CH-3 Electrochemistry

Ques 1. **Define electrochemical cell. What happens if external potential applied becomes greater than E^0_{cell} of electrochemical cell?**

Ans 1.   Electrochemical cell is a device which converts chemical energy into electrical energy i.e., produced as a result of redox reaction taking place in the electrolyte.
The reaction gets reversed and it becomes non-spontaneous. It starts acting as an electrolytic cell.

Ques 2. **Why an electrochemical cell stops working after some time? The reduction potential of an electrode depends upon the concentration of solution with which it is in contact?**

Ans 2.   As the cell works, the concentration of reactants decreases. Then according to Le chatelier's principle it will shift the equilibrium in backward direction. On the other hand, if the concentration is more on the reactant side, then it will shift the equilibrium in forward direction. When cell works concentration in anodic compartment in cathodic compartment decreases and hence E° cathode will decrease. Now EMF of cell is
$E^0_{cell} = E^0_{cathode} - E^0_{anode}$
A decrease in E°$_{cathode}$ and a corresponding increase in E°$_{anode}$ will mean that EMF of the cell will decrease and will ultimately become zero i.e., cell slops working after some time.

Ques 3. **Following reactions can occur at cathode during the electrolysis of aqueous silver nitrate solution using Pt electrodes :**
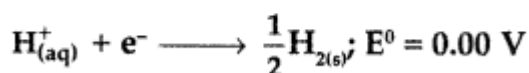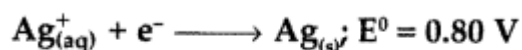
$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}; \; E^0 = 0.80 \text{ V}$$

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(s)}; \; E^0 = 0.00 \text{ V}$$

On the basis of their standard electrode potential values, which reaction is feasible at cathode and why?

Ans 3.   As the standard electrode potential of silver is greater than that of the other hydrogen electrode, so reduction of silver takes place and reaction (i) will be feasible
i.e., $Ag+(aq) + e^- \rightarrow Ag_{(s)}$

Ques 4. **Following reactions may occur at cathode during the electrolysis of aqueous CuCl₂ solution using Pt electrodes:**
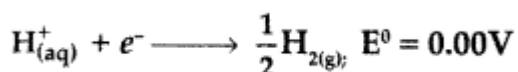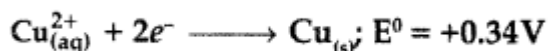
$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}; \; E^0 = +0.34V$$

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}; \; E^0 = 0.00V$$

On the basis of their standard electrode potential values, which reaction is feasible at cathode and why?

Ans 4.   Since the standard electrode potential of Cu^{2+} is greater than that of H^+, so reaction (i) will be feasible at cathode

i.e. $Cu^{2+}(aq) + 2e \rightarrow Cu$
Cu^{2+} has higher reduction potential.

Ques 5. **Given that the standard electrode potentials (E°) of metals are :**
K^+/K = -2.93 V, Ag^+/Ag = 0.80 V, Cu^{2+}/Cu = 0.34 V,
Mg^{2+}/Mg = -2.37 V, Cr^{3+}/Cr = -0.74 V, Fe^{2+}/Fe = -0.44 V.
Arrange these metals in increasing order of their reducing power.

Ans 5. $Ag^+/Ag < Cu^{2+}/Cu < Fe^{2+}/Fe < Cr^{3+}/Cr < Mg^{2+}/Mg < K^+/K$
More negative the value of standard electrode potentials of metals is, more will be the reducing power.

Ques 6. **Two half cell reactions of an electrochemical cell are given below :**
$MnO^-_4(aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4H_2O$ (I), E° = + 1.51 V
$Sn^{2+} (aq) \rightarrow 4 Sn^{4+} (aq) + 2e^-$, E° = + 0.15 V
Construct the redox equation from the two half cell reactions and predict if this reaction favours formation of reactants or product shown in the equation.

Ans 6.   The reactions can be represented at anode and at cathode in the following ways :
At anode (oxidation) :
$Sn^{2+} \rightarrow = Sn^{4+} (aq) + 2e^-] \times 5$ E° = + 0.15 V

At cathode (reduction) :
$MnO^-_4(aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4H_2O$ (l)] $\times 2$ E° = + 1.51 V

The Net reactions is $2MnO^-_4(aq) + 16H^+ + 5Sn^{2+} \rightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$

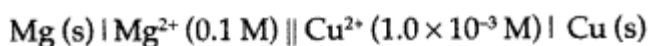Now $E°_{cell} = E°_{cathode} - E°_{anode}$
         $= 1.51 - 0.15 = + 1.36$ V
∴ Positive value of $E°_{cell}$ favours formation of product.

Ques 7. **Calculate the emf of the following cell at 298 K :**
$Mg (s) | Mg^{2+} (0.1 M) || Cu^{2+} (1.0 \times 10^{-3}M) | Cu (s)$
[Given = E0 Cell = 2.71 V].

Ans 7.

$$Mg\,(s)\,|\,Mg^{2+}\,(0.1\,M)\,\|\,Cu^{2+}\,(1.0 \times 10^{-3}\,M)\,|\,Cu\,(s)$$

Given: $E^0_{Cell} = 2.71\,V$

Applying Nernst equation

$$Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu$$
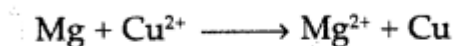
$$E_{Cell} = E^0_{Cell} - \frac{0.0591}{n} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$= 2.71 - \frac{0.0591}{2} \log \frac{0.1}{1 \times 10^{-3}}$$

$$= 2.71 - \frac{0.0591}{2} \log \frac{0.1}{0.001}$$

$$= 2.71 - 0.02955 \log 100$$

$$= 2.71 - 0.02955 \times 2$$

$$= 2.71 - 0.0591$$

$$\therefore \quad E_{Cell} = \mathbf{2.65\,V}$$

Ques 8. Calculate the equilibrium constant (log K_c) and $\Delta_r G°$ for the following reaction at 298 K.

$Cu\,(s) + 2Ag^+\,(aq) \rightleftharpoons Cu^{2+}\,(aq) + 2Ag\,(s)$
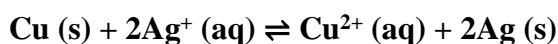
Given $E^0_{cell} = 0.46\,V$ and $1F = 96500\,C\,mol^{-1}$

$$\log K_c = \frac{nE^0 cell}{0.059} \qquad \log K_c = \frac{2 \times 0.46V}{0.059}$$

$$\log K_c = \frac{0.92}{0.059} \qquad \log K_c = 15.59$$

$$\Delta_r G^0 = -nF\,E^0_{cell}$$

$$= -2 \times 96500\,C\,mol^{-1} \times 0.46\,V$$

$$= -88,780\,J\,mol^{-1}\ or\ -88,78\,kJ\,mol^{-1}$$

Ans 8.

Ques 9. A voltaic cell is set up at 25°C with the following half cells :

Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50 M)
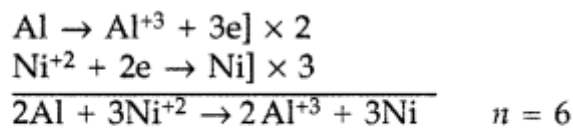
Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

$E^0_{Ni2+/Ni} = -0.25V$ and $E^0_{Al3+/Al} = -1.66V$

(Log $8 \times 10^{-6} = -0.54$)

Ans 9.   Half-cell reactions and overall cell reaction are

$$Al \rightarrow Al^{+3} + 3e] \times 2$$
$$Ni^{+2} + 2e \rightarrow Ni] \times 3$$
$$\overline{2Al + 3Ni^{+2} \rightarrow 2\,Al^{+3} + 3Ni} \qquad n = 6$$

$$E^0{}_{cell} = E^0_{Cathod} - E^0_{Anode}$$

$$\Rightarrow E^0{}_{cell} = -0.25 - (-1.66) = 1.41\ V$$

$$E_{M^{n+}/M} = E^0{}_{cell} - \frac{0.0591}{6}\log\frac{[Al^{+3}]^2}{[Ni^{+2}]^3}$$

$$\therefore E^0_{M^{n+}/M} = 1.41 - \frac{0.0591}{6}\log\frac{(1\times10^{-3})^2}{(5\times10^{-1})^3}$$

$$= 1.41 - 0.00985\log\frac{10^{-6}}{125\times10^{-3}}$$

$$= 1.41 - 0.00985$$
$$(-\log10^{-3} - \log 125)$$

$$= 1.41 + 0.0985 \times 5.0970$$

$$= 1.41 + 0.05 = \textbf{1.46 volts}$$

Ques 10. Calculate emf of the following cell at 298 K : Mg(s) | Mg^{2+} (0.1 M) || Cu^{2+} (0.01) | Cu (s)
[Given E$^0{}_{cell}$ = +2.71 V, 1 F = 96500 C mol^{-1}]

Ans 10.   Cell reaction : $Mg + Cu^{2+}\ Mg^{2+} + Cu (n = 2)$
Using Nernst equation,

$$E_{cell} = E^0{}_{cell} - \frac{0.0591}{2}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$\Rightarrow E_{cell} = 2.71 - \frac{0.0591}{2}\log\frac{0.1}{0.01}$$

$$\Rightarrow E_{cell} = 2.71 - \frac{0.0591}{2}\log 10$$

$$\Rightarrow E_{cell} = 2.71 - 0.02955 \therefore \textbf{E}_{cell} = \textbf{2.68 V}$$

Ques 11. A zinc rod is dipped in 0.1 M solution of ZnSO₄. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential.
[E°$_{Zn^{2+}}$ /Zn = – 0.76 V]
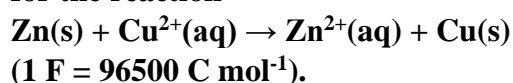
Ans 11.   The electrode reaction is given as
$$Zn^{+2} + 2e^- \rightarrow Zn$$
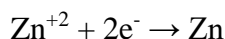
Using Nernst Equation

$$E_{Zn^{+2}/Zn} = E°_{Zn^{2+}/Zn} - \frac{0.0591}{2} \log \frac{1}{[Zn^{+2}]}$$

$$[Zn^{+2}] = \frac{95}{100} \times 0.1 = 0.095$$

$$E_{Zn^{+2}/Zn} = -0.76 - 0.0295 \log \frac{1}{0.095}$$
$$= -0.76 - 0.0295 [\log 1000 - \log 95]$$
$$= -0.76 - 0.0295 [3 - 1.9777]$$
$$= -0.76 - 0.03016 = \textbf{-0.79 volt}$$

Ques 12. **The standard electrode potential (E°) for Daniel cell is +1.1 V. Calculate the ΔG° for the reaction**
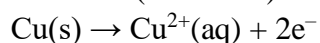**Zn(s) + Cu²⁺(aq) → Zn²⁺(aq) + Cu(s)**
(1 F = 96500 C mol⁻¹).

Ans 12. We know, $\Delta G° = -nFE°cell$
Given : E°cell = 1.1 volt
∴ $\Delta G° = -2 \times 96500$ C mol⁻¹ × 1.1 volt
= -212300 CV mol⁻¹
= -212300 J mol⁻¹ = -212.3 KJ mol⁻¹

Ques 13. **A copper-silver cell is set up. The copper ion concentration in it is 0.10 M. The concentration of silver ion is not known. The cell potential is measured 0,422 V. Determine the concentration of silver ion in the cell.**
Given : E°_{Ag⁺}/Ag = + 0.80 V, E° _{Cu²⁺}/Cu = + 0.34 V.

Ans 13. The reaction takes place at anode and cathode in the following ways :
At anode (oxidation) :
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
At cathode (reduction) :
$Cu(s) + 2Ag^{2+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
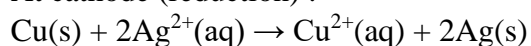
The complete cell reaction is

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$

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

$$\text{or} \quad E^0_{cell} = + 0.80 - (+ 0.34)$$
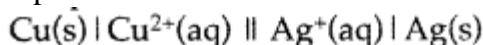
$$\text{or} \quad E^0_{cell} = 0.80 - 0.34 = 0.46 \text{ V}$$

Using *Nernst equation*

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} \log \frac{[Cu^{2+}(aq)]}{[Ag^+(aq)]^2}$$

$$0.422 = 0.46 - \frac{0.059}{2} \log \frac{(0.1)}{[Ag^+]^2}$$

$$0.422 - 0.46 = - \frac{0.059}{2} \log \frac{10^{-1}}{[Ag^+]^2}$$

$$-0.038 = -0.0295 \, [\log 10^{-1} - \log [Ag^+]^2]$$

$$-0.038 = -0.0295 \, [-1 - 2 \log [Ag^+]]$$

$$-0.038 = 0.0295 + 0.059 \log [Ag^+]$$

$$\text{or} \quad -0.059 \log [Ag^+] = 0.038 + 0.0295$$

$$\text{or} \quad -0.059 \log [Ag^+] = 0.0675$$

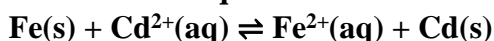$$\text{or} \quad -\log [Ag^+] = \frac{0.0675}{-0.059}$$

$$\text{or} \quad \log [Ag^+] = 1.14407$$

$$\text{or} \quad [Ag^+] = \text{Antilog } 1.14407$$

$$\therefore \quad [Ag^+] = \textbf{13.93 M}$$

Ques 14. Calculate the equilibrium constant for the reaction

$$\textbf{Fe(s) + Cd}^{2+}\textbf{(aq)} \rightleftharpoons \textbf{Fe}^{2+}\textbf{(aq) + Cd(s)}$$

(Given : $E^0_{Cd2+/Cd} = -0.40$ V,

$E^0_{Fe2+/Fe} = -0.44$ V).

$$(b) \quad E^0_{cell} = \frac{0.059}{n} \log K_c$$

$$\therefore \quad 0.04 = \frac{0.059}{2} \log K_c$$
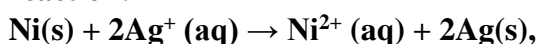
$$\log K_c = \frac{2 \times 0.04}{0.059} = \frac{0.08}{0.059} = 1.356$$

$$\text{or} \quad K_c = \text{antilog } 1.356$$

$$\therefore \quad \textbf{K}_c = \textbf{22.70}$$

Ans 14.

Ques 15. Determine the values of equilibrium constant (K_c) and $\Delta G°$ for the following reaction:

$$\textbf{Ni(s) + 2Ag}^+ \textbf{(aq)} \rightarrow \textbf{Ni}^{2+} \textbf{(aq) + 2Ag(s),}$$

$E° = 1.05$ V

($1F = 96500$ C mol^{-1})

Ans 15.   According to the formula

$$\Delta G° = -nFE° = - 2 \times 96500 \times 1.05$$

or $\Delta G° = -202650$ J mol$^{-1} = -202.65$ KJ mol^{-1}

Now $\Delta G° \Rightarrow -202650$ J Mol^{-1}
R = 8.314 J/Mol/K, T = 298 K

$$\log K = \frac{\Delta G°}{2.303\,RT}$$

$$\text{or } \log K = \frac{-202650}{2.303 \times 8.314 \times 298}$$

$$\log K = \frac{-202650}{5705.84831} = 35.52$$

K = Antilog of 35.52 $\therefore$ **K = 0.35 × 10^7**

Ques 16. **The cell in which the following reaction occurs :**
$2Fe^{3+}$ (aq) + $2I^-$ (aq) → $2Fe^{2+}$ (aq) + I_2 (s) has E^0_{cell} = 0.236V at 298K. Calculate
the standard Gibbs energy and the equilibrium constant of the cell reaction.
(Antilog of 6.5 = 3.162 × 10^6; of 8.0 = 10 × 10^8; of 8.5 = 3.162 × 10^8)

Ans 16. $\log K_C = \frac{nE^0_{cell}}{0.0591} = \frac{2 \times 0.236}{0.0591} = 8$
K_C = antilog 8 = 1×10^8

$\Delta G° = -nFE^0_{cell} = -2 \times 96500 \times 0.236$
= -45548 J/mol^{-1}
= -45.548 kJ/mol^{-1}

Ques 17. **Calculate the potential for half-cell containing**
0.10 M $K_2Cr_2O_7$ (aq), 0.20 M Cr^{3+} (aq) and 1.0×10^{-4} M H^+ (aq).
The half-cell reaction is
$Cr_2O_7^{2-}$(aq) + 14 H^+ (aq) + 6e$^-$ → 2 Cr^{3+} (aq) + 7 H_2O (l)
and the standard electrode potential is given as E^0 = 1.33 V.

Ans 17.   E = ? E^0 = 1.33 V
E^0_{cell} = 1.33 – 0.05916 $\log\frac{[Cr^{+3}]^2}{[Cr_2O^{2-}_7][H^+]^{14}}$

$$= 1.33 - \frac{0.0591}{6}\log\frac{(0.2)^2}{0.1 \times (10^{-4})^{14}}$$

$$= 1.33 - \frac{0.0591}{6}\log\frac{4 \times 10^{-2}}{10^{-57}}$$

$$= 1.33 - \frac{0.0591}{6}\log 4 \times 10^{55}$$

$$= 1.33 - \frac{(0.0591 \times 55.6020)}{6}$$

$$= 1.33 - 0.5467 = \textbf{0.783 volts}$$

Ques 18. **Calculate the emf of the following cell at 298 K: Fe(s) | Fe^{2+} (0.001 M) || H^+ (1M) |**
H_2(g) (1 bar), Pt(s) (Given $E°_{cell}$ = +0.44V)

Ans 18. As $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$ (n = 2)
According to Nernst equation

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Fe^{2+}]}{[H^{+2}]^2}$$

$$\Rightarrow \quad E_{cell} = 0.44 - \frac{0.0591}{2} \log \frac{10^{-3}}{1^2}$$

$$\therefore \quad E_{cell} = 0.44 - \frac{0.0591}{2} \times (-3)$$

$$= 0.44 + 0.0887 = \mathbf{0.529\ V}$$

Ques 19. Represent the galvanic cell in which the reaction
Zn (s) + Cu^{2+} (aq) → Zn^{2+} (aq) + Cu (s) takes place.

Ans 19. The galvanic cell may be represented as Zn (s) | Zn^{2+} (1M) || Cu^{2+} (1M) | Cu (s)

Ques 20. Calculate Δ_rG^0 for the reaction
Mg (s) + Cu^{2+} (aq) → Mg^{2+} (aq) + Cu (s)
Given : E^0_{cell} = + 2.71 V, 1 F = 96500 C mol^{-1}

Ans 20. $\Delta_rG^0 = - nFE^0$
$= -2 \times 96500 \times 2.71$ (∵ n = 2)
$= -523,030$ J mol^{-1} = -523.03 KJ mol^{-1}

Ques 21. Calculate $\Delta_rG°$ and log K_c for the following reaction at 298 K.
2Cr(s)+3Cd2+(aq)→2Cr3+raq+3Cd(s)
[Given : E0Cell = +0.34 V, IF = 96500 C mol^{-1}]

Ans 21.

$$2Cr_{(s)} + 3Cd^{2+}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 3Cd_{(s)}$$

$$2Cr \longrightarrow 2Cr^3 + 6e^-$$

or, $3Cd^{2+} + 6e^- \longrightarrow 3Cd$
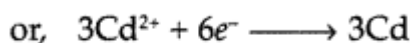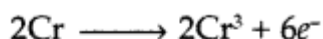
Hence, $n = 6$

$$\Delta_r G^0 = -nFE^0_{Cell}$$
$$\Delta_r G^0 = -6 \times 96500\ C\ mol^{-1} \times (+0.34\ V)$$
$$= -196860\ J\ mol^{-1}$$
$$\therefore \quad \Delta_r G^0 = -196.86\ KJ\ mol^{-1}$$
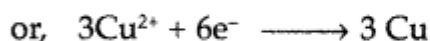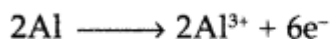$$\Delta_r G^0 = -2.303\ RT\ \log K_c$$

$$\log K_c = \frac{-\Delta G^0}{2.303\ RT} \quad \log K_c = \frac{+196860 J\ mol^{-1}}{2.303 \times 8.314 \times 298}$$

$$\log K_c = \mathbf{34.5014}$$

Ques 22. Calculate $\Delta_r G°$ and log K. for the following reaction at 298 K. (Comptt. All India 2017)

$$2Al_{(s)} + 3Cu^{2+}_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3Cu_{(s)}$$

$$(E^0_{Cell} = 2.02 \text{ V}), \text{ IF} = 96500 \text{ C mol}^{-1}]$$

$$2Al_{(s)} + 3Cu^{2+}_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3Cu_{(s)}$$

$$2Al \longrightarrow 2Al^{3+} + 6e^-$$

or, $3Cu^{2+} + 6e^- \longrightarrow 3 Cu$

Hence, $n = 6$

$$\Delta G^0 = -nFE^0_{Cell}$$
$$\Delta G^0 = -6 \times 96500 \times 2.02 = -1169580 \text{ J mol}^{-1}$$
$\therefore$ $\Delta G^0 = \mathbf{-116.958 \text{ KJ mol}^{-1}}$

Now, $\Delta G^0 = -2.303 \text{ RT log K}_c$

$$\log K_c = \frac{-\Delta G^0}{2.303RT} = \frac{1169580}{2.308 \times 8.314 \times 298}$$

$$= \frac{1169580}{5705.84}$$

Ans 22. $\therefore$ $\log K_c = \mathbf{205.009}$

Ques 23. Calculate emf of the following cell at 25°C :
Fe | Fe^{2+} (0.001 M) || H$^+$ (0.01 M) | H$_2$(g) (1 bar) | Pt(s)
E^0(Fe^{2+} | Fe) = -0.44 V E^0(H$^+$ | H$_2$) = 0.00V

Ans 23.   Fe | Fe^{2+} (0.001 M) || H$^+$ (0.01 M) | H$_2$(g) (1 bar) | Pt(s)

$$E^0_{cell} = E^0_c - E^0_a$$
$$= [0 - (-0.44)] \text{ V} = 0.44 \text{ V}$$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Fe^{+2}]}{[H^+]^2}$$

$$\Rightarrow E_{cell} = 0.44 \text{ V} - \frac{0.0591}{2} \log \frac{0.001}{0.01 \times 0.01}$$

$$= 0.44 \text{ V} - \frac{0.0591}{2} \log 10$$

$$= 0.44 \text{ V} - \frac{0.0591}{2} = (0.44 - 0.0295) \text{ Volts}$$

$= 0.4105$ Volts

Ques 24. Calculate e.m.f. of the following cell at 298 K: 2Cr(s) + 3Fe^{2+} (0.1 M) →
2Cr^{3+} (0.01 M) + 3 Fe(s)
Given: E^0(Cr^{3+}| Cr) = -0.74 V E^0(Fe^{2+} | Fe) = -0.44 V

Ans 24.

$$E_{cell} = ?$$
$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$
$$= (-0.44) - (-0.74)$$
$$= -0.44 + 0.74 = +0.30 \text{ V}$$

Using Nernst equation:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

$$= 0.30 - \frac{0.0591}{6} \log \frac{(0.01)^2}{(0.1)^3}$$

$$= 0.30 - 0.00985 \log \frac{0.0001}{0.001}$$

$$= 0.30 - 0.00985 \log \left(\frac{1}{10}\right)$$

$$= 0.30 - 0.00985 (\log 1 - \log 10)$$

$$= 0.30 - 0.00985 (0 - 1) = 0.30 + 0.00985$$

$$\therefore \quad E_{cell} = \mathbf{0.3098 \text{ V}}$$

Ques 25. **(a) Calculate E^0_{cell} for the following reaction at 298 K:**
$2Al(s) + 3Cu^{2+} (0.01M) \rightarrow 2Al^{2+} (0.01M) + 3Cu(s)$
Given: $E_{cell} = 1.98$ V
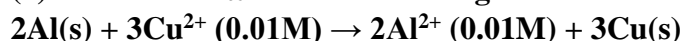
Ans 25.   For the reaction
$$2Al(s) + 3Cu^{2+} (0.01M) \rightarrow 2Al^{3+} (0.01M) + 3Cu(s)$$
Given: $E_{cell} = 1.98$ V $E^0_{cell} = ?$
Using Nernst equation
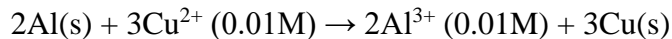
$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$

$$\text{or} \quad 1.98 \text{ V} = E^0_{cell} - \frac{0.0591}{6} \log \frac{(0.01)^2}{(0.01)^3}$$

$$\begin{bmatrix} \because \ \mathbf{\log 100 = 2 \log 10} \\ \mathbf{\log 10 = 1} \end{bmatrix}$$

or $1.98 \text{ V} = E^0_{cell} - 0.00985 \log 100$
or $1.98 \text{ V} = E^0_{cell} - 0.00985 \times 2$
$1.98 \text{ V} = E^0_{cell} - 0.0197$
$\therefore \quad E^\circ_{cell} = 1.98 \text{ V} + 0.0197$
$\therefore \quad E^\circ_{cell} = \mathbf{1.9997 \text{ V}}$

Ques 26. **Using the E^0 values of A and B, predict which is better for coating the surface of iron $[E^0(Fe^{2+}/Fe) = -0.44$ V$]$ to prevent corrosion and why?**
**Given: $E^0(A^{2+}/A) = -2.37$ V; $E^0(B^{2+}/B) = -0.14$ V**

Ans 26.   Element A will be better for coating the surface of iron than element B because its E° value is more negative.

Ques 27. A voltaic cell is set up at 25°C with the following half cells :
Ag^+ (0.001 M) | Ag and Cu^{2+} (0.10 M) | Cu What would be the voltage of this cell?
(E^0_{cell} = 0.46 V)

Ans 27.　The reaction takes place in cell as

$$Cu + 2Ag^+ \longrightarrow Cu^{+2} + 2Ag$$
$$\quad\quad (0.001\ M) \quad\quad (0.10)$$

$$Cu/Cu^{+2}\ (0.10) \parallel Ag^+\ (0.001M)/Ag$$
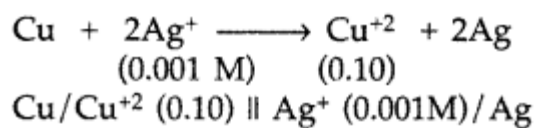
$$E_{cell} = E°_{cell} - \frac{0.059}{n} \log \frac{[Cu^{+2}]}{[Ag^+]^2}$$

$$E_{cell} = 0.46 - \frac{0.059}{2} \log \frac{0.1}{(0.001)^2}$$

$$= 0.46 - \frac{0.059}{2} \log 10^5$$

$$= 0.46 - \frac{0.059}{2} \times 5 \log 10$$

$= 0.46 - 0.0592 \times 5$
$= 0.46 - 0.1475 = 0.3125$

Ques 28. Define conductivity and molar conductivity for the solution of an electrolyte.
Discuss their Variation with change in temperature.

Ans 28.　**Conductivity:** 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. It is represented by K.
Its unit is S cm^{-1}
Molar conductivity: Molar conductivity of a solution at a dilution V is the conductance of
all the ions produced from one mole of the electrolyte dissolved in V cm^3 of the solution
when the electrodes are 1 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.
Its unit is S cm^2 mol^{-1}
Conductivity and molar conductivity of electrolytes increase with increasing temperature.

Ques 29. Describe how for weak and strong electrolytes, molar conductivity changes with
concentration of solute. How is such change explained?

Ans 29.　In case of strong electrolytes there is a small increase in conductance with dilution because a
strong electrolyte is completely dissociated in solution and the number of ions remains
constant. Moreover, there will be greater inter-ionic attractions at higher concentrations
which retards the motion of ions and conductance decreases. In case of weak electrolytes
there is increase in conductance with decrease in concentration due to the increase in the
number of ions in the solution.

The graph between Λ_m and concentration also rectifies the above statement.
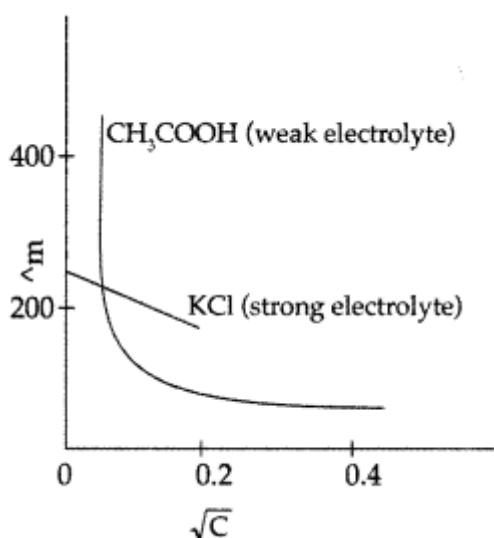
Ques 30. **What is meant by 'limiting molar conductivity'?**

Ans 30. The molar conductivity of a solution at infinite dilution is called limiting molar conductivity and is represented by the symbol Λ_m.

Ques 31. **State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution?**

Ans 31. **Kohlrausch law of independent migration of ions:** The limiting molar conductivity of an electrolyte (i.e. molar conductivity at infinite dilution) is the sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of the electrolyte
$\Lambda°m$ for $A_xB_y = x\lambda°_+ + y\lambda°_-$
For acetic acid $\Lambda° (CH_3COOH) = \lambda°_{CH3COO^-} + \lambda°_{H^+}$
$\Lambda°(CH_3COOH) = \Lambda° (CH_3COOK) + \Lambda° (HCl) - \Lambda° (KCl)$

Ques 32. **The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1} ?**

Ans 32. $R = \rho (l/a)$
Cell constant $la=R\rho = RK$
$= (1500\ \Omega) \times 0.146 \times 10^{-3}$ S cm^{-1} = 0.219 cm^{-1}

Ques 33. **The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution.**

Ans 33. $C = 1.5$ M, $\Lambda_m = 138.9$ S cm^2 mol^{-1}
$\Lambda_m = K\times1000c$
$\therefore K = \Lambda m \times C/1000 = 138.9 \times 1.5/1000 = 0.20835$ S cm^{-1}

Ques 34. **The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity.**

Ans 34.   Molar conductivity $\Lambda_m = 1000 \times \kappa M$
Given: $K = 0.025$ S cm^{-1}, $M = 0.20$ M
Hence, $\Lambda_m = 0.025 \times 1000 0.20$ $\therefore \Lambda_m = 125$ S cm^2 mol^{-1}

Ques 35.   The measured resistance of a conductance cell was 100 ohms. Calculate (i) the specific conductance and (ii) the molar conductance of the solution.
(KC1 = 74.5 g mol^{-1} and cell constant = 1.25 cm^{-1})

Ans 35.   Given : $R = 100$ Ω Cell constant $= 1.25$ cm^{-1}
Molarity $= 74.5$ g mol^{-1}

(i) Specific conductance, $K = \dfrac{1}{R} \times$ Cell constant

$$= \dfrac{1}{100} \times 1.25$$

$$\therefore \qquad = 0.0125 \ \Omega^{-1} \ cm^{-1}$$

(ii) Molar conductance $(\Lambda_m) = \dfrac{K \times 1000}{\text{Molarity}}$

$$= \dfrac{0.0125 \times 1000}{74.5}$$

$$= 0.167 \ \Omega^{-1} \ cm^2 \ mol^{-1}$$

Ques 36.   The conductivity of 0.001 M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2/mol.

Ans 36.   Given : $K = 4 \times 10^{-5}$ S/cm, $M = 0.001$ M
$\Lambda^{\circ}m = 390$ S cm^2/mol, $k = ?$
Using the formula

$$\Lambda_m^c = \dfrac{K \times 1000}{\text{Molarity}}$$

$$= \dfrac{4 \times 10^{-5} \text{S cm}^{-1} \times 1000 \text{ cm}^3 \text{L}^{-1}}{0.001 \text{mol L}^{-1}}$$

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

$$\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^{\circ}} = \dfrac{40}{390} = 0.1025$$

$$CH_3-COOH \rightleftharpoons CH_3-COO^- + H^+$$
$$\quad C \qquad\qquad\qquad 0 \qquad\quad 0$$
$$C(1-\alpha) \qquad\qquad C\alpha \qquad C\alpha$$
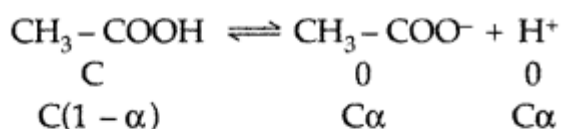
$$k_\alpha = \dfrac{[CH_3-COO^-][H^+]}{[CH_3-COOH]} = \dfrac{C\alpha.C\alpha}{C(1-\alpha)} = \dfrac{C\alpha^2}{1-\alpha}$$

$$k = \dfrac{10^{-3} \times (1.025 \times 10^{-1})^2}{1 - 0.1025} = \dfrac{10^{-5} \times 0.105}{0.8975}$$

$$\therefore \quad k = 1.46 \times 10^{-6}$$

Ques 37. The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1} Calculate the conductivity of the solution.

Ans 37.   Given:

$$\Lambda_m = \frac{k \times 1000}{c} \ S \ cm^2 \ mol^{-1}$$

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

$$k = \frac{1}{200} \times 1 \ S \ cm^{-1}$$

$$k = \frac{1}{200} \ S \ cm^{-1}$$

$$\Lambda_m = \frac{1 \times 1000}{200 \times 0.01} \ S \ cm^2 \ mol^{-1}$$

$$\Lambda_m = 500 \ S \ cm^2 \ mol^{-1}$$

Ques 38. Calculate the degree of dissociation (a) of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}. Given: $\lambda°(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda°(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}

Ans 38. $\Lambda°_m(HAc) = \lambda°_{H^+} + \lambda°_{Ac^-}$

$\lambda°_{CH3COOH} = \lambda°_{H^+} + \lambda°_{CH3COO^-}$

$= 349.6 \ S \ cm^2 \ mol^{-1} + 40.9 \ S \ cm^2 \ mol^{-1}$

$= 390.5 \ S \ cm^2 \ mol^{-1}$

$$\alpha = \frac{\Lambda_m}{\Lambda°_m} = \frac{39.05 \ cm^2 \ mol^{-1}}{390.05 \ cm^2 \ mol^{-1}} = 0.1$$

Ques 39. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Ans 39. $A = \pi r^2 = 3.14 \times (0.5)^2 = 0.785 \ cm^2, l = 50 \ cm$

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

$$\therefore \quad \rho = \frac{RA}{l} = \frac{5.55 \times 10^{-3} \times 0.785}{50} = 87.135 \ \Omega \ cm$$

$$Conductivity, \ K = \frac{1}{\rho} = \frac{1}{87.135}S \ cm^{-1}$$

$$= 0.01148 \ S \ cm^{-1}$$

Molar conductivity,

$$\Lambda_m = \frac{K \times 1000}{C} = \frac{0.01148 \times 1000}{0.05}$$

$$= 229.6 \ S \ cm^2 \ mol^{-1} \qquad where \ [C = 0.05 \ m]$$

Ques 40. When a certain conductance cell was filled with 0.1 M KCl, it has a resistance of 85 ohms at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.
[Specific conductance of 0.1 M KCl = 1.29×10^{-2} ohm^{-1} cm^{-1}]

Ans 40. Cell contant = Conductivity × Resistance
$G^* = K \times R$
$= 1.29 \times 10^{-2} \Omega^{-1} \times 85$
$= 109.65 \times 10^{-2} \Omega^{-1}$
$= 1.0965$ cm^{-1}

Conductivity of 0.052 M KCl, $\left[\because K = \dfrac{1}{R}\left(\dfrac{l}{A}\right) \right.$
$\left. \therefore \dfrac{l}{A} = K \times R \right]$

$K = \dfrac{G^*}{R} = \dfrac{1.0965}{96} = 0.0114 \ \Omega^{-1}$cm^{-1}
$= 1.14 \times 10^{-2} \ \Omega^{-1}$cm^{-1}

Λ^m for 0.052 M $= \dfrac{K \times 1000}{M}$
$= \dfrac{1.14 \times 10^{-2} \times 1000}{0.052} = \mathbf{219.23 \ \Omega^{-1}cm^2 \ mol^{-1}}$

Ques 41. The conductivity of 0.001 M acetic acid is 4×10^{-5} S/m. Calculate the dissociation constant of acetic acid if $\Lambda0m$, for acetic acid is 390 S cm^2 mol^{-1}.

Ans 41. Conductivity (K) $= 4 \times 10^{-5}$ S cm^{-1}
Concentration (C) = 0.001M

Molar conductivity $\Lambda_m^C = \dfrac{K \times 1000}{C}$

$\Lambda_m^C = \dfrac{4 \times 10^{-5} \times 1000}{0.001} = 40$ S cm^2 mol^{-1}

Degree of dissociation $(\alpha) = \dfrac{\Lambda_m^C}{\Lambda_m^0} = \dfrac{40}{390}$
$= 0.102$

$\therefore \ K = \dfrac{C\alpha^2}{1-\alpha} = \dfrac{0.001 \times (0.102)^2}{1 - 0.102} = \dfrac{1.04 \times 10^{-5}}{0.898}$
$= \mathbf{1.158 \times 10^{-5}}$

Ques 42. The resistance of 0.01 M NaCl solution at 25° C is 200 Ω. The cell constant of the conductivity cell used is unity. Calculate the molar conductivity of the solution.

Ans 42. For 0.01 M NaCl solution,
R = 200 Ω, cell constant is unity.
∴ Conductivity (K) = Cell constant Resistance
= 1200 = 0.005 Sm^{-1}
Concentration of solution = 0.01 M = 0.01 mol L^{-1}

= 0.01 × 10³ mol m⁻³ = 10 mol m⁻³

Molar conductivity = KCm=0.00510

5×10^{-4} Sm² mol⁻¹

Ques 43. The conductivity of 0.001 mol L⁻¹ solution of CH₃COOH is 3.905 × 10⁻⁵ S cm⁻¹. Calculate its molar conductivity and degree of dissociation (α).
Given: λ⁰(H⁺) = 349.6 S cm² mol⁻¹ and λ⁰ (CH₃COO⁻) = 40.9 S cm² mol⁻¹

Ans 43.   Concentration = 0.001 mol L⁻¹

$K = 3.905 \times 10^{-5}$ S cm⁻¹ $\Lambda^c_m = ?$

Using formula,

$$\Lambda^c_m = \frac{K \times 1000}{C} = \frac{3.905 \times 10^{-5} \times 1000}{0.001}$$

$$= 39.05 \text{ S cm}^2 \text{ mol}^{-1}$$

Molar conductivity at infinite dilution:

$$CH_3COOH \longrightarrow CH_3COO^- + H^+$$
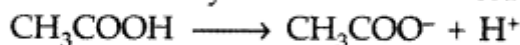
$$\Lambda^°_m = \lambda^°H^+ + \lambda^°CH_3COO^-$$

$$= (349.6 + 40.9)$$

$$\Lambda^°_m = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

Degree of dissociation:

$$\alpha = \frac{\Lambda^c_m}{\Lambda^°_m} = \frac{39.05}{390.5} \qquad \therefore \ \boldsymbol{\alpha = 0.1}$$

Ques 44. Conductivity of 2.5 × 10⁻⁴ M methanoic acid is 5.25 × 10⁻⁵ S cm⁻¹. Calculate its molar conductivity and degree of dissociation.
Given : λ⁰(H⁺) = 349.5 Scm² mol⁻¹
and λ⁰(HCOO⁻) = 50.5 Scm² mol⁻¹.

Ans 44.   Concentration is 2.5 x 10⁻⁴ M

$K = 5.25 \times 10^{-5}$ Scm⁻¹.

Λcm=K×1000 Concentration

$$= \frac{5.25 \times 10^{-5} \times 1000}{2.5 \times 10^{-4}} \text{ Scm}^2 \text{ mol}^{-1}$$

$$= \frac{5.25 \times 10^2}{2.5} = \frac{525}{2.5} = 210 \text{ Scm}^2 \text{ mol}^{-1}$$

Molar conductivity at infinite dilution,

$$\Lambda^0_m = \lambda^0H^+ + \lambda^0HCOO^- = (349.5 + 50.5)$$

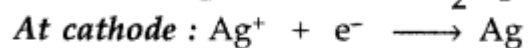$$= 400 \text{ Scm}^2 \text{ mol}^{-1}$$

Degree of dissociation,

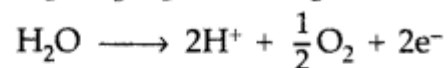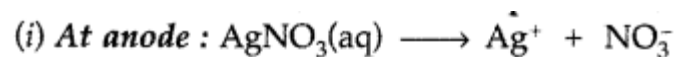$$\alpha = \frac{\Lambda^c_m}{\Lambda^0_m} = \frac{210}{400} = \frac{21}{40} = 0.525$$

Ques 45. **Predict the products of electrolysis in each of the following:**
(i) An aqueous solution of AgNO₃ with platinum electrodes.
(ii) An aqueous solution of H₂SO₄ with platinum electrodes.

Ans 45.   The following products are obtained in each case:

(i) *At anode :* $AgNO_3(aq) \longrightarrow Ag^+ + NO_3^-$

$$H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$$

At cathode : $Ag^+ + e^- \longrightarrow Ag$
Product of electrolysis of aq soln of H_2SO_4
is H^+ and SO_4^{2-} and OH^-

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

(ii) *At anode :* $H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

At cathode : $2H^+ + 2e^- \longrightarrow H_2$