Long Answer Questions

Long Answer Questions

Q.1. Answer the following questions

[*CBSE Central 2016*]

Q. The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).

Given $\lambda^0 (H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda^0(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}

Ans.

Given, $c = 0.001 \text{ mol L}^{-1} = 1 \times 10^{-3} \text{ mol L}^{-1}$, $k = 3.905 \times 10^{-5} \text{ S cm}^{-1}$

Substituting these values in the expression,

$$\Lambda_m^c = \frac{k \times 1000}{c} \text{, we get}$$

$$\Lambda_m^c = \frac{3.905 \times 10^{5}\ S\,cm^{1} \times 1000\ cm^{3}\ L^{1}}{1 \times 10^{3}\ mol\ L^{1}} = 39.05 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^0\ (CH_3COOH) = \lambda^o_{(CH_3COO\ )} + \lambda^o_{(H^+)}$$

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

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

Degree of dissociation, $\alpha = \frac{\Lambda_m^c}{\Lambda_m^0}$

$$= \frac{39.05\ S\ cm^{2}\ mol^{1}}{390.5\ S\ cm^{2}\ mol^{1}} = 0.1$$

or $\alpha = 10\%$

Q. Define electrochemical cell. What happens if external potential applied becomes greater than E^o_{cell} of electrochemical cell?

Ans. A device which is used to convert chemical energy produced in a redox reaction into electrical energy is called an electrochemical cell.

If external potential applied becomes greater than E^o_{cell} of electrochemical cell, the reaction gets reversed and the electrochemical cell function as an electrolytic cell.

Q. 2.

Calculate e.m.f and ΔG for the following cell at 298 K:

$\text{Mg(s)} \mid \text{Mg}^{2+}\ (0.01\ \text{M}) \parallel \text{Ag}^{+}\ (0.0001\ \text{M}) \mid \text{Ag(s)}$

Given: $[\, E^o_{\text{Mg}^{2+}/\text{Mg}} = -\,2.37\ \text{V},\ E^o_{\text{Ag}^{+}/\text{Ag}} = +\,0.80\ \text{V}]$

[CBSE Guwahati 2015]

Ans.

At anode : $\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^{-}$

At cathode: $[\text{Ag}^{+} + e^{-} \rightarrow \text{Ag}] \times 2$

$$\overline{\underline{\text{Mg} + \ 2\text{Ag}+ \rightarrow + \text{Mg}\,2 + +2\ \text{Ag}\,;}}\ n = 2$$

$$E^{o}{}_{\text{cell}} = E^o_{\text{cathode}} - E^o_{\text{anode}} = E^o_{\text{Ag}^{+}/\text{Ag}} - E^o_{\text{Mg}^{2+}/\text{Mg}} = 0.80\ \text{V} - (-\,2.37\ \text{V}) = 3.17\ \text{V}$$

Substituting $E^{o}{}_{\text{cell}} = 3.17$ V, $n = 2$, $[\text{Mg}^{2+}] = 1 \times 10^{-2}$ M, $[\text{Ag}^{+}] = 1 \times 10^{-4}$ M in Nernst equation for above cell reaction,

$$\text{E}_{\text{cell}} = E^o_{\text{cell}} - \frac{0.059}{n} \log \frac{/\ \text{Mg}^{2+}\ /}{/\ \text{Ag}^{+}\ /^{2}}, \text{ we get}$$

$$E_{\text{cell}} = 3.17 - \frac{0.059}{2} \log \frac{10^{-2}}{(10^{-4})^{2}}$$

$$E_{\text{cell}} = 3.17 - 0.0295 \log 10^{6}$$

$$E_{\text{cell}} = 3.17 - 0.177\ \text{V} = 2.993\ \text{V}$$

$$E_{\text{cell}} = \mathbf{2.993\ V}$$

Substituting $n = 2$, $F = 96500\ \text{C mol}^{-1}$, $E_{\text{cell}} = 2.993$ V in the expression, $\Delta G = -\,nFE_{\text{cell}}$ we ge

$$\Delta G = -\,nFE_{\text{cell}} = -\,2 \times 96500\ \text{C mol}^{-1} \times 2.993\ \text{V}$$

$$\Delta G = -\,577649\ \text{J mol}^{-1} = -\,577.649\ \text{kJ mol}^{-1}$$

Q.3. Answer the following questions

Q. State the relationship amongst cell constant of a cell, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solute related to conductivity of its solution?

Ans.

$k = \frac{1}{R} \times \left(\frac{l}{A}\right)$ = where, k = Conductivity, $\frac{l}{A}$ = Cell constant, R = Resistance

$\Lambda_m = \frac{k \times 1000}{M}$ where, Λm = Molar conductivity, k = Conductivity, M = Molarity of solution

Q.

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

$Al \mid Al^{3+}$ (0.001 M) and $Ni \mid Ni^{2+}$ (0.50 M)

Calculate the cell voltage $E^o_{Ni^{2+}/Ni}$ $[= -\,0.25\ \text{V},\ E^o_{Al^{3+}/Al} = -\,1.66\ \text{V}]$

Ans.

At anode: $[Al(s) \rightarrow Al^{3+}(aq) + 3e^-] \times 2$

At cathode: $[Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)] \times 3$

$$\underline{\overline{2\,AL\,(s) + 3\,Ni^{2+}\,(aq) \rightarrow 2\,Al^{3+}\,(aq) + 3\,Ni\,(s),}}\quad n = 6$$

$$E_{\text{cell}} = E^o_{\text{cell}} - \frac{0.0591}{n} \log \frac{/\ Al^{3+}\ /^{2}}{/\ Ni^{2+}\ /^{3}}$$

Here, $n = 6$, $[Al^{3+}] = 0.001\ M = 1\times 10^{-3}\ M$, $[Ni^{2+}] = 0.5\ M$

$$E^{o}_{cell} = E^{o}_{Ni^{2+}/Ni} - E^{o}_{Al^{3+}/Al} = -0.25\ V - (-1.66\ V) = 1.41\ V$$

$$E_{cell} = 1.41 - \frac{0.0591}{6}\log\frac{(10^{-3})^2}{(0.5)^3} = 1.41 - \frac{0.0591}{6}\log\frac{10^{-6}}{0.125}$$

$$= 1.41\ \frac{0.0591}{6} - \log(10^{-6}\times 8) = 1.41 - \frac{0.0591}{6}\log(10^{-6} + \log 2^{3})$$

$$= 1.41 - \frac{0.0591}{6}\log(-6\log 10 + 3\log 2)$$

$$= 1.41 - \frac{0.0591}{6}\log(-6 + 3\times 0.3010)$$

$$= 1.41 - \frac{0.0591}{6}(-5.097)$$

$$= 1.41 + \frac{0.3012}{6} = 1.41 + 0.0502 = 1.4602\ V$$

$E_{cell} =$ **1.46 V**

Q.4.

Given that Λ^{0}_{m} (HCl) $= 426\ S\ cm^{2}\ mol^{-1}$, Λ^{0}_{m} (NaCl) $= 126\ S\ cm^{2}\ mol^{-1}$

Λ^{0}_{m} (CH_3COONa) $= 91\ S\ cm^{2}\ mol^{-1}$

Ans.

$$\Lambda^{0}_{m}(CH_3COOH) = \Lambda^{o}_{CH_3COO^-} + \Lambda^{o}_{H^+}$$

$$= \Lambda^{o}_{CH_3COO^-} + \Lambda^{o}_{Na^+} + \Lambda^{o}_{H^+} + \Lambda^{o}_{Cl^-} - (\Lambda^{o}_{Na^+} + \Lambda^{o}_{Cl^-})$$

$$= \Lambda^{o}_{m(CH_3COONa)} + \Lambda^{o}_{m(HCl)} - \Lambda^{o}_{m(NaCl)}$$

$$= (91 + 426 - 126)\ S\ cm^{2}\ mol^{-1}$$

$$= \mathbf{391\ S\ cm^{2}\ mol^{-1}}$$

Q.5. A voltaic cell is set up at 25°C with the following half-cells Al^{3+} (0.001 M) and 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.

$$\left(\text{Given: } E^{o}_{Ni^{2+}/Ni} = -\ 0.25\ V,\ E^{o}_{Al^{3+}/Al} = -\ 1.66\ V\right)$$

Ans.

At anode: $[Al \rightarrow Al^{3+} + 3e^{-}] \times 2$

At cathode: $[Ni^{2+} + 2e^{-} \rightarrow Ni] \times 3$

Cell reaction: $\underline{\overline{2Al + 3\,Ni^{2+} \rightarrow 2\,Al^{3+} + 3\,Ni}}$

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = E^{o}_{Ni^{2+}/Ni} - E^{o}_{Al^{3+}/Al}$$

$$= -\ 0.25\ V - (-\ 1.66\ V) = 1.41\ V$$

$$[Al^{3+}] = 1 \times 10^{-3}\ M;\ [Ni^{2+}] = 0.5\ M;\ n = 6$$

Substituting the values in the Nernst equation,

$$E_{cell} = E^{o}_{Ni^{2+}/Ni} - E^{o}_{Al^{3+}/Al}$$

$$E_{cell} = 1.41\ V - \frac{0.059}{6}\log\frac{(10^{-3})^2}{(0.5)^3}$$

$$= 1.41\ V - \frac{0.059}{6}\log(8 \times 10^{-6}) = 1.41\ V - \frac{0.059}{6}(-\ 0.54)$$

$E_{cell} = 1.41\ V + 0.0053\ V = \mathbf{1.4153\ V}$

Q.6. Calculate the potential for half-cell containing

0.10M $K_2Cr_2O_7$ (*aq*), 0.20 M Cr^{3+}(*aq*) and 1.0×10^{-4} M H^{+}(*aq*). The half cell reaction is

$Cr_2O_7^{2-}(aq) + 14H^{+}(aq) + 6e^{-} \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

and the standard electrode potential is given as E^{o} =1.33V.

Ans.

For half cell reaction

$$Cr_2O_7^{2} (aq) + 14H^{+}(aq) + 6e^{-} \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log\frac{/ Cr^{3+} /^{2}}{/ Cr_2 O_7^{2}][H^{+}/^{14}}$$

Here, $E^{o} = 1.33$ V, n = 6, $[Cr^{3+}] = 0.2$ M

$[Cr_2O_7^{2}] = 0.1$ M, $[H^{+}] = 1 \times 10^{-4}$ M

Substituting these values in the given expression, we get

$$E_{cell} = 1.33\text{ V} - \frac{0.0591}{6}\log\frac{(0.20)^{2}}{(0.1)(10^{-4})^{14}}$$

$$= 1.33\text{ V}\ \frac{0.0591}{6} - \log\left(4 \times 10^{55}\right) = 1.33\text{ V} - \frac{0.0591}{6}\left[\log 4 + \log 10^{55}\right]$$

$$= 1.33\text{ V} - \frac{0.0591}{6}\left[2\log 2 + 55\log 10\right] = 1.33\text{ V} - \frac{0.0591}{6}\left[2 \times 0.3010 + 55\right]$$

$= 1.33$ V $- 0.548$ V $=$ **0.782 V**

Q.7.

Using the E^{o} values of A and B, predict which is better for coating the surface of iron

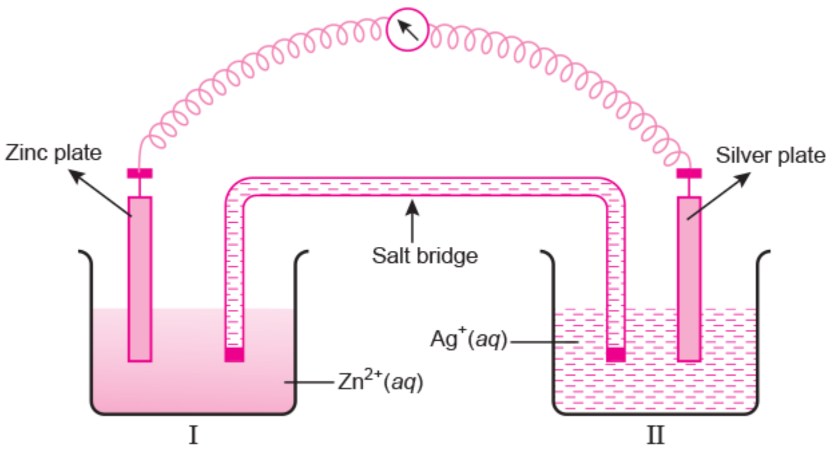
$\left[E^{o}_{Fe^{2+}/Fe} = -0.44\text{ V}\right]$ to prevent corrosion and why?

Given: $\left[E^{o}_{A^{2+}/A} = -2.37\text{ V}, E^{o}_{B^{2+}/B} = -0.14\text{ V}\right]$

Ans. A, as its standard reduction potential is less than B, therefore, it will undergo oxidation more easily than B.

Long Answer Question (OIQ)

Q.1. Consider the figure given below and answer the questions (i) to (vi):



- **i. Write the direction of electron flow.**
- **ii. Is silver plate the anode or cathode?**
- **iii. What will happen if salt bridge is removed?**
- **iv. When will the cell stop functioning?**
- **v. How will concentration of Zn^{2+} ions and Ag^+ ions be affected when the cell functions?**
- **vi. How will the concentration of Zn^{2+} ions and Ag^+ ions be affected after the cell becomes 'dead'?**

[*NCERT Exemplar] [HOTS*]

Ans.

- **i.** Electrons move from Zn to Ag.
- **ii.** Ag is the cathode.
- **iii.** Cell will stop functioning.
- **iv.** When Ecell = 0.
- **v.** Concentration of Zn^{2+} ions will increase and concentration of Ag^+ ions will decrease.
- **vi.** When Ecell = 0, equilibrium is reached and concentration of Zn^{2+} ions and Ag^+ ions will not change.

Q.2. The electrochemical cell given alongside converts the chemical energy released during the redox reaction

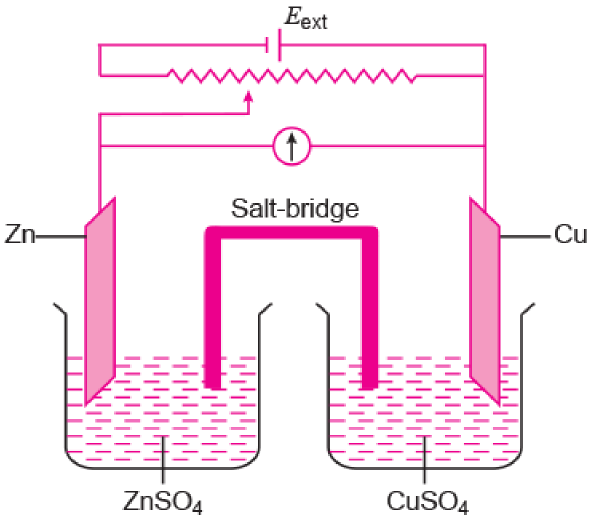
$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

to electrical energy. It gives an electrical potential of 1.1 V when concentration Zn^{2+} and Cu^{2+} ions is unity. State the direction of flow of current and also specify whether zinc and copper are deposited or dissolved at their respective electrodes when:

- **i. an external opposite potential of less than 1.1 V is applied.**

ii. an external potential of 1.1 V is applied.
iii. an external potential of greater than 1.1 V is applied.

[*HOTS*]



Ans.

- **i.** Reaction continues to take place. Electrons flow from Zn electrode to copper electrode, hence current flows from Cu to Zn. Zn dissolves and copper deposits at their respective electrodes.
- **ii.** The reaction stops and no current flows. A state of equilibrium is achieved and no change is observed at zinc and copper electrodes.
- **iii.** Reaction takes place in opposite directions. Electrons flow from copper electrode to zinc electrode and hence current flows from Zn to Cu. Zinc deposits and copper dissolves at their respective electrodes. The cell functions as an electrolytic cell.

Q.3. Answer the following questions

Q. Define the following terms:

a. Limiting molar conductivity

b. Fuel cell

Ans.

- **a.** The molar conductivity when concentration approaches to zero is called limiting molar conductivity.
- **b.** A fuel cell is a device which converts energy produced during the combustion of fuels like hydrogen, methane, methyl alcohol etc. directly into electrical energy. One such successful fuel cell is hydrogen-oxygen fuel cell.

Q. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is $1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$.

Ans. For 0.1 mol L^{-1} KCl solution,

Conductivity, k = $1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$, Resistance, R = 100 W

Cell constant = Conductivity × resistance

= 1.29×10^{-2} Ω–1 cm^{-1} × 100 Ω = 1.29 cm^{-1}

For 0.02 mol L^{-1} solution,

Resistance = 520 Ω, Cell constant = 1.29 cm^{-1},

$$\text{Conductivity, k} = \frac{\textit{Cellconstant}}{\text{Resistance}}$$

$$= \frac{129\ \ cm^{-1}}{520\ \ \Omega} = 0.00248\ \Omega^{-1}\ cm^{-1}$$

$$\text{Molar conductivity, } \Lambda m = \frac{\text{Conductivity } (k) \times 1000\ \ cm^{3}\ \ L^{-1}}{\text{Molarity}}$$

$$= \frac{0.00248\ \ \Omega^{-1}\ cm^{-1} \times 1000\ \ cm^{3}\ \ L^{-1}}{0.02\ \ mol\ \ L^{-1}}$$

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

Q.4. Answer the following questions

[*HOTS*]

Q. Calculate the standard free energy change for the following reaction at 25°C.

$$Au(s) + Ca^{2+}(1\ M) \quad \rightarrow \quad Au^{3+}(1\ M) + Ca(s)$$

$$E^{o}_{Au^{3+}/Au} = +\ 1.50\ V\ ,\ = E^{o}_{Ca^{2+}/Ca}\ -\ 2.87\ V$$

Predict whether the reaction will be spontaneous or not at 25°C. Which of the above two half cells will act as an oxidising agent and which one will be a reducing agent?

Ans.

$$E^{o}_{cell} = E^{o}_{Ca^{2+}/Ca} - E^{o}_{Au^{3+}/Au}$$

$$= (-2.87\ V) - (1.50\ V) = -4.37\ V$$

$$\Delta_r G^{o}_{cell} = -6 \times 96500 \times (-4.37\ V)$$

$$= +2530.230\ kJ/mol$$

Since $\Delta_r G^{o}$ is positive, therefore, reaction is non-spontaneous.

Au^{3+}/Au half cell will be an oxidising agent while Ca^{2+}/Ca half cell will be a reducing agent.

Q. Tarnished silver contains Ag_2S. Can this tarnish be removed by placing tarnished silver ware in an aluminium pan containing an inert electrolytic solution such as NaCl? The standard electrode potential for half reaction:

$$Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-} \text{ is } -0.71V$$

and for $Al^{3+} + 3e^- \rightarrow 2Al(s)$ is $-1.66V$

Ans. E^{o}_{cell} for reaction of tarnished silver ware with aluminium pan is

(– 0.71 V) – (– 1.66 V) *i.e.*, + 0.95 V

Tarnished silver ware, therefore, can be cleaned by placing it in an aluminium pan as E^{o}_{cell} is positive.

Q.5. At 291 K, the molar conductivities at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 S cm^2 mol^{-1} respectively. If the molar conductivity of a centinormal solution of NH_4OH is 9.33 S cm2 mol^{-1}, what is the percentage dissociation of NH_4OH at this dilution? Also calculate the dissociation constant of NH_4OH.

[*HOTS*]

Ans.

Here, we are given:

Λ_m^0 for NH_4Cl = 129.8 S cm^2 mol^{-1}

Λ_m^0 for NaOH = 217.4 S cm^2 mol^{-1}

Λ_m^0 for NaCl = 108.9 S cm^2 mol^{-1}

By Kohlrausch's law,

Λ_m^0 for NH_4OH = $\lambda^o_{NH_4^+} + \lambda^o_{OH^-}$

$= \Lambda^o_m(\mathbf{NH_4\,Cl}) + \Lambda^o_m(\mathbf{NaOH}) - \Lambda^o_m(\mathbf{NaCl})$

$= [129.8 + 217.4 - 108.9]$ S cm^2 mol^{-1}

$= 238.3$ S cm^2 mol^{-1}

$\Lambda_m^c = 9.33$ S cm^2 mol^{-1} (Given)

$\therefore$ Degree of dissociation $(\alpha) = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{9.33}{238.3} = 0.0392$

or Percentage dissociation = 0.0392 × 100 = **3.92%**

Calculation of dissociation constant

$$NH_4OH \rightleftharpoons \mathbf{NH_4^+} + OH^-$$

Initial conc. c 0 0

Equilibrium conc. $c - c\alpha$ $c\alpha$ $c\alpha$

$= c(1 - \alpha)$

$$K = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

Substituting, $c = 0.01$ N $= 0.01$ M, and $\alpha = 0.0392$, we get

$$\text{We get,} \quad K = \frac{(0.01)\ (0.0392)^2}{1 - 0.0392}$$

$$= \frac{10^{-2} \times (3.92 \times 10^{-2})^2}{0.9608}$$

$$= 1.599 \times 10^{-5}$$

Q.6. Answer the following questions

Q. State two advantages of H_2–O_2 fuel cell over ordinary cell.

Ans. Advantages of fuel cell:

- **a.** It is a pollution-free device since no harmful products are formed.
- **b.** Its efficiency is about 75% which is considerably higher than conventional cells.
- **c.** It is a continuous source of energy if the supply of gases is maintained. (Any Two)

Q. Silver is electrodeposited on a metallic vessel of total surface area 500 cm^2 by passing a current of 0.5 amp for two hours. Calculate the thickness of silver deposited.

[Given: Density of silver = 10.5 g cm^{-3}, Atomic mass of silver = 108 amu, *F* = 96,500 C mol^{-1}]

Ans.

$$m = Z\,I\,t = \frac{108}{96500} \times 0.5 \times 2 \times 3600 = 4.029 \text{ g}$$

$$d = \frac{m}{V} \quad \Rightarrow \quad V = \frac{m}{d}$$

$$V = \frac{4.029\ g}{10.5\ g\ \text{cm}^{-3}} = 0.3837 \text{ cm}^3$$

Let the thickness of silver deposited be x cm.

$$\therefore \quad V = A \times x \quad \text{or} \quad x = \frac{V}{A}$$

$$x = \frac{0.3837}{500} = 7.67 \times 10^{-4} \text{ cm.}$$