

Electrochemistry

Topic 1

1. Mg, Al, Zn, Fe, Cu

2. Higher the oxidation potential, more easily it is oxidized and hence greater is the reducing power. Thus, increasing order of reducing power will be

Ag < Hg < Cr < Mg < K.

3. The cell will be represented as



(i) Anode, *i.e.*, zinc electrode will be negatively charged.

(ii) Electrons are current carriers. The current will flow from silver to zinc in the external circuit.

(iii) At anode : $\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2e^{-}$

At cathode : $\text{Ag}^{+}_{(aq)} + e^{-} \rightarrow \text{Ag}_{(s)}$

4. (i) $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$
 $= -0.40 \text{ V} - (-0.74 \text{ V}) = +0.34 \text{ V}$

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

$= -196860 \text{ J mol}^{-1} = -196.86 \text{ kJ mol}^{-1}$

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

$196860 = 2.303 \times 8.314 \times 298 \times \log K$

or $\log K = 34.5014$

$K = \text{Antilog } 34.5014 = 3.172 \times 10^{34}$

(ii) $E^{\circ}_{\text{cell}} = +0.80 \text{ V} - 0.77 \text{ V} = +0.03 \text{ V}$

$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} = -1 \times 96500 \times 0.03$

$= -2895 \text{ J mol}^{-1} = -2.895 \text{ kJ mol}^{-1}$

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

$-2895 = -2.303 \times 8.314 \times 298 \times \log K$

or $\log K = 0.5074$

$K = \text{Antilog } (0.5074) = 3.22$

5. (i) The electrode reactions are

At anode : $\text{Mg}_{(s)} \rightarrow \text{Mg}^{2+} (0.001 \text{ M}) + 2e^{-}$

At cathode : $\text{Cu}^{2+} (0.0001 \text{ M}) + 2e^{-} \rightarrow \text{Cu}_{(s)}$

Net reaction :

$\text{Mg}_{(s)} + \text{Cu}^{2+} (0.0001 \text{ M}) \rightarrow \text{Mg}^{2+} (0.001 \text{ M}) + \text{Cu}_{(s)}$

The Nernst equation for this cell at 25°C

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

Where $E^{\circ}_{\text{anode}} = -2.37 \text{ V}$; $E^{\circ}_{\text{cathode}} = +0.34 \text{ V}$

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

$$= (+0.34 \text{ V}) - (-2.37 \text{ V}) = +2.71 \text{ V}$$

The cell EMF is then given by

$$E_{\text{cell}} = 2.71 - \frac{0.0591}{2} \log \left(\frac{0.001}{0.0001} \right)$$

$$= \left(2.71 - \frac{0.0591}{2} \log 10 \right) \text{ V} = \left(2.71 - \frac{0.0591}{2} \right) \text{ V}$$

$$= 2.71 - 0.03 = 2.68 \text{ V}$$

(ii) The electrode reactions are

At anode : $\text{Fe}_{(s)} \rightarrow \text{Fe}^{2+} (0.001 \text{ M}) + 2e^{-}$

At cathode : $2\text{H}^{+} (1 \text{ M}) + 2e^{-} \rightarrow \text{H}_2 (1 \text{ bar})$

Net reaction :

$\text{Fe}_{(s)} + 2\text{H}^{+} (1 \text{ M}) \rightarrow \text{Fe}^{2+} (0.001 \text{ M}) + \text{H}_2 (1 \text{ bar})$

The Nernst equation of this cell at 25°C

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}](p_{\text{H}_2})}{[\text{H}^{+}]^2}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = E^{\circ}_{\text{H}^{+}|\text{H}_2} - E^{\circ}_{\text{Fe}^{2+}|\text{Fe}}$$

$$= 0.000 \text{ V} - (-0.44 \text{ V}) = +0.44 \text{ V}$$

The cell EMF is then given by

$$E_{\text{cell}} = 0.44 - \frac{0.0591}{2} \log \frac{0.001 \times 1}{(1)^2}$$

$$= 0.44 - 0.0296 \log(10^{-3})$$

$$= 0.44 + (3 \times 0.0296) = 0.44 + 0.0888$$

Therefore, $E_{\text{cell}} = +0.53 \text{ V}$

(iii) The electrode reactions are

At anode : $\text{Sn}_{(s)} \rightarrow \text{Sn}^{2+} (0.05 \text{ M}) + 2e^{-}$

At cathode : $2\text{H}^{+} (0.02 \text{ M}) + 2e^{-} \rightarrow \text{H}_2 (1 \text{ bar})$

Net reaction :

$\text{Sn}_{(s)} + 2\text{H}^{+} (0.02 \text{ M}) \rightarrow \text{Sn}^{2+} (0.05 \text{ M}) + \text{H}_2 (1 \text{ bar})$

The Nernst equation of this cell at 25°C

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}](p_{\text{H}_2})}{[\text{H}^{+}]^2}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{H}^{+}|\text{H}_2} - E^{\circ}_{\text{Sn}^{2+}|\text{Sn}}$$

$$= 0.000 \text{ V} - (-0.14 \text{ V}) = +0.14 \text{ V}$$

$$\text{or, } E_{\text{cell}} = E^{\circ}_{\text{cell}} - 0.0296 \log \frac{0.05 \times 1}{(0.02)^2}$$

$$\begin{aligned}
 &= E^\circ_{\text{cell}} - 0.0296 \log \left(\frac{0.05}{0.0004} \right) \\
 &= E^\circ_{\text{cell}} - 0.0296 (\log 125) \\
 &= E^\circ_{\text{cell}} - 0.0296 \times 2.0969 = E^\circ_{\text{cell}} - 0.06
 \end{aligned}$$

$$E_{\text{cell}} = 0.14 - 0.06 = 0.08 \text{ V}$$

(iv) The electrode reactions are



Net reaction :



The Nernst equation of this cell at 25°C is

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Br}_{2(l)}](p_{\text{H}_2})}{[\text{H}^+]^2 [\text{Br}^-]^2}$$

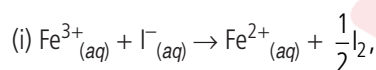
$$E^\circ_{\text{cell}} = E^\circ_{\text{H}^+/\text{H}_2} - E^\circ_{\text{Br}_2/\text{Br}^-} = 0 - 1.08 = -1.08 \text{ V}$$

$$\begin{aligned}
 E_{\text{cell}} &= -1.08 - 0.0296 \times \log \frac{1}{(0.03)^2 (0.01)^2} \\
 &= -1.08 - 0.0296 \log \left[\frac{1}{(9 \times 10^{-4})(1 \times 10^{-4})} \right] \text{ V}
 \end{aligned}$$

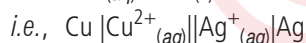
$$\begin{aligned}
 &= -1.08 - 0.0296 \times \log \left(\frac{10^8}{9} \right) \\
 &= -1.08 - 0.0296 (\log 10^8 - \log 9) \text{ V} \\
 &= -1.08 - 0.0296 (8 - 0.9542) \text{ V} \\
 &= -1.08 - 0.0296 (7.0457)
 \end{aligned}$$

$$E_{\text{cell}} = -1.08 - 0.21 = -1.29 \text{ V}$$

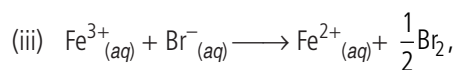
6. A reaction is feasible if EMF of the cell reaction is positive.



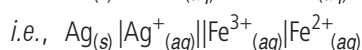
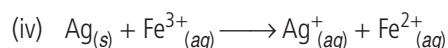
$$\begin{aligned}
 \therefore E^\circ_{\text{cell}} &= E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^\circ_{\text{I}_2/\text{I}^-} \\
 &= 0.77 - 0.54 = 0.23 \text{ V (Feasible)}
 \end{aligned}$$



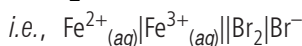
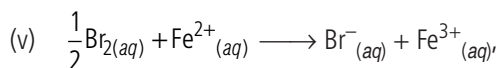
$$\begin{aligned}
 E^\circ_{\text{cell}} &= E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Cu}^{2+}/\text{Cu}} \\
 &= 0.80 - 0.34 = 0.46 \text{ V (Feasible)}
 \end{aligned}$$



$$\begin{aligned}
 E^\circ_{\text{cell}} &= E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^\circ_{\text{Br}_2/\text{Br}^-} \\
 &= 0.77 - 1.09 = -0.32 \text{ V (Not feasible)}
 \end{aligned}$$



$$\begin{aligned}
 E^\circ_{\text{cell}} &= E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^\circ_{\text{Ag}^+/\text{Ag}} \\
 &= 0.77 - 0.80 = -0.03 \text{ V (Not feasible)}
 \end{aligned}$$



$$\begin{aligned}
 E^\circ_{\text{cell}} &= E^\circ_{\text{Br}_2/\text{Br}^-} - E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} \\
 &= 1.09 - 0.77 = 0.32 \text{ V (Feasible)}
 \end{aligned}$$

Topic 2

1. The reciprocal of resistivity is known as specific conductance or simply conductivity. It is denoted by κ (kappa). Thus, if κ is the specific conductance and G is the conductance of the solution, then

$$R = \frac{1}{G} \text{ and } \rho = \frac{1}{\kappa} \therefore \frac{1}{G} = \frac{1}{\kappa} \times \frac{l}{A} \Rightarrow \kappa = G \times \frac{l}{A}$$

Now, if $l = 1 \text{ cm}$ and $A = 1 \text{ sq. cm}$, then $\kappa = G$.

Hence, conductivity of a solution is defined as the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section. Alternatively, it may be defined as conductance of one centimeter cube of the solution of the electrolyte.

Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from 1 mole of the electrolyte dissolved in $V \text{ cm}^3$ of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole of the solution is contained between them. It is represented by Λ_m .

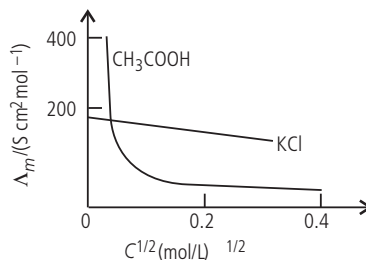
$$\Lambda_m = \frac{\kappa A}{l}$$

Since $l = 1 \text{ cm}$ and $A = V$ (volume containing 1 mole of electrolyte)

$$\Lambda_m = \kappa V$$

Variation of conductivity and molar conductivity with concentration :

Conductivity always decreases with decrease in concentration, for both weak and strong electrolytes. This is because the number of ions per unit volume that carry the current in a solution decreases on dilution.



Molar conductivity versus $C^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

Molar conductivity increases with decrease in concentration. This is because that total volume, V , of solution containing one mole of electrolyte also increases.

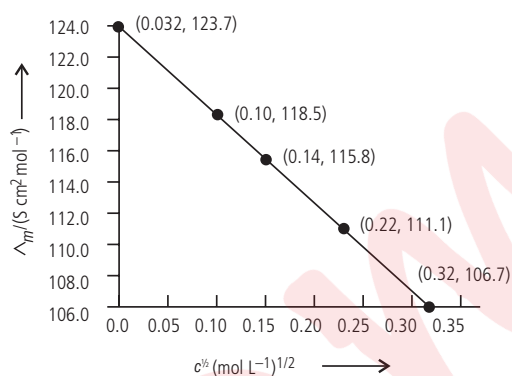
2. Given $\kappa = 2.48 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$, $M = 0.20 \text{ mol L}^{-1}$

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1000 \times 2.48 \times 10^{-2}}{0.20} = 124 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

4. $1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1}$, $\frac{1 \text{ S cm}^{-1}}{100 \text{ S m}^{-1}} = 1$ (unit conversion factor)

3. Cell constant = $\kappa \times R = 0.146 \times 10^{-3} \times 1500 = 0.219 \text{ cm}^{-1}$

Conc. (M)	$\kappa (\text{S m}^{-1})$	$\kappa (\text{S cm}^{-1})$	$\Lambda_m = \frac{1000 \times \kappa}{\text{Molarity}} (\text{S cm}^2 \text{ mol}^{-1})$	$c^{1/2} (\text{M}^{1/2})$
10^{-3}	1.237×10^{-2}	1.237×10^{-4}	$\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$	0.0316
10^{-2}	11.85×10^{-2}	11.85×10^{-4}	$\frac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 118.5$	0.100
2×10^{-2}	23.15×10^{-2}	23.15×10^{-4}	$\frac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}} = 115.8$	0.141
5×10^{-2}	55.53×10^{-2}	55.53×10^{-4}	$\frac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$	0.224
10^{-1}	106.74×10^{-2}	106.74×10^{-4}	$\frac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$	0.316



Λ^0 = Intercept on the Λ_m axis $\approx 124.0 \text{ S cm}^2 \text{ mol}^{-1}$ (on extrapolation to zero concentration).

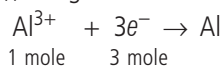
5.
$$\Lambda_m^c = \frac{\kappa \times 1000}{M} = \frac{(7.896 \times 10^{-5}) \times 1000}{0.00241} = 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

$$K_a = \frac{\alpha^2}{1 - \alpha} = \frac{0.00241 \times (8.4 \times 10^{-2})^2}{1 - 0.084} = 1.86 \times 10^{-5}$$

Topic 3

1. (i) The given reaction is

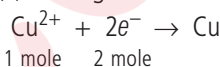


\therefore 3 mole electrons are needed for reduction of 1 mole of Al^{3+} to Al.

3 mole electrons = 3 Faraday

$$= 3 \times 96500 \text{ coulombs} = 2.895 \times 10^5 \text{ coulombs}$$

(ii) The given reaction is

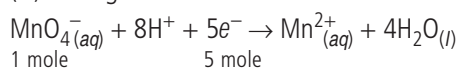


\therefore 2 mole electrons are needed for reduction of 1 mole of Cu^{2+} to Cu.

2 mole electrons = 2 Faraday

$$= 2 \times 96500 \text{ coulombs} = 1.93 \times 10^5 \text{ coulombs}$$

(iii) The given reaction is

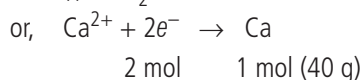


\therefore 5 mole electrons are needed for reduction of 1 mole of MnO_4^- to Mn^{2+} .

5 mole electrons = 5 Faradays

$$= 5 \times 96500 \text{ coulombs} = 4.825 \times 10^5 \text{ coulombs}$$

2. (i) $\text{CaCl}_2 \rightarrow \text{Ca}^{2+} + 2\text{Cl}^-$

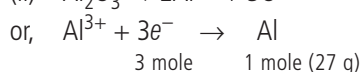


\therefore 40 g of calcium needs = 2 mole of electrons

$$= 2 \times 96500 \text{ coulombs}$$

\therefore 20 g of calcium needs = 96500 coulombs (1F).

(ii) $\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^{3+} + 3\text{O}^{2-}$



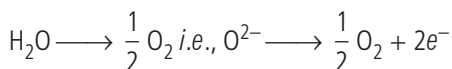
\therefore 27 g of aluminium needs = 3 mole of electrons

$$= 3 \times 96500 \text{ coulombs}$$

$$\therefore 40.0 \text{ g of aluminium needs} = \frac{3 \times 96500 \times 40.0}{27} \text{ coulombs}$$

$$= 4.28888 \times 10^5 \text{ coulombs (4.44 F)}$$

3. (i) The electrode reaction for 1 mol of H_2O is given as



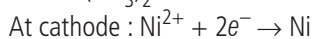
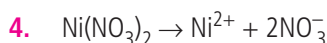
$$\therefore \text{Quantity of electricity required} = 2F$$

$$= 2 \times 96500 \text{ C} = 193000 \text{ C}$$

(ii) The electrode reaction for 1 mol of FeO is given as



$$\therefore \text{Quantity of electricity required} = 1 \text{ F} = 96500 \text{ C}$$



For getting 1 mole of Ni, we require 2 Faradays of electricity.

$$I = 5 \text{ A, } t = 20 \text{ min} = 20 \times 60 = 1200 \text{ sec,}$$

$$Q = I \times t = 5 \times 20 \times 60 = 6000 \text{ C}$$

$$\therefore 2 \times 96500 \text{ C of electricity will produce 58.7 g of nickel}$$

$$\therefore 6000 \text{ C of electricity will produce}$$

$$\frac{58.7 \times 6000}{2 \times 96500} = 1.825 \text{ g of nickel}$$

5. Given : $I = 1.5 \text{ A, } W = 1.45 \text{ g Ag, } t = ?, M = 108, n = 1$

Using Faraday's 1st law of electrolysis, $W = ZIt$ or, $W = \frac{M}{nF} It$

$$\text{or, } 1.45 \text{ g} = \frac{108}{1 \times 96500} \times 1.5 t$$

$$\text{or, } t = \frac{1.45 \times 96500}{1.5 \times 108} = 863.73 \text{ seconds}$$

Now for Cu,

$$W_1 = 1.45 \text{ g Ag, } E_1 = 108, W_2 = ?,$$

$$E_2 = \frac{63.5}{2} = 31.75$$

From Faraday's 2nd law of electrolysis,

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

$$\frac{1.45}{W_2} = \frac{108}{31.75} \Rightarrow W_2 = \frac{1.45 \times 31.75}{108} = 0.426 \text{ g of Cu}$$

Similarly, for Zn,

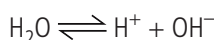
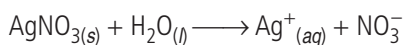
$$W_1 = 1.45 \text{ g Ag, } E_1 = 108, W_2 = ?,$$

$$E_2 = \frac{65.3}{2} = 32.65$$

$$\text{Using formula, } \frac{W_1}{W_2} = \frac{E_1}{E_2}$$

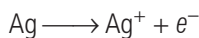
$$\frac{1.45}{W_2} = \frac{108}{32.65} \Rightarrow \frac{1.45 \times 32.65}{108} = 0.438 \text{ g of Zn}$$

6. (i) Electrolysis of aqueous solution of AgNO_3 with silver electrodes,



At cathode: Ag^+ ions have lower discharge potential than H^+ ions. Hence, Ag^+ ions will be deposited as Ag in preference to H^+ ions.

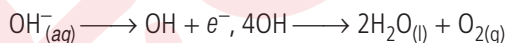
At anode: As Ag anode is attacked by NO_3^- ions, Ag of the anode will dissolve to form Ag^+ ions in the solution.



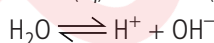
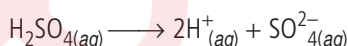
(ii) Electrolysis of aqueous solution of AgNO_3 using platinum electrodes,

At cathode: Ag will be deposited.

At anode: As anode is not attacked, out of OH^- and NO_3^- ions, OH^- ions have lower discharge potential. Hence, OH^- ions will be discharged in preference to NO_3^- ions, and OH^- will then decompose to give out O_2 .



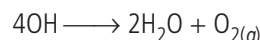
(iii) Electrolysis of dilute H_2SO_4 with platinum electrodes,



At cathode: $\text{H}^+ + e^- \longrightarrow \text{H}$,

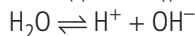
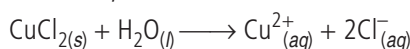


At anode: $\text{OH}^- \longrightarrow \text{OH} + e^-$,

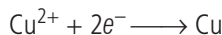


Thus, H_2 is liberated at the cathode and O_2 at the anode.

(iv) Electrolysis of aqueous solution of CuCl_2 with platinum electrodes,



At cathode: Cu^{2+} ions will be reduced in preference to H^+ ions.



At anode: Cl^- ions will be oxidized in preference to OH^- ions.



Thus, Cu will be deposited on the cathode and Cl_2 will be liberated at the anode.

Topic 4

1. Zn is oxidised and Ag_2O is reduced (as Ag^+ ions change into Ag)

$$E^\circ_{\text{cell}} = E^\circ_{\text{Ag}_2\text{O}/\text{Ag}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} = 0.344 - (-0.76) = 1.104 \text{ V}$$

$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}} = -2 \times 96500 \times 1.104 = -2.13 \times 10^5 \text{ J}$$

