2

CHAPTER

Electrochemisty

Level - 1 CORE SUBJECTIVE QUESTIONS

MULTIPLE CHOICE QUESTIONS (MCQs)

(1 Mark)

1. **Option (D) is correct.**
   Explanation: At the cathode H_2O is reduced more easily than Na^+ ion. (SRP of $H_2O > Na^+$)
2. **Option (C) is correct.**
   Explanation: NASA has used H_2—O_2 fuel cells since the mid 1960, in Apollo-series missions and on the space shuttle.
3. **Option (A) is correct.**
   Explanation: During the electrolysis of aqueous sodium chloride H_2 gas is liberated at cathode and Cl_2 gas is liberated at anode.
4. **Option (D) is correct.**
   Explanation: Limiting conductance of Ca^{2+} and Cl^- is 119 and 76.3 S cm^2 mol^{-1}.
   Limiting conductance of $CaCl_2$ is 119 + 76.3 × 2
   $$=271.6 \text{ S cm}^2 \text{ mol}^{-1}$$
5. **Option (D) is correct.**
   Explanation: When a solution is diluted there are more ions and they have more space to move i.e. ions are more far away from each other and mobility of ions increases which leads to increase in molar conductivity of solution. Conductivity of solution decreases with increasing the dilution because number of ions per unit volume decrease with dilution.
6. **Option (A) is correct.**
   Explanation:
   $$E^o_{\frac{S_n^{+4}}{S_n^{+2}}} = 0.15 \text{ V}$$
   $$E^o_{\frac{C_r^{+3}}{Cr}} = –0.73\text{V}$$
   $$\begin{aligned} E^\circ_{Cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= 0.15\ (–0.73) \\ &= +0.88\text{V} \end{aligned}$$
7. **Option (B) is correct.**
   Explanation: When concentrated brine is electrolysed, the following two half reaction are most likely to happen
   At Anode
   $$2Cl^- \longrightarrow Cl_2 + 2e^-$$
   At Cathode
   $$2H^+ + 2e^- \longrightarrow H_2$$
8. **Option (C) is correct.**
   Explanation: For a spontaneous cell reaction, the change in Gibbs free energy (ΔG) is negative and the cell potential (E^o_{Cell}) is positive.
9. **Option (A) is correct.**
   Explanation: The molar conductivity (Δ_m) of KCl increases as the concentration decreases. This is because at lower concentrations, ions experience less inter-ionic attraction and can move more freely, resulting in higher molar conductivity. Thus, 0.01 M KCl has the highest molar conductivity among the options.
   $$\boxed{\Lambda_m \alpha \frac{1}{M}}$$
10. **Option (D) is correct.**
    Explanation: At Anode:
    $$Zn \longrightarrow Zn^{2+} + 2e^-$$
    At Cathode:
    $$2Ag^+ \longrightarrow 2Ag$$
11. **Option (B) is correct.**
    Explanation:
    $$E^\circ_{Cell} = E^\circ_{cathode} - E^\circ_{anode}$$
    as
    Fe is cathode and Sn is anode
    $$\begin{aligned} E_{cell} &= 0.77 - (-0.14) \\ &= 0.91\text{V} \end{aligned}$$
12. **Option (D) is correct.**
    Explanation: $MnO_4^- + 5e^- \longrightarrow Mn^{2+}$
    ∴ 5 F are required to reduce / 1 mol of MnO_4^- to Mn^{2+}
13. **Option (B) is correct.**
    Explanation: The Kohlrausch equation is a relationship between the molar conductivity ($\wedge_m$) and concentration (c) of electrolytes. When the concentration approaches zero at infinite dilution then $A\sqrt{C}$ becomes zero, hence at infinite dilution molar conductivity approaches the limiting molar conductivity.
14. **Option (B) is correct.**
    Explanation: Y is a strong electrolyte since it is already almost completely ionised (α ≈ 1). Dilution simply help in its dissociation i.e. ions get separated. Therefore, the increase in molar conductivity upon dilution is small.
15. **Option (D) is correct.**
    Explanation: If an external opposite potential is applied on the galvanic cell and increased reaction

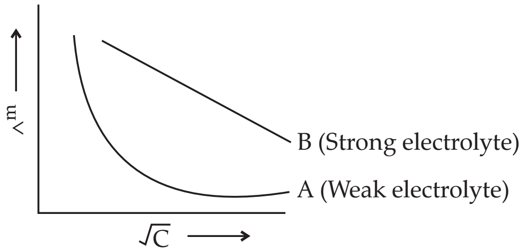
continues to take place till the opposite voltage reaches the value of cell's standard potential, then no current flows through the cell. Further increase in external potential starts the reaction in opposite direction and galvanic cell behaves as a electrolytic cell.

ASSERTION-REASON QUESTIONS (1 Mark)

1. **Option (D) is correct.**
   Explanation: $\Lambda_m^\circ = \Lambda_m - AC^{1/2}$ is an incorrect equation, the correct equation is $\Lambda_m = \Lambda_m^\circ - AC^{1/2}$
2. **Option (C) is correct.**
   Explanation: The Zn-Cu Daniel cell will change from being a galvanic cell to an electrolytic cell with the direction of electron flow reversed, if the opposing potential rises over 1.10 vol. The external potential will cause the flow of electrons from Cu to Zn, instead of the spontaneous flow from the zinc electrode to the copper electrode.
3. **Option (D) is correct.**
   Explanation: Δ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.
4. **Option (A) is correct.**
   Explanation: In the electrolysis of aqueous NaCl, chloride ions (Cl^-) are oxidised to chlorine gas (Cl_2) at the anode, while hydrogen gas (H_2) is produced at the cathode. Overpotential is the extra voltage needed for a non-spontaneous reaction to occur. While oxygen gas (O_2) can be formed at the anode via the oxidation of water, it requires application of higher potential/ overpotential compared to the oxidation of chloride ions to chlorine.
5. **Option (A) is correct.**
   Explanation: It is because the number of ions per unit volume drops with dilution the solutions current carrying capacity reduces as well. As a result conductivity decreases with dilution.

VERY SHORT ANSWER TYPE QUESTIONS (2 Marks)

1. (i) $Y(s)|Y^{2+}(aq)\,||\,X^{+}(aq)|\,X(s)$
   (ii) ions are carrier of current in salt bridge
   (iii) $Y(s) \rightarrow Y^{2+}(aq) + 2e^-$
2. We know $$E = E^\circ - \left(\frac{0.0592}{n}\right) \times \log \theta$$
   Applying Nernst equation,
   $$E = -0.45 - \frac{0.0592}{2} \times \log\frac{1}{0.01}$$
   $$E = -0.45 - \frac{0.0592}{2} \times 2$$
   $$E = -0.45 - 0.0592$$
   $$E = -0.5092V$$
3. $$\text{Cell constant} = \text{Conductivity} \times \text{resistance}$$
   $$= 0.0248 \text{ S/cm} \times 200$$
   $$= 4.96 \times \text{cm}^{-1}$$
   For 0.05 mol L KCl solution
   $$\text{Conductivity} = \frac{\text{cell constant}}{\text{resistance}}$$
   $$= \frac{4.96}{620}$$
   $$= 0.008 \text{ S cm}^{-1}$$
   $$\text{Molar conductivity} = \frac{\text{Conductivity}}{\text{Concentration}}$$
   $$= \frac{0.008 \times 1000}{0.05}$$
   $$= 160 \text{ S cm}^2 \text{mol}^{-1}$$
4. (i) Kohlraush law of independent migration of ions state that the limiting molar conductivity of an electrolyte can be represented as the sum of individual contributions of its cations and anions.
   (ii) Faraday's first law of electrolysis state that the amount of a substance produced at an electrode during electrolysis is directly proportional to the amount of electricity that passes through the electrolytic cell.
5. (i) Hydrogen-Oxygen Fuel cell
   (ii) Lead storage cell
   (iii) Mercury cell
   (iv) Leclanche cell or Dry cell
6. (i) E°_{Cell} = positive
   ΔG° = Negative
7. $$E^\circ_{Cell} = 0.44V$$
   $$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$
   $$E_{Cell} = E^\circ_{Cell} - \frac{0.0591}{n}\log\frac{\left[Fe^{2+}_{(aq)}\right]}{\left[H^+_{(aq)}\right]^2}$$
   $$n = 2$$
   $$E_{Cell} = 0.44 - \frac{0.0591}{2}\log\frac{0.01}{1}$$
   $$= 0.44 - \frac{0.0591}{2}(-2\log 10)$$
   $$= 0.44 + 2 \times \frac{0.0591}{2}$$
   $$= 0.4991 \text{ V}$$
8. Oxidation potential of Fe = 0.44 V
   Oxidation potential of X = 2.36 V
   Oxidation potential of Y = 0.14 V
   X is better.
   As X has higher oxidation potential than Iron, it can be used for coating the surface of iron. As it will be preferentially oxidised before iron and iron can be protected from corrosion.
9. A is a weak electrolyte whereas 'B' is a strong electrolyte



10. (i) A mercury cell has a constant cell potential throughout its' life time because the overall reaction does not involve any ion in the solution whose concentration can change.

(ii) When DC is used it will polarize the electrode and electrolyte which will lead to an error in measured conductivity.

11. A fuel cell can be defined as an electro chemical cell that generate electrical energy from fuel via an electrochemical reaction. Example H_2—O_2 fuel cell. Fuel cell run continuously as long as the reactants are supplied to it. They do not run down or need recharging like primary and secondary batteries.

SHORT ANSWER TYPE QUESTIONS (3 Marks)

1. (i) Product of electrolysis of copper chloride

Cathode(–) $Cu^{2+} + 2e^- \rightarrow Cu(s)$

Anode(+) $2Cl^- \rightarrow Cl_2 + 2e^-$

Product of electrolysis of concentrated copper sulphate

Anode(+) $SO_4^{2-} \rightarrow S_2O_8 + 2e^-$

Cathode (–) $Cu^{2+} + 2e^- \rightarrow Cu(s)$

(ii) $\Lambda_m^0[Al_2(SO_4)_3] = 2\,\lambda_m^0(Al^{3+}) + 3\,\lambda_m^0\,(SO_4^{2-})$

2. (i)

$$E_{cell} = E°_{cell} - \frac{2.303RT}{nF}.\log K_c$$

At 298 K,

$$E_{cell} = E°_{cell} - \frac{0.0591}{n}.\log K_c$$

At equilibrium, $E_{cell} = 0$, $n = 6$

$$E^o_{Cell} = \frac{0.0591}{n}.\log K_c$$

$$= \frac{0.059}{6} \log 4.617 \times 10^{184}$$

$$= 0.00983 \times 184.6644$$

$$E^o_{Cell} = 1.8152$$

(ii)

$$E^o_{Cell} = E°_{Sn^{4+}/Sn^{2+}} - E°_{Al^{3+}/Al}$$

$$1.81 = -0.15 - E°_{Al^{3+}/Al}$$

$$E°_{Al^{3+}/Al} = -1.66 \text{ V}$$

3.

$$E°_{Cell} = E_{cathode} - E_{anode}$$

$$= -0.14 - (-0.76)$$

$$= -0.14 + 0.76$$

$$E°_{Cell} = 0.62$$

$$EMF = E°_{Cell} - \frac{0.0591}{n}\log\frac{[Z_n^{2+}]}{[S_n^{2+}]}$$

$$= 0.62 - \frac{0.0591}{2}\log\frac{0.1}{0.001}$$

$$= 0.62 - \frac{0.0591}{2}\log 100$$

$$= 0.62 - \frac{0.0591}{2} \times \log 10^2$$

$$= 0.62 - \frac{0.0591}{2} \times 2$$

$$= 0.62 - 0.0591$$

$$= 0.561\text{V}$$

4. Given, Resistance $= 100\ \Omega$

Conductivity $= 1.35 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$

$$\text{Cell constant } (G^*) = \text{Conductivity} \times \text{Resistance}$$

$$= 100 \times 1.35 \times 10^{-2}$$

$$= 1.35 \text{ cm}^{-1}$$

$$\text{Conductivity} = \frac{\text{Cell constant}}{\text{Resistance}}$$

$$= \frac{1.35}{90} = 0.015 \text{ S cm}^{-1}$$

$$\text{Molar conductivity} = \frac{K \times 1000}{M} = \frac{1.35 \times 1000}{90 \times 0.02}$$

$$= 750 \text{ S cm}^2 \text{ mol}^{-1}$$

5.

$$\text{Molar conductivity } (\Lambda_m) = \frac{K \times 1000}{M}$$

$$= \frac{2.48 \times 10^{-2} \times 10^3}{0.2}$$

$$= 124 \text{ S cm}^2 \text{ mol}^{-1}$$

Given

$$\Lambda°_{k^+} = 73.5 \text{ S cm}^2 \text{ mol–1;}$$

$$\lambda°_{k^+} = 73.5 \text{ S cm}^2 \text{ m}$$

$$\lambda°_{Cl^-} = 76.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 73.5 + 76.5$$

$$= 150 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\wedge_m}{\wedge°_m} = \frac{124}{150}$$

$$= 0.82$$

6. $Sn + 2H^+ \longrightarrow Sn^{2+} + H_2$ $n = 2$

Applying Nernst equation:

$$E_{Cell} = E°_{Cell} - \frac{0.0591}{2}\log\frac{[Sn^{2+}]}{[H^+]^2}$$

$$= [0 - (-0.14)] - \frac{0.0591}{2}\log\frac{0.001}{(0.01)^2}$$

$$= 0.14 - \frac{0.0591}{2}$$

$$= 0.14 - 0.02955$$

$$= 0.11045 \text{ V or } 0.11 \text{ V}$$

7. $Ni + 2Ag^+ \longrightarrow Ni^{2+} + 2Ag$

$n = 2$

$$E_{Cell} = E°_{Cell} - \frac{0.0591}{n}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$E_{Cell} = 1.05 - \frac{0.0591}{2}\log\frac{(0.1)}{(0.01)^2}$$

$$= 1.05 - \frac{0.0591}{2}\log\frac{0.1}{0.01\times 0.01}$$

$$= 1.05 - \frac{0.0591}{2}\log 10^3$$

$$= 1.05 - \frac{0.0591}{2}\times 3$$

$= 1.05 – (0.0955 \times 3)$

$= 1.05 – (0.08865)$

$= 0.96135$ V

8. Cell constant $= 50\ \text{cm}^{-1}$

Electrical resistance $= 4.5 \times 10^3\ \Omega$

Concentration $= 0.05$ M

We know $$R = \rho\times\frac{l}{\alpha}$$

$$\rho = \frac{R}{l/\alpha}$$

$$= \frac{4.5\times 10^3}{50}$$

$= 9 \times 10^1$

$= 90\ \Omega$ cm

$$\text{Conductivity} = \frac{1}{\text{Resistivity}}$$

$$= \frac{1}{90}$$

$= 0.0111\ \text{S cm}^{-1}$

$$\text{Molar conductivity } \wedge_m = \frac{K}{C}\times 1000$$

$$= \frac{1/90}{0.05}\times 1000$$

$= 222.22\ \text{S cm}^2\ \text{mol}^{-1}$

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. (i)
$$E^\circ_{Cell} = E^\circ_{Cathode} - E^\circ_{Anode}$$
$$= 0.80 - (-0.44) = 1.24$$
$$\Delta^\circ_G = -nFE^\circ_{Cell}$$
$$= -2 \times 96500 \times 1.24$$
$$= -239320 \text{ J/Mol}$$
$$E^\circ_{Cell} = \frac{0.059}{n}\log K_C$$
$$\log K_C = \frac{1.24\times 2}{0.0591} = 41.96$$

(ii) Two advantages of fuel cell over primary and secondary batteries are:

1. Fuel cells are more efficient

2. Fuel cells can produce electricity continously.

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

(iii) 4 Faradays are required for oxidation of 2 moles of H_2O to O_2. Therefore, 1 equivalent mass of H_2O will require 1 Faraday electric charge to oxidise to O_2.

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

1 mole = $2e^-$

2. (i)
$$\wedge_m = \frac{K}{C}\times 1000$$
$K = 5.25 \times 10^{-5}\ \text{S cm}^{-1}$

$C = 0.0025$
$$\wedge_m = \frac{5.25\times 10^{-5}\times 1000}{0.0025}$$
$$= \frac{5.25\times 10^{-2}}{2.5\times 10^{-3}}$$
$= 21\ \text{S cm}^2\ \text{mol}^{-1}$
$$\propto = \frac{\wedge_m}{\wedge^\circ_m} = \frac{21}{390} = \frac{2.1}{39} = 0.05384$$

(ii) At Anode:

$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

At Cathode:

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

Overall: $Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$

3. (i) Electrolyte conductivity $K = \frac{1}{R}\times$ Cell constant
$$= \frac{1}{100}\times 0.0354$$
$= 3.54 \times 10^{-4}\ \pi^{-1}\ \text{cm}^{-1}$
$$\therefore \text{Molar conductivity} = \frac{1000\times 3.54\times 10^{-4}}{0.05}$$
$= 7.08\ \text{S cm}^2\ \text{mol}^{-1}$

(ii) Faraday's First law of electrolysis states that the amount of a substance produced at an electrode during electrolysis is directly proportional to the amount of electricity that passes through the electrolyte.

The balanced chemical equation is

$8H^+ + 5e^- + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

According to chemical equation, to reduce one mole of MnO_4^- to Mn^{2+} 5 electrons are required.

5 moles of electron = 5 Faraday

4. $Zn + Cd^{2+} \longrightarrow Zn^{2+} + Cd$

$n = 2$

According to Nernest equation
$$E_{Cell} = E^\circ_{Cell} - \frac{2.303\ RT}{nF}\log\frac{[Zn^{2+}]}{[Cd^{2+}]}$$
$$= (-0.40 + 0.76) - \frac{0.0591}{2}\log\frac{(0.001)}{(0.1)}$$
$$= 0.36 - \frac{(0.059)}{2}\log 10^{-2}$$
$$= 0.36 - \frac{0.0591}{2}\times(-2)$$
$= 0.36 + 0.0591$

$= 0.4191$ V

(ii) Faraday's second law of electrolysis states that the mass of different substance liberated from the same quantity of electric current through an electrolytic solution is directly proportional to their equivalent weight

When an aqueous solution of sodium chloride (NaCl) is electrolysed, the pH of the solution increases.

5. (i) Lead storage battery is a secondary cell.

At Anode:

$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

At Cathode:

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

Overall: $Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$

(ii) The reaction at the cathode is

$Ag^+ + e^- \rightarrow Ag\,(s)$

108 g 96500 C

108 g of silver is deposited by passing charge = 96500 C.

1.5 g of silver is deposited by passing charge

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

$$= 1340.27 \text{ C}$$

$$\text{Time to deposit 1.5 g of silver} = \frac{\text{Charge}}{\text{Current}}$$

$$= \frac{1340.27}{1.5}$$

$$= 893.51 \text{ S}$$

or 14.89 min

6. (i) Kohlrausch's law of independent migration of ions states that the molar conductivity of an electrolyte is the sum of the contribution of its individual ions.

$\wedge^\circ_m$ for $NH_4OH = \wedge^\circ_m\, NH_4Cl + \wedge^\circ_m\, NaOH - \wedge^\circ_m NaCl$

$$= (110 + 100) - 105$$
$$= 210 - 105$$
$$= 105 \text{ S cm}^2 \text{ mol}^{-1}$$

(ii)

$$\Delta^\circ G = -nFE^\circ_{Cell}$$
$$E^\circ_{Cell} = 0.34 - (-0.76)$$
$$= 1.10V$$
$$\Delta^\circ G = -2 \times 96500 \times 1.10$$
$$= -212300 \text{ J/mol.}$$

7. (i)

$$\wedge^\circ_m NH_4Cl = \wedge^\circ_m NH_4^+ + \wedge^\circ_m Cl^-$$
$$= 73.8 + 76.2$$
$$= 150 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\% \text{ of } \alpha = \frac{\wedge_m}{\wedge^\circ_m} \times 100$$

$$= \frac{129 \times 100}{150}$$

$$= 86\%$$

(ii)

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$E = -0.76 - \frac{8.314 \times 298}{2 \times 96500} \ln \frac{1}{0.1}$$

$$E = -0.76 - 0.02956$$
$$E = -0.7895 \text{ V}$$

8. (i) Molar conductivity

$$\wedge_m = \frac{K \times 1000}{C}$$

$$= \frac{8 \times 10^{-5} \times 1000}{2 \times 10^{-3}}$$

$$= \frac{8 \times 10^{-2}}{2 \times 10^{-3}}$$

$$= 40 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Degree of dissociation } (\alpha) = \frac{\wedge_m}{\wedge^\circ_m} = \frac{40}{404}$$

$$= 0.099$$

(ii) $Ni + 2Ag^+ \rightleftharpoons 2Ni^{2+} + 2Ag$

$$E^\circ_{Cell} = 0.80 - (-0.25)$$
$$= 1.05V$$

We know

$$\Delta_r{}^\circ G = -nFE^\circ_{Cell}$$
$$= -2 \times 96500 \times 1.05$$
$$\Delta_r{}^\circ G = -202,650 \text{ J mol}^{-1}$$

$$E^\circ_{Cell} = \frac{0.0591}{n} \log K_C$$

$$\log K_C = \frac{1.05 \times 2}{0.0591}$$

$$\log K_C = 35.5329$$

9. (i)

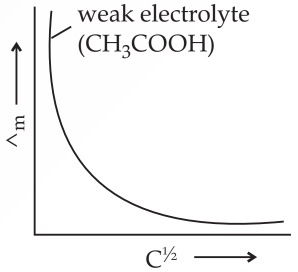
$$E_{Cell} = E^\circ_{Cell} - \frac{0.0591}{n} \log \frac{[Al^{+3}]^2}{[Ni^{2+}]^3}$$

$$E^\circ_{Cell} = E^\circ_{Cathode} - E^\circ_{Anode}$$
$$= -0.25 - (-1.66)$$
$$= 1.41V$$

$$E_{Cell} = 1.41 - \frac{0.059}{6} \log \frac{[10^{-3}]^2}{[10^{-1}]^3}$$

$$E_{Cell} = 1.41 + 0.0295$$
$$= 1.4395 \text{ V}$$

(ii) The plot of $\wedge_m$ against $\sqrt{C}$ is not linear. Therefore the value of $\wedge^\circ_m$ for weak electrolyte cannot be obtained by extrapolation.



10. (i) Kohlrausch's law of independent migration of ions states that each ion migrates independently of its co-ion at infinite dilution and contributes to the total molar conductivity of an electrolyte on its own, regardless of the other ion it is associated.

Limiting molar conductivity of acetic acid

$\Lambda^\circ_m\,(CH_3COOH) \longrightarrow \lambda^\circ\,(CH_3COO^-) + \lambda^\circ\,(H^+)$

(ii) $Ni + 2Ag^+ \rightarrow Ni^{2+} + 2Ag$

$$E^\circ_{Cell} = 0.80 - (-0.25)$$
$$= 1.05 \text{ V}$$

$$E^\circ_{Cell} = \frac{0.059}{n} \log K_C$$

$$1.05 = \frac{0.059}{n} \log K_C$$

$$\log K_C = \frac{1.05 \times 2}{0.059} = 35.59$$

$$\begin{aligned} \Delta_r G^\circ &= -nFE^\circ_{Cell} \\ &= -2 \times 96500 \times 1.05 \\ &= -202650 \text{ J mol}^{-1} \\ &= -202.65 \text{ kJ mol}^{-1} \end{aligned}$$

11. (i) Faraday's first law of electrolysis states that the amount of a substance deposited or liberated at an electrode is directly proportional to the amount of electricity that passes through the electrolyte.

The amount of charge require to reduce one mole of Cu^{2+} to Cu is 2F. This is because the reaction involves two moles of electrons.

(ii) $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$

According to Nernst equation

$$E_{Cell} = E^\circ_{Cell} - \frac{0.0591}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

Given $E^\circ_{Cell} = 2.71$ V, $[Mg^{2+}] = 0.1$ M

$[Cu^{2+}] = 0.01$ M, $n = 2$

$$\begin{aligned} E_{Cell} &= 2.71 - \frac{0.0591}{2} \log \frac{0.1}{0.01} \\ &= 2.71 - 0.02955 \times 1 \\ &= 2.68 \text{ V} \end{aligned}$$

12. (i) Half cell reactions

At Anode: $H_2 \rightarrow 2H^+ + 2e^-$

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

$H_2 + Cu^{2+} \rightarrow 2H^+ + Cu$

(ii) $\Delta^\circ G = -2.303\, RT \log_{10} K_C$

(iii) $Mg + Cu^{2+} \rightarrow Cu + Mg^{2+}$

$$\begin{aligned} n &= 2 \\ E^\circ_{Cell} &= 0.34 - (-2.37) \\ &= 2.71\text{V} \\ E_{Cell} &= E^\circ_{Cell} - \frac{0.0591}{n} \log \frac{[Mg^{2+}]}{[Cu^{2+}]} \\ &= 2.71 - \frac{0.0591}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]} \\ &= 2.71 - \frac{0.0591}{2} \log \frac{1 \times 10^{-1}}{1 \times 10^{-3}} \\ &= 2.71 - \frac{0.0591}{2} \log 10^{-1} \times 10^{+3} \\ &= 2.71 - \frac{0.0591}{2} \log 10^{2} \\ &= 2.71 - \frac{0.0591}{2} \times 2 \\ &= 2.71 - 0.0591 \\ E_{Cell} &= 2.65 \text{ V} \end{aligned}$$

Level - 2 ADVANCED COMPETENCY FOCUSED QUESTIONS

MULTIPLE CHOICE QUESTIONS (MCQs) (1 Mark)

1. **Option (C) is correct.**

   Explanation: For spontaneous reaction.

   $$E^\circ_{Cell} = +ve$$
   $$\Delta G = -ve$$

2. **Option (D) is correct.**

   Explanation: When voltage greater than 1.10 v is applied, the cell act as an electrolytic cell and start converting electrical energy into chemical energy.

3. **Option (B) is correct.**

   Explanation:

   $$\begin{aligned} E^\circ_{Cell} &= E^\circ_{Cathode} - E^\circ_{anode} \\ &= 0.77 - 0.54 \\ &= +\, 0.23\text{V} \end{aligned}$$

4. Option (C) is correct

   Explanation: This is a Daniel cell, where Zinc is the anode, so oxidation takes place here:

   $Zn(s) \rightarrow Zn^{2+} + 2^{e-}$

   Copper is the cathode, so reduction takes place here:

   $Cu^{2+} + 2^{e-} \rightarrow Cu(s)$

5. Option (A) is correct

   Explanation: A more negative E° means stronger reducing agent (more easily oxidised). A more positive E° means stronger oxidising agent (more easily reduced).

   Fe has a lower (more negative) E° → stronger reducing agent than Cu. Therefore, Fe can reduce Cu^{2+} to Cu and itself gets oxidised to Fe^{2+}.

   So, the correct redox reaction is:

   $Fe(s) + Cu^{2+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + Cu_{(s)}$

   This means iron can displace copper from copper sulphate solution.

6. Option (B) is correct

   Explanation: A Daniell cell is represented as Zn (s) $|Zn^{2+}$ (aq)$||Cu^{2+}$ (aq)$|$Cu (s)

   Anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)

   Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)

   Nernst Equation (for cell potential):

   $$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \left(\frac{|Zn^{2+}|}{|Cu^{2+}|} \right)$$

   Where:

   $n = 2$ (number of electrons transferred)

   $$E^\circ_{cell} = E^\circ_{cathode} - E^0_{anode}$$

   Increasing $[Cu^{2+}]$ increases the denominator in the log term → log value decreases → E_{cell} increases.

7. Option (A) is correct

   Explanation: At the Cathode (reduction):

   $Na^+ + e^- \rightarrow Na$ (liquid)

   Sodium ions gain electrons to form liquid sodium metal.: Na^+ is reduced to Na

   At the Anode (oxidation): $2Cl^- \rightarrow Cl_2(g) + 2^{e-}$

   Chloride ions lose electrons to form chlorine gas. Cl^- is oxidised to Cl_2 gas

ASSERTION-REASON QUESTIONS (1 Mark)

1. Option (C) is correct
   Explanation: Assertion is true. In a galvanic cell, oxidation occurs at the anode and reduction occurs at the cathode. This is a fundamental principle of electrochemistry.
   Reason is false. Electrons actually flow from anode to cathode through the external circuit, not from cathode to anode.
2. Option (C) is correct
   Explanation: Assertion is true. The standard electrode potential of the $\frac{Zn^{2+}}{Zn}$ half-cell is -0.76 V, which is negative relative to the standard hydrogen electrode (SHE, which is defined as 0 V).
   Reason is false. A negative electrode potential means zinc has a higher tendency to lose electrons (i.e., it is more easily oxidised) than hydrogen—not to gain them. So, zinc has a lower tendency to gain electrons than hydrogen.
3. Option (C) is correct
   Explanation: Assertion is true. The salt bridge maintains electrical neutrality by allowing the migration of ions (not electrons) between the two half-cells. This prevents charge buildup and allows the redox reaction to continue.
   Reason is false. The salt bridge does not allow electron flow. Electrons flow through the external wire, while the salt bridge permits the flow of ions to balance the charges in the two half-cells.
4. Option (A) is correct
   Explanation: Assertion is true. In the electrolysis of aqueous NaCl, H^+ gas is liberated at the cathode instead of sodium metal. This is because water (H_2O) provides H^+ ions, which are preferentially reduced over Na^+ ions.
   Reason is also true. The reduction potential of H^+ (0.00 V) is higher than that of Na^+ (–2.71 V). Thus, H^+ ions are reduced more easily than Na^+ ions during electrolysis.
5. Option (A) is correct
   Explanation: Assertion is true. Corrosion of iron (rusting) is indeed an electrochemical process, where iron reacts with water and oxygen, leading to the formation of rust ($Fe_2O_3.xH_2O$).
   Reason is also true. The process involves:
   Oxidation of iron ($Fe \rightarrow Fe^{2+} + 2e^-$) at the anode.
   Reduction of oxygen ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) at the cathode (in presence of moisture and air).

VERY SHORT ANSWER TYPE QUESTIONS (2 Marks)

1. Aman should use the Copper spoon.
   The reduction potential of Aluminium is lower than Fe metal, hence Aluminium spoon (metal) cannot be used as it undergoes oxidation i.e. it would lose *e*.
   $$Al_{(s)} \longrightarrow Al^{3+}{}_{(aq)} + 3e^-$$
   Thus, the solution will slowly turn into Aluminium sulphate and it will not serve the purpose.
   Copper, on the other hand, has a reduction potential higher than Fe (both in ionic state) or we can say it is less reactive than Fe.
   $Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$
   Moreover, Cu here is in the solid state. Hence, Cu spoon can be used to stir the solution as it will not bring any change in the $FeSO_4$ solution.
2. For SHE :
   $H^+ + e^- \longrightarrow 1/2H_2$
   Applying Nernst equation.
   $$E = E° - \left(\frac{0.0591V}{n}\right)\log\frac{1}{[H^+]}$$
   $$E = 0 - \left(\frac{0.0591V}{n}\right)\log\frac{1}{1\times10^{-10}}$$
   $$E = -0.0591V \times 10 \log 10$$
   $$E = -0.591V \ (\log 10 = 1)$$
3. Lithium-ion cells are suitable for portable electronic devices because:
   (i) **High Energy Density:** They can store a large amount of energy in a small and lightweight battery, making them ideal for compact devices like phones and laptops.
   (ii) **Rechargeability and Long Cycle Life:** They can be recharged multiple times with minimal loss of capacity, providing long-lasting performance.
4. Galvanisation prevents corrosion of iron by coating it with a thin layer of zinc. Zinc is more reactive than iron and lies above iron in the electrochemical series, meaning it has a higher tendency to lose electrons (oxidise).
   If the zinc layer is damaged and both zinc and iron are exposed to moisture and air, zinc acts as the anode and gets preferentially oxidised, while iron remains protected as the cathode. This sacrificial protection ensures that zinc corrodes instead of iron, thus preventing rusting of iron tools and gates. Hence, galvanisation utilises zinc's electrochemical properties to protect iron from corrosion.
5. Tin is used to coat steel cans because:
   (i) Tin is less reactive than iron and resists corrosion, especially in acidic environments like soft drinks.
   (ii) It provides a protective barrier that prevents the steel (iron) from coming into contact with moisture and acids in the drink.
   If the tin coating is scratched, the underlying iron is exposed. Since iron is more reactive than tin, and tin is below iron in the electrochemical series, the exposed iron becomes the anode and starts to corrode faster due to galvanic corrosion. This can lead to rust formation and contamination of the drink.
6. Two essential characteristics of electrochemical cells used in medical implants like pacemakers and hearing aids are:

(i) **High energy density in a small size:** Medical implants require miniature cells that can deliver sufficient power over long durations without frequent replacement.

(ii) **Biocompatibility and safety:** The materials used must be non-toxic and stable inside the human body to avoid harmful reactions or leakage.

7. In moist air, copper wires corrode due to an electrochemical reaction involving water, oxygen, and carbon dioxide present in the atmosphere. The process is as follows:

(i) Oxidation of copper occurs at anodic sites on the wire surface:

$Cu_{(s)} \rightarrow Cu^{2+} + 2^{e-}$

(ii) Reduction of oxygen occurs at cathodic sites in the presence of water:

$O_2 + 4H^+ + 4^{e-} \rightarrow 2H_2O$ (in acidic medium)

or in neutral/basic medium:

$O_2 + 2H_2O, + 4^{e-} \rightarrow 4OH^-$

The Cu^{2+} ions react with hydroxide ions or carbonate in water to form basic copper carbonate (green layer of patina):

$2Cu^{2+} + H_2O + CO_2 + O_2 \rightarrow Cu(OH)_2.CuCO_3$

This electrochemical corrosion occurs because moist air acts as an electrolyte, facilitating redox reactions on the copper surface.

8. Lead-acid batteries are preferred in vehicles due to the following two key features:

(i) **High Current Output:** They can deliver a large amount of current quickly, which is essential for starting vehicle engines.

(ii) **Rechargeability and Long Life:** They are rechargeable, durable, and can withstand numerous charge-discharge cycles, making them suitable for long-term use in automobiles.

9. A sacrificial anode is a more reactive metal (such as magnesium, zinc, or aluminum) that is intentionally connected to a less reactive metal structure (like a ship hull or pipeline) to prevent corrosion.

The sacrificial anode undergoes oxidation (loses electrons) preferentially, protecting the more valuable metal. It "sacrifices" itself by corroding instead of the protected metal. This is an application of the electrochemical series, where the more reactive metal acts as the anode and corrodes, while the protected metal acts as the cathode and remains intact.

SHORT ANSWER TYPE QUESTIONS

(3 Marks)

1. (i) In experimental set up I, the blue colour of $CuSO_4$ solution will fade away.

It is because $CuSO_4$ solution will turn into H_2SO_4 solution.

Oxidation of water leaves behind H^+ and reduction of Cu^{2+} ion leaves SO_4^{2-} ion in the solution.

$2H^+ + SO_4^2 \longrightarrow H_2SO_4$

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

(iii) Oxygen (O_2)

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

(iv) Set up II depict the refining of Cu metal.

In this setup, an impure copper rod is made anode, where oxidation takes place,

At anode—

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

and a pure thin wire of copper is made cathode.

At cathode

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

2. **(i)** The electrolyte used is a solution of a soluble nickel salt, typically nickel(II) sulphate ($NiSO_4$).

(ii) The object to be plated is made the cathode because reduction occurs at the cathode, allowing Ni^{2+} ions to gain electrons and deposit as metallic nickel on the surface of the object.

(iii) Electroplating enhances the appearance and increases the resistance to corrosion of the object, making it more durable and attractive. For example, in cutlery, jewellery, and bathroom fittings.

3. **(i)** Rusting is an electrochemical process where iron acts as the anode and gets oxidised:

$Fe \rightarrow Fe^{2+} + 2e^-$

At the cathodic regions, oxygen from air is reduced in the presence of water:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (in acidic medium)

The Fe^{2+} ions further react with water and oxygen to form hydrated iron(III) oxide ($Fe_2O_3.xH_2O$), commonly known as rust.

(ii) In coastal areas, the presence of moisture and salt (NaCl) increases the electrolytic conductivity of water, accelerating the rusting process due to enhanced ionic movement.

(iii) One method to reduce rusting is galvanisation, i.e., coating the iron surface with a thin layer of zinc, which acts as a sacrificial anode and protects the iron from corrosion.

4. **(i)** During discharge, the overall reaction is:

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

(ii) These batteries are rechargeable because the discharge reaction is reversible. On applying an external electric current, the lead sulphate and water can be converted back into lead, lead dioxide, and sulphuric acid.

(iii) One major limitation of lead acid batteries is that they are heavy and bulky, which makes them less suitable for portable devices.

5. **(i)** A sacrificial anode is a more reactive metal that is deliberately connected to a less reactive metal (like iron or steel) to protect it from corrosion. The anode corrodes (oxidises) instead of the protected metal.

(ii) Zinc, magnesium, and aluminium are commonly used because they are more electropositive (higher in the electrochemical series) than iron.

(iii) The sacrificial metal oxidises (loses electrons) in place of the iron pipeline. As a result, the pipeline remains unoxidised and protected. This is an application of the principle of electrochemical series, where a more reactive metal sacrifices itself to prevent corrosion of the less reactive metal.

CASE BASED QUESTIONS (4 Mark)

1. (i) The main difference between primary and secondary batteries is that primary batteries are non-rechargeable while secondary batteries are rechargeable.

(ii) The cell potential of mercury cell is 1.35V and remain constant throughout its life because it does not involve any ions in the solution whose concentration may change during its life lime.

(iii) (a) The reactions involved in the recharging of lead storage battery.

At Cathode:

$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$

At Anode :

$PbSO_4(s) + 2H_2O(l) \longrightarrow PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$

Overall reaction

$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 4H^+(g) + 2SO_4^{2-}(aq)$

OR

(b) Two advantages of fuel cell over other galvanic cell are

(1) Fuel cells are more efficient than galvanic cell.

(2) Fuel cells does not cause pollution.

2. (i) A salt bridge is used to maintain electrical neutrality inside the circuit of galvanic cell.

(ii) A galvanic cell behaves like an electrolytic cell when an external oppsoite potential is applied to the galvanic cell and the opposing voltage reaches higher than 1.1 V.

(iii) (a) No, it is not possible. The E° value of the copper and zinc electrode are $E^\circ_{Cu^{2+}/Cu}$ = 0.34 V and $E^\circ_{zn^{2+}/Zn}$ = –0.76. This show that zinc is stronger reducing agent than copper. It will lose electron to Cu^{2+} ion.

OR

(b) (1) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

We need 5 moles of electrons to reduce 1 mole of MnO_4^-.

Faraday required = 5 moles of electron

= 5 Faraday

(2) $H_2O \longrightarrow 2H^+ + 1/2O_2 + 2e^-$

Eelectricity required to oxidise 1 mole of H_2O to O_2 = 2 Faraday

3. (i) Conductivity decreases with dilution because the number of ions per unit volume of the solution decreases on dilution.

(ii) $\wedge^\circ_m$ KCl = 150.0 5 $cm^2\ mol^{-1}$

$\wedge_m$ 0.01 MKCl = 141 S cm^2/mol

As we know,

$$\text{degree of dissociation} = \frac{\wedge_m}{\wedge^\circ_m} = \frac{141}{150}$$

$$= 0.94$$

(iii) (a) The conductivity ($\wedge_m$) values would be more for HCl than for KCl for a given concentration because HCl is fully ionised and H^+ has higher mobility than K^+ ions.

OR

(b) **Similarity:** $\wedge_m$ increases with dilution for both electrolytes.

Difference: For KCl, the $\wedge_m$ increases gradually whereas for CH_3COOH, $\wedge_m$ increases steeply on dilution.

In case of CH_3COOH, $\wedge^\circ_m$ cannot be obtained by extrapolation of $\wedge_m$ to zero concentration whereas for KCl it can be obtained.

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. (i) Corrosion of iron is an electrochemical process where iron acts as the anode and undergoes oxidation:

$Fe_{(s)} \rightarrow Fe^{2+} + 2^{e-}$

These electrons travel through the metal to another site exposed to air and moisture, which acts as the cathode, where oxygen is reduced:

$O_2 + 4H^+ + 4^{e-} \rightarrow 2H_2O$ (in acidic medium)

Or $O_2 + 2H_2O + 4^{e-} \rightarrow 4OH^-$ (in neutral/basic medium)

The Fe^{2+} ions combine with OH^- to form ferrous hydroxide:

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

This further gets oxidised to $Fe_2O_3.xH_2O$, which is rust.

(ii) The conditions necessary for rusting are:

(1) **Presence of moisture (water):** Acts as the medium for ionic conduction.

(2) **Presence of oxygen (air):** Necessary for the cathodic reaction.

(3) **Electrolytes (e.g., salts):** Speed up corrosion by increasing conductivity.

(iii) The methods to prevent corrosion are:

(1) **Galvanisation (Zinc coating):** Zinc is more reactive than iron. It oxidises preferentially, offering sacrificial protection, even if the coating is scratched.

(2) **Painting or Coating with oil/grease:** Forms a barrier that prevents air and moisture from reaching the metal surface, interrupting the electrochemical process.

(iv) Corrosion is faster in coastal areas because coastal air contains high humidity and dissolved salts (like NaCl). These salts act as electrolytes, enhancing the conductivity of water and speeding up the electrochemical corrosion process.

2. (i) A galvanic cell (or voltaic cell) is an electrochemical cell that converts chemical energy into electrical energy through a redox reaction.

It consists of two half-cells:

Anode: Where oxidation occurs (loss of electrons)

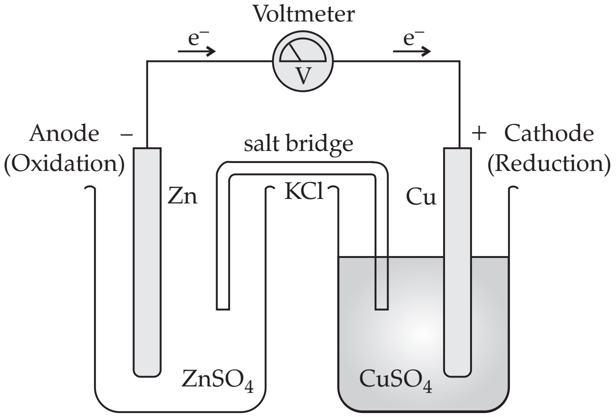
Cathode: Where reduction occurs (gain of electrons)

Example: Daniel Cell

Anode: Zinc ($Zn \rightarrow Zn^{2+} + 2e^-$)

Cathode: Copper ($Cu^{2+} + 2e^- \rightarrow Cu$)

Electrons flow from Zn to Cu through the external wire.



$Zn(s) + 2e^- \rightarrow Zn^{2+}$ $Cu^{2} + 2e^- \rightarrow Cu(s)$

$Zn(s) \mid ZnSO_4(aq) \mid\mid CuSO_4(aq) \mid Cu(s)$

(ii) EMF (Electromotive Force) is the potential difference between the two electrodes of a galvanic cell when no current is drawn.

$$EMF = E^0_{cathode} - E^0_{anode}$$

For Daniel Cell:

$$E^0_{Cell} = E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}$$

$$= (+ 0.34 \text{ V}) - (-0.76 \text{ V}) = + 1.10 \text{ V}$$

(iii) Salt bridge:

(1) Maintains electrical neutrality by allowing the flow of ions.

(2) Prevents accumulation of charges in half-cells.

(3) Closes the circuit internally, allowing the cell to function.

(4) Typically contains an inert electrolyte like KNO_3 or Na_2SO_4 in agar gel.

(iv) In a galvanic cell, chemical energy from redox reactions is converted into electrical energy. Electrons released at the anode (oxidation) travel through the external circuit to the cathode (reduction).This flow of electrons generates electric current, powering devices.