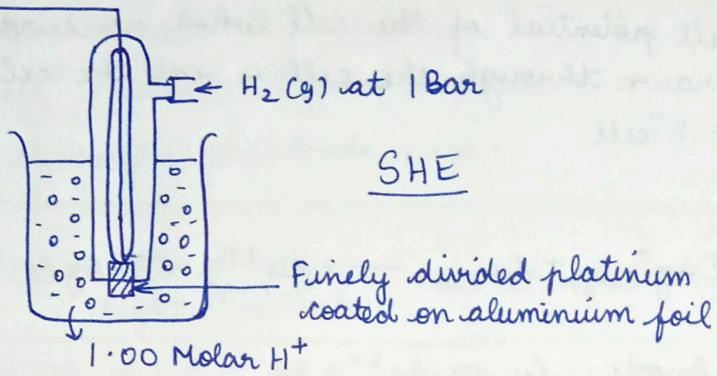
SHE - Standard Hydrogen Electrode.

- The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell.
- If we arbitrarily choose the potential of one electrode (half-cell) then that of the other can be determined with respect to this.
- According to convention, a half-cell called SHE represented by $\boxed{\text{Pt}(\text{s}) | \text{H}_2(\text{g}) | \text{H}^+_{(\text{aq})}}$, is assigned a zero potential at all temperatures

SHE - platinum electrode coated with platinum black

- $\underline{\text{H}_2(\text{g}) = 1 \text{ Bar}}$

- $\underline{\text{H}^+_{(\text{aq})} = 1 \text{ M}}$



$$E_{\text{cell}}^{\circ} = E_{\text{R}}^{\circ} - E_{\text{L}}^{\circ}$$

$$-0.76 \text{ V} = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} - 0$$

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

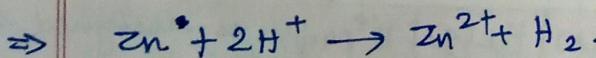
Inert electrode (Pt, Au) do not participate in the reaction but provide their surface for oxidation/reduction reactions and for conduction of electrons.

ELECTROCHEMICAL SERIES

Arrangement of elements in increasing order of standard electrode potential.

Applications of ECS:

- More -ve value = strong reducing agent (Li)
More +ve value = strong oxidising agent (F)
- All elements below Hydrogen (i.e. -ve E° value) can displace Hydrogen from mineral acid.
All elements above Hydrogen (i.e. +ve E° value) cannot displace Hydrogen from mineral acid.



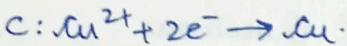
$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ} = 0 - (-0.76) \\ &= +0.76. \end{aligned}$$

$E_{\text{cell}}^{\circ} = +\text{ve}$: spontaneous

$E_{\text{cell}}^{\circ} = -\text{ve}$: Non-spontaneous

3. To predict the feasibility or to predict whether the reaction happens or not (displacement reaction)

⇒ CuSO_4 in Zn container - safe?



$$E^\circ_{\text{cell}} = E^\circ_C - E^\circ_A$$

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

$$= 0.34 - (-0.76)$$

$$= 0.34 + 0.76$$

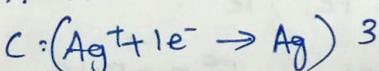
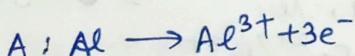
$$= 1.10 \text{ V},$$

$E^\circ_{\text{cell}} = +ve$: spontaneous

↓
Zn displaces Cu from CuSO_4 .

∴ Zinc containers are not used in storing CuSO_4 solution as Zn is oxidised and Cu metal ions are reduced to metal Cu.

⇒ Why is Aluminium foil used in cleaning silver utensils?



$$E^\circ_{\text{cell}} = E^\circ_A - E^\circ_C$$

$$= 0.8 - (-1.66)$$

$$= 0.8 + 1.66$$

$$= 2.46 \Rightarrow +ve E^\circ \Rightarrow \text{spontaneous.}$$

Hence aluminium foil is wrapped around silver articles and boiled to remove the outer Ag_2S (black) layer.

Note: since Voltage is an intensive property (does not depend upon the amount of matter), we do not have to multiply the EMF by any stoichiometric coefficient to cancel out the electrons in calculating emf.

In text Questions

- 3.1) Pt using $\text{Pt}(\text{s})/\text{H}_2(\text{g})/\text{H}^+(\text{aq})$ electrode - (SHE) - as anode and find out E° cell.

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

$$E^\circ_{\text{cel}} = E^\circ_{\text{Mg}^{2+}/\text{Mg}} - 0$$

$$-2.36 \text{ V} = E^\circ_{\text{Mg}^{2+}/\text{Mg}}.$$

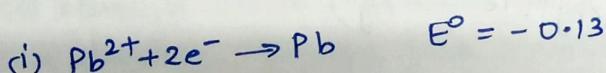
$$\therefore E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.36 \text{ V.}$$

- 3.2) No. refer previous pages.

- 3.3) Anode: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^- . \quad E^\circ = -0.44$.

Cathode = ?

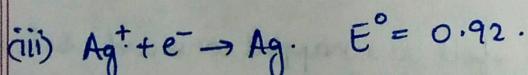
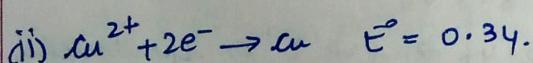
Cathode's E° value must be greater than -0.44 , i.e., > -0.44 , i.e., above $\text{Fe}^{2+}/\text{Fe}^{3+}$.



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

$$= -0.13 - (-0.44)$$

$$= -0.13 + 0.44 = 0.31 \Rightarrow \text{Spontaneous}$$



EXERCISE Q's.

- 1) $\text{Al} = -1.66$ — ②
 $\text{Cu} = 0.34$ — ⑤
 $\text{Fe} = -0.44$ — ④
 $\text{Mg} = -2.36$ — ①
 $\text{Zn} = -0.76$ — ③

order in which they displace each other.
 i.e., Increasing order of SRP (-ve to +ve).

∴ Mg, Al, Zn, Fe, Cu.

- 2) Increasing order of reducing power,
 decreasing order of SRP (+ve to -ve).

$$\text{K}^+/\text{K} = -2.93\text{V}$$

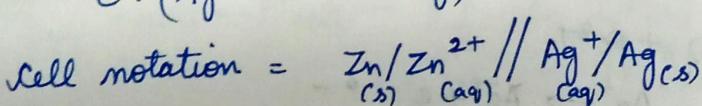
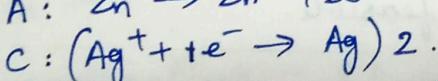
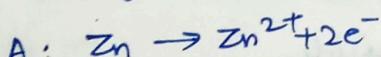
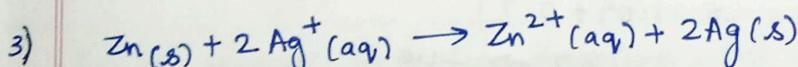
$$\text{Ag}^+/\text{Ag} = 0.80\text{V}$$

$$\text{Hg}^{2+}/\text{Hg} = 0.79\text{V}$$

$$\text{Mg}^{2+}/\text{Mg} = -2.37\text{V}$$

$$\text{Cr}^{3+}/\text{Cr} = -0.74\text{V}$$

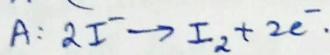
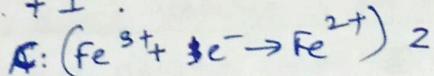
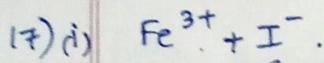
∴ Ag, Hg, Cr, Mg, K.



(i) Negatively charged electrode = Anode. (Zn electrode)

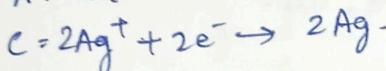
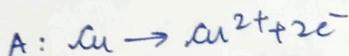
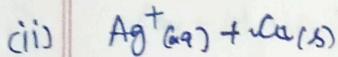
(ii) Carriers of current in the cell = electrons from A to C outside Zn to Ag.

(iii) Anode: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$ | ions flow within the cell.
 Cathode $2\text{Ag}^+ + 2e^- \rightarrow 2\text{Ag}$.



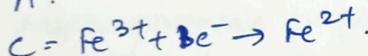
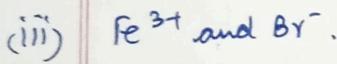
$$\begin{aligned}E_{\text{cell}}^{\circ} &= E_C^{\circ} - E_A^{\circ} \\&= 0.77 - (0.54) \\&= 0.23 \text{ V.} \rightarrow +ve.\end{aligned}$$

∴ Feasible.



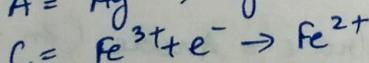
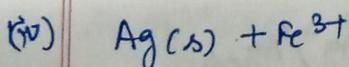
$$\begin{aligned}E_{\text{cell}}^{\circ} &= E_C^{\circ} - E_A^{\circ} \\&= 0.80 - (0.34) \\&= 0.46 \text{ V} \Rightarrow +ve\end{aligned}$$

∴ Feasible



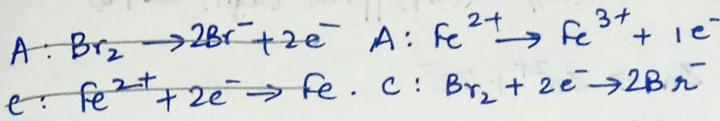
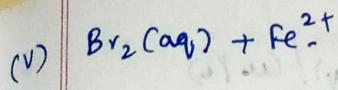
$$\begin{aligned}E_{\text{cell}}^{\circ} &= E_C^{\circ} - E_A^{\circ} \\&= 0.77 - (1.09) \\&= -1.09 + 0.77 \\&= -0.32 \Rightarrow -ve\end{aligned}$$

∴ Not feasible



$$\begin{aligned}E_{\text{cell}}^{\circ} &= E_C^{\circ} - E_A^{\circ} \\&= 0.77 - (0.80) \\&= -0.03 \text{ V} \Rightarrow -ve\end{aligned}$$

∴ Not feasible.



$$E^\circ_{\text{cell}} = E^\circ_C - E^\circ_A \Rightarrow 1.09 - (0.77)$$

$$= -0.44 - (1.09) = 1.09 - 0.77$$

$$= -1.53 V \Rightarrow -ve = +0.32 \Rightarrow +ve$$

∴ Not feasible. ∴ Feasible.

Applications of Electrochemical cell → Can determine:

- pH of solutions
- solubility product
- equilibrium constant
- Thermodynamic properties like ΔG & K_{eq} .
- Potentiometric titrations.

Factors affecting cell potential :

- Temperature
- Concentration.

↳ How will it affect? — Given by Nernst equation.

NERNST EQUATION

For a general reduction reaction, the cell potential is given as:

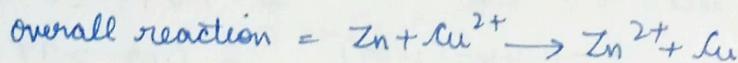
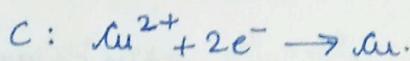
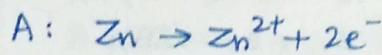
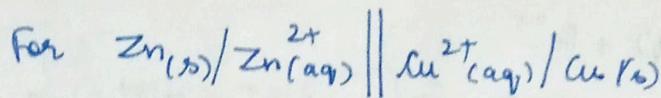
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+}(aq)]}$$

$$\Rightarrow E_{\text{cell}} = E^\circ_{M^{n+}(aq)/M(s)} - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+}(aq)]}$$

$$\Rightarrow E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}(aq)]}$$

cone. of solids taken as unity

e.g.



$n=2$

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

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

$$E_{\text{Zn}^{2+}/\text{Zn}} = E^\circ_{\text{Zn}^{2+}/\text{Zn}} - \frac{0.059}{2} \log \frac{1}{[\text{Zn}^{2+}]}$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

$$E_{\text{cell}} = \left\{ E^\circ_{\text{Cu}^{2+}/\text{Cu}} - \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]} \right\} - \left\{ E^\circ_{\text{Zn}^{2+}/\text{Zn}} - \frac{0.059}{2} \log \frac{1}{[\text{Zn}^{2+}]} \right\}$$

$$\left\{ E^\circ_{\text{Cu}^{2+}/\text{Cu}} - \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]} \right\}$$

$$E_{\text{cell}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} \left[\frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]} + \frac{0.059}{2} \log \frac{1}{[\text{Zn}^{2+}]} \right]$$

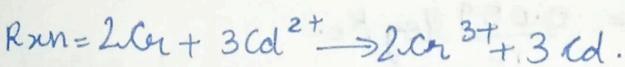
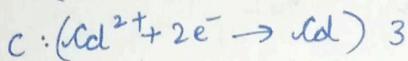
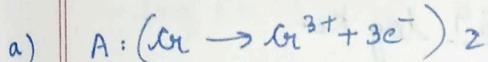
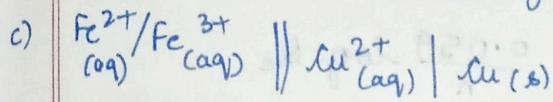
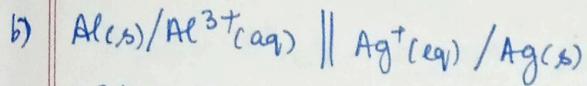
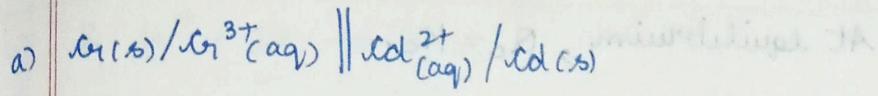
$$E_{\text{cell}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} -$$

$$\left(\frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)$$

In general: $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log Q_c$

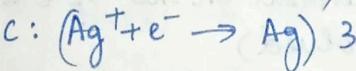
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

Q) Write the Nernst equation for:

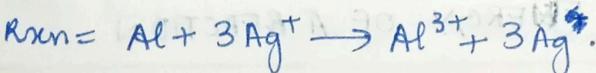


$$\underline{n=6}$$

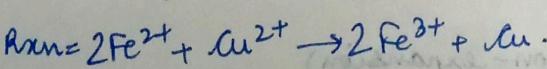
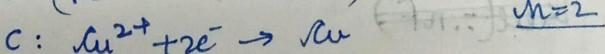
$$\text{Equation} = E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Cd}^{2+}]^3}$$



$$\underline{n=3}$$



$$\text{Equation} = E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{3} \log \frac{[\text{Al}^{3+}]}{[\text{Ag}^+]^3}$$



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Fe}^{3+}]^2}{[\text{Fe}^{2+}]^2 [\text{Cu}^{2+}]}$$

$E_{\text{cell}} = \text{RT} \ln K_p$

Equilibrium const. from Nernst eqn.

At equilibrium, $Q_c = K_c$

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

$$\therefore E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n} \log Q_c$$

↓

$$0 = E^{\circ}_{\text{cell}} - \frac{0.059}{n} \log K_c.$$

$$E^{\circ}_{\text{cell}} = \frac{0.059}{n} \log K_c.$$

$$\log K_c = \frac{n E^{\circ}_{\text{cell}}}{0.059}$$

Note:

E° value - intensive

K_c value - extensive (dependent on no. of e⁻s involved)

GIBBS ENERGY OF A REACTION

Electrical work done in one second is equal to the electrical potential multiplied by total charge passed.

$$\text{Elec. WD} = E_{\text{cell}} \times nF$$

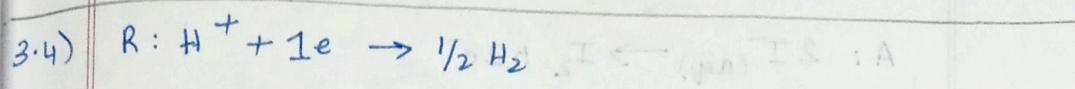
$$\Delta G = -W_{(\text{non-expansion})}$$

$$W_{(\text{non-expansion})} = \text{Elec. WD.}$$

$$\therefore \Delta G = -nFE_{\text{cell}}$$

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

In test questions



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{1}{[\text{H}^+]}$$

$$\text{pH} = 10$$

$$-\log [\text{H}^+] = 10$$

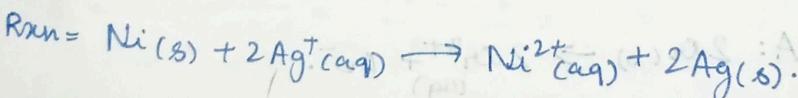
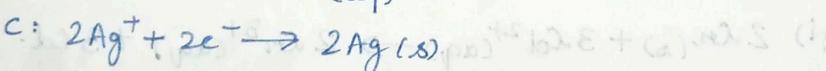
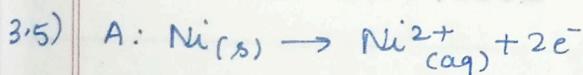
$$[\text{H}^+] = 10^{-10}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - 0.059 \log$$

$$= 0 - 0.059 \log 10^{10}$$

$$= -0.059 (10)$$

= -0.59 V. \Rightarrow non spontaneous



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

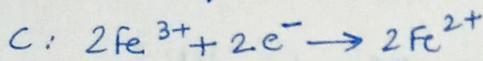
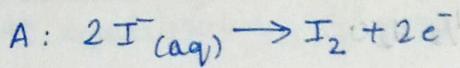
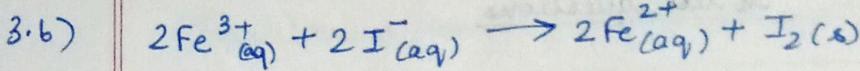
$$= 1.05 - \frac{0.059}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 1.05 - 0.03 \log \frac{40}{(4 \times 10^{-3})^2}$$

$$= 1.05 - 0.03 \log 4 \times 10^4 = 1.05 - 0.03 (4 + \log 4)$$

$$= 1.05 - 0.03 (4.6021) = 1.05 - 0.148$$

$$= 0.902 \text{ V.}$$



$$\underline{M=2}$$

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

$$= -2 \times 96500 \times 0.236$$

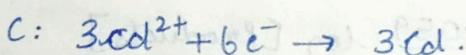
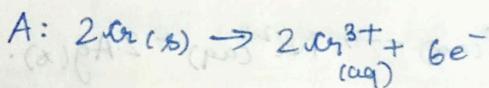
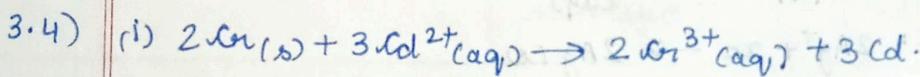
$$= 193 \times 236$$

$$= -45.548 \text{ kJ/mol.}$$

$$\log K_c = \frac{nE^\circ_{\text{cell}}}{0.059} = \frac{2 \times 0.236}{0.059} \approx 7.87.$$

$$\therefore K_c = 10^{7.87}$$

EXERCISE QUESTIONS



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

$$= -0.40 - (-0.74)$$

$$= 0.74 - 0.40$$

$$E^\circ_{\text{cell}} = 0.34 \text{ V.}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -6 \times 96500 \times 0.34$$

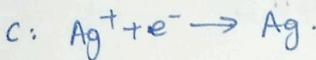
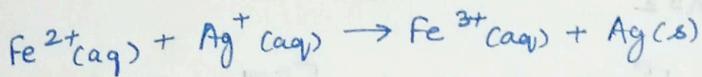
$$= -5790 \times 34$$

$$= -196860 \text{ J/mol}$$

$$= -196.86 \text{ kJ/mol}$$

$$\log K_c = \frac{n E^\circ_{\text{cell}}}{0.059} = \frac{6 \times 0.34}{0.06} = 34.$$

$$\therefore K_c = 10^{34}.$$



$$n=1$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{C}} - E^\circ_{\text{A}} = 0.71 - (0.44 + 0.80) = -0.03$$

$$= 0.80 - (0.71)$$

$$= 0.03 \text{ V}$$

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

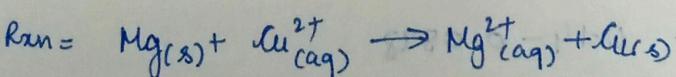
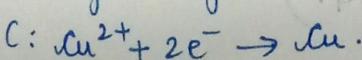
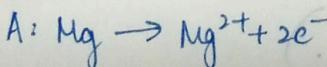
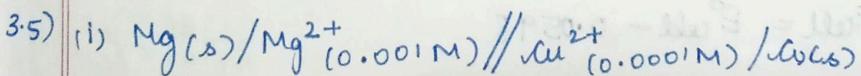
$$= -1 \times 96500 \times 0.03$$

$$= -2895 \text{ J}$$

$$= -2.895 \text{ kJ}$$

$$\log K_c = \frac{n E^\circ_{\text{cell}}}{0.059} = \frac{1 \times 0.03}{0.06} = 0.5.$$

$$K_c = 10^{0.5} = \sqrt{10} \approx 3.2$$

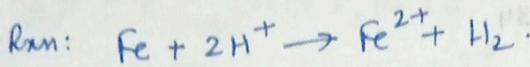
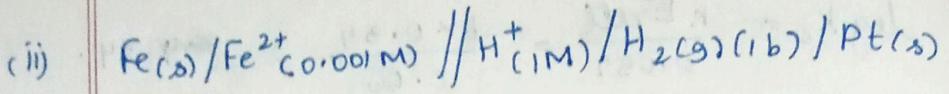


$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log$$

$$\frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\frac{1 \times 10^{-3}}{1 \times 10^{-4}} = 10.$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0295 \times [0.34 - (-2.37) - 0.0295] = 2.71 \text{ V}$$



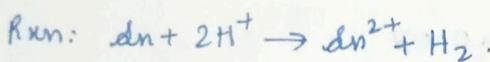
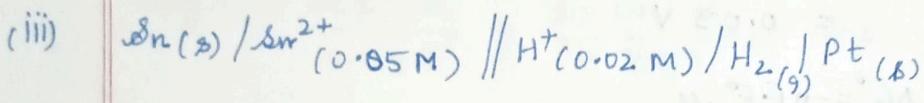
$$M=2$$

$$\begin{array}{l} 2.68 \vee \\ 0.53 \vee \\ 0.08 \vee \\ -1.298 \vee \end{array}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2} \times 10^{-3}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0285 (-3)$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} + 0.0855 = 0.44 + 0.085 = 0.525 \text{ V}$$



$$M=2.$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2} \times \frac{5 \times 10^{-2}}{4} \times 10^4$$

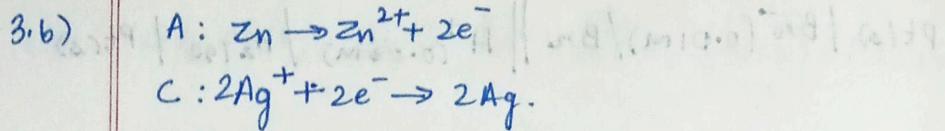
$$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0285 \log 125$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0285 (2.0969)$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0598$$

$$(E_{\text{cell}} = 0 + 0.14 = 0.14.)$$

$$\begin{aligned} E_{\text{cell}} &= 0.14 - 0.0598 \\ &= 0.08 \text{ V} \end{aligned}$$



$$E_{cell}^\circ = E_C^\circ - E_A^\circ$$

$$= 0.80 - (-0.76)$$

$$= 1.56 V.$$

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

$$= -2 \times 96500 \times 1.56$$

$$= -1930 \times 156$$

$$= -30108$$

$$= -30.108 \text{ kJ/mol}$$

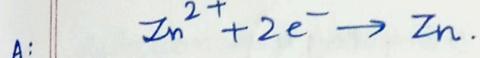
$$\begin{array}{r}
 193 \\
 156 \\
 \hline
 1561 \\
 14498 \\
 \hline
 30108
 \end{array}$$

- Note: (For electrochemical cell)

E_{cell} decreases when concentration of
 Anode / Products \uparrow
 Cathode / Reactants \downarrow

E_{cell} Increases when concentration of
 Anode / Products \downarrow
 Cathode / Reactants \uparrow

Q.1) Zn rod dipped in 0.1 M solⁿ of $ZnSO_4$. The salt is 95.1% dissociated at this dilution at 298 K. Calculate the electrode potential $[E^{\circ}_{Zn^{2+}/Zn} = -0.76 V]$



$$n=2.$$

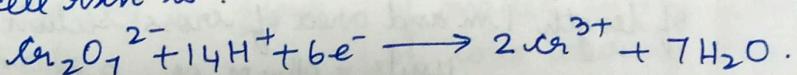
$$\Omega_c = \frac{[Zn]}{[Zn^{2+}]} = \frac{1}{[Zn^{2+}]} = \frac{1}{\frac{0.1 \times 95}{100}}$$

$$= \frac{100}{9.5} = 10.5$$

$$\log \Omega_c = \log 10.5 = 1.0212$$

$$\begin{aligned} E_{cell} &= E^{\circ}_{cell} - \frac{0.059}{n} \log \Omega_c \\ &= -0.76 - \frac{0.059}{2} \times 1.02 \\ &= -0.76 - (0.03 \times 1.02) \\ &= -0.76 - 0.0306 \\ &= -0.7906 V. \end{aligned}$$

Q.2) Calculate the potential for half cell containing 0.1 M $K_2Cr_2O_7$, 0.2 M Cr^{3+} and 1×10^{-4} M H^+ ions. The half cell rxn is :



$$[E^{\circ}_{cell} = 1.33 V].$$

A: $n=6.$

$$\Omega_c = \frac{[Cr^{3+}]^2}{[K_2Cr_2O_7^{2-}][H^+]^{14}} = \frac{(2 \times 10^{-1})^2}{(1 \times 10^{-1})(1 \times 10^{-4})^{14}}$$

$$= \frac{4 \times 10^{-2} \times 10^{56}}{1 \times 10^{-1}} = 4 \times 10^{55}.$$

$$\begin{aligned}
 E_{\text{cell}} &= E'_{\text{cell}} - \frac{0.059}{n} \log Q_c \\
 &= 1.33 - \frac{0.059}{6} \log 4 \times 10^{55} \\
 &= 1.33 - \left(\frac{0.01}{6} \times 55 + \log 4 \right) \\
 &= 1.33 - (0.01 \times (55 + 0.6021)) \\
 &= 1.33 - 0.556 \\
 &= 0.774 \text{ V}
 \end{aligned}$$

ELECTROLYTIC CELL

- Resistance - R : ohm (Ω) \rightarrow .

$R \propto$ length of wire.

$$R \propto \frac{1}{\text{Area of Cross sec.}}$$

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

- $\rho =$ specific resistance (or) Resistivity

It is defined as the resistance offered by a wire of length 1 m and area of cross section 1 m^2

units = ohm m or $\Omega \text{ m}$

- Cell constant $= \frac{l}{a} = G^*$

units = m^{-1} .

- Conductance (G): Reciprocal of Resistance.

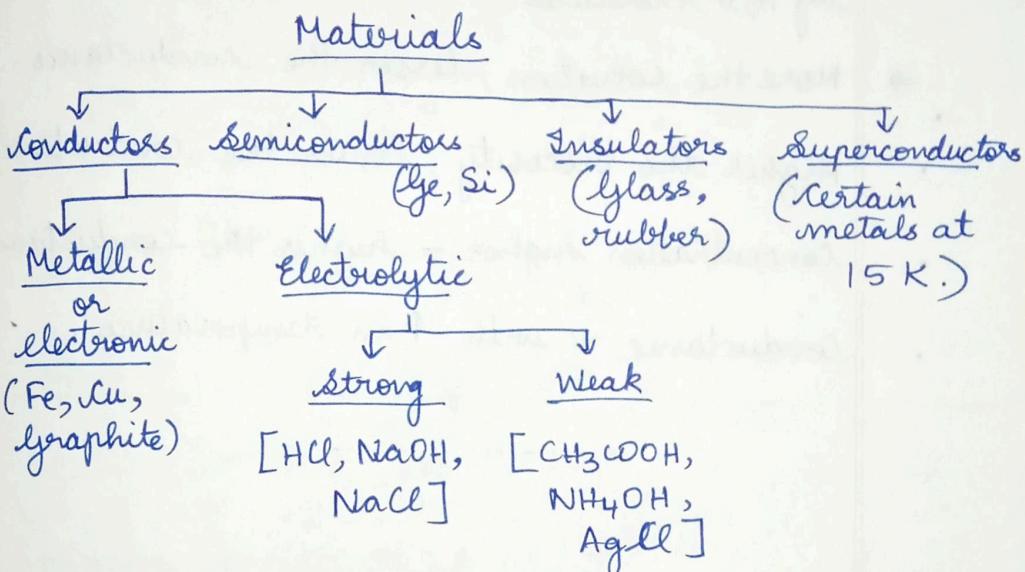
$$G = \frac{1}{R} = \frac{1}{\rho \frac{l}{A}} = \frac{1}{\rho} \times \frac{A}{l} = K \frac{A}{l}$$

units for $\sigma = \text{ohm}^{-1}$. or S (siemen)

K - conductivity - reciprocal of resistivity
units = $\text{ohm}^{-1}\text{m}^{-1}$. or S m^{-1}

Relationship between Resistance and Conductivity

(R and K) : cell constant $\frac{l}{a} = R \times K$



Metallic conductors

- Flow of electric current is due to flow of e^- s.
- There is no transport of matter during the flow of electricity.
- Metallic conductance \downarrow with \uparrow in temperature
- The flow of electricity occurs without any chemical composition

Electrolytic conductors

Flow of current is due to flow of ions

There is actual transport of matter in the form of ions during the flow of electricity.

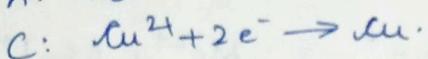
Electrolytic conductance \uparrow with \uparrow in temperature.

The flow of electricity takes place with chemical decomposition of the electrolyte.

- Resistance ↑ with ↑ in temperature because the kernels are vibrating
- Strong electrolytes have more conductance.
- Among LiCl and NaCl, NaCl has more conductance as Li^+ ions would get trapped by H_2O molecules.
- More the solvation, lesser the conductance.
- Higher the viscosity, lower the conductance.
- Concentration higher - higher the conductance.
- Conductance ↓ with ↑ in temperature.

REVISION FOR UNIT TEST - 2

- 1) calculate the electrode potential of Ni^{2+}/Ni electrode if the EMF of the cell $\text{Ni}^{2+}/\text{Ni}^{2+} \parallel \text{Cu}^{2+}/\text{Cu}$ is 0.59 V. ($E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$) ($[\text{Cu}^{2+}] = 0.01 \text{ M}$)



(n = 2)

$$\alpha_c = \frac{[\text{Ni}^{2+}]}{[\text{Cu}^{2+}]} = \frac{1 \times 10^{-2}}{1 \times 10^{-1}} = 10^{-1}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \alpha_c$$

$$0.59 = E^\circ_{\text{cell}} - \frac{0.059}{2} \log 10^{-1}$$

$$0.59 = E^\circ_{\text{cell}} + 0.03$$

$$E^\circ_{\text{cell}} = 0.59 - 0.03 \\ = 0.56 \text{ V.}$$

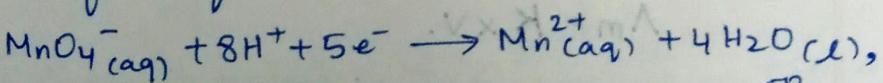
$$E^\circ_{\text{cell}} = E^\circ_A - E^\circ_B$$

$$0.56 = 0.34 - E^\circ_B$$

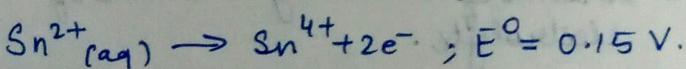
$$E^\circ_B = E^\circ_{\text{Ni}^{2+}/\text{Ni}} = 0.34 - 0.56 \\ = -0.22 \text{ V.}$$

$$\therefore E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -(-0.22 \text{ V}) = \underline{\underline{0.22 \text{ V}}}$$

- 2) 2 Half cell of an electrochemical cell is given as

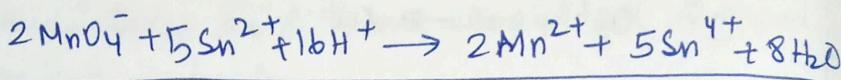
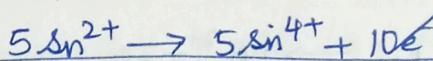


$$E^\circ = 1.51 \text{ V}$$



Construct the redox eqn. from the 2 half cell rxn and predict if this rxn favours formation of reactants or products

A:



$$E_{\text{cell}}^\circ = E_C^\circ - E_A^\circ$$

$$= 1.51 - 0.15 = 1.36\text{V.}$$

reaction is Feasible \downarrow \leftarrow favours the formation of products.

Variation of conductivity with concentration

conductivity always decreases with decrease in concentration of both weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in the solution decreases on dilution.

Molar conductivity (Λ_m):

Molar conductivity of a solution at a given concentration is the conductance of Volume V of the solution containing 1 M of electrolyte kept between 2 electrodes with area of cross section A and distance of unit length.

$$\Lambda_m = K A/l \quad (l = \text{unity})$$

$$\Lambda_m = K \times A$$

$$\Lambda_m = K \times V.$$

$A = V = \text{Volume of containing one mole of electrolyte.}$

In terms of molarity :

$$c = \frac{\text{no. of moles}}{\text{V of soln}(\text{L})} = \frac{1}{\text{V of soln}(\text{L})}$$

$$\text{V. of soln in L} = \frac{1}{c}; V = \frac{1000 \text{ cm}^3}{c}$$

$$\therefore \Lambda_m = \frac{K \times 1000}{c}$$

unit for $\Lambda_m = \text{S cm}^2/\text{mol.}$

When dil \uparrow , $\Lambda_m \downarrow$.

(dil \uparrow , $V \uparrow$, $K \downarrow$, $c \downarrow$. $\Lambda_m \downarrow$)

Variation of molar conductivity with concentration

Molar conductivity increases \uparrow with decrease \downarrow in concentration. This is because the total volume V of the solution containing one mole of the electrolyte also increases. It has been found that decrease in K on dilution of a solution is more than compensated by increase in its volume.

Pg 79, eg 3.4

0.1 mol/L KCl

$$R = 100 \Omega$$

$$K = 1.29 \text{ S m}^{-1}$$

$$l/a = R \times K$$

$$= 100 \times 1.29$$

$$= 129 \text{ m}^{-1}$$

0.02 mol/L KCl

$$R = 520 \Omega$$

$$K = ?$$

$$K = l/a \times 1/R$$

$$= 1.29 \times \frac{1}{520}$$

$$\approx 0.24 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$$

$$\Lambda_m = \frac{K \times 1000}{c} = \frac{0.24 \times 10^{-2} \times 10^3}{2 \times 10^{-2}} = 120 \Omega^{-1} \text{cm}^{-1} \text{mol}^{-1}$$

Pg 80, Eg - 3.5

$$A = \frac{\pi}{4} = \frac{3.14}{4} = 0.785 \text{ cm}^2.$$

$$R = 5.55 \times 10^3 \Omega$$

$$K = \frac{l}{R \times A} = \frac{50}{5.55 \times 10^3 \times 78.5 \times 10^{-2}} = \frac{10}{871.35} = 0.0115$$

$$\rho = \frac{1}{K} = \frac{1}{0.0115} = 87.135$$

$$\Lambda_m = \frac{K \times 1000}{c} = \frac{0.0115 \times 1000}{0.05}$$

$$\text{molar conductivity} = \frac{11.5}{0.05} = 230.5 \text{ cm}^2/\text{mol}$$

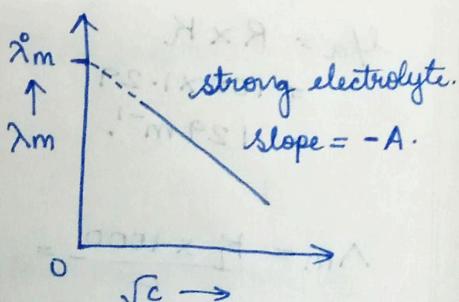
Variation of molar conductance with concentration for a strong electrolyte.

Molar conductivity of a strong electrolyte is found to vary with concentration according to Debye-Hückel-Onsager equation.

$$\Lambda_m = \lambda_m^0 - A \sqrt{c}$$

$$y = c + mx$$

λ_m^0 = limiting molar conductivity which is defined as molar conductivity at infinite dilution or at zero concentration of electrolyte.



For a strong electrolyte, ionisation is almost complete at all concentrations. On increasing dilution, +ve ions move apart and the inter ionic interactions are decreased.

∴ Mobility of ions increases, thereby the value of molar conductivity also increases.

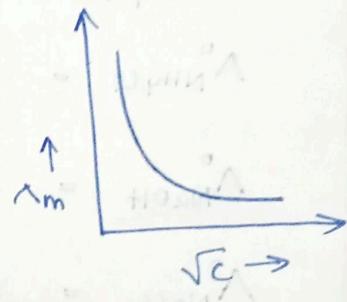
Variation of molar conductance with concentration for a weak electrolyte

For a weak electrolyte, degree of ionisation increases ↑ with increase ↑ in dilution. This increases ↑ the no. of ions and thus the value of molar conductivity.

$$\alpha = \sqrt{\frac{ka}{c}}$$

\propto directly proportional

$$\text{to } \frac{1}{\sqrt{c}}$$



KOHLRAUSCH'S LAW

The law states that the limiting molar conductivity of an electrolyte can be represented as the sum of individual contributions of anions and cations of the electrolyte, where λ°_+ and λ°_- are molar limiting molar conductivities of cation and anion respectively, v^+ and v^- are no. of cations and anions respectively.

$$\Lambda_m^{\circ} = v^+ \lambda^{\circ}_+ + v^- \lambda^{\circ}_-$$

$$\lambda^{\circ}_{\text{NaCl}} = \lambda^{\circ}_{\text{Na}^+} + \lambda^{\circ}_{\text{Cl}^-}$$

$$\lambda^{\circ}_{\text{MgCl}_2} = \lambda^{\circ}_{\text{Mg}^{2+}} + 2 \lambda^{\circ}_{\text{Cl}^-}$$

$$\lambda^{\circ}_{\text{Na}_2\text{SO}_4} = 2 \lambda^{\circ}_{\text{Na}^+} + \lambda^{\circ}_{\text{SO}_4^{2-}}$$

$$\lambda^{\circ}_{\text{Al}_2(\text{SO}_4)_3} = 2 \lambda^{\circ}_{\text{Al}^{3+}} + 3 \lambda^{\circ}_{\text{SO}_4^{2-}}$$

APPLICATIONS OF KOHLRAUSCH'S LAW

1. Calculating limiting molar conductivity of weak electrolytes.

$$\lambda^{\circ}_{\text{NH}_4\text{OH}} = \lambda^{\circ}_{\text{NH}_4^+} + \lambda^{\circ}_{\text{OH}^-}$$

$$\lambda^{\circ}_{\text{NH}_4\text{Cl}} = \lambda^{\circ}_{\text{NH}_4^+} + \lambda^{\circ}_{\text{Cl}^-}$$

$$\lambda^{\circ}_{\text{NaOH}} = \lambda^{\circ}_{\text{Na}^+} + \lambda^{\circ}_{\text{OH}^-}$$

$$\lambda^{\circ}_{\text{NaCl}} = \lambda^{\circ}_{\text{Na}^+} + \lambda^{\circ}_{\text{Cl}^-}$$

$$\therefore \lambda^{\circ}_{\text{NH}_4\text{OH}} = \lambda^{\circ}_{\text{NH}_4\text{Cl}} + \lambda^{\circ}_{\text{NaOH}} - \lambda^{\circ}_{\text{NaCl}}$$

$$\lambda^{\circ}_{\text{HCOOH}} = \lambda^{\circ}_{\text{H}^+} + \lambda^{\circ}_{\text{HCOO}^-}$$

$$= \lambda^{\circ}_{\text{HCl}} + \lambda^{\circ}_{\text{HCOONa}} - \lambda^{\circ}_{\text{NaCl}}$$

2. To calculate the degree of dissociation of weak electrolyte:

$$\alpha = \frac{\lambda_m}{\lambda^{\circ}_m}$$

3. To calculate the dissociation constant of weak electrolyte:

$$K_a = \frac{C \alpha^2}{1-\alpha} \quad (a)$$

$$= \left(\frac{\lambda_m}{\lambda_m^\circ} \right)^2 \times C = \frac{C \lambda_m^2}{\lambda_m^\circ} \times \frac{\lambda_m^\circ}{\lambda_m^\circ - \lambda_m} \quad (b)$$

$$\therefore K_a = \frac{C \lambda_m^2}{\lambda_m^\circ (\lambda_m^\circ - \lambda_m)} \quad (c)$$

4. Calculating solubility of sparingly soluble salt:

$$\lambda_m^\circ = \frac{K \times 1000}{s} \text{ mol/l} = \text{molar soln} \quad (d)$$

$$\therefore s = \frac{K \times 1000}{\lambda_m^\circ} \quad (e)$$

P.E.Q

$$\text{Eg. } P.S. : \frac{2.1 \times 2.9 \times 10^{-4}}{2.1 \times 85.1} = \frac{0.001 \times 10^{-4}}{10} = \text{mA}$$

$\lambda^\circ_{\text{CaCl}_2}$ and $\lambda^\circ_{\text{MgSO}_4}$.

$$\lambda^\circ_{\text{CaCl}_2} = \lambda^\circ_{\text{Ca}^{2+}} + 2 \lambda^\circ_{\text{Cl}^-} = \frac{\text{mA}}{\text{mA}} = 271.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\begin{aligned} \lambda^\circ_{\text{MgSO}_4} &= \lambda^\circ_{\text{Mg}^{2+}} + \lambda^\circ_{\text{SO}_4^{2-}} \\ &= 106 + 160 = 266 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

Calculate the λ_m° values of i) and ii)

a) CaCl_2

b) $\text{Mg}(\text{CH}_3\text{COO})_2$

c) Na_2SO_4 .

By referring the λ° values from the table.

$$\begin{aligned}
 a) \quad \lambda^\circ_{\text{CaCl}_2} &= \lambda^\circ_{\text{Ca}^{2+}} + 2 \lambda^\circ_{\text{Cl}^-} = 119 \\
 &= 119 + 2(76.3) \\
 &= 119 + 152.6 \\
 &= 271.6 \text{ S cm}^2 \text{ mol}^{-1}.
 \end{aligned}$$

$$\begin{aligned}
 b) \quad \lambda^\circ_{\text{Mg}(\text{CH}_3\text{COO})_2} &= \lambda^\circ_{\text{Mg}^{2+}} + 2 \lambda^\circ_{\text{CH}_3\text{COO}^-} \\
 &= 106 + 2(40.9) \\
 &= 106 + 81.8 \\
 &= 187.8 \text{ S cm}^2 \text{ mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 c) \quad \lambda^\circ_{\text{Na}_2\text{SO}_4} &= 2 \lambda^\circ_{\text{Na}^+} + \lambda^\circ_{\text{SO}_4^{2-}} \\
 &= (50.1) 2 + 160 = 260.2 \text{ S cm}^2 \text{ mol}^{-1}
 \end{aligned}$$

Eg. 3.9

$$\Lambda_m = \frac{K \times 1000}{c} = \frac{4.95 \times 10^{-5}}{1.028 \times 10^{-3}} \approx 49.5$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{49.5}{390.5} = 0.1233$$

$$K = \frac{c \alpha^2}{1 - \alpha} = \frac{1.78 \times 10^{-5}}{0.8767} = 2.01 \times 10^{-5}$$

Interest Questions under molar conductivity

3.7) No. of ions per unit volume decreases, $K \downarrow$

$$3.8) \quad \lambda^\circ_{\text{H}_2\text{O}} = \lambda^\circ_{\text{H}^+} + \lambda^\circ_{\text{OH}^-}$$

$$\lambda^\circ_{\text{H}_2\text{O}} = \lambda^\circ_{\text{NaOH}} + \lambda^\circ_{\text{HCl}} - \lambda^\circ_{\text{NaCl}}$$

$$3.9) \quad \lambda^{\circ}_{\text{HCOOH}} = \lambda^{\circ}_{\text{H}^+} + \lambda^{\circ}_{\text{HCOO}^-}$$

$$\begin{aligned} &= 349.6 + 54.6 \\ &= 404.2 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\alpha = \frac{\lambda m}{\lambda^{\circ} m} = \frac{46.1}{404.2} \approx 0.114.$$

$$K_a = \frac{C \alpha^2}{1 - \alpha} = \frac{0.00025 \times 10^{-3} \times 0.13^2}{0.886} \approx 3.67 \times 10^{-4}$$

$$\rho \propto w$$

$$\rho \Sigma = W$$

Antoniuspa lásd meghatározását = Σ

minimális telítettségi térfogat, je. Tör az összes
szem. Tör A1 fej törme.

$$\frac{\rho A}{\rho A_1} \times \text{szem. térfogat} = W$$

$$\approx 0.02 \text{ dB}$$

$$\rho A \leftarrow \rho A_1$$

egyszerűbb számítás \rightarrow fej térfogat!

$$0.018 \mu \text{F} = \rho A_1 \times d \times \frac{\rho A_1}{\rho A_1 + d + 1}$$

$$\rightarrow \frac{\rho A_1}{\rho A_1 + d + 1} = \text{fej térfogat / egész fej}$$

$$\rho A_1 \times 0.02 \text{ dB} \times 1 = 7.3 \text{ fej térfogat / egész fej}$$

$$0.018 \mu \text{F} =$$

$$0.002 \mu \text{F} = 7.1$$

ELECTROLYSIS

Electrolysis is defined as the process of decomposition of an electrolyte by the passage of electric current in the molten state or through its aqueous solution.

Faraday's first law of electrolysis

The amt. of chemical reaction which occurs at any electrode during electrolysis by a current, is proportional to the quantity of electricity passed through the electrolyte.

$$W \propto Q$$

$$W = ZQ$$

W = weight of substance (g)

Q = Quantity of electricity (C)

$$Q = It$$

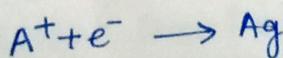
I = current (A)

t = time (s)

Z = Electrochemical equivalent:

defined as wt. of metal deposited by passing current of 1 A for 1 sec.

$$W = \frac{\text{Atomic mass} \times It}{96500n}$$



1 mole of e^- \Rightarrow How much charge?

$$= 1.6 \times 10^{-19} \times 6 \times 10^{23} = 96487 C.$$

$$\text{charge on one } e^- = 1.602 \times 10^{-19} C.$$

$$\therefore \text{charge on one mole of } e^- = N_A \times 1.602 \times 10^{-19}$$
$$= 96487 C$$

$$1 F = 96500 C.$$

one faraday is defined as the quantity of electricity contained by one mole of electrons.

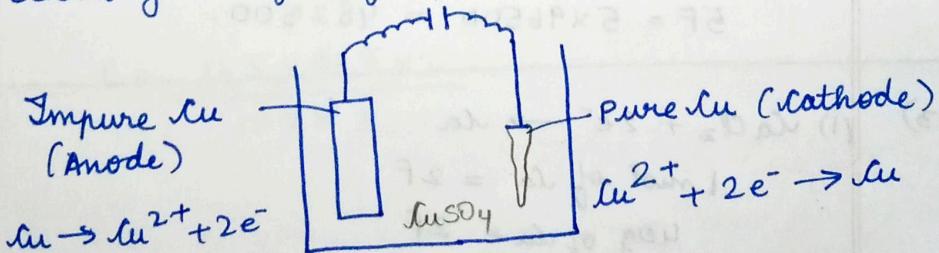
Faraday's second law of electrolysis

Amount of different substances liberated by the same quantity of electrolyte passing through the electrolytic solution are proportional to their chemical equivalent weights.

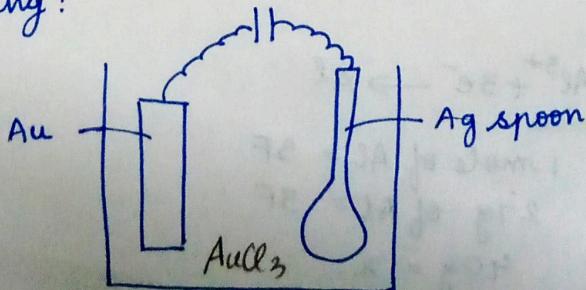
$$\frac{W_{Cu}}{W_{Zn}} = \frac{E_{Cu}}{E_{Zn}} \quad (\text{for Daniell cell})$$

APPLICATIONS OF FARADAY'S LAW

- 1) To determine the volume of gas liberated at an electrode during electrolysis.
- 2) To determine the equivalent mass and valency of metal.
- 3) In electrolytic extraction of metals
- 4) Electrolytic refining of metals:



- 5) Electropatenting:



Exercise Questions

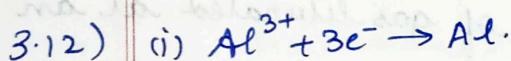
3.8) $\Lambda_m = \frac{K \times 1000}{c} = 124 \text{ S cm}^2/\text{mol}$

3.9) $\frac{l}{a} = R \times K = 1500 \times 0.146 \times 10^{-3}$
 $= 219 \times 10^{-3} \text{ cm}^{-1}$

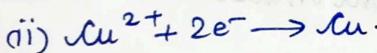
3.11) $\Lambda_m = \frac{K \times 1000}{c} = \frac{7.896 \times 10^{-5} \times 10^3}{2.41 \times 10^{-3}}$
 $= \frac{78.96}{2.41} \approx 32.78 \text{ cm}^2/\text{mol.}$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{32.7}{390.5} \approx 0.083.$$

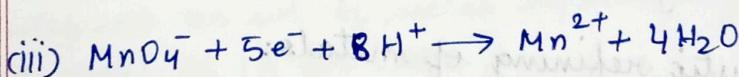
$$\therefore \alpha = 8.3\%$$



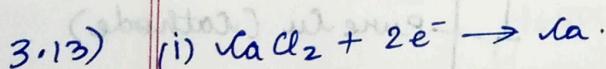
$$3F = 3 \times 96500 = 289500 \text{ e.}$$



$$2F = 2 \times 96500 = 193000 \text{ e.}$$



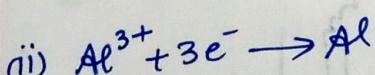
$$5F = 5 \times 96500 = 482500.$$



$$1 \text{ mol of Ca} = 2F$$

$$40 \text{ g of Ca} = 2F$$

$$\underline{20 \text{ g of Ca} = 1F.}$$



alumina

$$1 \text{ mole of Al} = 3F$$

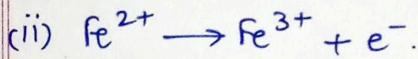
$$27 \text{ g of Al} = 3F$$

$$40 \text{ g} = x.$$

$$x = \frac{40 \times 3}{27} \approx 4.44 F$$



$$\begin{aligned}1 \text{ mole of } H_2O &= 2F \\&= 2 \times 96500 \\&= 193000 C\end{aligned}$$



$$\begin{aligned}1 \text{ mole} &\rightarrow 1F \\&= 1 \times 96500 C \\&= 96500 C.\end{aligned}$$

3.15) $I = 5A$

$$t = 20 \times 60$$

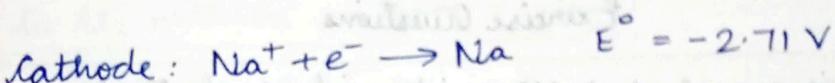
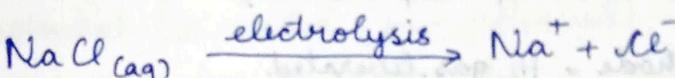
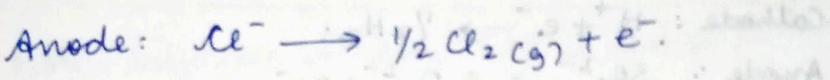
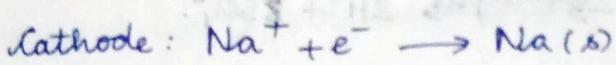
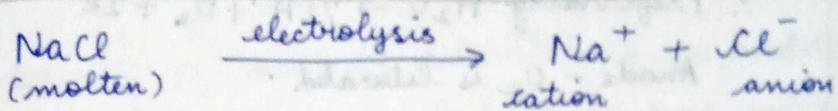
$$W = \frac{\text{At.-mass} \times It}{96500 \times n} = \frac{59 \times 5 \times 1200}{96500 \times 2}$$
$$\approx 1.84 g.$$

3.16) $I = 1.5 A$

$$1.45 = \frac{108 \times 1.5 \times t}{96500}$$

$$t = \frac{145 \times 965 \times 2}{108 \times 3}$$

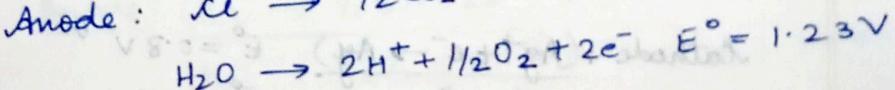
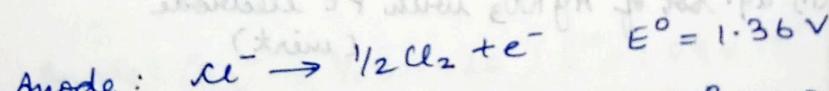
Predicting the product of Electrolysis



One with higher SRP \rightarrow gets reduced at cathode

$\therefore \text{H}^+$ gets reduced. $\therefore \text{H}_2$ is liberated

$\therefore \text{Na}^+$ ions remain in the solution itself.

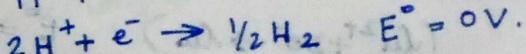
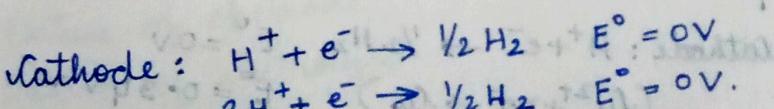
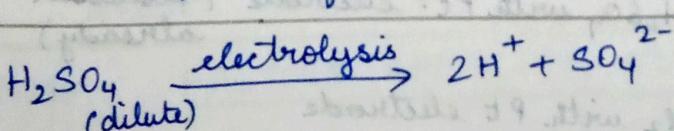


Expected product at anode = O_2 .

Actual = Cl_2 — Why?

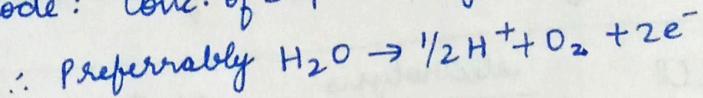
Reason: Diff in E° values — less and water — weak electrolyte — over potential needed.

\therefore Release of Cl_2 is favoured.

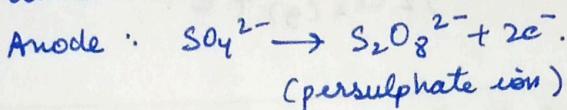
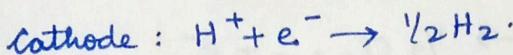
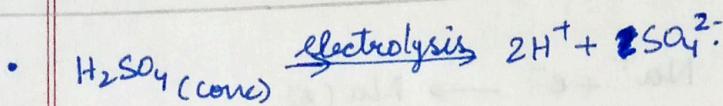


$\therefore \text{H}_2$ is liberated at Cathode

Anode: Conc. of SO_4^{2-} - very less.



Anode - O_2 is liberated.

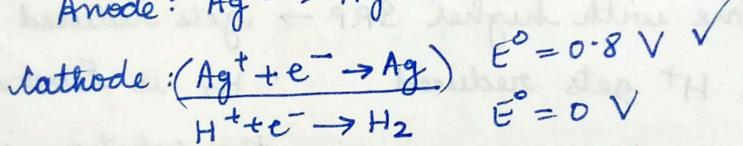
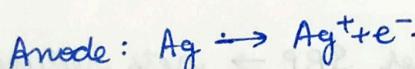


At cathode = H_2 gas liberated.

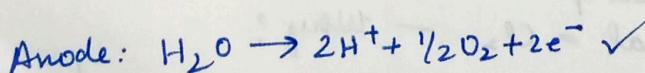
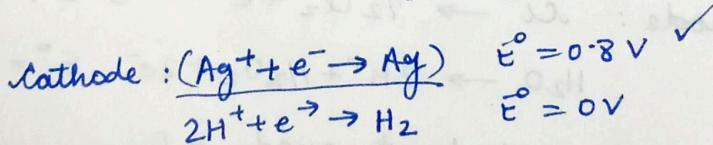
At anode = persulphate ion liberated.

Exercise Questions

- 3.18) (i) aq. sol. of AgNO_3 with silver electrode (active)



- (ii) aq. sol of AgNO_3 with Pt electrode (inert)

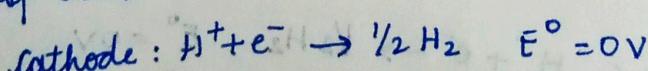


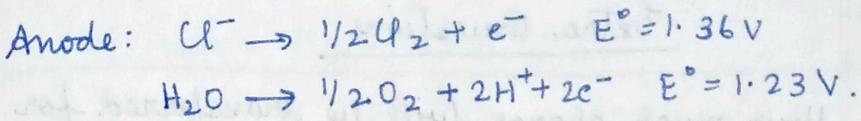
Cathode: Ag gets deposited

Anode: O_2 is liberated.

- (iii) dil H_2SO_4 with Pt. electrode (discussed already)

- (iv) aq. CuCl_2 with Pt electrode





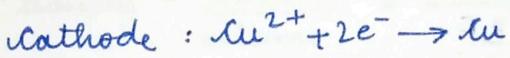
Actually O_2 must be liberated as, in anode:
 lower E° value wins. But due to over potential
 needed for O_2 's release, Cl_2 's release is favoured.

Note: Difference between SRP is less.

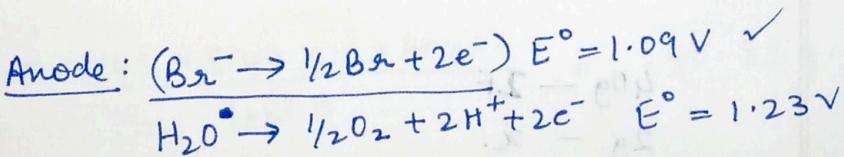
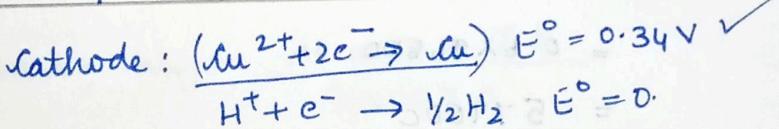
Kinetically unfavoured. Hence supply of external
 potential is needed (over potential)

↳ only for Cl_2 's case (X)

- CuCl_2 with Cu electrode (active)



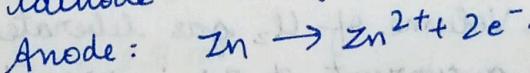
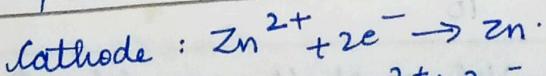
- $\text{CuBr}_2(\text{aq})$ with Pt electrode (inert)



Cathode: Cu is deposited

Anode: Br_2 is liberated.

- ZnSO_4 with Zn electrode (active)



NOTE: FACTORS AFFECTING ELECTROLYSIS

- Nature of electrode
- Nature of electrolyte.

26/7/22

Extra Questions

- 1) How much charge will be transferred for 3.6g of H_2O ?

$$18\text{g} - 2\text{F}$$

$$3.6\text{g} - x.$$

$$x = \frac{2 \times 3.6}{18} = 0.4\text{F}$$

$$= 0.4 \times 96500$$

$$= 36500\text{C.}$$

- 2) Calculate the amount of charge required to deposit 5.4g of Al and 2g of calcium.

$$27\text{g} - 3\text{F}$$

$$5.4\text{g} - x$$

$$x = \frac{5.4 \times 3}{27} = 0.6\text{F}$$

$$= 0.6 \times 96500$$

$$= 57900\text{C.}$$

$$40\text{g} - 2\text{F}$$

$$2\text{g} - x.$$

$$x = \frac{2 \times 2}{40} = \frac{1}{10}\text{F}$$

$$= \frac{96500}{10} = 9650\text{C.}$$

- 3) calculate the Volume of Cl_2 gas liberated at anode when a current of 2A is passed for 10 minutes through molten NaCl .

$$W_{\text{Cl}} = \frac{\text{At. mass} \times It}{96500 \times n} = \frac{71 \times 2 \times 10 \times 60}{2 \times 96500}$$

$$\approx 0.44\text{g.}$$

$$1 \text{ mole} = 71 \text{ g} = 22.4 \text{ F}$$

$$0.44 \text{ g} = x$$

$$x = \frac{0.44 \times 22.4}{71} \text{ L}$$

$$= 0.138 \text{ L}$$

- 4) A current of 8.46 A is passed for 8 hours through a solution containing Ag^+ ion for plating a silver plate. What is the area of tray if the thickness of silver plating is 0.00254 cm ? (density of silver is 10.5 g/cc).

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{\text{mass}}{\text{thickness}}$$

$$\therefore \text{Area} = \frac{\text{mass}}{\text{density} \times \text{thickness}}$$

$$\text{mass} = W_{\text{Ag}} = \frac{A t \cdot \text{mass} \times I t}{96500 \times n}$$

$$= \frac{108 \times 8.46 \times 10 \times 60 \times 60}{96500} = 340.85 \text{ g.}$$

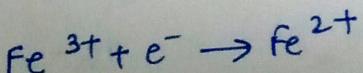
$$\text{Area} = \frac{340.85}{10.5 \times 254 \times 10^{-5}} = 12780.3 \text{ cm}^2$$

$$= 12780.3 \times 10^{-2} \times 10^{-2} \text{ m}^2$$

$$= 1.278 \text{ m}^2$$

$$\approx 1.28 \text{ m}^2$$

- 5) How many hours does it take to reduce 3 moles of Fe^{3+} to Fe^{2+} with 2 Ampere current?



$$\begin{aligned}
 1 \text{ mol-1 F} &= 96500 \text{ coulombs} \\
 3 \text{ mol-3 F} &= 3 \times 96500 \\
 &= 289500 \text{ C.}
 \end{aligned}$$

$$Q = It \Rightarrow t = \frac{Q}{I} = \frac{289500}{2}$$

$$= 144750 \text{ s} = \frac{144750}{60 \times 60}$$

$$= 40.21 \text{ hours} \approx 1.676 \text{ days}$$

$$\frac{\text{sec}}{\text{second} \times \text{amps}} = \frac{\text{sec}}{\text{amp}} = \text{farad}$$

$$\frac{\text{sec}}{\text{second} \times \text{amps}} = \frac{\text{sec}}{\text{amp}} = \text{farad}$$

$$\frac{1 \text{ A} \times 1 \text{ sec}}{1 \times 1000 \text{ amp}} = \frac{1 \text{ A} \times 1 \text{ sec}}{1000 \text{ amp}} =$$

$$128.018 = \frac{128.018 \times 10^{-3} \times 8 \times 30}{1000 \times 10^{-3}} =$$

$$128.018 \times 10^{-3} = \frac{128.018}{1000 \times 10^{-3}} = 128.018 \text{ A}$$

$$128.018 \times 10^{-3} \times 8 \times 0.8751 =$$

$$128.018 \times 10^{-3} \times 8 \times 0.8751 =$$